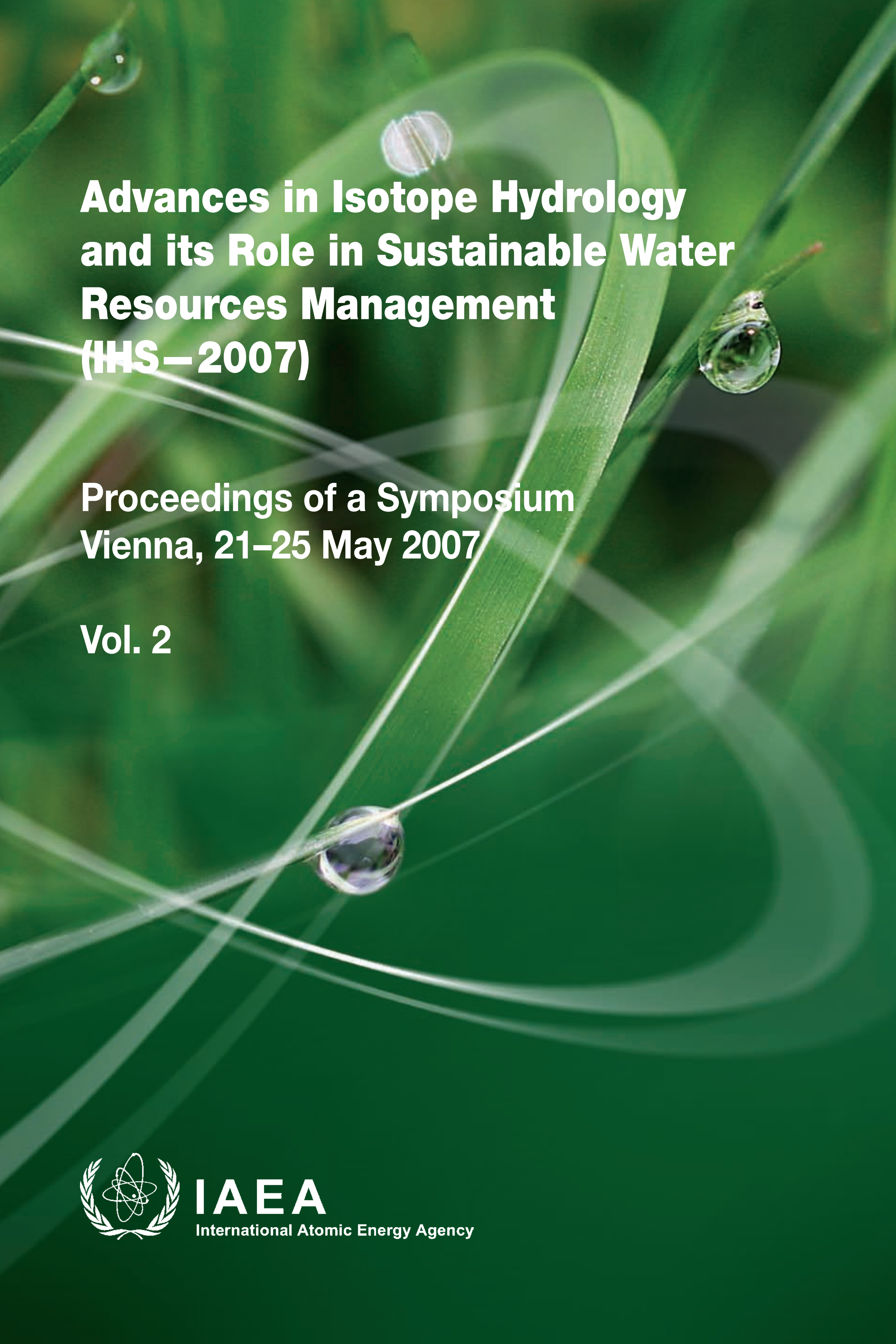

Advances in Isotope Hydrology and its Role in Sustainable Water Resources Management (IHS—2007)

Proceedings of a Symposium
Vienna, 21–25 May 2007

Vol. 2

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ADVANCES IN ISOTOPE HYDROLOGY AND ITS ROLE IN SUSTAINABLE WATER RESOURCES MANAGEMENT
(IHS–2007)

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FOREWORD

Access to safe freshwater is considered a basic human right. However, in many parts of the world, surface water and ground water resources are at risk because of indiscriminate use, rapidly growing populations, increasing agricultural demands, and the threat of pollution. These risks are often compounded by a lack of understanding about local conditions governing the occurrence, distribution and movement of surface and groundwater resources.

Historically, the IAEA has played a key role in advancing isotope techniques and in promoting the use of isotopes to address water resource sustainability issues worldwide. The quadrennial IAEA symposia continue to be an important component of the IAEA's mission in water resources management. The 12th symposium in the series was convened from 21 to 25 May 2007 in Vienna with the objectives of: reviewing the state of the art in isotope hydrology; outlining recent developments in the application of isotope techniques to water resources management; and identifying future trends and developments for research and applications.

Over 200 participants from 59 Member States participated in a series of invited lectures, poster sessions, round table discussions, and a scientific visit to the Danube River. The breadth of topics addressed was extensive and included analytical developments, the use of isotopes to understand land–atmosphere–biosphere interactions, rivers and surface water, development of deep groundwater resources, ecohydrology, urbanization and water resources management, carbon sequestration, waste management, artificial recharge, contamination problems, coastal zone hydrology, geothermal systems, agriculture and water resources management, and research frontiers.

Out of 152 oral and poster presentations, 136 contributions submitted by the authors are included in two volumes of the proceedings with editorial corrections. These proceedings are intended for those using isotopes for applied problems in hydrology as well as the research community. It is also hoped that these proceedings will promote increased use of isotopes for water resource sustainability problems and greater utilization of these techniques by hydrologists in general.

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GEOTHERMAL SYSTEMS

SUMMARY

The 12th international symposium on Advances in Isotope Hydrology and its Role in Sustainable Water Resources Management (IHS–2007) was held in Vienna, from 21 to 25 May 2007. The symposium was divided into an opening session, a series of nine invited lectures, a series of eight case study lectures, three poster sessions (at which 135 posters were presented), a scientific side visit, two roundtable discussions, technology demonstrations, and a closing session. The poster sessions were very well attended and generated substantial interactions among participants. Technical presentations were organized through a series of themes which are described below. There were 213 registered participants, 14 observers, and 6 exhibitors. Participants came from 59 Member States, and 32 grants were provided to participants from developing countries. Four new aspects of this symposium were the focus on poster sessions over oral presentations, the scientific side visit, the roundtable discussions, and the technology demonstrations.

SURFACE WATER DYNAMICS AND QUALITY, INCLUDING THE UNSATURATED ZONE AND ARTIFICIAL RECHARGE

One highlight of this theme was a case study on a large wetlands area in Spain. Another was the large number of posters that described a wide range of water flow and water quality studies involving rivers, streams, lakes, artificial impoundments, and the role of the unsaturated zone. The number of posters on nitrate contamination was substantial, and this is an area where compound specific isotope analyses can be very important. Other studies demonstrated usefulness of isotope methods for quantifying artificial recharge through dams and enhanced bank infiltration.

SURFACE WATER–GROUNDWATER INTERACTIONS

A scientific side event on the River Danube was held mid-conference. The visit involved a boat trip from Melk to Vienna, and participants learned about the importance of surface water–groundwater interactions while on the river. Two keynote presentations were made on the boat and demonstrated the critical value of isotope methods in rivers and catchment studies, and the role of such data for development of conceptual and predictive models that integrate both surface water and groundwater aspects. In addition, various rivers and aquifers interactions were discussed during the poster sessions.

GROUNDWATER DYNAMICS AND QUALITY

Two invited presentations showed how diverse isotope applications can be for addressing important issues involving groundwater dynamics. One presentation described the application of isotopes and geochemistry to carbon sequestration in brine aquifers. This work was also described in an article on the IAEA web page the week before the symposium. The second presentation showed how isotopes can be used to understand groundwater flow in systems with clay aquitards. These systems can isolate aquifers for long periods of time, making them potentially attractive for hazardous or radioactive waste disposal. Case studies described isotopes and aquifer hydraulic data that can be integrated to understand groundwater flow in Uganda, use of nitrogen isotopes to understand the origin of nitrate pollution in groundwaters of Côte d'Ivoire, and how isotopes and hydrogeochemical methods can be used to quantify groundwater dynamics in coastal sedimentary aquifers in India. Posters described many examples of application of isotopes used to understand groundwater flow and pollution problems.

GROUNDWATER SUSTAINABILITY, INCLUDING GEOTHERMAL SYSTEMS

Many of the posters presented focused on sustainability issues, showing the significance of this problem across the world. The highlights of this theme included an invited presentation on the Nubian aquifer in Africa, which described how isotopes are being used to characterize this large, complex, and important transboundary aquifer system. In addition, case studies described isotope studies of groundwater sustainability issues in semiarid/arid areas in China and Mexico. There were many posters on the application of isotopes in geothermal systems.

ANALYTICAL DEVELOPMENTS AND SAMPLING METHODS

New analysis and sampling methods help increase the breadth of isotope applications for water cycle problems, and in some cases make it easier to apply and use isotopes for applied problems and research. Highlights of this theme include invited presentations on compound specific isotope analyses for understanding contaminant degradation and advanced laser methods for water cycle studies. Demonstrations of new laser analysis instrumentation for water samples and an automated precipitation/water sampling device for isotope studies were also highlights of this theme and drew a great deal of interest from participants. Several posters also presented innovative analysis or sampling methods for both stable isotopes and radioisotopes.

LAND–ATMOSPHERE AND GROUNDWATER–MARINE CONNECTIONS

The highlights of this session included an invited presentation of how radioisotopes can be used to quantify submarine groundwater discharge and how important this process is in many coastal areas. A second invited presentation described how isotopes are critical for understanding land–atmosphere interactions in the water, carbon, and oxygen cycles and that there is still much work to do in this area. Two case study lectures reinforced the importance of these connectivity issues. One case study presentation described the links between groundwater and coastal wetlands in Brazil and the factors that are impacting this important ecosystem. The other case study described how isotopes can be used to understand the relation between precipitation and atmospheric circulation patterns in Turkey.

ROUNDTABLE SESSIONS

The roundtable sessions were held to provide open forums for conference participants to discuss key issues related to the application of isotope methods. They were used as a way of identifying research needs and priority application areas, and to hear about isotopes application issues in developing countries. The roundtable outcomes will help the IAEA understand how best to align programmatic efforts and resources for future needs. One roundtable focused on the use of isotopes in developing countries, while the other focused on general issues involving the application of isotope techniques. Three of the main conclusions of the developing country roundtable were:

— The IAEA continues to play a critical role in promoting and facilitating the use of isotope methods in developing countries, and is helping to address important water issues. It can play an even stronger role, for example, by increasing integrated isotope–geochemistry–basic hydrology training options with other UN organizations.

- The development of new isotope tools and approaches which can be more easily applied under the challenging circumstances in developing countries should be continued. The increasing need for developing countries to address contaminant and climate change issues requires new and/or easier to implement isotope methods.
- Isotope laboratories are difficult to operate, and maintaining analytical quality can be a problem in small laboratories in some developing countries. Isotope laboratories should not be established indiscriminately in developing countries. A focus on a few regional laboratories would enable those laboratories to have enough economy of scale for routine operation and to provide quality analyses. New ‘simpler’ technologies, such as laser machines, can also make it easier for countries to maintain isotope capabilities and adequate analytical quality.

The main conclusions of the roundtable on general isotope issues were as follows:

- There is a clear need for the increased use of isotopes in numerical modelling studies which is being driven by new regulations such as the European Union water framework. International organizations and research agencies should increase their focus on the integration of isotopes and modelling.
- The IAEA/WMO global network of isotopes in precipitation (GNIP) is more important than ever, not only because of groundwater/surface water applications, but also for understanding the role of the water cycle in climate and atmospheric processes, ecology and other disciplines. Moisture isotopes in the biosphere and atmosphere (MIBA) and global network of isotopes in rivers are also important, but because they are in the development stage, their impact is not currently as large.
- As a community, we need to identify problems where isotopes can have large impacts, and focus efforts on those problems. This focus includes doing more work to understand linkages and coupled processes. To this end, we need to encourage more collaborative research and interactions at meetings between isotope hydrologists and those working in fields such as ecohydrology, carbon and oxygen cycling, and the climate

POSTER PRESENTATIONS

GROUNDWATER DYNAMICS

CONTRIBUTION OF ISOTOPIC INDICATORS TO THE ASSESSMENT OF GROUNDWATER MIXTURE BETWEEN CONTINENTAL INTERCALAIRE AND DJEFFARA AQUIFERS (SOUTH-EASTERN TUNISIA)

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Abstract

The Continental Intercalaire and the Djeffara aquifers are the most important groundwater resources in Southern Tunisia. Previous hydrogeologic and isotopic studies (^{18}O, ^{2}H, ^{3}H, ^{14}C) allow to define the main hydrodynamic and hydrochemical characteristics for each aquifer. The Continental Intercalaire aquifer, which has important water reserves contains very old groundwater with low ^{14}C activities and very depleted values of stable isotopes (^{18}O, ^{2}H). This is why this aquifer is considered as fossil and contains non renewable resources. Compared to the Continental Intercalaire aquifer, Djeffara aquifer has more scattered stable isotopes values which confirms that there are different water origins. Near to the El Hamma faults, isotopic contents of Djeffara aquifer are very similar to the isotopic signature of the Continental Intercalaire, indicating mixing flows between the two systems and showing that the recharge of Djeffara of Gabes is partially ensured by the discharge of the old water of the Continental Intercalaire through faults.

1. INTRODUCTION

The climate of Southern Tunisia is classified as semi-arid to arid, precipitation is scarse and occurs mostly during winter. Large amounts of water are lost by runoff and evaporation, and surface waters are insufficient for domestic, industrial and agricultural needs. Therefore, groundwater constitute

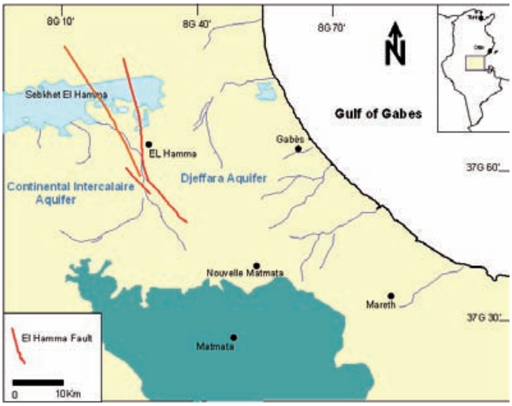

FIG. 1. Location map of the study area.

the main water resource in Southern Tunisia. The plain of Djeffara of Gabes, located at South-Eastern Tunisia, is limited to the North by the Skhira region, at the west by the El-Hamma faults and Matmatas reliefs and at the South by the Djeffara of Medenine (Fig. 1). This plain is declining regularly eastward to the Gulf of Gabes (Mediteranean Sea).

During the last decades, the Gabes region knew an increase in population from 240 160 in 1984 to 341 800 in 2003, which corresponds to a yearly increase of 1.87% during this period. The increase of population is related mainly to the creation of new irrigated perimeters around several deep drillings which allowed the devopement of agricultural, touristic and industrial sectors.

In 2004, the exploitation of the Djeffara aquifer reached 103 Mm^3 (28 Mm^3 for the drinking water supply, 70 Mm^3 for agriculture uses and 5 Mm^3 for industry uses) [1]. The current exploitation had induced a disturbance of hydrodynamic functionning and hydrochemical characteristics of the Djeffara aquifer and thus brings about a decrease of its potential (recharge rate, quality, sustainalibity).

2. HYDOGEOLOGICAL SETTING

The hydrogeological framework of Southern Tunisia is formed by three important aquifers: the Continental Intercalaire aquifer, the Complexe Terminal aquifer and the Djeffara aquifer. In this paper, the study is focused in flow exchanges between the Djeffara and the Continental Intercalaire aquifers in the Gabes region.

The Djeffara plain is underlied by a multilayered aquifer system, characterized by a lithostratigraphic and structural complexity induced by the combination of three important phenomena: a lithological variability of the aquifer formations, a tectonic complexity and a post-tectonic erosion leading to the karstification and the reduction of the aquifereous formations.

The Djeffara aquifer of Gabes has been structured according to two main layers [2]:

(a) The continental Miocene sands containing the main aquifer on the north of Gabes;

(b) Cretaceous and Jurassic limestones containing the main aquifer on the south of Gabes.

The Continental Intercalaire aquifer system is one of the largest groundwater systems in the North West Sahara and extends over 84 000 km^2 in the southern Tunisia. The Continental Intercalaire aquifer is formed by a succession of Lower Cretaceous clastic sediments (Neocomian, Barremian, Aptian and Albian).

The hydraulic continuity between the Continental Intercalaire and the Djeffara aquifers has been proven through a set of boreholes showing concordant hydrogeologic and hydrodynamic parameters. In fact, the Continental Intercalaire aquifere presents a decrease of permeability and thickness and at the end, disappears under the Djeffara plain. Moreover, the piezometric map of the Djeffara aquifer indicates a West–East flow direction from Matmata relief and El Hamma region towards the Mediterranean Sea (Fig. 2). Near El Hamma faults, the hydraulic head is about 50 m, explained by the raise of Continental Intercalaire groundwaters through El Hamma faults to flow in the aquifereous formations of the Djeffara system (Fig. 3). Also, water temperature and chemical characteristics of Djeffara groundwaters in this region indicate the influence of the Continental Intercalaire aquifer. Indeed, in Hamma and Chenchou boreholes water temperature values exceed the average of 25 to 30°C. These thermal anomalies are accompanied by chemical similarities between the Continental Intercalaire and the Djeffara groundwaters which present the same chemical facies explained by the hydraulic connection between the two aquifers.

3. ISOTOPIC STUDY

Previous isotopic studies carried out on groundwater resources in Southern Tunisia allowed to identify isotopic characteristics of each aquifer, in particular, those of Continental Intercalaire, Complexe Terminal and Djeffara. However, many questions remain unanswered and several hypotheses need

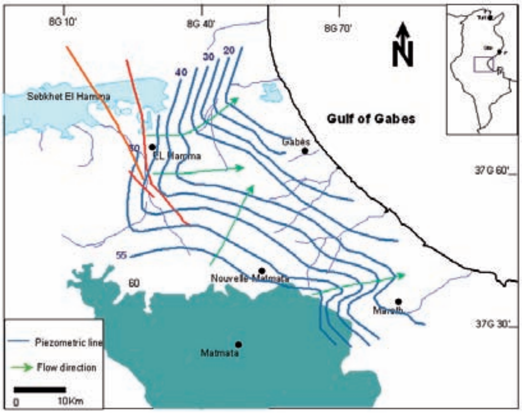

FIG. 2. *Potentiometric map of Djeffara Aquifer in 2002 [4].*

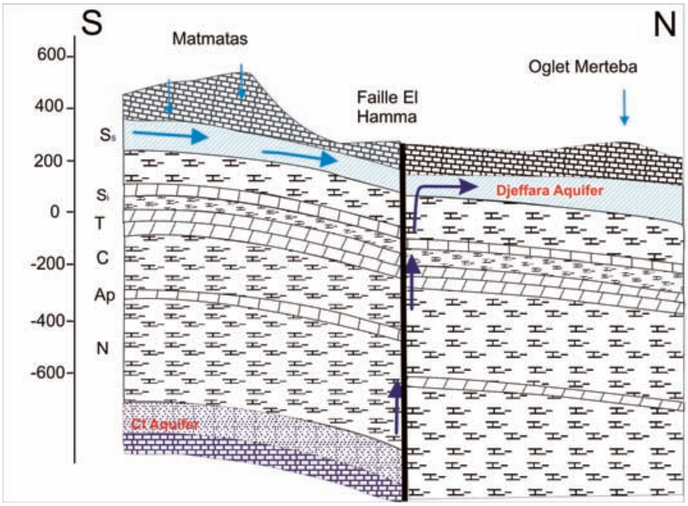

FIG. 3. Simplified geologic cross section showing internonnection between Djeffara and Continental Intercalaire aquifers [3].

to be confirmed, such as hydraulic connections between these aquifers. This study is carried out under the inter-regional IAEA project RAF/8/035. Stable isotopes analysis (^{18}O, ^{2}H) and tritium concentrations were analysed under the International Atomic Energy Agency coordination while carbon-14 dating have been made in the Laboratory of Radio-Analysis and Environment of the National School of Engineers of Sfax.

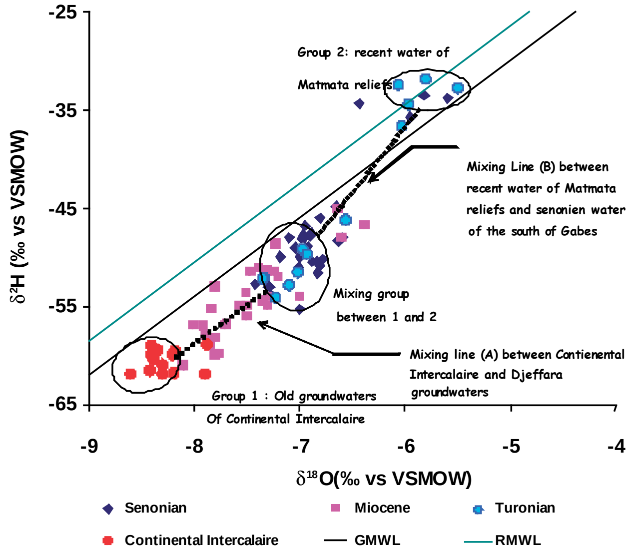

FIG. 4. The $^{18}O/^{2}H$ diagram of the Continental Intercalaire and the Djeffara groundwaters.

The Djeffara groundwaters have stable isotopic contents ranging from –8.3 to –5.2‰ $\delta^{18}O$ and from –58.8 to 33.5 ‰ $\delta^{2}H$, while Continental Intercalaire groundwaters present very depleted values with a more homogenous isotopic composition with an average value equal to –8.23‰ and –61.1‰ for oxygen 18 and deuterium, respectively.

The ($^{18}O/^{2}H$) diagram (Fig. 4) shows that the Djeffara groundwaters plot slightly below the Global Meteoric Water Line (GMWL) and the Regional Meteoric Water Line of Sfax (RMWL). Oxygen-18 contents decrease toward the El Hamma fault where they fall down to –8.3‰ $\delta^{18}O$ vs VSMOW which is very similar to the isotopic signature of the Continental Intercalaire groundwaters. The great similarity in the isotopic composition of Djeffara with that of the Continental Intercalaire (CI) groundwaters in the area of Chenchou and El Hamma suggests the existence of a leakage of Continental Intercalaire groundwaters through the fault system of El Hamma.

In this diagram (Fig. 4) two mixing lines can be distinguished:

(a) The mixing line (A): Old, isotopically depleted groundwaters of the Continental Intercalaire aquifer raise up through El Hamma fault and mix with groundwaters lodged in Mio–Pliocene formations in the North of Gabes. Then, these groundwaters mix with those from the Senonian formations in the South of Gabes. Mixed groundwater have isotopic present values ranging around –7‰ for oxygen-18 and around –50‰ for deuterium.

(b) The mixing line (B): Recent waters infiltrated on the Matmata reliefs through Turonien outcrops mixes with those of the Senonian formation in the South of Gabes.

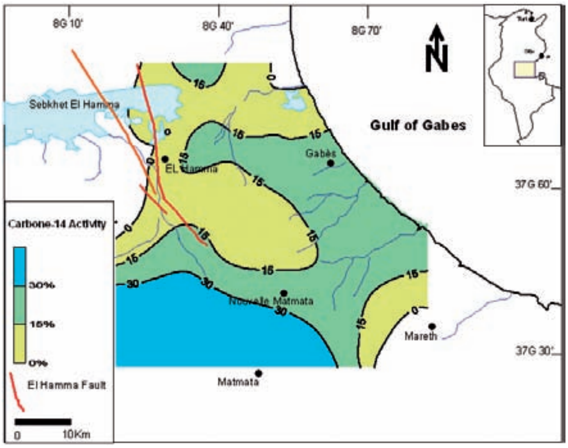

FIG. 5. *Carbon-14 activities contour map in the Djeffara region of Gabes.*

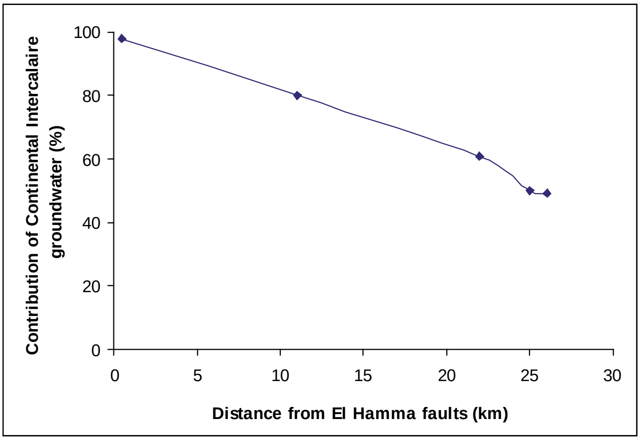

FIG. 6. Graphic presenting the decrease of Continental Intercalaire contribution from El Hamma faults towards the coastal area.

TABLE 1. CONTRIBUTION OF CONTINENTAL INTERCALAIRE GROUNDWATER TO THE RECHARGE OR THE DJEFFARA AQUIFER (%).

Borehole Name	Mass balance using ^{14}C actvities	Mass balance using ^{18}O
Baten Trajma	42	48
Chenchou 1bis	80	44
Chenchou 2 bis	69	57
Od khalifa Mahmoud	57	80
Aouinet 4	76	70
Rass el Aioun	45	60
Sidi Daoud	71	49
Ambar	61	50
Godfa 2 bis	62	83
El boniane 3	71	61
Rmathie 2	63	48
Gourai	74	63
Garet Ltaifa	71	47
Aéroport Militaire	47	58
Beni Zelten 3	0	9
El Hani 1	95	44
Mereth 6	79	44
Mareth 6	90	53
Henchir Jehha	78	49
Henchir Jehha	82	52
Matmata 5	73	45

Tritium activities of the Djeffara groundwaters are very low and close to the detection limit, except for Beni Zelten 3 borehole, located on the Matmata relief, which presents an activity of 1.3 TU. This value proves that rainwater infiltrates through Turonian outcrops.

Moreover, carbon-14 activities of the Djeffara of Gabes groundwaters are relatively low with an average value of about 12.6%. This is explained by the mixture between very old Continental Intercalaire groundwaters with no carbon 14 activity and recent infiltrated rainfall in Matmata reliefs. Lowest carbon 14 activities are observed near the El Hamma-Chenchou region and support the existence of a leakage from the Continental Intercalaire through El Hamma faults. The recent recharge is very low and seems to take place only in the sectors where the aquifer formationw outcrops, as it is the case of Beni Zelten sector (Cretaceous limestones) (Fig. 5) where carbon-14 activity reaches 43%. On the North of Gabes, carbon-14 activities are very close to those of Continental Intercalaire aquifer which can be explained by the fact that, in this area, the aquifer formations of the Continental Intercalaire are directly in contact with Miocene sands. It is possible that the Continental Intercalaire discharge takes place directly through Miocene sands, which is the main aquifer in the North of Djeffara.

In order to evaluate the contribution of the Continental Intercalaire groundwater to the recharge of the Djeffara aquifer, a mass balance equation has been used for oxygen-18 contents and carbon-14 activities. In this equation, we calculate the mixing ratio between two end-members: old groundwater of the Continental Intercalaire (^{14}C activity = 0% and $\delta^{18}O$ mean value = –8.3‰) and recent groudwater of Turonian outcrops (^{14}C activity = 43% and $\delta^{18}O$ mean value = –5.84‰).

Using this equation for oxygen-18 contents, we notice that the leakage up of the Continental Intercalaire aquifer through El Hamma faults constitutes the most significant contribution to the Djeffara aquifer recharge. It represents about 90% to 98% close to the fault and in the northen part of Gabes, and reaches 63% on the south of Gabes. This contribution decreases from El Hamma faults to the coastal area of Gabes (Fig. 6). The contribution of the recent water is very small and takes place only on Turonian outcrops on Matmata reliefs.

The results given by mass the balance equation using ^{18}O and ^{14}C activities are different but the differences range around the same magnitude (Table 1). This can be explained by the fact that the groundwater carbon-14 activity is quickly reduced by exchange with the carbonated matrix during its transit in the aquifer.

4. CONCLUSION

The Djeffara aquifer is one of the most important systems in the South-Eastern Tunisia. Its renewable resources are estimed to 115.2 Mm^3 per year in the Gabes region. Isotopic studies have proven that the contribution of the Continental Intercalaire to the recharge of Djeffara aquifer is very significant and may reach 95% in the El Hamma region and in the northern part of Gabes. This process is supported by the hydrogeological setting and by the existing faults in this area. In fact, stable isotopes analyses show the existence of mixing flows between Djeffara aquifer formations with depleted Continental Intercalaire groundwater on the one hand and with the enriched water of Turonian on the other hand. Low carbon-14 activities obtained for the Djeffara groundwaters sampled near the El Hamma region in the North of Gabes support the up-leakage of Continental Intercalaire groundwaters. Higher carbon 14 activities observed in groundwaters sampled in the Matmata reliefs region confirm the infiltration of recent water through Turonian outcrops. We can conclude the water resources management of the Djeffara aquifer depends on the Continental Intercalaire aquifer.

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USE OF ENVIRONMENTAL ISOTOPES OF HYDROGEN AND OXYGEN TO DETERMINE RED RIVER AND GROUNDWATER MIXING IN HANOI AREA OF VIETNAM

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Abstract

The paper presents a study on the interaction between groundwater and surface water; water of Red River together with water of large lakes in Hanoi area. The isotope data show that almost all groundwater in study area is recharged in recent time and only one site in the south contains groundwater older than 1100 years. Proportions of the Red River water in groundwater depend on the distance to the Red River; Groundwater of six Groundwater Production Stations is mostly recharged by Red River water in the rainy season when the water level of Red River is high. In the Ngoc Ha Station, groundwater relates to water of West Lake. Groundwater of Ha Dinh, Mai Dich, Phap Van Stations is the mixture of Red River water and meteoric water and the proportion of Red River water in these Stations is as follows: 50%, 52% and 57% respectively. Stable isotope ^{18}O was also used for determining the residence time of groundwater recharged by Red River at some groundwater producing boreholes of Yen Phu Station.

1. INTRODUCTION

Isotope techniques were applied for studying groundwater resources in Hanoi area from the end of the 1990s in projects carried out by the institutions of Vietnam and other countries [1]. Since 2002, being supported by the Ministry of the Science and Technology of Vietnam and IAEA, through the technical cooperation projects, the Institute for Nuclear Science and Technology (INST) has been applying isotope techniques for estimating groundwater resources in Hanoi area with a larger and detailed scale. This paper presents some initial results of using the radioactive ^{3}H and stable isotopes ^{18}O, ^{2}H to estimate the hydraulic relationship between groundwater and surface water in Hanoi area.

2. REGIONAL GEOLOGY AND HYDROGEOLOGY

Hanoi City, the Capital of SRV (The Socialist Republic of Vietnam) is located to the north of country and lies near to the Red River, which is one of the two largest rivers of Vietnam. The resident population of Hanoi city is about 4 millions.

The aquifer system under the city is made of Quaternary deposits, which have been simplified to an Upper and Lower aquifer system. The Upper aquifer system (UAS) comprises one or the two minor aquifers separated by less permeable clays or aquitard. The Lower aquifer system (LAS) is normally called as the Hanoi aquifer of lower-middle Pleistocene age. This is the main water supply aquifer for Hanoi City and is a highly permeable sand and gravel aquifer.

3. SAMPLING AND ANALYTICAL METHODS

3.1. Sampling

The sampling area is about 250 km^2 and the main sampling boreholes are the observation holes in Hanoi monitoring network (signed by letter P) and the National monitoring network (signed by letter Q). Surface water samples were

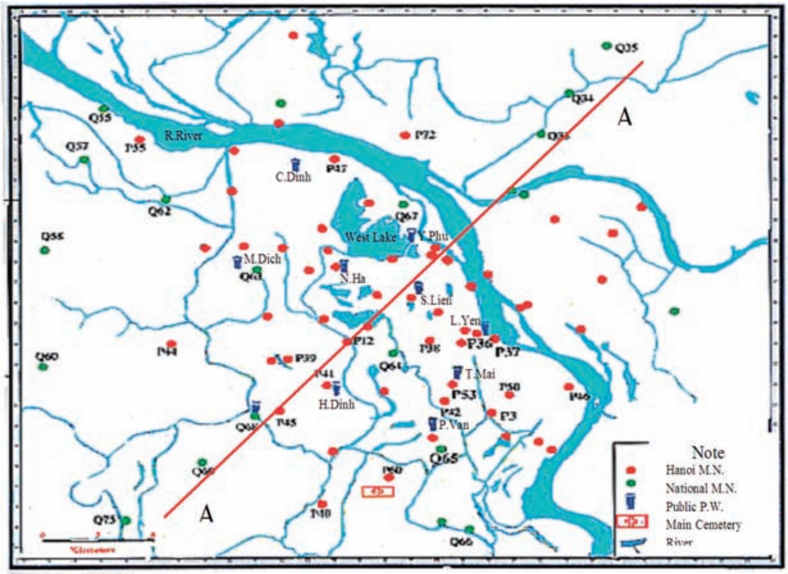

FIG. 1. The map of the study area.

collected from some lakes, Red River and the Wastewater River. The study area is presented in Fig. 1. Almost all samples were collected in two seasons in 2004 and 2005.

3.2. Analytical methodology

All measurements of radioisotopes and stable isotopes were carried out in the laboratories of INST. The radioisotope ^{3}H was enriched by electrolysis before its measurements on a liquid scintillation spectrometer. The stable isotope ratios δ^{18}O and δ^2H were measured by the isotope ratio mass spectrometer using the elemental analyzer for pyrolysing water at high temperature to produce gases CO for analyzing δ^{18}O and H_2 for analyzing δ^2H.

4. RESULTS AND DISCUSSION.

4.1. Data of isotope in precipitation

The concentration of tritium in precipitation has been being monitored since 2003. The results show that the concentration of ^{3}H varies monthly and has values between 0.5 TU and 6.3 TU. However, the seasonal variations are not marked. On the contrary, there are clear seasonalvariations of the stable isotope composition. The stable isotopecontents in precipitation are enriched at the end of dry season and depleted at the end of rainy season. The plots of δ^2H and δ^{18}O are presented in Fig. 2. All points of plot δ^2H vs δ^{18}O lie along the GMWL and after removing the points whith positive values, the regression line of measurement data is the same as the GMWL.

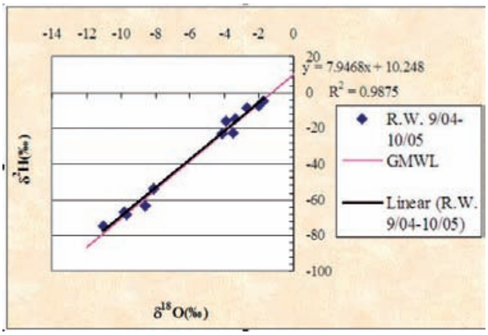

FIG. 2. The plot of δ^2H vs δ^{18}O in precipitation.

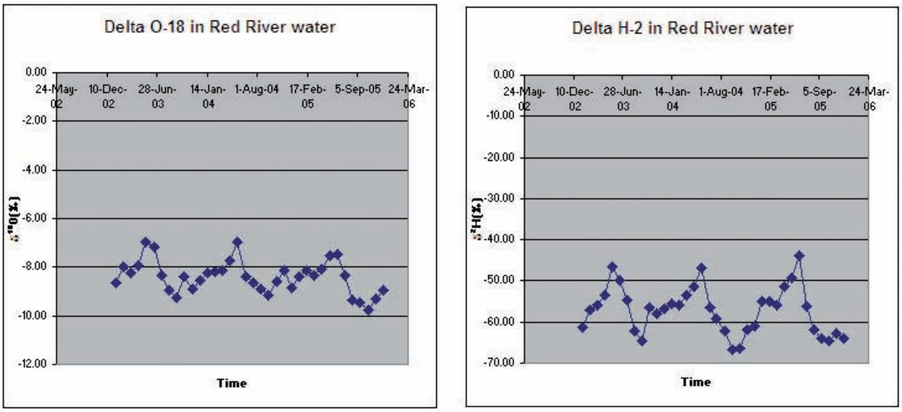

FIG. 3. The variation of composition of ^{18}O and ^{2}H in Red River water.

TABLE 1. THE AVERAGE VALUES OF $\delta^{18}O$ AND $\delta^{2}H$ IN RED RIVER WATER.

Year	$\delta^{18}O$	$\delta^{2}H$
2003	–8.27 ‰	–56.43 ‰
2004	–8.33 ‰	–58.08 ‰
2005	–8.59 ‰	–57.02 ‰

4.2. Isotope contents in Red River water

Tritium and stable isotopes ^{18}O and ^{2}H in Red River water have been being monthly monitored since 2003. The results show that there is a seasonal variation of tritium concentration. The average ^{3}H concentration in Red River water is as follows: 2003 3.4 TU; 2004 4.0 TU; 2005 5.5 TU. There is also seasonal variation of the stable isotope composition and the variations are presented in Fig. 3. The average values for $\delta^{18}O$ and $\delta^{2}H$ are presented in Table 1.

4.3. Isotope contents in groundwater

Isotope ^{3}H: Almost all of groundwater samples show a ^{3}H concentration in the range 0.4 TU–5.8 TU, except a groundwater sample in borehole P40A in the southern part, which shows 0 TU. It means that groundwater in Hanoi area is recharged in recent times. At borehole P40A, the measured ^{14}C activity

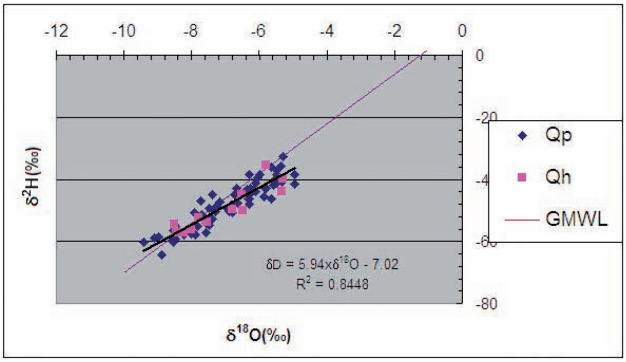

FIG. 4. The plot of δ^2H and δ^{18}O of groundwater in Hanoi area.

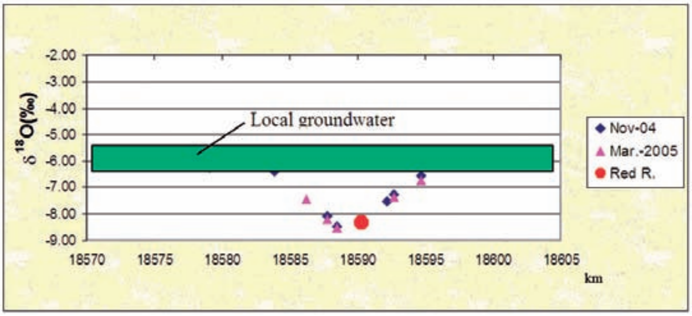

FIG. 5. The composition of stable isotope ^{18}O in groundwater depends on the distance to Red River after removing points affected by evaporation process.

in groundwater is corrected by the isotope mass balance model based on the activity of ^{14}C, δ^{13}C value, concentration of the dissolved inorganic carbon [2]. The age of 1100 years is calculated by using the correction model. This is the oldest age of groundwater in the study area.

***Stable isotope*:** In 2005, the stable isotope composition ^{18}O and ^{2}H of 113 groundwater samples were analyzed. The relationship of δ^2H and δ^{18}O is presented in Fig. 4. The majority of the points is on an evaporation line and the intersection point of evaporation line and Global Meteoric Water Line is –8.26 for ^{18}O and –56.09‰ for ^{2}H. These values are close to the average values of the stable isotope composition in Red River water. This fact suggests that Red River water recharges groundwater in the unconfined aquifer where groundwater is evaporated before recharging to the LAS.

TABLE 2. THE PROPORTION OF RED RIVER WATER IN GROUNDWATER AT SOME BOREHOLES.

Boreholes in North-East	Proportion of Red River water, p	Boreholes in South-West	Proportion of Red River water, p
Q33	57%	P58	100%
P13	46%	P38	87%
Q35	10%	P60	53%

For estimating the proportion of recharged water from Red River to groundwater in some places which lie near the bank of Red River, the monitoring boreholes on a line AA' across the Red River is chosen as presented in Fig. 1. These are boreholes P13A, P38A, P54A, P58A, P60A, Q33A, Q35A, Q37A, Q66A, Q69A, P41A, Q75A. Groundwater samples were collected in November 2004 and in March 2005. After removing the points where groundwater in LAS recharged from unconfined aquifer concerning the evaporation process, groundwater of remaining points is only mixture of Red River water and local groundwater. The stable isotope ^{18}O contents of these points are presented Fig. 5.

The stable isotope composition of groundwater of the above points is attributed to the mixing of Red River water and local groundwater, as shown in the following formula:

$$\delta^{18}O_{BH} = p \times \delta^{18}O_{RR} + (1-p) \times \delta^{18}O_{LG} \quad (1)$$

with $\delta^{18}O_{BH}$, $\delta^{18}O_{RR}$, $\delta^{18}O_{LG}$ respectively is the composition of ^{18}O in a borehole, Red River water and local groundwater. $\delta^{18}O_{RR}$ is determined with the average value of –8.40‰ . After determining the stable isotope composition of groundwater in 10 boreholes distributing around the study area, the value of –6.24‰ for ^{18}O were chosen for $\delta^{18}O_{LG}$ with standard deviation 0.20‰. p is the proportion of Red River water in groundwater of a borehole. The calculating results of p is presented in Table 2.

Stable isotopes have also been used for estimating the proportion of Red River water in groundwater exploited at the pumping stations in Hanoi city. The names of 9 stations are Ha Dinh, Luong Yen. Mai Dich, Nam Du, Ngoc Ha, Cao Dinh, Ngo Sy Lien, Phap Van, Tan Mai. The positions of the stations are presented in Fig. 1. The stable isotope composition at each station is the average value of two sampling campaigns in a year. The plot of δ^2H and $\delta^{18}O$ of the samples is shown in Fig. 6.

The results show that almost points of the plot of δ^2H and δ^{18}O lie on the GMWL. The pumping stations are divided into three groups: the first group consists of Luong Yen, Nam Du, Cao Dinh, Ngo Sy Lien, Tuong Mai which are located very close to the Red River and show stable isotope composition of groundwater more depleted than the average value in Red River water. It means that groundwater of these pumping well stations is only recharged from Red River water during the rainy season when, the water level in Red River is high. Groundwater exploited in the pumping stations of the second group (Ha Dinh, Mai Dich and Phap Van) is the mixture of Red River water and local groundwater. Using equation (1), the proportions of Red River water in these stations is as folows: 50%, 52% and 57%. Third group is Ngoc Ha station where a fraction of the g West Lake.

The variation of stable isotopes compositions ^{18}O, ^{2}H in the Red River water is also used as a tracer to determine the residence time of groundwater recharged by Red River water at a groundwater producing borehole of Yen Phu Station. The residence time of 3.6 months is calculated by using FlowPC software [3].

5. CONCLUSION

Almost all groundwater in Hanoi area is recharged in recent times. Especially the area close to the Red River, the aquifers close to to the Red River. Groundwater in this part of study area is recharged from Red River water during the rainy season. In the central part, groundwater is the mixture of local groundwater, Red River water and surface water. In the southern part,

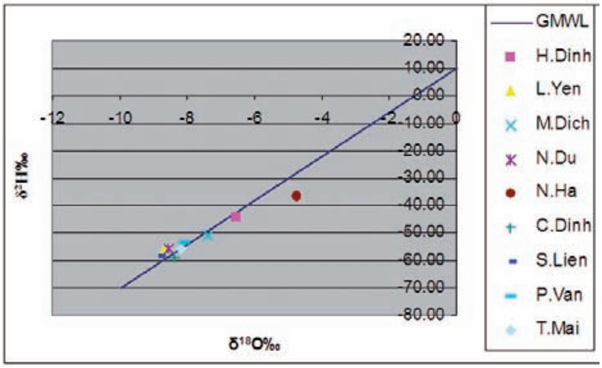

FIG. 6. The plot of δ^2H and δ^{18}O of groundwater at pumping stations in 2004.

groundwater was recharged before the recent times, or there is the mixture of water recharged before and after 1950.

ACKNOWLEDGEMENTS

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LOCATION OF RECHARGE AREA OF GORGOVIVO SPRING, CENTRAL ITALY

A contribution from isotope hydrology

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Abstract

The present study deals with the problem of characterization of the recharge zone and the mechanisms of water renewal at the Gorgovivo spring, which feeds the aqueduct of the Ancona province. For achieving with precision the hydrogeological and geochemical dynamics, analyses of chemical, isotopic and tritium contents have been used. The presence of different meteorological stations to measure of rainfall amount and isotopic contents in precipitation has allowed to evaluate the altitude gradient which correlates the oxygen-18 content in the underground waters with the isotopic height of infiltration. This gradients (about –0.24‰ per 100 m) allowed to establish around 1400 m asl the intake altitude for Gorgovivo spring. Tritium contents (about 8–13 TU for shallow springs present in the area, 6–8 TU for Gorgovivo spring) and the different isotopic composition indicate the presence in groundwater of a double flowpath. The first one is shallow and very fast: to this pathway belong the ooze springs in the studied area. The second pathway is slow and deeper. It reaches the bottom part of bedrock (Massive Limestone). As result, the groundwater recharging Gorgovivo spring can be considered as a mixing between these two pathways. The liquid discharge of the spring is exceptional, thus Gorgovivo spring is one among the greatest Apennine springs both in terms of importance and quality. The stable isotopic composition and tritium contents have allowed to investigate the recharge area and the mechanisms of recharge of such spring.

1. INTRODUCTION

The study area in examination is situated 50 km from the Adriatic Sea, in the Central Apennine (Fig.1). Gorgovivo spring is located in a zone of deep erosive incision near the bed of the Esino River. The total discharge is very high (between 2 and 3 m^3/s), of which only one third is tapped for drinkable purposes. In this zone several other springs exist. They are of lower flow, and they represent the discharge of shallow aquifers at different elevations. Such ooze springs had been considered together with the most important one, in order to characterize shallow flowpath (Fig. 1). Different authors [1–5] admit in fact the presence of a double pathway in the underground waters: the first one is extremely rapid (what it happens for macro fracture and Karst small ducts), the second one is slower (flow through micro fractures in the saturated aquifer zone). The first pathway occurs in little deep catchments, with limited water's volumes and high rate of withdrawal. Such type of pathway — fed from direct meteoric supplies of local origin — is superimposed to the slowest and deeper pathway, in which the recharge is frequently not local and occurs in landscapes at different elevations. Gorgovivo spring is the result of mixing between these two types of waters. The observation of chemical and isotopic contents and their time fluctuations in the different points investigated, has allowed to validate such interpretation.

2. CLIMATE, GEOLOGY AND HYDROGEOLOGICAL SETTINGS

A low-mountain climate with considerable maritime influence occurs in the investigated area. Regions at low elevation (200 m asl) show maximum precipitation in October, November and December. Regions at higher elevation (1400 m asl) have maximum rainfall in December and January [1], [6]. Precipitation amount increases with altitude, with mean annual precipitation lower than 1000 mm (for landscapes around 500 m asl), and about 1500 mm (for zones near to 900 m asl).

From a geological point of view, the investigated area belongs to the Umbro-Marchigiana carbonatic ridge. The complete sequence is constituted —by: Lower part — "Burano" Anhydrites, Massive Limestone, "Corniola", Formation of "Bosso", Jasper Limestones, "Maiolica", "Fucoidi" Marls, White Red and Variegated "Scaglia", Ashy "Scaglia", "Bisciaro" and "Schlier" (Figs 1 and 2). The massive Limestone, "Maiolica" and "Scaglia" represent the main hydrogeological complexes, and they feed several springs characterized by extremely varying flow velocities [3]. The massive Limestone aquifer symbolize the principal bedrock for the structure. Inside the massive, karst phenomena

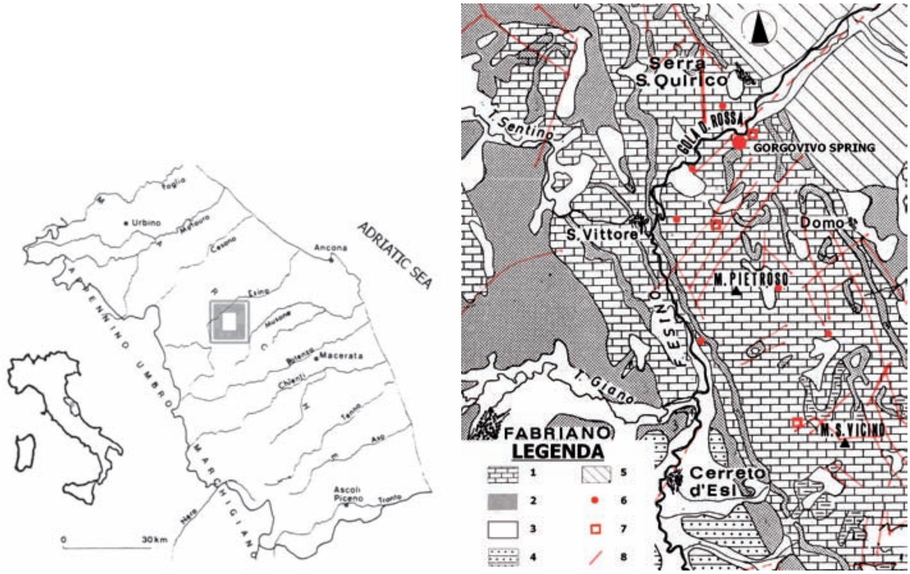

FIG. 1. Location of the investigated area and geological map of the area. 1. Limestones (Massive Limestone, "Corniola", "Maiolica", "Scaglia"); 2. Marly limestones (Jasper limestones, Jasper); 2. Marly limestones and marls ("Fucoidi" Marls, "Scaglia Cinerea"); 3. Alluvial deposits; 4. Sandstones and conglomerates; 5. Marly Clay; 6. Spring; 7. Rain gauge; 8. Fault.

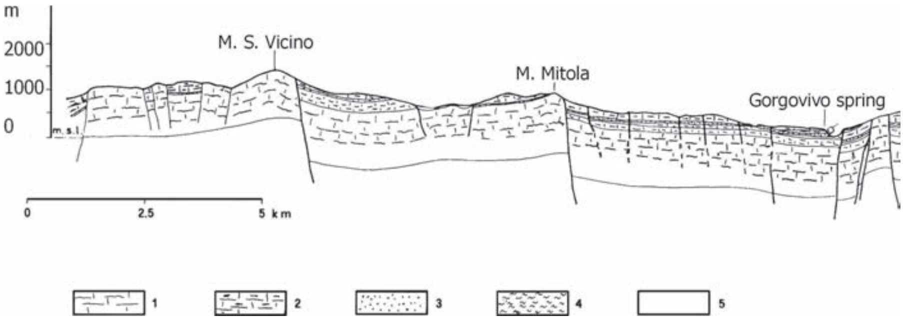

FIG. 2. Geological cross-section representing the recharge basin of Gorgovivo spring. 1. Massive Limestone; 2. "Maiolica", "Corniola", "Scaglia bianca e rosa"; 3. Nodular Limestones, Jaspers; 4. "Fucoidi" Marls; 5. "Burano" Anhydrites.

are very developed. It is made of limestones and dolomitic limestones in thick hard fractured layers. In this area, the limestones of the "Maiolica" formation are directly based on the Massive Limestone, thus constituting a single hydrogeological complex spacing from the "Burano" Anhydrites to the "Fucoidi" Marls (as aquiclude, Fig. 2). In this point, high discharge springs have been found. In the "Scaglia" formation permeability is due to micro and macro cracking and fissures. Such aquifer is suspended on Massive Limestone, supported by the aquiclude of "Fucoidi" Marls. Here there are many springs with low discharge and quick renewal.

3. CHEMISTRY

The shallow springs rising from "Scaglia" aquifer have TDS contents of 200–270 mg/L, with concentration of chloride and nitrate higher than the "Maiolica" springs. They are primarily of calcium bicarbonate type. The waters rising from Massive Limestone are different from the others because of the presence of a more elevated salt content, with enrichment in sulphate, magnesium and chloride (Fig. 3). All the springs generally exhibit homogeneous chemical characteristics, apart from the rock reservoir, with strong similar values of the chemical ratios. The relationship rMg^{++}/rCa^{++}, for example, ranges from 0.01 to 0.02; the only exception is represented by Gorgovivo spring, in which the aforesaid ratio is equal to 0.25. This is mainly due to the water leaching the basal part of the Massive Limestone, in contact with the "Burano" Anhydrites — primarily made of evaporites — at its basis. It has been recorded an increase

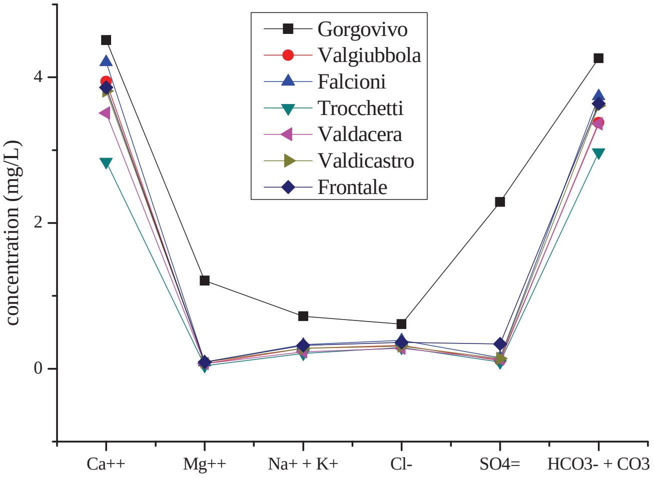

FIG. 3. Schöeller diagram for the shallow springs in the area and Gorgovivo spring.

of the magnesium content from 2–3 mg/L to 13–14 mg/L, and a similar increase in sulphate content from 15–20 mg/L to 60–80 mg/L. This fact ratifies the presence of a deeper pathway that crosses dolomitic limestones and anhydritic nodules, located in the lower part of the Massive Limestone formation. The temperature of the springs changes along the year from a minimum of 8°C to a maximum of 13°C, except for Gorgovivo spring, which presents a constant temperature during the year equal to 12.2°C.

4. RECHARGE AREA EVALUATION

The input data for the hydrogeological cycle has been measured in rain gauge stations located at different elevations in this area. First of all, the input values of tritium were achieved from a rain gauge station — managed by our research group for over 20 years — situated in the North slope of the Monte San Vicino, at 950 m asl. In such station monthly samples of meteoric water are collected on which a series of isotopic and tritium analysis have been done during the period 2002–2006. In Fig. 4 the tritium trend since 1986 to 2006 for the Pian dell'Elmo station is reported. The data relevant to the isotopic contents of deuterium and oxygen-18, allow to locate the intake areas for the springs. Preliminarily the altitude gradient for the zone in examination has been estimated. The altitude effect of local precipitation on isotopic composition has been obtained by using values of rain gauge stations and several shallow

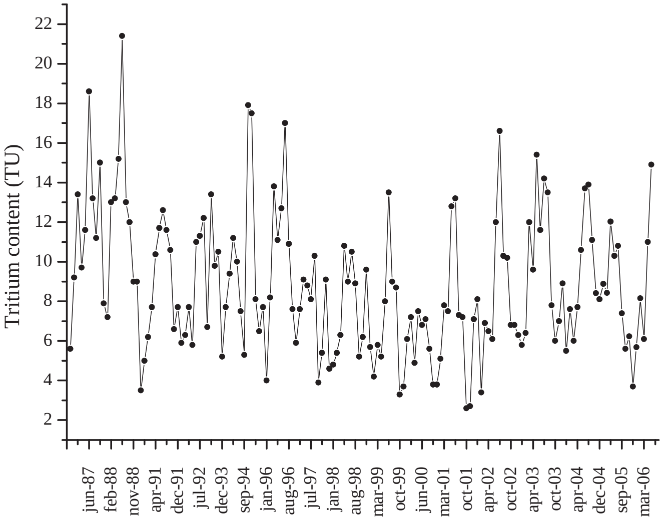

FIG. 4. Tritium trend for Pian dell'Elmo Rain gauge station (950 m asl).

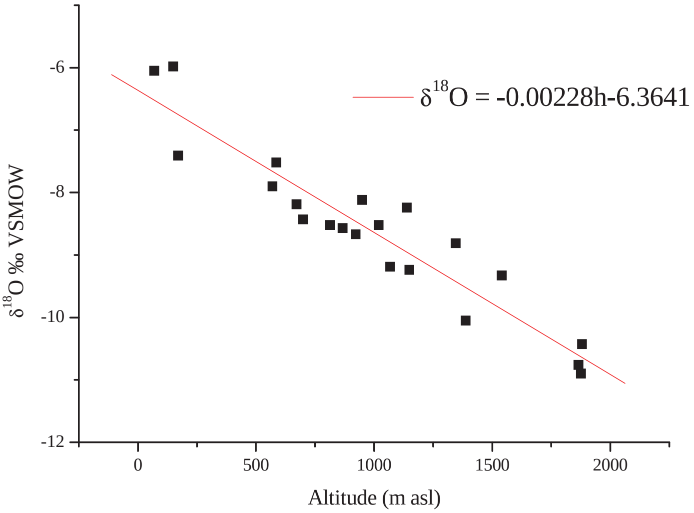

FIG. 5. Altitude gradient for the Marche and Umbria Apennine Region (Central Italy).

springs located at different altitudes above sea level. These values give an altitude gradient of about 0.235‰ per 100 m (Fig. 5). The gradient evaluated in this work is quite different from others [7, 6], calculated for the entire Middle Apennines in Central Italy. Such gradient has been used for evaluating the altitude of groundwater replenishment of Gorgovivo spring. Previous surveys [8], [4] individualized the intake area of the spring in the zone at North of Monte San Vicino (Figs. 1 and 2). Since the mean values of oxygen-18 monthly measured within 4 years has resulted equal to –9.45‰ VSMOW, from such values an infiltration altitude of around 1400 m asl. can be estimated. This infiltration area is therefore extended to the whole North slope of Monte San Vicino, nearly the peak, located at about 10 km South of the spring (Fig. 2). Evidences of the contact with evaporitic rocks — present in the basal part of the Massive Limestone — also come from the values of $\delta^{34}S$ in the sulphates, equal to +13.1‰ CDT [6]. Such values are with Triassic evaporites, present in the formation of the “Burano” Anhydrites.

5. ISOTOPIC AND TRITIUM DATA

Tritium contents of the springs discharging from “Scaglia” and from “ Maiolica” — and characterized by low and variable discharges during the year — generally are high, and they follow the course of meteoric waters, with a delay in the peak of 1–2 month. This usually underlines probable recharge from

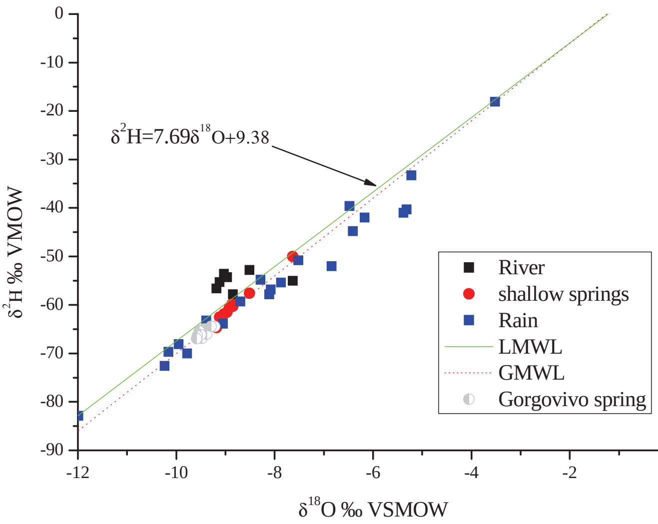

FIG. 6. Isotopic plot of $\delta^{18}O$ and δ^2H values for groundwater, surface water and rain water.

perched and low flow groundwater. Tritium content of the shallow springs in 2002 was variable between 8 and 13 TU. Tritium contents of Gorgovivo spring, monthly measured in the tap wells from 2001 to 2004, have underlined a more homogeneous trend, less variable and with lower values (6–8 TU). This fact confirms the presence of a wide reservoir and a deeper water circulation. In reality, such values are probably the consequence of mixing between more recent waters of the shallow pathway and groundwater of the deepest circuit, which have log-term renewal times. Isotopic composition of different waters involved in this study can be appreciated by observing the plot in Fig. 6, representing the relationship between δ^2H and $\delta^{18}O$ for groundwater, surface water and meteoric water. As we can see, the differences among all kind of waters are well-marked. In particular, it is clear that Gorgovivo spring has isotopic composition quite different with respect to shallow springs, and that surface water of Esino River becomes more enriched than groundwaters. The slope of the local meteoric water line (LMWL) is almost equal to the one found by other authors [9] for Northern Italy.

6. CONCLUSIONS

The former considerations and the experimental data gathered in these years allow to delineate the following conclusions as regards to the recharge mechanism of Gorgovivo spring. It is mainly recharged by the basal circulation in the Massive Limestone, which is slow and characterized by a long pathway; but — at the same time — it has typical elements of a shallow circulation, very fast and with a flowpath of limited length. The first type of circulation has been identified through the observation of chemical and isotopic data measured in some deep wells (over 150 m depth) placed near the Esino River (about 200 m asl). In these wells a variation of such characters has been noticed over a certain depth. The second type of circulation has been investigated analyzing the hydrogeochemical behaviour of different shallow springs in the zone, which are directly recharged from local meteoric waters, and therefore characterized by great variability in discharge and temperature. In these kind of springs, chemical and isotopic parameters reflect the different composition of the rocks reservoir and the difference in pathways. For these springs, time of renewal inthe order of a month and local and fast recharges are established. The shallow path, therefore, is able to reach the basal aquifer of Massive Limestone, in some cases mixing itself in various proportions to the slower base-flow. The result is a groundwater with typical chemical characteristics, with constant temperature over the year, and with short but well defined isotopic variations, and with tritium contents lower than that of recent rainfall waters. The discharge of the spring is exceptional, thus Gorgovivo spring is one among the greatest Apennine springs in terms of importance and quality.

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FIRST RESULTS OF THE ISOTOPIC STUDY (^{18}O, ^2H, ^3H) OF THE DOUALA QUATERNARY AQUIFER (CAMEROON)

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Abstract

The Quaternary sandy aquifer of the Douala sedimentary basin generally shows homogeneous isotopic abundances (^{18}O, ^2H, ^3H) of water sampled at different depths. The large majority of these samples indicated a direct and fast infiltration of precipitation, without significant evaporation. This homogeneity can moreover be accentuated under the pumping effects, connecting various levels of the multilayer aquifer. These results show that pollution from the surface can quickly reach the deeper layers, and seems to corroborate those obtained on the basis of field measurements and chemical analyses.

1. INTRODUCTION

The method known as "traditional method" of investigation in hydrogeology appears to be effectively efficient where important databases are available. At present, data collection is presently in progress in the Douala basin where information on many parameters is still sparse. Data collection includes hydrodynamic characteristics, piezometric surface and detailed stratigraphy. The lenticular nature of the deposits together with the lateral and vertical variations of facies — which are the rule in this environment of fluvial and deltaic type — provides a complex structure to the aquifer. Furthermore the use of water resources without proper control, are not likely to facilitate hydrogeologic studies in this area. This is in this context of particular technical constraints, where the use of isotopic techniques can be particularly useful —

than a specific project has been launched in collaboration with the IAEA to be included in the hydrogeologic study of the Douala basin.

2. HYDROLOGICAL SETTING

The Douala sedimentary basin, which covers an area of about 7000 km^2 onshore, is located at the centre of the Gulf of Guinea, between the latitudes 3°00' and 4°30' N and longitudes 9°20' and 10°20' E (Fig. 1). Variation of altitudes in the study area do not exceed 100 m.a.s.l. The climate is of equatorial type, with a long rainy season (March–November) and a short dry season (December–February). The annual rainfall is about 4000 mm. The interannual average temperature (1961–2005) is of 27°C.

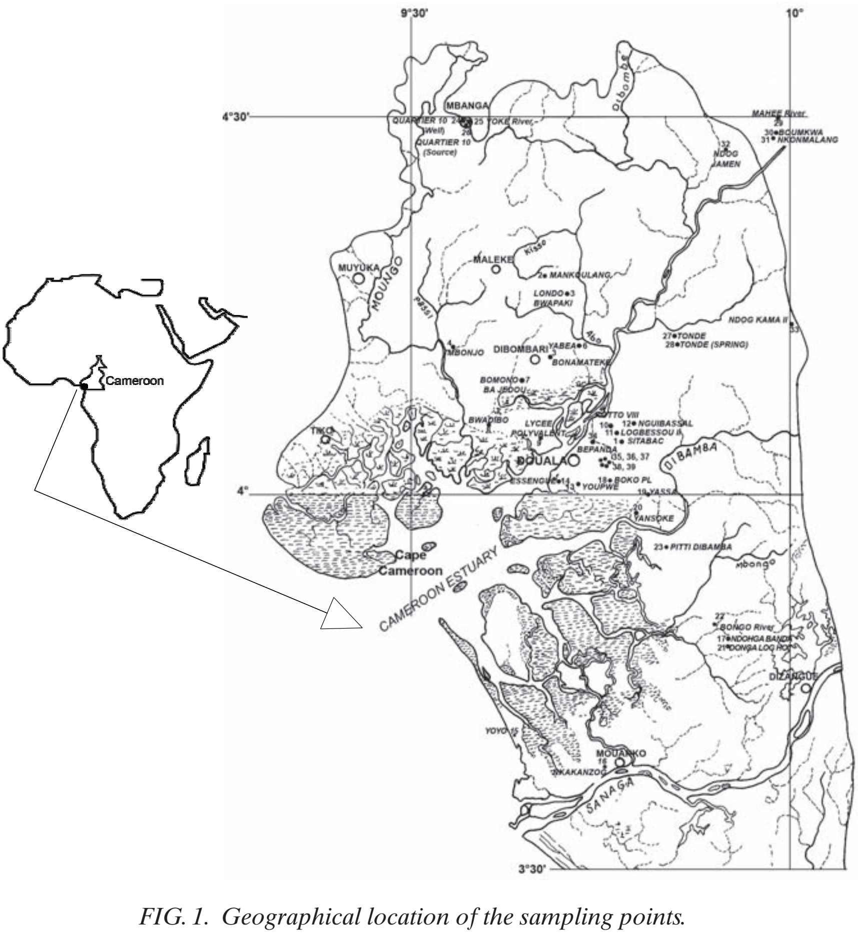

FIG. 1. Geographical location of the sampling points.

The overall structure of the Douala basin has the shape of a monoclinous. The sedimentary sequences (Apto-Albian to Quaternary) is generally composed by conglomeratic sandstones at the base, evolving to more sandy clay formations at the top. Four aquifers can be identified in the sedimentary unit: (1) the basal sandstones, (2) the Paleocene sands, (3) the Mio-Pliocene sands, and, (4) the Late Quaternary aquifer, made by the recent fluviogenic deposits (clay and sands in variable proportions). The Quaternary aquifer is a multilayer system with confined and semi-confined units, surmounted by a shallow groundwater system. The aquifers are currently exploited without real quantitative and qualitative monitoring.

3. SAMPLING AND ANALYTICAL PROCEDURES

The first sampling campaign was conducted during the rainy season (May-June 2004). It concerned 39 points, selected from the deep and dug wells distributed over the whole of the studied area (Fig. 1). This relatively limited number of points results from the criteria of representativeness of sampling sites (the majority of wells collects several water levels were indeed excluded from sampling). The samples were dispatched to the CNESTEN laboratory (Rabat, Morocco) for chemical analyses and to the IAEA laboratory in Vienna (Austria) for isotopic analyses. The results are reported on Table 1.

4. RESULTS AND DISCUSSION

4.1. Field measurements

The temperature of groundwater is in general very similar to the average annual atmospheric values. The interval of variation of conductivity is very large and depends on the type of aquifer. In the zone of outcrop of the basal sandstones, average conductivity is around 130 µS/cm. In the zone of bedrock average conductivity is 40 µS/cm. Quaternary sands have the lowest conductivities (9 µS/cm). In this context, high values of conductivity (947, 908 and 878 µS/cm) are clear indication of water pollution, as already mentioned by previous studies [5]. Sample (15), with a conductivity of 12 430 µS/cm, corresponds to an invasion of marine water. pH of most samples is (79%) lower than 6. This acidity is probably related to the hydrolysis of silicates and the reaction in the ground with humic acids resulting from the decomposition of organic matter in the infiltration zones. Alkalinity, the essential anion

TABLE 1 : CHEMICAL AND ISOTOPIC COMPOSITION OF GROUNDWTER FROM THE QUATERNARY SANDS OF DOUALA SEDIMENTARY BASIN.

Sample	Lithologie	Deepth	pH	Cond.	T°C	Alkalinity	Ca++	Mg++	Na++	K+	Cl--	SO4--	HCO3-	^{18}O	^{2}H	^{3}H
				(µS/cm)					(mg/L)					(‰)	(‰)	(TU)
1	sand	46.40	4.14	28.50	28.00	18.30							0.30	–3.62	–16.19	1.60
2	sand	35.00	4.90	9.10	28.30	27.45	0.02	0.28	0.06	0.01	0.02	0.00	0.42	–3.67	–16.85	1.80
3	sand	32.20	3.98	83	27.80	36.60	0.08	0.20	0.23	0.22	0.21	0.06	0.60	–3.87	–18.15	1.20
4	sand	40.37	4.12	49	27.90	30.50	0.08	0.18	0.14	0.08	0.09	0.01	0.50	–3.54	–16.78	1.60
5	sand	61.01	4.39	18	26.40	27.45	0.16	0.32	0.04	0.01	0.08	0.01	0.45	–3.17	–13.57	1.70
6	sand	82.60	7.28	379	28.30	247.05	1.68	1.66	0.30	0.20	0.04	0.22	4.05	–4.75	–26.19	0.00
7	sand	38.20	4.00	15	27.50	12.20	0.00	0.00	0.00	0.00	0.00	0.00	0.20	–2.96	–14.17	5.30
8	sand	54.70	4.40	52	27.90	33.50	0.11	0.09	0.15	0.08	0.11	0.02	0.55	–2.97	–12.04	1.20
9	sand	46.20	6.14	149	28.40	94.55	0.22	0.28	0.46	0.11	0.14	0.04	1.55	–3.63	–15.34	0.10
10	sand	49.78	3.88	31	27.30	33.55	0.07	0.03	0.04	0.00	0.02	0.05	0.55	–3.26	–12.86	1.90
11	sand	47.20	4.08	27	27.60	42.70	0.12	0.01	0.09	0.02	0.06	0.00	0.70	–3.56	–14.47	1.90
12	sand	39.50	4.18	47	27.20	67.10	0.02	0.14	0.16	0.06	0.10	0.00	0.07	–3.54	–15.40	2.10
13	sand	36.20	6.45	908	28.40	195.20	0.10	0.30	2.93	0.24	11.63	0.00	3.20	–3.91	–13.70	0.10
14	sand	31.28	6.63	878	27.30	286.70	0.38	1.03	3.91	0.35	7.37	0.00	4.70	–3.68	–13.51	0.10
15	sand	29.30	6.40	12430	28.20	521.55	3.10	23.19	72.84	2.86	88.22	0.00	8.56	–3.09	–14.96	0.00
16	sand	29.30	4.15	16	27.20	15.25	0.01	0.01	0.05	0.00	0.03	0.02	0.25	–3.73	–15.70	0.90

TABLE 1 : CHEMICAL AND ISOTOPIC COMPOSITION OF GROUNDWTER FROM THE QUATERNARY SANDS OF DOUALA SEDIMENTARY BASIN (cont.).

17	sand	37.20	3.91	24	25.80	24.40	0.01	0.23	0.03	0.02	0.01	0.01	0.40	–3.63	–13.55	2.70
18	sand	30.30	4.11	55	27.30	36.60	0.12	0.14	0.32	0.02	0.10	0.00	0.60	–3.52	–14.33	1.50
19	sand	53.30	3.92	20	26.60	21.35	0.00	0.00	0.00	0.00	0.00	0.00	0.35	–3.52	–13.62	6.10
20	sand	46.20	4.73	26	27.10	48.80	0.08	0.32	0.05	0.05	0.06	0.04	0.80	–3.58	–14.81	2.20
21	sand	39.20	4.06	17	26.60	21.35	0.03	0.03	0.04	0.01	0.01	0.01	0.35	–3.44	–17.48	2.50
22	river		4.41	20	24.80	39.65	0.03	0.19	0.05	0.02	0.04	0.04	0.65	–2.35	–12.21	2.90
23	sand	48.20	4.20	20	26.80	30.50	0.02	0.06	0.05	0.01	0.03	0.01	0.50	–3.58	–15.80	1.80
24	river		5.19	142	27.70	33.55	0.53	0.40	0.33	0.08	0.30	0.01	0.55	–3.30	–16.72	1.90
25	river		6.11	120	27.00	33.55	0.46	0.32	0.31	0.07	0.23	0.04	0.55	–3.37	–15.70	2.30
26	sand	12.00	5.40	121	27.40	45.75	0.40	0.47	0.29	0.08	0.25	0.01	0.75	–3.34	–15.65	2.60
27	sand	40.20	4.40	28	28.20	36.60	0.50	0.22	0.12	0.01	0.03	0.01	0.60	–3.48	–15.90	2.20
28	river		3.92	43	27.30	30.07	0.09	0.03	0.04	0.03	0.04	0.11	0.49	–3.45	–13.64	5.90
29	river		6.83	31	25.80	42.70	0.10	0.16	0.16	0.05	0.02	0.00	0.70	–3.29	–12.12	2.80
30	Bed rock	21.40	5.30	42	28.20	36.60	0.07	0.15	0.20	0.11	0.06	0.02	0.60	–3.68	–16.29	2.80
31	Bed rock	33.78	5.29	54	27.40	41.75	0.20	0.02	0.17	0.06	0.06	0.00	0.69	–3.72	–15.52	1.70
32	Bed rock	33.16	6.66	345	27.50	247.05	0.08	0.20	0.29	0.06	0.02	0.02	4.05	–3.45	–14.06	1.70
33	Bed rock	18.30	5.48	46	26.90	51.85	2.56	0.45	0.70	0.12	0.04	0.02	0.85	–3.75	–15.01	0.00

TABLE 1 : CHEMICAL AND ISOTOPIC COMPOSITION OF GROUNDWTER FROM THE QUATERNARY SANDS OF DOUALA SEDIMENTARY BASIN (cont.).

34	sand	38.20	6.96	947	28.40	280.60	4.34	4.09	0.90	0.38	9.15	0.00	4.61	–4.55	–21.57	0.60
35	river		4.58	11	25.90	18.50	0.02	0.02	0.06	0.01	0.03	0.00	0.30	–3.49	–11.90	2.10
36	sand	91.60	5.51	110	27.00	70.15	0.43	0.46	0.12	0.10	0.07	0.17	1.15	–3.87	–14.64	0.40
37	sand	87.00	4.75	37	28.00	33.55	0.12	0.39	0.07	0.04	0.03	0.14	0.55	–3.63	–12.52	0.10
38	sand	90	4.54	42	27.60	48.80	0.15	0.09	0.05	0.09	0.04	0.18	0.80	–3.64	–13.50	0.00
39	sand	34.4	3.96	120	27.20	33.55								–3.64	–14.33	4.30

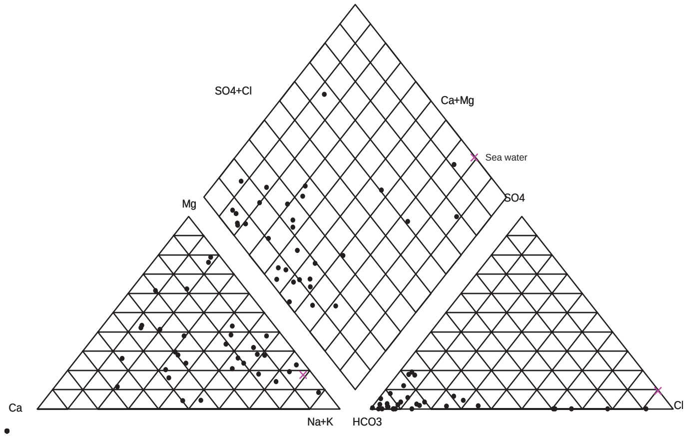

FIG. 2. Chemical composition of Quatermary sand groundwater.

component of water, shows a large range of values (4 and 286.7 mg/L). This attests that mineralization is acquired in the unsatured zone.

4.2. Ionic contents

Chemical composition of water indicates that there is a very weak mineralization in the whole Douala basin. The most common water type is the calcic and sodic bicarbonate type (Fig. 2). The most abundant cation changes according to the sectors of aquifer, which reflects the variety of the mineralogical groups subjected to alteration. The relative weakness of the ions of meteoric origin such as chloride suggests that the evaporating process does not affect mineralization. These results show that nfiltration is relatively fast on the whole Douala basin

4.3. Stable isotopes (oxygen-18 and deuterium)

The isotope contents vary between –2.10 ‰ and –6.10 ‰ for $\delta^{18}O$ (Fig. 4a), and between –11.90 ‰ and –26.19 ‰ for $\delta^{2}H$. Three points deviate from this group (6), (22) and (34). Diagram $\delta^{18}O$ *vs* $\delta^{2}H$ (Fig. 4b) shows that the large majority of the points is located at the top of the Global Meteoric Water Line (GMWL). This reflects the local climatic conditions (cycle evaporation/ precipitation close to the cost[1]). Three groups can be identified on the graph:

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[1] The equatorial climate and the presence of the ocean, induce in the area a "very pure" mechanism of fractional distillation of the vapour masses. That contributes to reduce the annual thermal amplitudes consequently, and, also reduced variation

(i) Group I, corresponds to the current refill in the Douala basin. The isotope contents lie between –4 and –3‰ $\delta^{18}O$ and account for 87‰ of the samples.
(ii) Group II, is represented by one sample (22) and corresponds to a small river, which is located below the GMWL with a content of stable isotopes testifying enrichment by evaporation.
(iii) Group III: constituted by two points, also close to the GMWL but more depleted with $\delta^{18}O$ contents lower than –4.55‰. These samples (6) and (34) seem to correspond to a recharge carried out under climatic conditions different from current conditions [6]. Their geographical position does not make it possible to consider as the result of the altitude effect.

The major part of water samples seem to derive from the fast infiltration of local precipitation, without significant contribution of another type of water. No obvious relation appears between the isotopic composition of water and depths (Fig. 4c). This testifies the homogeneity of the recharge conditions in the surface horizons of the Quaternary aquifer. The isotopically depleted water compared to present day water can come from major aquifer formations facilited by a particular lithological structures or by the influence of pumping.

Finally some points of group I seem to approach the evaporated pole (“group II”), suggesting under certain geomorphological conditions, the influence of surface water.

4.4. Tritium

The tritium concentration measured on surface water and one well allows, in the absence of measurements in precipitation, to estimate the tritium concentration of water of precipitation [7]. In the Douala basin, the tritium concentration of precipitations is close to 2.5 TU. These low concentrations correspond to the contents expected in the tropical coastal areas[1].

The frequency distribution of the tritium concentrations indicates that the majority of ground waters have contents lower than 2 TU (Fig. 3d). A small proportion shows a content higher than 4 TU, which can correspond

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of the isotopic composition of precipitation. Fontes and Olivry in 1976 show that condensations in the area of the Cameroon Mount have the character of a system of fractional distillation which functions in a way very close to the theoretical conditions of Rayleigh, probably exceptional on a worldwide scale.

[1] The natural tritium concentration of precipitation lies between 0 and 5 UT. Because of importance of the marine masses, this content is lower in the Southern Hemisphere than the northern hemisphere. The marine masses which correspond to long residence times are obviously very low in tritium. In general, the tritium concentration of rainwater is lower in coastal zones [8, 9].

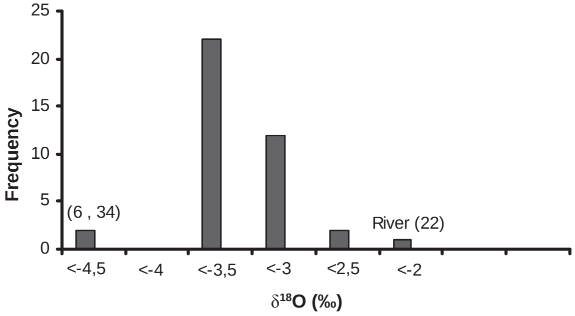

FIG. 3a. Histogram showing the distribution of δ^{18}O.

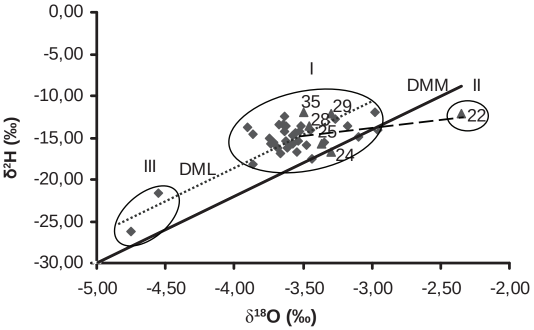

FIG. 3b. Relationship between δ^{2}H and δ^{18}O.

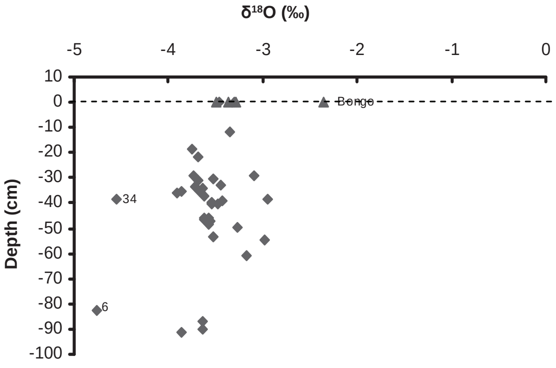

FIG. 3c. Relationship between δ^{18}O and depth.

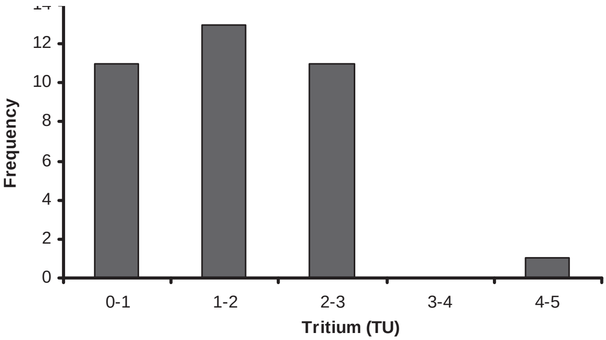

FIG. 3d. Histogram showing the distribution of ^{3}H.

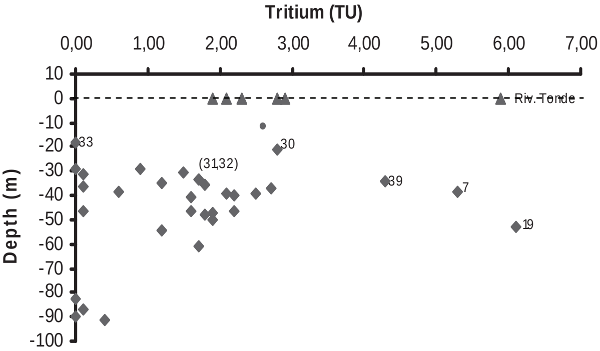

FIG. 3e. Relationship between ^{3}H and depth.

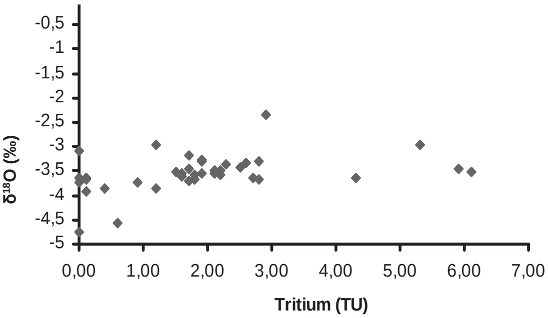

FIG. 3f – Relationship between δ^{18}O and tritium.

to a remanence of the post nuclear tritium whose content dropped because of atmospheric dilution and by the radioactive decay. The distribution of tritium concentrations with depth (Fig. 3e) does not seem to show an univocal relation. Until 60 m of depth, water presents some variations in the tritium concentrations between 0 and 7 TU. The sample collected at greatest depth, between 80 and 100 m, is completely dfree of tritium.

The relation between tritium and the oxygen-18 contents (Fig. 3f) reflects the isotopic homogeneity underlined previously. It seems moreover to reveal a tendency gathering the most depleted water of heavy isotopes with tritium concentrations below the limit of detection.

In order to confirm the assumptions concerning ascent of the local deeper and older water, in particular under the influence of certain pumping, measurements of the carbon-14 activity in dissolved carbonates should be carried out, in particular on water free of tritium.

5. CONCLUSION

The interpretation of the first isotopic results reveals for the major part of the sampled groundwaters, an isotopic homogeneity, indicating the similarity of the processes of recharge. This takes place mainly by direct and fast infiltration of non evaporated precipitation. This homogeneity in the Quaternary aquifer can moreover be accentuated under the effect of pumping, by putting in communication various levels of the multi-layer aquifer, characterized by its lenticular aspect. Some points seem influenced by water with enriched isotopic contents probable due to contribution of a local evaporated surface water. Two points show isotopic characteristics significantly depleted compared to the other points, in different conditions from the whole of the group. These conditions are certainly to be found in natural hydraulic relations or, artificially caused by pumping with lower levels containing of the older water and recharged under previous conditions different from those prevailing at present. The distribution of the tritium concentration confirms this preliminary interpretation. These assumptions will have to be checked by further analyses, including analyses of the carbon-14 activity, in particular on the water free of tritium.

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HYDROCHEMICAL AND ISOTOPIC GROUNDWATER INVESTIGATION IN THE OLTREPÒ REGION (PO VALLEY, NORTHERN ITALY)

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Abstract

A hydrogeologic investigation was conducted using hydrochemistry and isotope techniques in the lowland of the Oltrepò region (Po valley, Northern Italy). Groundwater generally displays a calcium bicarbonate facies. Along major discontinuities, the Po valley brines moves upward and mix with fresh groundwater. Stable isotopes of the water molecule indicate the main aquifer recharge areas, corresponding to the alluvial fans of the major rivers flowing from the Apennine towards the Po river. The observed different deuterium excess in groundwater relates to the origin of precipitation and the location of the river drainage basins. A hydraulic connection, underneath the Po river, between the deep aquifers of the Lomellina and the Oltrepò is also evidenced, implying that deep groundwater is recharged in the pre-alpine area and is several thousand years old.

1. INTRODUCTION

The Oltrepò Pavese lowland has in recent years shown symptoms of increased aquifer vulnerability. Surface water shortage, especially during summer, has resulted in an increased exploitation of groundwater not only for domestic and industrial use, but also for irrigation. The peculiar hydrogeological conditions determine the presence of low productivity aquifers in several sectors of the plain. The lack of a regional hydrogeological investigation providing adequate tools for rational groundwater exploitation has led to this study, aiming at defining the origin of groundwater through the joint interpretation of hydrogeological, hydrochemical and isotopic data.

2. GEOLOGICAL AND HYDROGEOLOGICAL SETTING

The lowland of the Oltrepò region is delimited to the North by the Po river and to the South by the hills of the Apennine chain. It is characterised by the presence of quaternary alluvial deposits derived from Apennine watercourses, creating coalescent alluvial fans when reaching the plain, and by the presence of the Po river. Alluvial deposits host the main regional aquifer, overlying the mostly impervious mio-pliocenic marine sequence. The tectonic disturbances, related to the presence of buried thrusts faults of the Apennine front, affect the marine substratum and control the distribution of the permeable deposits forming the Oltrepò aquifer [1]. In particular, the presence of a "structural high", delimited to the North by an important buried discontinuity, known in the literature as "Voghera fault" [2], strongly conditions the hydrological asset of the investigated area. In the Oltrepò area, the fault is oriented SW-NE and runs from the town of Casteggio to the Po river (Fig. 1). South of the Voghera fault, the alluvial deposits are reduced in thickness to only a few tens of meters and have an uneven distribution, ranging from a minimum of 2 km close to Casteggio, to a maximum of 5–6 km in Central and Eastern Oltrepò.

The area located north of the Voghera fault shows instead a rapid increase in the aquifer thickness, reaching more than 100 m, because of the deepening of

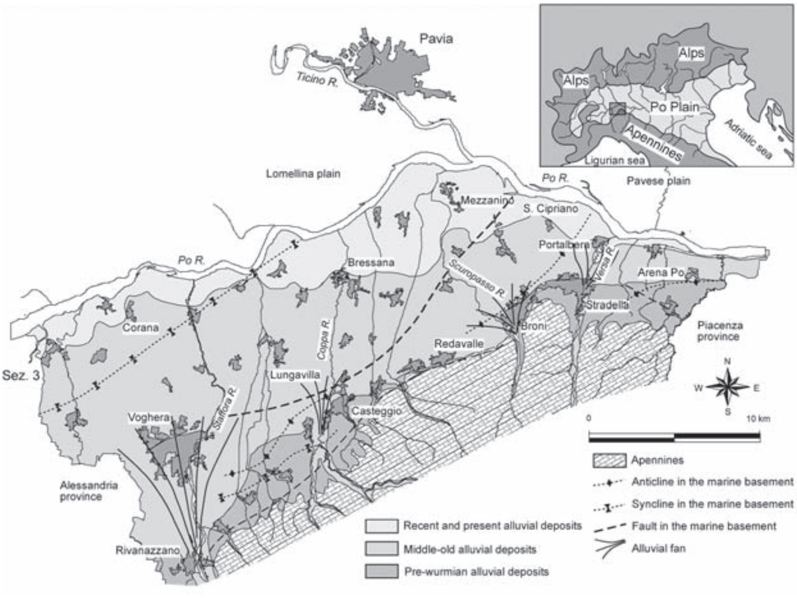

FIG. 1. Geological map of the investigated area .

the mio-pliocenic substratum [3]. An important aquifer thickness is also found in western Oltrepò, where the impervious marine substratum is excavated in a large depression corresponding to the Staffora river alluvial fan. Nevertheless, the lack of deep wells allows neither the reconstruction of the deep aquifer to the North, nor the derivation of its hydrodynamic parameters.

Groundwater in Oltrepo aquifer flows northward to the regional drainage axis corresponding to the Po river.

3. METHODS OF INVESTIGATION

A detailed reconstruction of the hydrogeological setting was performed through the well inventory and the stratigraphic data interpretation, serving as a basis for groundwater sampling. More than 80 samples and 60 samples from municipal and private wells respectively were analysed for major ions and for some trace elements. Among those, more than 50 samples were selected for the determination of stable isotopes of the water molecule. In addition, ^{14}C dating was performed on one well. Chemical analyses were done by the Dipartimento di Scienze della Terra, University of Pavia. Anions and cations were determined by ion chromatography. All reported values have ionic balance within 5%. Samples for stable isotope analysis were collected and prepared according to the standard procedures [4]. A ^{14}C dating was performed by conventional beta-counting. Its result is reported in Percent Modern Carbon (pMC) along with the analytical error.

4. HYDROCHEMISTRY

Two main groundwater groups may be distinguished based on hydrochemical characteristics: calcium-bicarbonate water, the most common, and sodium-chloride water (Fig. 2).

The first group displays a medium grade mineralisation, with an E.C. ranging from 800 and 1200 μS/cm; the hydrofacies is mainly calcium-bicarbonate, locally with a magnesium contribution. Bicarbonates range between 300 and 700 mg/L, calcium between 50 and 200 mg/L, while magnesium varies between 10 and 50 mg/L, sometimes reaching 80 mg/L. Sulphates normally range between 50 and 180 mg/L, although some samples show higher values (up to 250 mg/L) or lower values (few or tens of mg/L); chloride concentration never exceeds 100 mg/L.

The distribution of bicarbonate content is not homogenous. Areas with low HCO_3^- correspond to the Apennine rivers alluvial fans and are related to

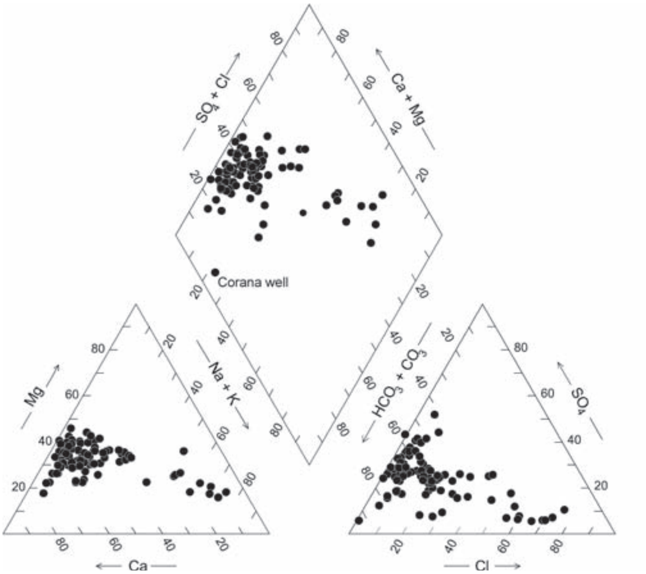

FIG. 2. Piper diagram.

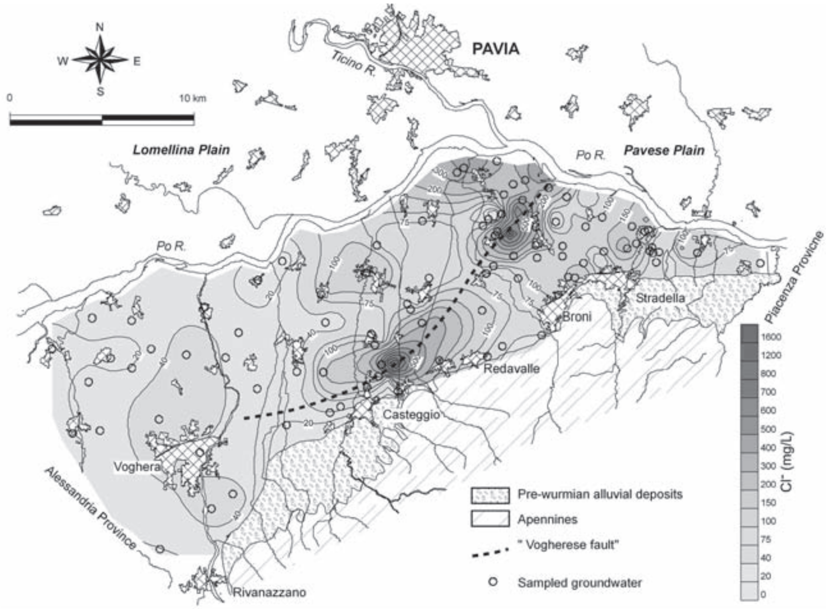

FIG. 3. Distribution of Cl^- concentration and location of sampled groundwater.

groundwater recharge, as evident in the Staffora river area. The Staffora river water displays a lower mineralization ($HCO_3^- \approx 300–350$ mg/L) and its recharge influence can be observed as far as the city of Voghera, reaching the Po river. Bicarbonates tend to increase moving North in the aquifer because of longer residence time and enhanced water rock interaction. South-west of the Ticino and Po rivers' confluence, the low bicarbonate content (350 mg/L) is due to mixing with groundwater coming from aquifers located North of the Po river. Indeed, groundwater from the phreatic aquifer of the Pavia plain is generally less mineralised, with bicarbonate content lower than 250 mg/L [5]. Therefore in the Oltrepò lowland, bicarbonate contents evidence the recharge areas and rise in content in areas with lower aquifer transmissivities.

The second groundwater type is characterised by an elevated mineralisation. E.C. reaches 4000–5000 µS/cm and chloride concentration may exceed 1600 mg/L. The highest chloride concentrations are observed in a narrow band running from the town of Casteggio to the confluence between the Po and Ticino rivers, corresponding to the buried structure of the Voghera fault (Fig. 3).

Highest salinities are found immediately North of the town of Casteggio and South of the Po river. Chloride contents range between 700 and 1600 mg/L, well above drinking water standards, making groundwater unsuitable even for irrigation. The origin of sodium-chloride water is attributed to groundwater mixing with the deep seated brines of the Po Plain [6]. These brines, displaying higher salinity than present-day sea water, are trapped in the deeper portions of the Po Valley aquifer since late Messinian. Their mobility, which is generally restricted because of their high density, can occur along the major discontinuities characterising the Apennine thrust belts.

5. ISOTOPE INVESTIGATION

Oxyen-18 ranges between –9.07‰ and –7.14‰, although most of the samples are comprised between –8.50‰ and –7.90‰. Deuterium ranges between –62.0‰ and –48.2‰; even in this case most of the samples fall in a narrow range between –57.5‰ and –51.5‰. A linear regression of all data provides an equation:

$$\delta^2H = 6.0 \times \delta^{18}O - 6.1$$

which is not in agreement with precipitation data for Northern Italy [7]. Considering instead a more likely slope value of approximately 8, samples fall instead between two lines differing in deuterium excess (Fig. 4), whose equations are:

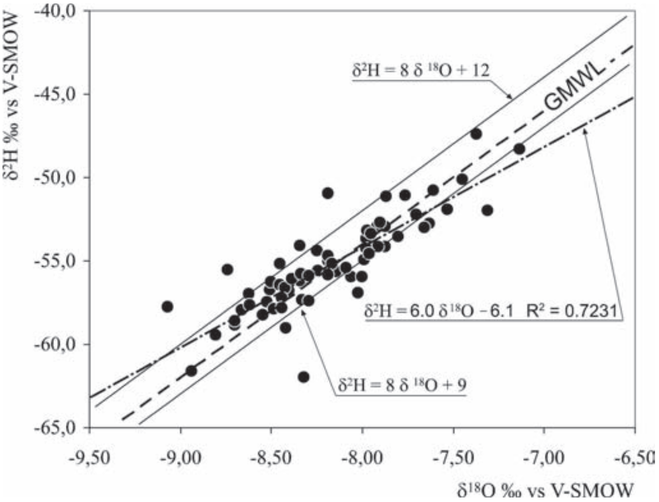

FIG. 4. $\delta^2H - \delta^{18}O$ plot for groundwater samples.

$$\delta^2H = 8 \times \delta^{18}O + 12$$

and

$$\delta^2H = 8 \times \delta^{18}O + 9.$$

The Oxygen-18 distribution is not uniform in the Oltrepò lowland (Fig. 5a). Depleted groundwater is clearly located in correspondence of areas where recharge by the Apennine streams occurs. Depleted values ($\delta^{18}O$ = –8.3‰ to –8.7‰) are related to the higher mean altitude of the river catchments found in the western sector of the Oltrepò area, corresponding to the recharge area of the Staffora river (Fig. 5b). Its catchment indeed extends to higher elevation and reaches the Apennine ridge. Therefore, the Staffora river can receive a higher contribution of precipitation derived from humid air masses coming from the Ligurian Sea. This deuterium excess is similar to the value reported by [7] for the Pontremoli station (d = 12.4), located on the South-western side of the Apennine ridge. The other Apennine catchments are instead fed by precipitation originating in the climatic context of the Po Valley.

A different origin, confirmed both by hydrochemistry and stable isotopes, can be evoked for groundwater tapped by the Corana well, in the north-western sector of the Oltrepò lowland. Groundwater extracted from a sand layer between 132 and 144 m depth shows a lower mineralisation (Fig. 2) and a quite depleted $\delta^{18}O$ composition (–9.07‰). These parameters are very similar

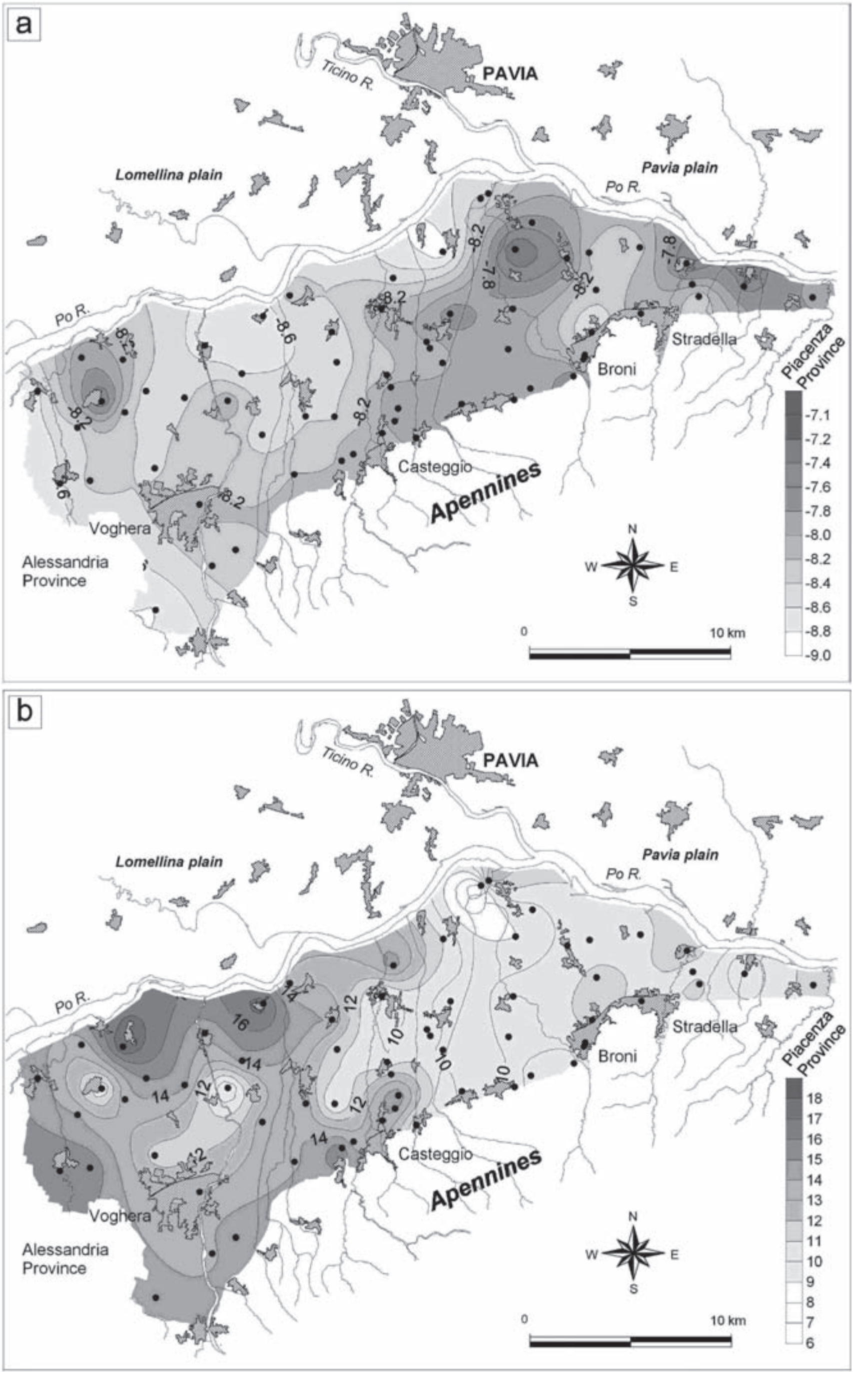

FIG. 5. Distribution map of δ^{18} (permil) (a) and deuterium excess (b).

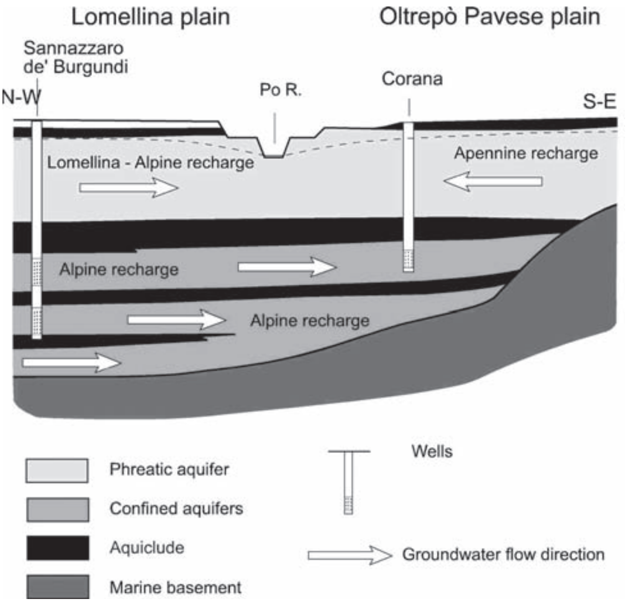

FIG.6. Schematic hydrogeological section across the Corana well.

to those characterising deep groundwater from the Lomellina plain, located North of the Po river [5]. ^{14}C dating was performed on this sample, providing a low activity value (A^{14}C = 27.2 ± 1.8 pMC and δ^{13}C of –16.50‰ ± 0.01‰ vs V-PDB). Groundwater age was calculated by correcting the raw activity according to the Pearson model [8] with the same input parameters used for the Lomellina aquifers [5], providing an estimated age of 7000 years. This value is in agreement with what is found at the same depth for the confined Lomellina aquifers.

Therefore stratigraphic, hydrochemical and isotopic data for the Corana well water point to a recharge area located in the Alpine foothills. Groundwater would then slowly flow from North to South in the confined aquifers of the Novara and Lomellina region, evidencing a hydraulic connection existing underneath the Po river (Fig. 6).

6. CONCLUSION

The results of this study clearly evidence how a hydrochemical and isotopic investigation coupled to detailed hydrogeological reconstructions can help defining groundwater circulation (location of the recharge area, mixing processes, interconnections). Recharge areas for the Oltrepò aquifer have been identified, corresponding to the alluvial fans of the major Apennine streams. This especially applies to the Staffora river. The Oltrepò aquifer is generally well protected from superficial input of exotic substances. On the other hand, critical areas where deep seated brines rise and contaminate groundwater have been identified. In addition, this study also allowed identifying interconnections with deep aquifers located North of the Po river and recharged in the Alpine area. The Corana area therefore, represents a promising area for the location of new wells.

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ISOTOPE AND TRACER TECHNIQUES APPLIED TO GROUNDWATER INVESTIGATIONS IN THE MUNICIPALITY OF ARAGUARI, MG, BRAZIL[1]

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Abstract

During the years 2004–2005 an investigation was carried out by CDTN and UFMG in the western border of the state of Minas Gerais, Brazil, aimed at assessing the water resources related to the Guarani Aquifer System in the region of Araguari. The project was supported by the Fund of Universities (BNPPW/OAS) and other donors and was designed to cover a whole hydrological year. The main water supply for domestic, industrial and agricultural consumption derives from groundwater extraction, and the hydrologic system is under permanent stress. Among other classical tools, isotopic techniques were used to study groundwater origin, recharge processes, transit times and infiltration rates. For such an accomplishment 51 water samples were analyzed for their stable (deuterium and oxygen-18) and radioactive (tritium) environmental isotopic composition. Tracer techniques applying artificial tritium were used to study infiltration rates in selected areas. The overall results show that local waters fit fairly well the GMWL, with a shift in the deuterium excess due to some previous evaporation; also, the groundwater is locally recharged. The exponential model was used to estimate water age, and the results show that most of the water samples (84%) contain young waters with a renewal time up to 30 years. Infiltration rates are high due to local conditions (high pluviosity,

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plain relief and high permeability of surface soil, and results seem to be in good agreement with figures assessed by means of classical water balance methods.

1. INTRODUCTION

The municipality of Araguari, situated at 569 km west of Belo Horizonte, the state capital, is located at the north-northeastern border of the sedimentary basin of Paraná River, between Paranaíba and Araguari Rivers. The area under investigation is restricted to the one in which the exposition of the sequence of rocks of the Paraná basin can be found. Its top is constituted by an extensive plateau, a watershed with altitudes ranging from 900 to 950 m, which spreads itself over an area of 1,405 km^2 (comprising 51% of the county area), over which most (91%) of the population, estimated to be of 108,672 inhabitants (IBGE, 2005), is concentrated.

Mean annual temperature is around 21.9ºC and the pluviometric regime is typical of tropical areas, presenting a mean annual value of precipitations of 1 589 mm/yr (IBGE, 2000, in www.almg.gov.br). The rainy season spans from October to March.

Water supply for the plateau (public supply, irrigation and industrial uses) is mostly from groundwate. Water is abstracted from tubular wells drilled predominantly in the Bauru aquifer.

The extreme dependency of the municipality upon the groundwater resources has already given rise to conflicts among users in areas of greater water demand, like the agricultural region of the sub-basin of Araras stream. Poor knowledge of the quantitative potential and of the dynamics of the Guarani Aquifer System (GAS) in the area have brought large insecurity to the state management organization and to the local water supply company.

The general objective of the project was a consistent investigation of the GAS in the municipality, including the application of isotope and tracer techniques in the water balance and flow dynamics assessment.

2. HYDROGEOLOGY OF THE AREA

The GAS lies over the metasedimentary neoproterozoic rocks of Araxá Group and of the gneissic-granulitic Complex and post-tectonic granitoids (Dardenne, 2000). The Mesozoic units, belonging to the Paraná sedimentary basin, are correlated to São Bento Group (Botucatu and Serra Geral Formations) and to Bauru Group (Marília Formation).

The Botucatu Formation is very restricted; only two occurrences lying directly upon the rock substrate have been identified, which is typical of a basin border. Thus, it does not seem to be feasible to exploit the spring from thus formation.

The basaltic rocks of Serra Geral Formation comprise the second aquifer in exploiting importance nowadays. It occurs directly upon Araxá Group, with mean thickness ranging from 200 to 250 m; it is highly fractured and forms columnar disjunction.

Bauru aquifer (Marília Formation) is formed, in its base, by a layer of conglomerates, 5 to 6 m thick, saturated, followed by a package of friable silt-clayish sandstones which, together with the eluvionary-colluvionary laterized tertiary covers (5 to 10 m), reaches mean thickness ranging from 50 to 60 m. The aquifer (832.4 km^2) extends itself for about 30% of the county area, with mean altitudes around 880 m.

Most of the natural recharge occurs from direct infiltration through the covering layer of silt-clayish soils. The aquifer has high storage capacity (0.12) and high permeability (2.3×10^{-3} cm/s). It is by far the most exploited aquifer, presenting a mean productivity of 21 m^3/h. Due to the fact that it is a shallow formation, and also owing to its natural lithologic constitution, uncontrolled and clandestine drilling of wells is a widespread practice. Taking also into account that the whole urban area is edificated over this system, it is not difficult to realize the high pollution risks imposed to the groundwater supplying system.

3. RESEARCH DEVELOPMENT

Available geologic studies, field reconnaissance of aquifer unities and of discharge areas (springs), associated with information derived from a database containing 122 selected tubular wells, were used as the base for the establishment of a physical hydrogeological model of the GAS in the municipality. Precise altimetric measurements of 98 wells were made.

The application of artificial tritium as radioactive tracer was used to assess the aquifer recharge. Five distinct areas were selected, all of them provided with rain gauges, three of them in the hydrogeologic domains of Bauru (B) sandstones and two in the domains of the Serra Geral (SG) basalts.

The hydrochemistry was characterized by the analysis of water samples collected in deep wells, shallow wells, springs and surface water bodies. Physical-chemical and chemical Parameters were analyzed (Ca^{2+}, Mg^{2+}, Na^+, K^+, Mn^{2+}, CO_3^{2-}, HCO_3^-, Cl^-, NO_3^-, SO_4^{2-}, total Fe, pH, electrical conductivity) in 34 samples. Basically, this characterization was aimed at establishing distinctions between waters from Bauru and Serra Geral aquifers and evaluating waters for different types of utilization.

Environmental tritium (^3H) and stable isotopes of oxygen (^{18}O) and hydrogen (^2H) were analyzed in 51 samples basically to determine transit times (water age) and to elucidate water origin and recharge processes.

4. RESULTS AND DISCUSSION

4.1. Water chemistry

Bauru aquifer waters are usually acidic; pH ranges between 4.6 and 5.3. They also have low salinity; values of TDS are usually under 15 mg/L and the electric conductivity is less than 30 µS/cm. This shows the large influence of precipitation waters in the recharge. On the other hand, waters from aquifer Serra Geral have a pH around 7, and higher salinity (TDS around 60 µS/cm).

4.2. Tritiated water to estimate groundwater recharge

Table 1 shows the result of the evolution of the water column as traced by the evolution of the tritium plume for the time period ranging from the end of October 2004 to the beginning of November 2005, during which 5 field campaigns were carried out. This way, the results cover the complete hydrologic year 2004/2005.

Although the figures for infiltration rates may seem very high, except for Piracaíba, it has to be taken into account that these values are coherent with the local high pluviosity, with the plain relief and with the high soil permeability.

Moreover, the percent values of recharge are in very good agreement with the values estimated by means of the water balance method for the sub-

TABLE 1. INFILTRATION IN AREAS SELECTED FOR TRITIUM INJECTION

Site	Infiltration (mm)	% of precipitation
Amanhece (B)	807	51
Viveiro Brasil (B)	614	43
Piracaíba (SG)	389	24
Piçarrão (SG)	651	41
Sacoman (B)	638	51

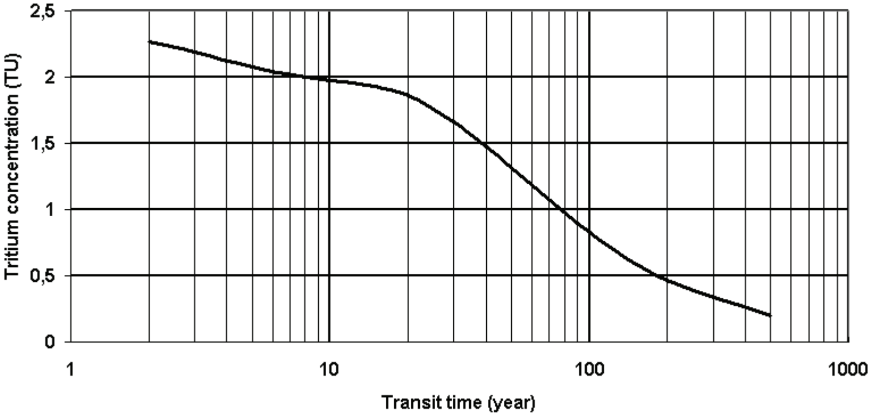

FIG. 1. Relationship between the tritium concentration and the transit time of groundwater in Araguari.

basins encompassing the sites of Amanhece (48%) and Sacoman (50%), also applied in this study. The sites Piracaíba and Piçarrão present covers composed predominantly by clayish soils, the former been located in a slope of the natural terrain. The site Viveiro Brasil is located at a naturally vegetated area, subject to water losses by evapotranspiration.

4.3. Environmental tritium to estimate water age

Mean residence time for the waters directly recharged into the Bauru formation was achieved by means of the measurement of environmental tritium concentration in groundwater and surface water samples. These figures were confronted with the ones obtained in the precipitation of selected GNIP – Global Network of Isotopes in Precipitation/IAEA — stations (Brasília, Porto Alegre and Kaitoke), taken as input data for the exponential model considered in this work.

Fig. 1 shows the tritium concentration versus residence time of groundwater curve for the local conditions. In a broad sense, it can be stated that waters presenting tritium concentrations close to or greater than 2 TU originate from recent precipitations and present transit times shorter than 10 years. On the other hand, waters with tritium concentrations less than 1.3 TU contain significant amounts of waters from precipitations previous to 1953. The results show the waters in Araguari to be relatively young, with transit times up to 30 years for 43 samples (84.3% of 51 samples), varying from 30 to 60 years for 7 samples (13.7%) and one single sample with 90 years, collected out of the interest area.

4.4. Stable isotopes in studying groundwater origin

Fig. 2 shows the values of ^{18}O and ^{2}H deviations for all samples (51) of surface and groundwater. The local water line obtained by plotting these deviations from the standard reference (VSMOW) appears to be well fitted to the global meteoric water line (GMWL), indicating that local recharge is basically originated from direct precipitation onto the soil surface.

Precipitation waters have not gone through important evaporation processes before their infiltration and have not either gone through isotopic exchange with endogenous gases or with rock minerals rich in oxygen.

The water samples collected in water points in Serra Geral unit constitute a group with its own characteristics, allowing the consideration of values between –6.1 to –6.5‰ for δ^{18}O and between –39 and –43‰ for δ^{2}H, for the waters directly infiltrated into the basalts. It was verified that these waters are relatively heavier than the waters from Bauru Aquifer, perhaps due to the altitude effect, taking into account that they were collected very close to the foot, or base, of the basaltic formation, some 300 m below the top of the plateau.

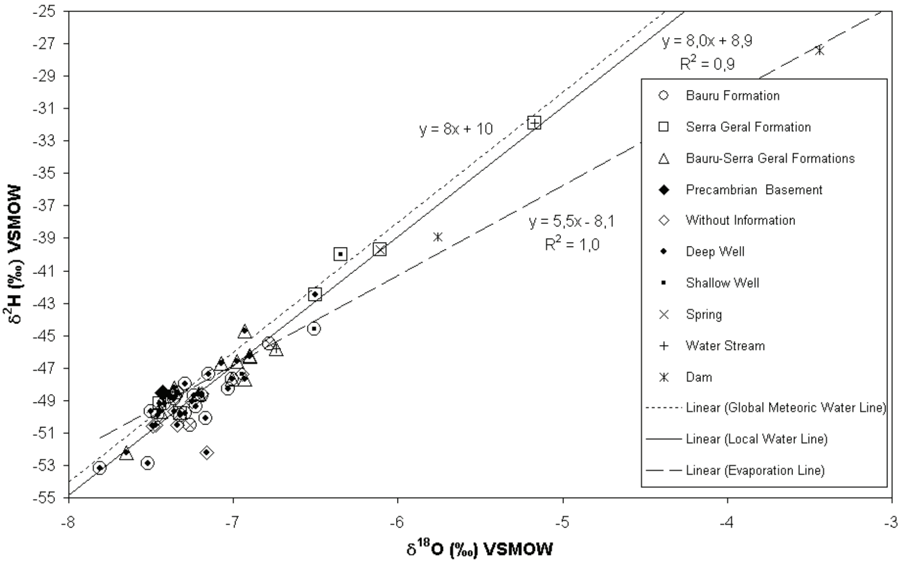

FIG. 2. The relationship for ^{18}O and ^{2}H in surface and groundwater of Araguari.

Another set of points in evidence in the diagram refers to those formed by samples coming from wells in Bauru Formation, wells crossing both formations and other wells without lithological information. This set of points shows values for $\delta^{18}O$ ranging from –6.9 to –7.5‰, and values for $\delta^{2}H$ ranging from –44.7 to –50.6‰, which could be taken as being typical for waters of the Bauru formation. These may contain a certain amount of waters from the basaltic formation (mixed wells). Wells included in this group present waters with a deuterium excess lower than 8‰, which could be an indication that these waters have gone through some evaporation prior to their infiltration.

5. CONCLUSIONS

The high values of the effective infiltration (recharge) obtained by the injection of tritiated water are coherent with the high pluviosity, plain relief and with the high permeability of the soil.

The low residence time of the groundwater, less than 40 years, as assessed by the concentration of environmental tritium, agrees with what should be expected for shallow flows, free aquifers locally recharged. This fact is corroborated by the results obtained by plotting the isotopic deviations of ^{18}O and ^{2}H for the groundwater in a local line, which will closely fit the global meteoric water line (GMWL). Therefore, the recharge is originated from direct precipitation, which is also shown by the hydro chemical characteristics of the groundwater, particularly the very low values of pH, electrical conductivity and dissolved solids.

Comparing the equipotential lines obtained by monitoring the static level of selected tubular wells with the isolines of the isotopic deviations of ^{18}O and ^{2}H and with the isolines for the environmental tritium concentrations, which were obtained through the spatial distribution of these parameters for water samples collected exclusively in the Bauru Aquifer, it can be concluded that: 1) the information about the recharge areas obtained by the isotopic tools are in good agreement with the equipotential lines in two regions (high course of Araras creek and at the southeastern extremity of the area); both present high concentration of young waters, enriched in heavier isotopes; 2) at the urban settlement there is a depletion of the stable isotopes, what could be indebted to the intensive aquifer exploitation.

The authors consider that the isotopic studies thus carried out should be considered as a preliminary approach and should be given due sequence in order to propitiate a better isotopic characterization of the aquifer units, including eventual seasonal variations, and a better understanding of the groundwater flow mechanisms in terms of pathways, transit times and definition of the overexploited areas.

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GROUNDWATER RESOURCES FROM CARBONATE ROCKS IN MOUNTAINOUS REGIONS: HYDROCHEMICAL AND ISOTOPIC SURVEY OF GROUNDWATERS IN THE WESTERN PYRENEES (FRANCE)

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Abstract

Carbonate rock aquifers are one of the main water supply sources for the French Western Pyrenees. The discontinuous structure of these reservoirs is a main obstacle to the development of such resources. By the way, since no other aquifer can be tapped, many communities have decided to improve their knowledge of the main springs over the whole region. Four sites have been considered from 2003 to 2006 and have been the object of multidisciplinary investigations including: geological mapping, geophysical investigations, dye tracing experiments and in situ hydrochemical survey. Stable isotopes have been analysed on both rainfall (^{18}O, ^{2}H) and spring waters (^{18}O, ^{2}H, ^{13}C, ^{34}S) in order to evaluate the origin of groundwaters, their residence time within the systems and to appreciate the occurrence of exchanges with other aquifers. Finally, this study provides a good example of how to include hydrogeochemistry and isotopic tools in a water supply management policy.

1. INTRODUCTION

In the French Pyrenees groundwater from carbonate rocks are considered as a huge potential, able to supply to drinking water needs. In the coming years, these resources will be called for to compensate superficial groundwater resources which are constantly decreasing because of the intense agricultural activity within the area and which quality is more and more unable to meet drinking water standards. The development of carbonate rocks groundwater is planned through the exploitation of many springs scattered over large areas and mainly concerns the South of the Béarn region and more precisely the area of the “Chaînons Béarnais”, here considered as a test zone.

The discontinuous structure of these reservoirs is a main obstacle to development and exploitation, but since no other aquifer can be tapped in these areas, many communities have decided to improve the knowledge of the main springs of the region, a few of them are already exploited for water supply, but problems linked to the lack of detailed management can lead in some cases to water supply disruption because of quality problems especially during strong rain episodes.

The rigorous French legislation on drinking water quality, inherited from the European Water Directive forces administrations in charge of groundwater management and distribution to pay minute attention to resource protection. Efficient management is strongly correlated to proper protection perimeter definition around springs and proactive regulation of land uses over impluvium. For water supply managers the objectives are to minimise the potential cost of water treatment and to guaranty the continuous delivery to consumers.

So the goal of this study is to provide new information on a selection of experimental sites representative of semi mountainous carbonate aquifers, to evaluate their potential as water supply sources and to propose recommendation concerning the management of their exploitation. To meet these objectives we propose a multidisciplinary approach combining geological field investigation and hydrochemical survey.

Two main case studies will be presented here, the Orbe spring and the Ourtau spring. Two additional sites will also be mentioned, the Mourtes spring and the Gourgouch spring. They all represent the main outlet of carbonate rock aquifers from Jurassic and Cretaceous age and can be considered as representatives of most reservoirs from this region of the Pyrenees.

Orbe, Ourtau and Mourtès springs were chosen because they are used as water supply by rural communities (respectively, Arette, Oloron-Sainte-Marie and Sarrance), and are thus particularly interesting in term of water quality and water resource availability. Gourgouch spring is also of major importance since it is used to supply an important fish breeding with pure cold waters.

During high rainfall periods, Orbe and Ourtau springs are turbid as is often the case for karstic springs and the turbidity values can exceed 200 NTU. This poses serious problems for the water treatment stations located near the springs. Turbid episodes mainly occur during high water when it reaches its peak and the spring water can become unfit for human consumption.

2. GEOGRAPHICAL AND GEOLOGICAL SETTING

2.1. Physiography

The study area is located in the southwestern part of France, around 50 km South from Pau city in the Western Pyrenees region (Fig. 1). The "Chaînons Béarnais" area constitutes the first piedmont relief of the Pyrenees coming from the North. The physiography of the region is an alternation of three semi-mountainous strong horizontal reliefs with depressions in between constituting the so-called "Chaînons Béarnais". These reliefs can reach an altitude of about 2050 m with an average of 1200 m. The "Chaînons Béarnais" are crossed through by three main rivers, the Vert d'Arette River, the Gave d'Aspe River and the Gave d'Ossau River, which all flow from South to North and reach the Adour Valley.

2.2. Geology

The geology of the "Chaînons Béarnais" structure is characterised by the abundance of carbonated formations from Jurassic to Cretaceous mainly composed of pure limestone with Urgonian facies, dolomitic limestone and dolomite (black dolomite from the Jurassic). These hard rocks constitute the three major reliefs of the area and often lye in sub vertical position; between them West-Est oriented valleys correspond to Albian marls and flysch from the Upper Cretaceous. The actual geometry of the deposits results from the Pyrenean orogenesis during the Eocene and is attributed to compression movements, as a result, the structure of the "Chaînons Béarnais" can be interpreted as a succession of tilted blocks with broken folds in between. During the Mesozoic, the region has endured many extension-distension phases entailing the intrusion of magmatic rocks like lherzolite and ophite (doleritic basalts) within Triassic and Cretaceous sediments. These ultramafic igneous rocks are always wrapped in versicolor and gypseous more or less endured dolomitic marls attributed to Keuper or to an hydrothermal layer resulting from the intrusion within the carbonates.

2.3. Hydrology

The average amount of rainfall in the “Chaînons Béarnais” is about 1450 mm per year (average from 1980 to 2004). This quite important amount can be explained by the proximity of the Atlantic Ocean which brings numerous cool and humid air masses and by the Pyrenees Mountains which play the role of a climatic barrier. The climate in the study area can be considered as oceanic attenuated and is characterized by very rainy autumn and beginning of winter, rainy spring and relatively dry summer with sometimes intense storm episodes. Temperatures are cool in winter (4.9°C) and mild in summer (18.7°C), the annual average temperature is close to 11.2°C (average from 1995 to 2005). So the most favourable period for recharge processes is the beginning of winter and the end of spring. The average evapotranspiration calculated from 2004 to 2005 is around 970 mm. Thus, on the same period of calculation, the average amount of effective recharge to the local aquifers can be estimated about 595 mm per year that is to say approximately 40% of the total amount of rainfall. The recharge processes of the aquifers are mainly diffuse.

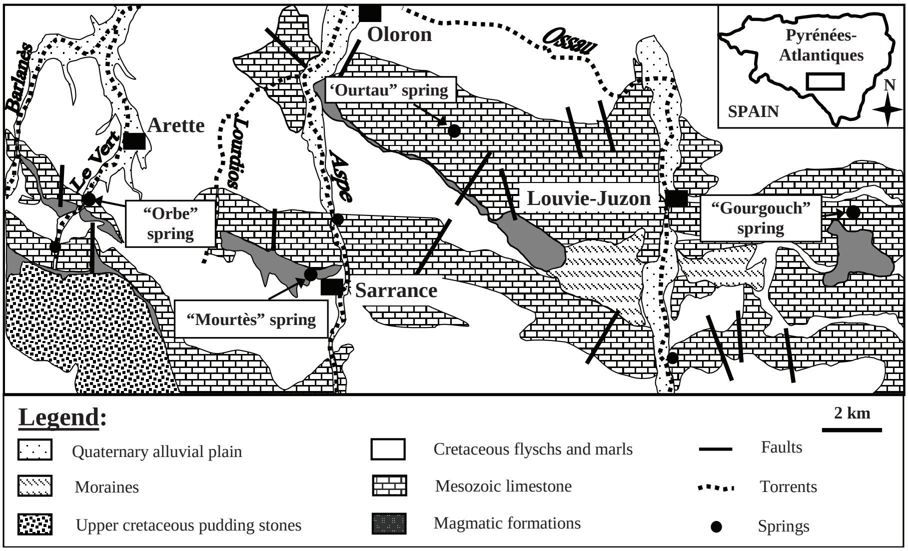

FIG. 1. Location of the springs and simplified geological map of the “Chaînons Béarnais”, from [1].

2.4. Soils and land uses

Land uses over the study area are mostly rural with deciduous forests on the highest reliefs and pasture lands in the valleys. Human settlements are limited and composed of small villages of no more than an hundred of inhabitants. Wastewater discharged by domestic residences is not collected by sewerage system but released in the environment via individual treatment devices. Soils are mainly thin brown soils developed on carbonate rocks and most of the time filling more or less developed lapiez.

3. METHOD

In order to characterise the framework in which the aquifers develop and the functioning of the systems, a multidisciplinary approach was chosen, including:

(a) Determination of the geometry of the systems. That aims at defining the most probable structure of the aquifers. To meet this objective a detailed study of the geology and structure of the systems was carried out, especially on Orbe and Ourtau systems.
(b) Characterization of the hydrodynamic functioning using hydrogeochemistry and natural tracing. Stable isotopes were analyzed on both rainfall (^{18}O, ^{2}H) and spring waters (^{18}O, ^{2}H, ^{13}C, ^{34}S) in order to evaluate the origin of groundwaters, their residence time within the systems and to appreciate the occurrence of exchanges with other aquifers.
(c) Characterization of turbid episodes in relation with dissolved transport. This information about particular transport will be interpreted in conjunction with electrical conductivity data which represents the dissolved transport within the systems.

4. RESULTS

Physical and chemical characteristics of the carbonate groundwaters and their variations during the hydrological year partly depend on the geologic environment. These characteristics are mainly ruled by the groundwater flow condition, flow velocity, residence time, confine or unconfined flow conduits, depending on the importance of the development of karst features, controlling the distribution of slow and quick flow in the infiltration zone as well as in the drowned zone. As a consequence, groundwater geochemistry can provide essential information concerning the dynamic of the aquifer systems [2].

This study includes physico-chemical parameter as temperature, electrical conductivity and pH data. Major ions (Ca^{2+}, Mg^{2+}, Na^{+}, K+, HCO_3^-, SO_4^{2-}, Cl^-, NO_3^-) were also measured every week on all four springs water.

4.1. Hydrochemistry

In the majority of the cases the Pyrenean groundwaters have a calcium bicarbonated chemical facies. However, the “Gourgouch”, “Ourtau” and “Mourtès” springs are supplied by the geological formations dated from the Jurassic. These last being primarily constituted of dolomites, water of these aquifers are systematically enriched in magnesium. This remark is in particular valid for the “Gourgouch” and Ourtau springs for which the magnesium concentrations can reach 25 mg/L. Rich magnesium water is the indication of relatively long residence time within the aquifer. For the “Ourtau” karstic spring this phenomenon is remarkable, after strong rainfall a significant fall of the magnesium concentration can be observed where values are reduced to half (10 mg/L) of that in low water periods. The sulphate concentrations are very interesting because of their hydrogeological meaning. Basically, a possible origin of these ions is the clayey level existing at the ophite and limestone contact; this kind of formation can actually contain some anhydrite ($CaSO_4$) or gypsum ($CaSO_4 \cdot 2H_2O$). This observation could confirm that the water would circulate along this low permeability clayey formation and thus, that the ophite would play an important role in the definition of the limits of spring catchment area.

From an environmental point of view and more particularly on the quality of water, the groundwater resources in the “Chaînons Béarnais” are rather good. Aside from the nitrate concentrations of the “Mourtès” ‘spring: 7 mg/L on average, but below the drinking water standard equal to 50 mg/L.

The “Orbe” spring emerges from the Lower Cretaceous limestones and the only fundamental difference between the Cretaceous and the Jurassic aquifers is underlined by the magnesium concentration in water. Nevertheless, the Urgonian limestones are often more fractured than the Jurassic formations and the Cretaceous aquifers are systematically of karstic type. These groundwater resources show really good characteristics (quality and quantity), but the problem of turbidity remains a factor limiting their use and is difficult to manage.

4.2. Isotope geochemistry

Stable isotopes of the water molecule were analyzed on rainfall collected from February 2004 to May 2005. Samples were collected every week. Data are presented in Fig. 2 and show the following regional meteoric water line for French Western Pyrenees: $\delta^2H = 6.6\ ^{18}O + 4.4$.

$\delta^{18}O$ and δ^2H data obtained from Orbe and Ourtau springs are consistent with the isotopic content of rainfall. That tends to prove the meteoric origin of groundwater of carbonate rocks in the region. Mixing between river waters which were suspected in the case of Orbe spring are not supported by any isotopic evidence.

The origin of sulphate was also investigated using ^{34}S and ^{18}O of dissolved SO_4^{2-}. The question was the exact origin of these ions considering the existence of two different potential sources of sulphur, in the Albian marls (as pyrite) and in the clayey layer between ophites and aquifer limestones (as gypsum crystals). Results show values from 6.5 to 11.5 $\delta^{34}S_{SO4}$‰ CDT and from 9.7 to 13.3 $\delta^{18}O_{SO4}$‰ VSMOW. These data are consistent with an evaporitic or atmospheric origin of sulphate, but not with pyrite oxidation.

In order to appreciate residence time and water rock interactions, $\delta^{13}C$ were also measured in Orbe and Ourtau groundwater. The relationship between rainfall and $\delta^{13}C$ content of dissolved inorganic carbon shows strong interactions between carbonate matrix and groundwater especially during dry season when $\delta^{13}C$ values are enriched (Fig. 3). This behavior suggests an important contribution of unsaturated zone to the summer discharge [3].

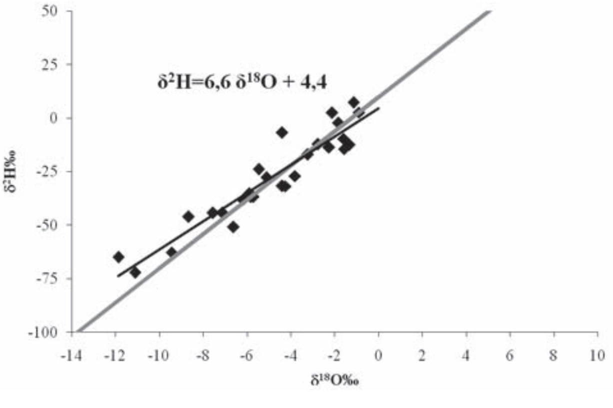

FIG. 2. Regional meteoric water line for the French Western Pyrenees.

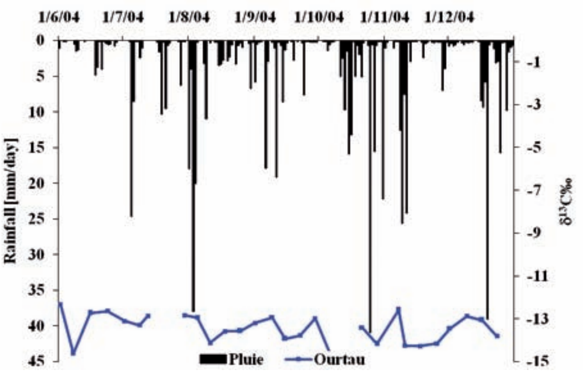

FIG. 3. Evolution of $\delta^{13}C$ of the total dissolved inorganic carbon in Ourtau.

4.3. Turbid episodes

Karstic aquifers like the "Orbe" and "Ourtau" springs remain very vulnerable especially to the turbidity problems. Fig. 4 shows an example of turbid episode of approximately 5 days long. In this case, people in charge of water delivery must use another resource to supply the inhabitants with drinking water. In such situations alluvial wells are often used. The detailed study of the turbidity/conductivity relationships according to [4, 5] allows identification of the processes causing turbid episodes. In the "Chaînons Béarnais" area the two following processes can be found: resuspension of

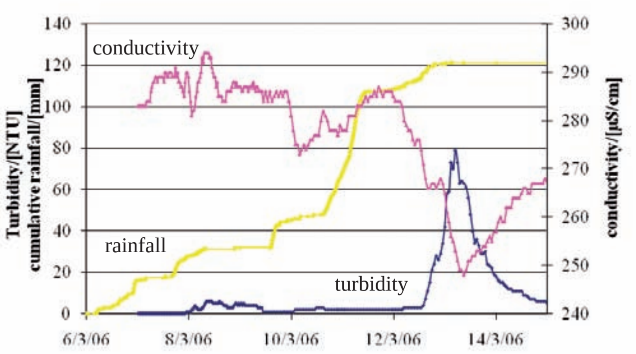

FIG. 4. Example of turbid episode (Orbe spring).

autochthonous material within the aquifer (Ourtau spring) or allochthonous suspended material (Orbe spring).

5. CONCLUSION

Groundwaters from French Western Pyrenees represent a huge potential in term of drinking water supply source. The detailed study of the geometry and hydrological functioning will help to the definition of the protection perimeters around the springs and at term will set up the basis of a better management of groundwater resource in mountainous areas.

ACKNOWLEDGEMENTS

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ISOTOPIC INDICATORS FOR THE PROCESSES FROM THE CHEMOAUTOTROPHIC ECOSYSTEM OF THE MOVILE CAVE, ROMANIA[1]

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Abstract

Measurements of the natural isotopic content for hydrogen, oxygen, sulphur and carbon for samples collected from cave served as the basis for the characterization of the cave components and processes. Based on the water isotopes, the surveys have elucidated the origin of the water from cave. The water has meteoric origin, from modern and submodern precipitation fallen over a higher altitude than that of the emergence. The cave is the buffer system between the deep confined aquifer and the unconfined aquifer from Sarmatian deposits. The $\delta^{34}S$ values in the sulphide and sulphate from the Movile Cave and from the Black Sea present distinct values. The sulphide comes from deep aquifers and sulphate is produced in cave by sulphide oxidizing in presence of microorganisms. All forms of inorganic carbon are isotopically light. CO_2 in the cave atmosphere is a mixture of heavier CO_2 resulting from the dissolution of limestone and lighter CO_2 resulting from the oxidization of the organic matter and/or methane. The bicarbonate in water is at isotopic equilibrium with CO_2. The organisms sampled from

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the cave are isotopically light versus surface congeners, suggesting dependence on the chemoautotrophic production occurring in the cave.

1. INTRODUCTION

The Movile Cave is one of the caves that have received the most attention during the last years from the scientific community because it is a peculiar ecosystem completely driven by chemosynthesis. The cave is located in the SE part of Romania, a few kilometers from the Black Sea. The cave area has a semi-arid climate with average temperatures of 11.5°C. Relatively small, presenting two levels (upper level is dry, lower level has a small lake connected with the groundwater table) and located at a depth approximately of 20 m bellow the surface, the cave is impermeable for infiltration of water and air from atmosphere. The Movile Cave is a groundwater ecosystem rich in H_2S (8–12 mg/L) and in contact with an atmosphere poor in O_2 (7–10%), rich in CO_2 (2–3.5%) and containing significant amounts of CH_4 (1–2%). The Movile Cave is populated with terrestrial and aquatic invertebrates (33 are endemic) adapted to their underground prison [1-3]. The geology was described in Ref. [4]. The detritic Paleozoic formation is intercepted between 560 and 1200 m. This is overlain by about 500m of compact limestone and dolomite belonging to the Mesozoic and Eocene. These deposits form a unified karstifiable complex separated from the upper layers by layers of clay and share by Romania and Bulgaria. Over them the Sarmatian limestones have been deposited in a thickness of 60 to 150 m. The quaternary deposits cover the Sarmatian limestones. Three karstification levels were described, the cave developing in the uppermost karstification level [2]. The tectonic structure for the South Dobrogea indicates the three major faults (Fig. 1) and three minor faults that intersect in the Mangalia Swamp, the last being major for the Mangalia area.

The aim of this study was to elucidate the water origin from cave, this problem being disputed (paleowater/ from Danube/ from sea/ from recent precipitation [1-4]), and to point out the evidence and constrains of the stable isotope signature in the cave processes.

2. METHODS

The method consists in measurements of natural isotope abundances and their interpretation. The data consist from measurements for the following elements: *hydrogen and oxygen* from water samples collected from three types of sources (wells, springs and residential fountains) located in surrounding of

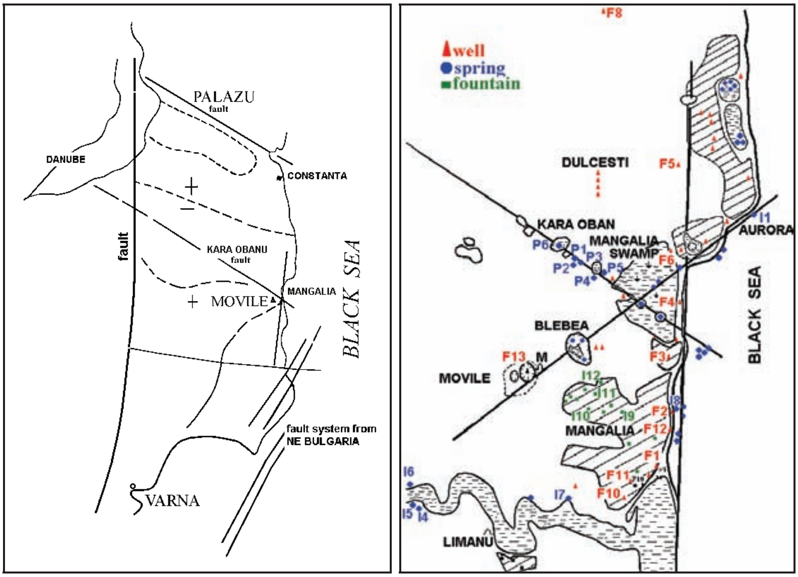

FIG. 1. The tectonic structure (left) and the location of the sampling points (right).

the cave, *carbon and oxygen* from samples of organic and inorganic matter (atmospheric CO_2, $CaCO_3$ of bedrock and bicarbonate from water samples) and *sulphur* from H_2S and SO_4^{2-} collected in the lower level of the cave. The map of the sampling points location is in Fig. 1.The isotopic measurements were performed in Romania (Cluj-Napoca and Rm. Valcea), USA (Univ. Michigan, the Geochron. Lab. Krueger Inc., Cambridge, MA, Univ. Alaska-Fairbanks and Indiana Univ.) and Canada (Univ. Hamilton). The isotopic analyses are reported as permil deviations against the international standards (VSMOW for water isotopes, VPDB for ^{13}C and CDT for ^{34}S). Measurement reproducibility was better than ±0.5‰ for ^{2}H, ±2 TU for ^{3}H and ±0.2‰ for ^{18}O, ^{13}C and ^{34}S.

3. RESULTS AND DISCUSSION

3.1. Water isotopes

The measurements of $^{2}H/^{1}H$ and $^{18}O/^{16}O$ ratios were made for the water collected in March 1994 and for water samples monthly collected during a meteoric cycle (Sept 95–Jan 97) were made the measurements of $^{2}H/^{1}H$ ratios, tritium concentrations and densities (ΔDens). The $\delta^{2}H$ values in precipitation over study area have been estimated with reasonable precision from the database of GNIP [5] and from δ^2H values calculated for temperature recorded in area with the equation established for precipitation fallen over Cluj-Napoca, Romania [6]:

$$\delta^2\text{H (‰)} = 3.2864 \times \text{T (°C)} - 103.79 \qquad R^2 = 0.959$$

The δ^{18}O values of the groundwater vary between –13.6‰ and –9.22‰, and for Danube River are about –10.1‰. The δ^2H values vary between –105.4‰ and –68.1‰ for monthly samples and between –98.8‰ and –72.9‰ for average values. These values are not typical for lowland local water, which present $\delta^2\text{H} > -70$‰. These values exclude the imported water from Black Sea ($\delta^2\text{H} \approx -25$‰) or the Danube River ($\delta^2\text{H} \approx -75$‰) as origin for the cave water.

The analysis of the δ^2H – $\delta^{18}O$ covariance. Comparing the δ^2H and δ^{18}O values for the groundwater with the values for precipitation (Fig. 2), most samples are depleted by 1.0–2.5‰ in ^{18}O and by 10–20‰ in ^{2}H. The groundwater samples are distributed along the GMWL [7] with a very good correlation between the δ^{18}O and δ^2H values. The slopes of the local MWLs are slightly higher than of GMWL and the y-intercepts for wells are of about 19‰, closing of those of the Mediterranean MWLs [8]. The surface water plots on a line with slope below 8 as a result of the evaporation in humid atmosphere (~85%), the lakes being located near the seacoast. Deuterium excess (d_{excess}), as an indicator

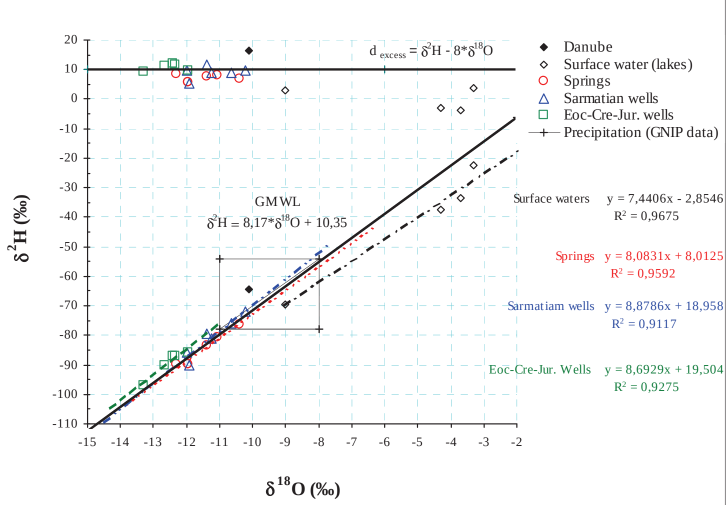

FIG. 2. δ^2H – $\delta^{18}O$ covariance.

of air circulation complexity, has the average values between 6‰ and 12.2‰ and is similar to SE Europe precipitation. These results suggest the meteoric origin of the groundwater and smaller kinetic effects during evaporation-condensation processes for the precipitation input into the ground.

δ^2H- time correlation. Fig. 3 presents the time variation of the δ^2H values for the groundwater samples. The seasonal deuterium variation from precipitation input is reproduced, after damping and delay. The deuterium concentration is lower in summer that in winter. Similar results were recorded by Flora and Longinelli [9] for karstic springs along the Adriatic coast, near Trieste. This six-month phase shift of the isotopic composition with respect to the seasonal variation of precipitation suggests that the contribution of the more elevated inland part of watershed is dominated during summer and water moves on a long way through channels in limestone. The δ^2H values suggest that part of the groundwater has been recharged at a much higher altitude (over 1000 m) than that of the emergence and the shifts of the δ values to more negative values are in correlation with the relations for altitude effect for precipitation. In the δ^2H-time variation the peak shape during spring indicates the contribution of the snowmelt from a region, with lower altitude and closer to the study area. It is an example of hydraulic interconnection between the upper aquifer and deeper aquifer.

The groundwater depleted in water isotopes in comparison to present precipitation can be due to the recharge during the Pleistocene, but the tritium concentration (between 1 and 14 TU) indicates the existence of two water types: one is a mix of submodern and modern water (Movile water) and the another represents modern recharge (<5 to 10 years), which means recent infiltration from precipitation to the aquifer system [10]. All measurements of the tritium activities show the six-month phase shift that appears with deuterium (values

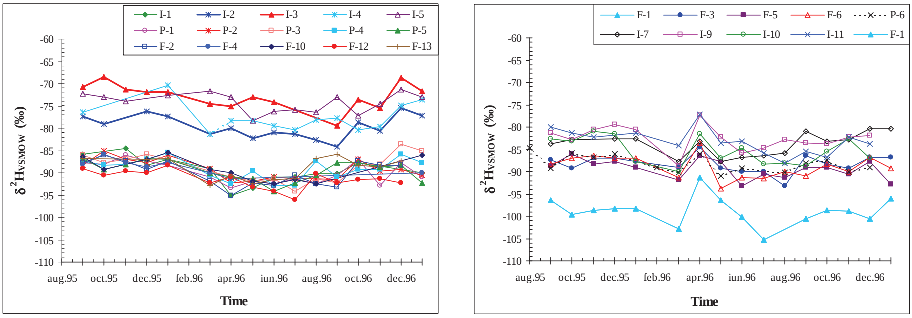

FIG. 3. The variation in time of the δ^2H values.

between 1 and 5.5 TU for samples collected in March and between 3.7 and 14.7 TU for those collected in September). This result supports the conclusion that the water from Movile Cave is not old water. The presence of post-bomb water in the cave and deep groundwater is due to the recent recharge by larger volumes of present-day precipitation from high altitude.

The correlation of the average values of δ^2H and ΔDens and mixing lines. The δ^2H and ΔDens average values are plotted in Fig.4 and delineate three

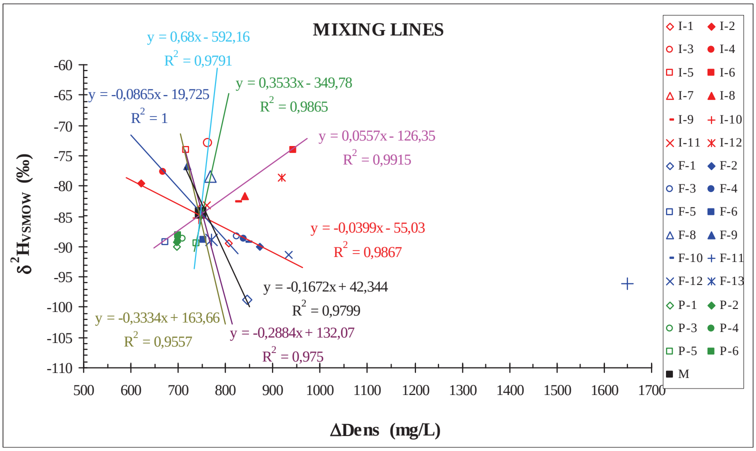

FIG. 4. The mixing lines for the water of cave on diagram δ^2H - ΔDens.

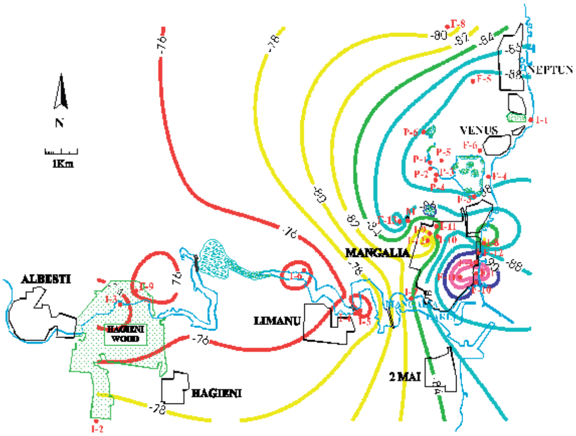

FIG. 5. The spatial distribution of the δ^2H average values.

water types: (1) waters with $\delta^2H < -88‰$; (2) samples with δ^2H of mean value; $\delta^2H \approx -85‰$; and (3) waters with $\delta^2H > -80‰$. For most samples the δ^2H values are lower than –80‰. On the diagram δ^2H–ΔDens, the mixing lines show that the water from residential fountains and the cave belong to a mixing water system. One end member is isotopically light water and another end member is isotopically enriched water.

The spatial variation of the δ^2H values. In the deuterium distribution maps (Fig. 5) the closed lines point out the areas with the water movement is vertical and delineate the sites with isotopically light water input, as the endmembers for isotopic mixing. The isotopically lightest waters are thermal sulphidic waters and are located in close proximity to the geological fault that brings sulphidic waters to the surface. The Movile Cave site appears to be a mix between isotopically light water from the high altitude coming on the faults and isotopically higher water following the Movile-Aurora fault.

3.2 Isotopic content for sulphur.

The $\delta^{34}S$ in H_2S and SO_4^{2-} samples fall in the range of the natural variation ($-40‰ < \delta^{34}S < +40‰$), but present distinct values. The $\delta^{34}S$ values in H_2S are of -40‰ for the Black Sea, between +5.9 and +8.3‰ for the Movile Cave and of +5.1‰ for the Vaclino Well (Bulgaria). The $\delta^{34}S$ values in SO_4^{2-} are of +26.6‰ for the Black Sea, of +1.1‰ for the Movile Cave and of –2.6‰ for the Vaclino Well. These values indicate that the Black Sea is not a source of H_2S in cave, the H_2S coming from deep aquifers (Mesozoic) spreads to Sarmatian aquifers through the faults [4]. Hydrogen sulfide was detected in the cave atmosphere only in the proximity of the air–water interface in concentrations of 1–5 ppm. No hydrogen sulfide was detected in the upper level of cave [1–3, 11]. The water entering Movile Cave is much lower in sulfate concentration (max. 0.01mmol) compared to the surface of the lake in the cave (max. 0.1 mmol). The presence of sulfate only at the water surface indicates that hydrogen sulfide is oxidized only at water-air interface. Hydrogen sulfide evaporates at the air-water interface and redissolves in the water-film covering the limestone cave walls. In aqueous phases, at pH of about 7, H_2S and HS^- occur in approximately equal amounts. Oxygen in the cave atmosphere also dissolves in the water and reacts with HS^- to form elemental sulfur. SO_4^{2-} is produced in cave by sulphide oxidizing (biochemical reactions) which are kinetic pathways by which the light isotopes are preferentially selected over the heavy isotopes. Studies of isotope effects during sulphide oxidation by chemosynthetic sulphur bacteria showed that in the transformation series $H^2S \rightarrow HS^- \rightarrow S \rightarrow SO_3^- \rightarrow SO_4^{2-}$ involves larger isotope effects, favoring ^{34}S in H_2S [12].

3.3 Carbon isotopes

The $\delta^{13}C$ values are shown in Fig. 6. All forms of inorganic carbon in the cave are isotopically light. The high levels of carbon dioxide in the atmosphere of Movile Cave accelerate dissolution by the condensed water on the surface of the limestone walls. Carbon dioxide in the cave atmosphere is isotopically light ($\delta^{13}C$ = –22 to –24‰) compared to surface carbon dioxide ($\delta^{13}C$ = –7.8‰) and is most probable a mixture of heavier carbon dioxide from the dissolution of limestone ($CaCO_3$) ($\delta^{13}C$ = –4‰) by sulfuric acid [13] and lighter carbon dioxide presumably oxidization of the organic matter ($\delta^{13}C$ = –44 ‰) or methane ($\delta^{13}C$ = –60 ‰). Decomposition of the OM follows a kinetic pathway by which the light isotopes (^{12}C and ^{1}H) are preferentially selected over the heavy isotopes and methane ascends, most probable, from the deep aquifer [12, 14]. Respiration of the cave biota is also source of isotopically light carbon dioxide. Assuming a fractionation of approximately –25‰ between inorganic carbon and the biomass of chemoautotrophs, the carbon isotope values for the microbial mat ($\delta^{13}C$ = –41 to –46‰) are as expected [12].

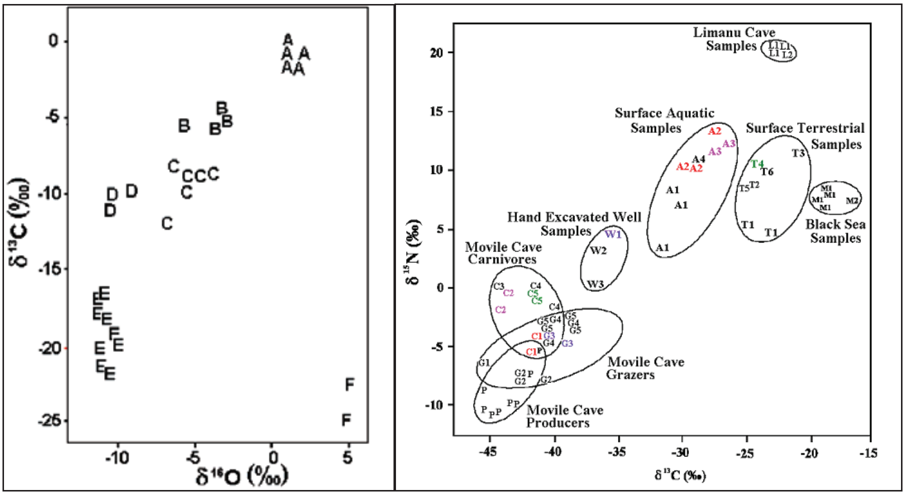

FIG. 6. Carbon isotope ratios in samples from Movile Cave.
Left: samples of CO_2 and $CaCO_3$. A.— Limestone bedrock not affected by corrosion. B.— Corroded surface of passages walls and detached oolites. C.—Boulders of limestone bedrock laying on the passage floor. D.— Botroidal calcite crusts filling the fractures within the bedrock. E. —Aragonite crust covering the passage floor and the base of the walls. F— Carbon dioxide from Movile Cave.
Right: samples of organisms from the Movile Cave area.

The content of ^{13}C for the samples of surface and cave dwelling communities show different concentrations (Fig 6 right). The $\delta^{13}C$ for cave organisms are very low due to the biochemical reactions mediated by bacteria for the production of food and energy. This is a kinetic pathway by which the ^{12}C are preferentially selected over the ^{13}C. Isotopic ratios observed in surface dwelling organisms reflect dependence on photosynthetic production, whereas values for organisms from Movile Cave suggest dependence on the chemoautotrophic production. For three pairs of surface — cave congeners pairs (pairs T_4 and C_5, A_3 and C_2, A_2 and C_1) the $\delta^{13}C$ reflect the habitats in which the species occur.

4. CONCLUSIONS

Movile Cave is a natural laboratory for complex research on the life of organisms based on chemoautotrophic processes. The following conclusions have been obtained:

- The origin of the water from the Movile Cave is meteoric, a mix of the modern (<5 to 10 years) and submodern (prior to 1950s) precipitation fallen over a higher altitude than that of emergence. Most probably, the water from the cave area comes from the Balkan Plateau. The cave is the buffer system between the deep confined aquifer and the upper unconfined aquifer from Sarmatian deposits. The lack of significant of water from the surface and the presence of highly corrosive sulfidic groundwaters in Mangalia region support the hypothesis that Movile Cave has a hypogenic origin.
- H_2S coming from deep aquifers (Mesozoic, Palaeogene) spreads to Sarmatian aquifers. The Black Sea is not the source of H_2S in cave and sulphate is result of the oxidation of sulphide.
- The organic matter is isotopically light due to the biochemical reactions mediated by the microorganisms. These are kinetic pathways by which the light isotopes are preferentially selected over the heavy isotopes.

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DETERMINATION OF TRANSBOUNDARY GROUNDWATER FLOW BY ISOTOPIC TRACING

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Abstract

The hydrodynamics of the groundwater flow in large sedimentary basins are very difficult to establish since detailed topographic data are often not available in connection with the lack of adapted topographic levelling. The only available topographic maps are small scales ones at 1/200 000 with contour lines equidistant of 40 metres and do not allow a characterisation of large scale flows in the case of the large trans-boundary basins such as the south-eastern edge of the Taoudenni sedimentary basin shared by Burkina Faso and Mali. An isotope hydrology investigation has been carried out in the basin of Taoudenni shared by Burkina Faso and Mali. It shows that the combination of independent information derived from isotope data with groundwater flow modelling can highly improve the understanding of the system including its structure (mono or multi-layer), boundary conditions and recharge mechanisms as well as the groundwater reserves renewal processes.

1. INTRODUCTION

Groundwater provides 85% of the water for human consumption in Burkina Faso while only 15% are supplied by surface water. These figures are much higher than the world average and demonstrate the urgent need to preserve the groundwater resources for both quantitative and qualitative reasons. Overall, the Burkina Faso aquifers can be divided into two large groups of formations: firstly, the crystalline bedrock, which covers 82% of the territory, but has a poor exploitation potential (low flow rates, frequent dry boreholes), secondly, the sedimentary zone in the extreme south-eastern part of the Taoudeni basin. Although this represents less than 20% of the surface area of the country, it contains a great multi-layered aquifer system which offers a large production potential: it provides considerable support for the economic development of the country.

2. HYDROGEOLOGICAL DESCRIPTION OF THE AQUIFER SYSTEM IN THE TAOUDENI SEDIMENTARY BASIN, BURKINA FASO

The Taoudeni basin is the largest sedimentary basin of Upper Precambrian and Palaeozoic age in Africa. It stretches across Mali, Mauritania and the two Guineas and overlaps slightly into Algeria, Senegal, Sierra Leon and Burkina Faso. Overall, its structure is simple: the most recent formations crop out in its sandy centre and the dip rarely exceeds 1°.

The south-eastern margin of the Taoudeni basin coincides with the right bank of the river Niger which cuts through the basin for almost 1500 km along a west-east axis (Fig.1). The surface area of the south-eastern margin of the sedimentary basin (Mali and Burkina Faso) is close to 260 000 km^2 of which 40 000 km^2 (i.e., less than 20%) belong to Burkina Faso.

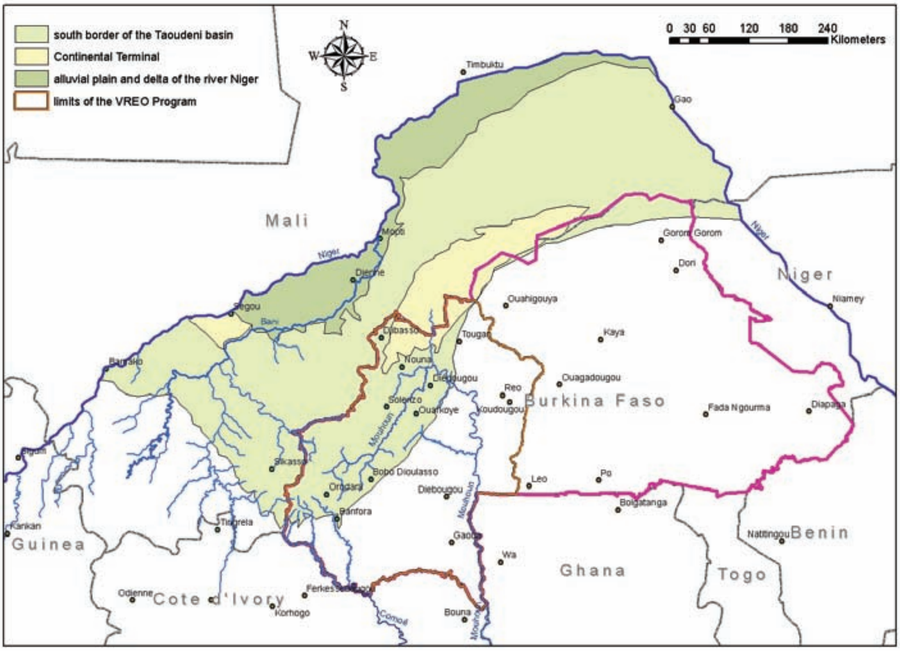

FIG. 1. Map showing location of study area.

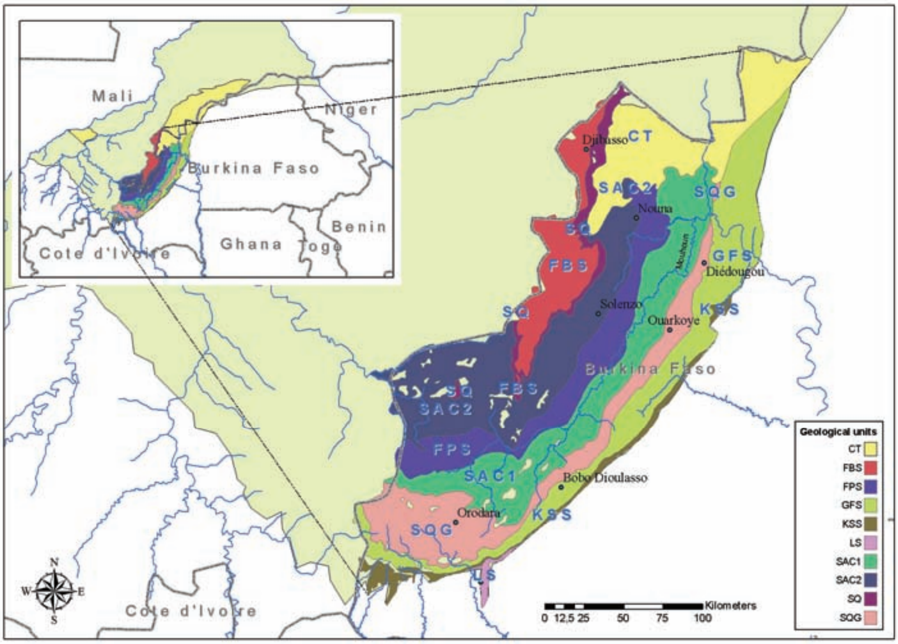

FIG. 2. Different formations in the Burkina Faso part of the basin.

In the Burkina Faso part of the basin, nine formations have been identified from the bottom up [1] as shown in Fig. 2: Lower Sandstone (LS), Kawara-Sindou Sandstone (KSS), Glauconitic Fine Sandstone (GFS), Sandstone with Quartz Grains (SQG), Guena-Souroukoundinga Siltstone, Argillite and Carbonate rocks (SAC 1), Fine Pink Sandstone (FPS), Samandeni-Kiébani Sandstone, Argillite and Carbonate rocks (SAC 2 or "Toun schist"), Fo Siltstone and Quartzite (SQ or "Koutiala sandstone") and Fo-Bandiagara Sandstone (FBS). These formations, mainly dominated by sandstones, are piled up in nearly horizontal layers with a slight dip toward the north-west (around 2°) and generally thicken toward the west.

The hydrogeological characteristics of the Burkina Faso sedimentary series can be determined by interpreting, among others, the available quantitative and qualitative data collected in the study area. Within the RESO programme [2] the hydrogeological data were summarised for each formation. The aquifers are assumed to be confined in about 30% of the boreholes where data required to estimate the storage coefficient are insufficient.

When the maps of aquifer depth and piezometry are examined together (Fig. 3), it seems clear that the principal rivers in the Banifing basin, in particular

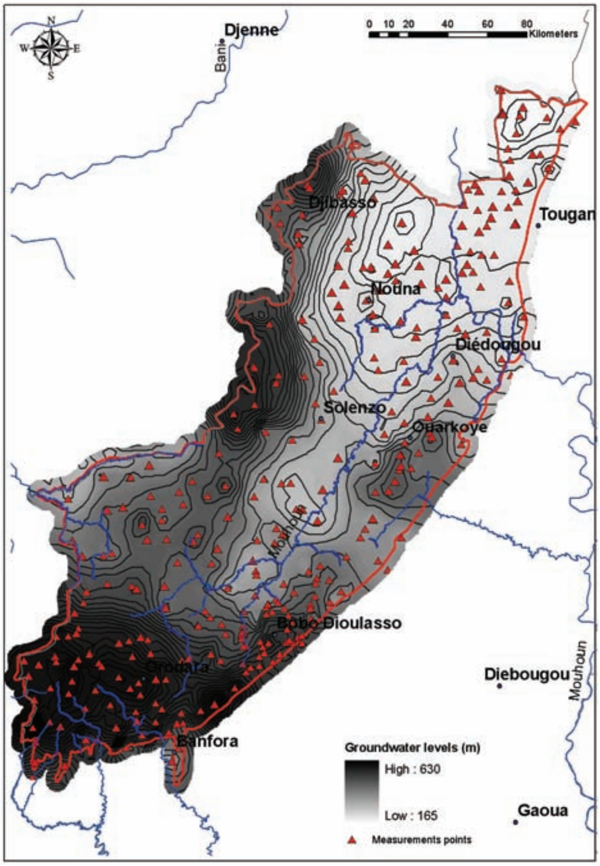

FIG. 3. Map showing aquifer and piezometry.

those along the administrative border with Mali, have marked drainage characteristics and are probably at equilibrium with the aquifer [3].

The analysis of the spatial interpretation of the piezometry highlights:

- the study area in Burkina Faso shows mean piezometric heights ranging between 635 and 165 m;
- there is a strong similarity between the topographical ridges that define the main watershed basins (Mouhoun, Camoé, Banifing) and the piezometric highs. For the groundwater flow in the sedimentary aquifers, there is generall conformity between the hydrogeological basins and the main surface basins;
- the piezometry indicates four main hydrogeological basins:

- the Mouhoun hydrogeological basin which covers almost 80% of the study zone and drains most of the groundwater in the Burkina Faso sedimentary zone along a north-northeast axis toward the plain of Sourou and even further downstream, in the direction of the Gondo depression. The effect of the Mouhoun River is clearly visible in the piezometry. The only natural outgoing groundwater flow occurs in the Mouhoun river where it is at equilibrium with the aquifer at the north-north-eastern limit of the study zone (frontier with Mali and northern boundary of the Sourou watershed basin);
- the Banifing hydrogeological basin which drains the groundwater along a north-west axis in the direction of Mali. The principal rivers in this basin, including those that flow along the frontier, have an effect on the piezometric map;
- the Comé hydrogeological basin in the extreme south-west of the study area. Overall, the groundwater flow in this basin has a westerly direction toward Mali and leaves at the frontier, and a southerly one where it leaves the sedimentary zone inside Burkina Faso in the direction of the crystalline bedrock;
- the Bougouriba-Grand Balé hydrogeological basin in which a piezometric ridge runs along the Bobo-Banfora cliff and its northern extension, i.e., on the inner margin of the sedimentary zone. It is inside the study area and is quite small. Groundwater flow is generally oriented toward the south-east and soon leaves the sedimentary zone in the direction of the crystalline bedrock.

The evolution over time of the piezometry, albeit based on a small number of observations, shows a general lowering of the water levels over the last five decades.

The hydrochemistry of the groundwater in the Burkina Faso sedimentary series has been described on the basis of analyses (ionic balance within 5%) of samples collected from around 500 observation points [4]. A distribution of the hydrochemical facies in the different formations in the sedimentary series was defined by statistical analysis, interpretation on Piper and Schoeller diagrams and Principal Component Analyses. The data show that the majority of the samples are of the calcium bicarbonate type (86%). There is a high degree of pollution. The Schoeller diagram illustrates the uniformity of the data on a regional scale and reflects a hydraulic continuum across the various basins.

Isotopic analyses [4], have been gathered over three sampling phases (1996–2002). These isotopic studies show that most of the water stored in the sedimentary reservoir is old (from 50 to over 1000 years old) which is not incompatible with the calculations of the present aquifer recharge given the large amount of water in storage. The currently interpretation is that of a mixing model containing contemporary and recent water mixed with the old water.

3. CONCEPTUAL GROUNDWATER FLOW MODEL FOR THE TAOUDENI SEDIMENTARY BASIN

It is assumed that there is hydraulic continuity between all the hydrogeological basins, and that the Burkina Faso sedimentary series contains a large single multi-layered aquifer. Although there are, locally, impervious horizons in the series, their horizontal extent is minor compared to the surface area of the basin.

The evolution of the water chemistry in the sedimentary series does not show any significant difference between individual aquifers. There is only calcium-magnesium bicarbonate type waters. An inspection of the major ions reveals an enrichment in bicarbonate as groundwater flows from the fine glauconitic sandstone or sandstone with quartz granules toward the Toun schist (SAC2). This is in keeping with a single continuous aquifer system in which all the groundwater types are mixed together. The available isotopic data are also consistent with the concept of a single aquifer. The mean residence time of the water ranges from less than 50 years in the fine glauconitic sandstone (Bobo-Dioulasso) to almost 500 years at the top of the sandstone with quartz granules (Nasso) and over 4000 years in the SAC1 (Fon). This evolution is consistent with slow and continuous flow in a general south-north direction. Thus, all the available data reflect a single multi-layered aquifer system, locally partitioned by a few discontinuous impervious layers of which the principal ones are situated at the base of the fine glauconitic sandstones (between Kékélesso and Péni) and at the top of the SAC1 (between Banzon and Samandéni) as well as inside the SAC2 (Toun schist).

4. GEOLOGICAL MODELLING OF THE TAOUDENI SEDIMENTARY BASIN, BURKINA FASO

The 3-D geometrical model of the Burkina Faso sedimentary series was developed within the VREO programme [3] for the purpose of:

- providing a complete 3-dimensional representation of the extent and boundaries of the 10 geological formations across the Burkina Faso sedimentary series, and to generate geological cross-sections;
- defining hydrogeological layers which could be used in a mathematical model to simulate groundwater flow.

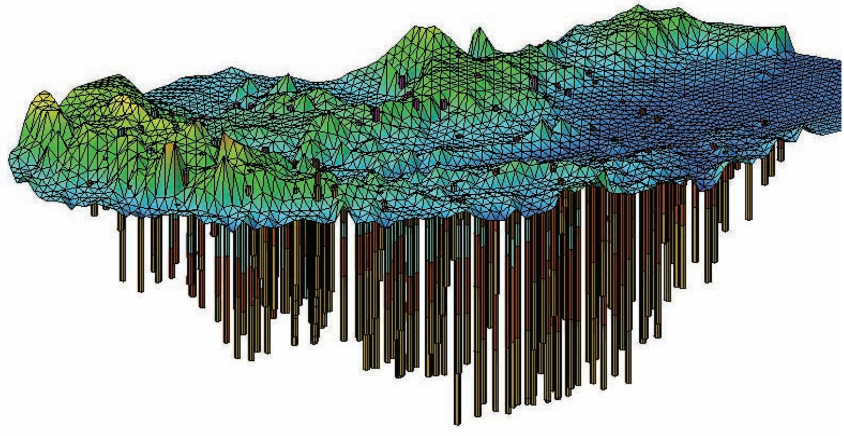

FIG. 4. Three dimensional view of topography and piezometers.

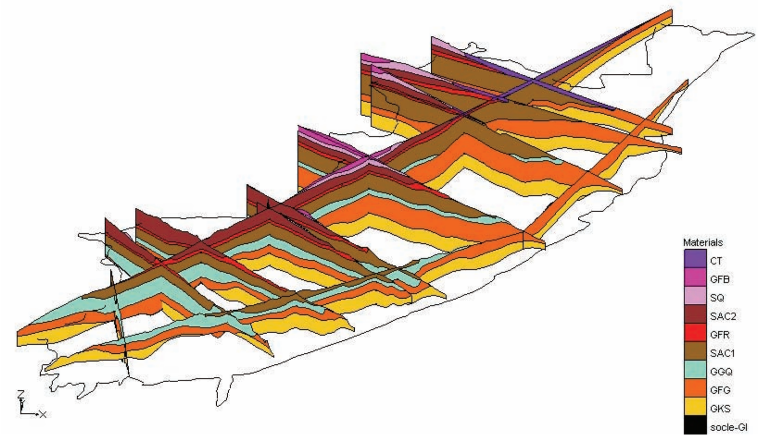

FIG. 5. 3D representation of geological formations provided by geometrical model.

The basic data for the geometrical model are the topography, the geological raster map and 18 available geological cross-sections. The results of the 3-D geometrical model are shown in Figs 4 and 5.

5. CONCLUSION

The understanding of the aquifer system on the south-eastern margin of the Taoudeni basin in Burkina Faso has gained by the interpretation of the piezometry across this 40 000 km^3 zone and the development of a 3-D geological model. This work was undertaken as a multi-disciplinary effort and combined stratigraphy, hydrodynamics, hydrogeochemistry and isotopic studies to support the geological and hydrogeological modelling.

The observed piezometry of the system comprises a typical large drainage basin with outflow towards the major Burkina Faso rivers. Given the low topographical relief compared to the depth of the base of the aquifer system, regional flow toward the Bani and Niger Rivers in Mali, cannot currently be excluded. The interpretation of all the available field data, supports the conceptual groundwater flow model.

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INTERACTION BETWEEN GROUNDWATER AND SURFACE WATER THROUGH EL HAOUAREB DAM *(Kairouan Plain, Central Tunisia)*

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Abstract

The alluvial aquifer of the Kairouan Plain is the most important aquifer in the semi-arid central Tunisia to provide the main water supply for agricultural and human needs. In 1989, the construction of the El Haouareb dam over a karstic sill completely changed the aquifer recharge process. Prior to the dam construction, recharge came from the infiltration of the Merguellil wadi floods in the plain and from the Ain el Beidha groundwater flow close to the dam site. Presently, recharge still comes from the Ain el Beidha aquifer but also from the dam reservoir through karstic fissures.

A detailed isotopic survey (^{18}O, ^{2}H, ^{3}H, ^{13}C, ^{14}C) completed the hydrodynamic analysis. The new recharge pattern is identified and the progress of water infiltrated after 1989 is visible. Ratios of Ain el Beidha and dam waters in the karst or in the plain aquifer vary with time. A first water budget is proposed for the period 1998–2000.

1. INTRODUCTION

In the semi-arid central Tunisia, the Kairouan Plain groundwater reservoir is contained in the Mio-Pliocene and Quaternary detrial deposits [1]. This aquifer is the most important aquifer in this region and also represents the main source for fresh and agriculture water supply. In order to protect the Kairouan city against the destructive floods of Merguellil, the El Haouareb

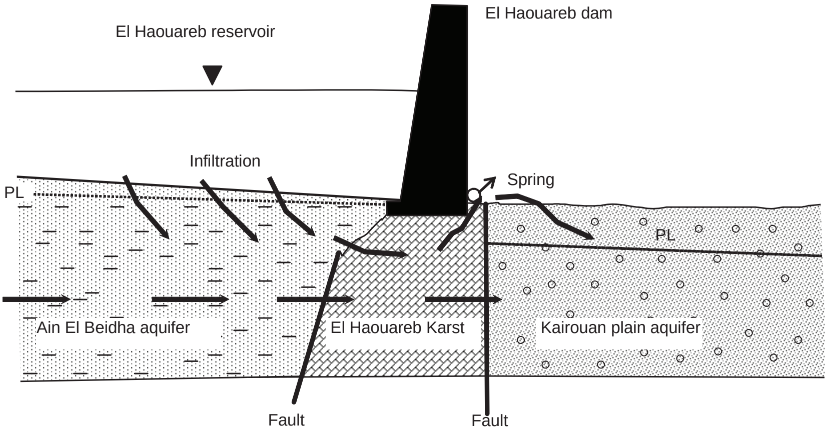

FIG. 1. Simplified hydrodynamic cross section of the El Haouareb karst.

dam was constructed in 1989. In addition, it promotes the artificial recharge of the Kairouan plain and the agriculture activity.

Under natural conditions, the recharge of the aquifer come from the infiltration of the Merguellil floods and from the Ain el Beidha groundwater flow close a karstic sill [2]. Since the construction of the El Haouareb dam over this karstic sill the natural mechanism was strongly disturbed: the dam water infiltrates into the karst (Fig.1), mixes with the Ain el Beidha groundwater, feeds the karst and pours later to the Kairouan Plain aquifer [3].

The main objective of this study is to apply integrated isotopic methods to follow the hydrodynamic transfer between the El Haouareb dam and the Kairouan Plain reservoir.

2. ISOTOPIC CHARACTERIZATION OF PRECIPITATIONS IN THE MERGUELLIL BASIN

For the rainfall isotopic characterization, 11 samples were collected from December 1997 until November 2000. Their mean values are about –4.23‰ and –24.1‰ for $\delta^{18}O$ and $\delta^{2}H$ respectively [4]. The deuterium excess for the local meteoric water line (LMWL) calculated from rainfall isotopic data with the theoretical slope of 8 is 10.87‰ [5]. This value is closer to the value defined for the precipitation in Tunisia (d = 11‰) [6] from the GNIP stations (Tunis and Sfax) data. Because of higher rainfall and altitude of the upstream catchment

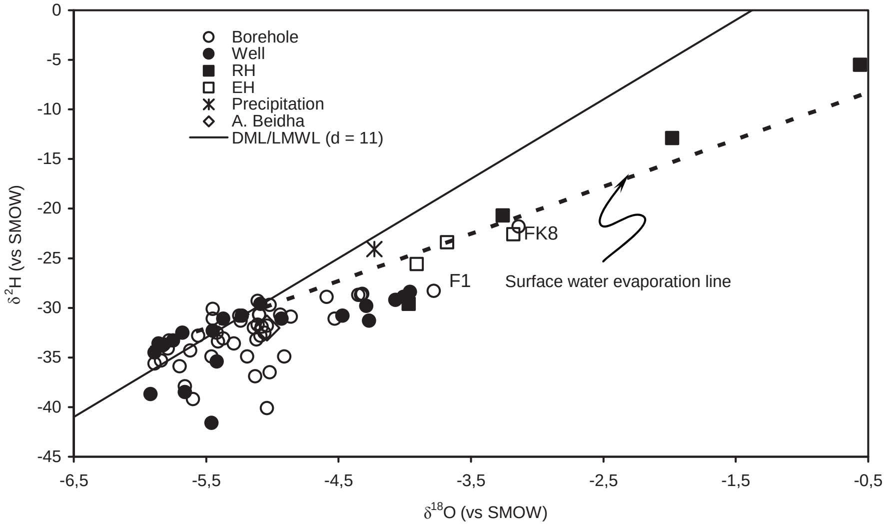

Fig. 2. Isotopic content of el Haouareb dam and Kairouan Plain groundwater.

in Merguellil basin, an altitude effect of –0.84 ‰ for ^{18}O was calculated using gradient of –0.2‰ [7, 8]. It suggests that rainfall ^{18}O composition in the Merguellil upstream ranges between –5.0 and –5.5‰.

3. DAM WATER AND KARSTIC SPRING

Dam reservoir isotope data, collected from November 1997 to May 2000 show a variation from –3.97 to 7.41‰ for ^{18}O and from –29.6 to 27.9‰ for ^{2}H. Stable isotope values measured in the karstic spring vary from –3.91 to –3.18‰ for ^{18}O and from –25.6 to –22.6‰ for ^{2}H. The evaporation line for surface water defined from stable isotopic data is $\delta^2H = 4.75 \times \delta^{18}O - 5.92$ (Fig. 2). For stream water, the isotopic signature of the upstream catchment can be estimated by the intercept of surface water line and the LMWL i.e. –5.2/–31.6‰ (^{18}O/^{2}H). The latter composition differs from the average composition of precipitation in Kairouan. This difference can be explained by an altitude effect and the higher rainfall in the Merguellil upstream basin.

The spring water shows an intermediate isotope composition between dam reservoir water and the upper catchment of Ain el Beidha basin. The contribution of these two systems was calculated using the following relationship: $\delta I_S = R_{AB}\, \delta I_{AB} + R_D\, \delta I_D$ (S – spring, AB – Ain el Beidha, D – dam, I – isotope composition, R – contribution rate). The contribution of dam water in mixed water (spring) varies between 21 to 66% depending on time. Values from ^{18}O and ^{2}H ratio are well correlated with the karstic spring flow and with the altitude of the reservoir.

4. GROUNDWATER IN KAIROUAN PLAIN

The isotopic composition of groundwater samples collected from the Kairouan Plain (Merguellil basin) shows that the mean isotopic content ($\delta^{18}O = -5.13$ and $\delta^{2}H = -32.60‰$) differs from rainfall in Kairouan and is closer to rainfall in the upstream Merguellil catchment. This suggests that most of the present groundwater in the Kairouan Plain aquifer comes from Merguellil floods and that the contribution of Plain borders in groundwater recharge is very small. This hypothesis is confirmed by radiogenic isotope values (^{14}C and ^{3}H): samples collected in Merguellil vicinity are characterised by high ^{3}H content and high ^{14}C activities.

Stable isotope values measured in the upstream part of Plain, closer the dam, differ from the rest of the aquifer, that suggests a “contamination” from evaporated dam water mixed with Ain el Beidha groundwater (spring water coming from the karst). This contamination can be observed as far as 7 km downstream. Three kilometres away from the dam the karst water contribution is estimated to 48%.

The isotopic signatures (^{18}O and ^{3}H) discriminate three geochemical water types with various mixing situations. The first group forms the present water (dam, spring and FK8). Its ^{18}O content vary widely from –3.97 to 7.4‰, whereas the ^{3}H values are in agreement with those of local precipitation (5 to 6 TU). High ^{3}H values in the second group are attributed to recent recharge coming in post nuclear tests period and before the dam construction. The third group represents old water infiltrated in a completely natural context. This groundwater is free from tritium and the ^{18}O content vary from –4 to –6‰ vs V-SMOW.

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ISOTOPIC AND CHEMICAL INVESTIGATION OF WATER SAMPLES IN ARGOLIS PENINSULA, GREECE

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Abstract

The area under study, located in the north-eastern part of Peloponnesus (Greece), is characterized by three major mountains (Arachnaio, Didima, Aderes), which constitute a complex orography and hydrogeology. Although the groundwater circulation in the peninsula is not very distinct due to the geological diversity, the objective of the study was to gain the first regional picture of groundwater recharge in the area. Samples were collected from springs, wells and rain collectors and analyzed for environmental isotopes as well as major ions. The interpretation of the results was carried out in the light of other geological and hydrogeological information in order to determine the sources and mechanisms of recharge in the area. Arachnaio Mountain, which shows the highest altitude and extent, appears to be the main recharge zone which replenishes a number of springs in the peninsula.

1. INTRODUCTION

The area studied (Fig. 1) is located in southern Greece, covers approximately 1300 km^2 and is bounded to the northeast by the Saronic Gulf and to the southwest by the Argolic Gulf, while it is limited to the north by the east-west trending ridge of Mt. Arachnaio. The aim of the study was to delineate the groundwater recharge in the area, based on the preliminary results obtained from the groundwater and rainwater isotopic and chemical data in Argolis Peninsula.

In several studies hydrochemistry, stable and radioactive isotopes have been extensively used as an important tool to overcome problems related to altitude effect, evaporation conditions and residence time and consequently give answers to issues that concern the comprehension of groundwater flow patterns [2, 3, 5].

2. HYDROGEOLOGICAL SETTING

Argolis Peninsula is characterized by dissimilar lithological formations with different permeabilities which contribute in the appearance of numerous springs. Actually, the studied area presents the following complex geological setting [4], as it is portrayed in Fig. 1.

The Quaternary sediments include alluvial deposits (G1), fans of clastic debris (G2) and volcanic sediments (G3), while the sequence of conglomerates, sandstones and marls is of Plio-Pleistocene age (G4). The Upper Cretaceous is represented by flyesh sediments built up by sandstones, conglomerates and shales together with a series of limestones (G5). Another flysch formation, consisting of marls, sandstones, breccias, conglomerates and limestone bodies (G6), is also present. Limestones and dolomites of L.Triassic — Jurassic age (G7) appear in a large extent, while there are occurences of basic and ultrabasic rocks (G8) together with part of an ophiolithic sequence of diabase, peridotite, serpentinite and pyroxenite (G9).

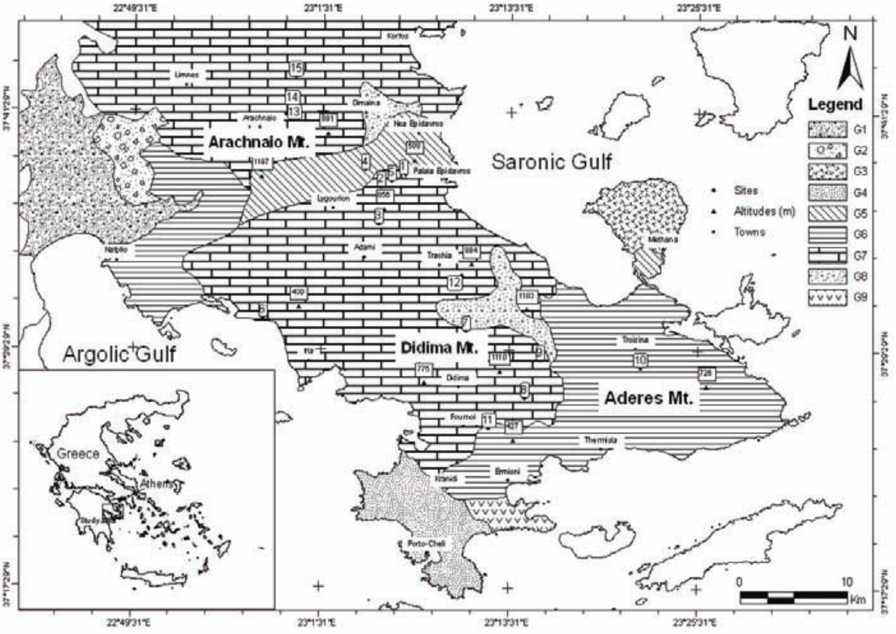

FIG. 1. A simplified geological map of the studied area [4] and the location of the sampling sites.

3. METHODOLOGY

We located and accurately determined the coordinates of fifteen sites which include ten springs, three wells/ boreholes and two rain tanks, presented in Fig.1. The samples were collected in polyethylene containers which were firstly rinsed in clear water several times and then filled to the top to minimize air entrapment. Most of the sites were sampled repeatedly during the period October 2005 – January 2007.

Groundwater and rainwater quality characteristics were defined by field measurements which included temperature, electrical conductivity (EC), pH and TDS using WTW 350i meters. Bicarbonate, chloride, calcium and magnesium were measured by titration using a Hach titrator. Sulphate and nitrate contents were measured photometrically with a HACH DR/2010 apparatus. Sodium and potassium analyses were perfomed with a flame photometer (JENWAY PFP7). Chemical analysis was routinely carried out at the University of Athens, Faculty of Geology and Geoenvironment.

The stable isotope ratios and tritium concentrations were measured at the Isotope Hydrology Laboratory of N.C.S.R. "Demokritos", Athens, Greece. The $^{18}O/^{16}O$ ratios were defined with the help of an Isotope Ratio Mass Spectrometer (SIRA Series II), while tritium analyses were performed with a low radiation counting device using the technique of Liquid Scintillation. Before the LSC counting the samples were electrolytically enriched. The $^{18}O/^{16}O$ ratios are expressed in δ‰, i.e. per mille deviation vs. the reference V-SMOW. The measurements standard uncertainties are 0.1 ‰ for $\delta^{18}O$. The Tritium concentration is expressed in tritium units (1 TU = 1 tritium atom per 10^{18} H atoms) and the uncertainty is defined as ±10% of the tritium value.

4. RESULTS AND DISCUSSION

4.1. Isotopic results and interpretation

The springs showed minor significant temporal variation in stable isotopic composition, while the wells/boreholes and rain tanks presented important variation. The tritium content fluctuated in most cases. In Table 1, we present the average stable isotopic values and the tritium variation range as well as its average concentration. Additionally, we classified the sampling sites in eight groups according to their mean isotopic concentration in ^{18}O (Table 2).

The mean tritium composition of precipitation, as observed in sampling sites 14-15, indicates relatively high values around 10 TU. The tritium range in groundwater outflows points out that the source supply in most of the springs originates from a mixture between modern precipitation and low-tritium older groundwater [1].

The sampling sites of Group C and Group E are located around the foot of Mt. Arachnaio. Their stable isotopic content is different and is attributed to the altitude effect [5], so that Group E is recharged from higher altitudes than Group C. In addition, their tritium values confirm the short residence time that characterizes the area [6]. However, although sampling site 5 (Group B) lies also close to the previous groups, its stable isotopic composition is heavier than that of the adjacent sites, and may be attributed to local recharge from lower altitudes or to evaporation effect. Unlike the stable isotopic values in site 5, its tritium measurements follow those of both Groups C and E. Additionaly, the sampling sites 5 and 6 of Group B have similar $\delta^{18}O$ values, even though they are found in very different locations. Sampling site 6 represents a borehole very close to the coast, but the chemical analysis (Table 3) shows no sign of sea

TABLE 1. SAMPLING SITES, NUMBER OF ANALYTICAL MEASUREMENTS (N) AND ISOTOPIC CONCENTRATIONS FOR THE PERIOD OCTOBER 2005 – JANUARY 2007.

No.	Sampling site	Type	Altitude (m)	$n_{oxygen-18}$	$\delta^{18}O$ (‰)	$n_{tritium}$	^3H (TU)	Mean TU
1	Ag. Marina	Spring	104	12	–6.17	6	2.9–11.9	7.6
2	Ag. Andreas	Spring	130	13	–6.13	7	4.0–10.0	7.4
3	Ag. Anna	Spring	403	11	–6.44	5	5.4–9.6	7.0
4	Ag. Paraskevi	Spring	269	12	–6.43	5	3.9–14.1	7.8
5	Epidavros	Spring	110	11	–5.76	4	3.8–10.9	7.1
6	Kantia	Borehole	7	13	–5.81	6	3.1–8.8	6.3
7	Pelei	Spring	309	12	–6.28	4	1.0–5.1	3.6
8	Loukaiti	Well	213	12	–5.26	4	1.2–10.5	5.0
9	Tsoukalia	Spring	379	11	–6.24	3	6.3–8.1	6.9
10	Monastery	Spring	343	11	–6.72	3	4.2–8.7	6.0
11	Fournoi	Spring	124	11	–5.06	3	4.4–9.1	6.3
12	Chiafa	Spring	430	10	–6.74	3	4.7–6.6	5.6
13	Arachnaio_1	Well	712	9	–7.10	1	–	9.5
14	Arachnaio_2	Rain tank	745	8	–7.21	2	8.6–13.1	10.9
15	Arachnaio_3	Rain tank	741	9	–7.40	2	9.0–12.9	10.9

TABLE 2. CLASSIFICATION OF THE SAMPLES ACCORDING TO THEIR MEAN STABLE ISOTOPIC COMPOSITION.

Group	A	B	C	D	E	F	G	H
Site No.	8, 11	5, 6	1, 2	7, 9	3, 4	10, 12	13	14, 15
Mean $\delta^{18}O$	–5.16	–5.79	–6.15	–6.26	–6.44	–6.73	–7.10	–7.31
SD	0.14	0.03	0.02	0.02	0.01	0.01	0.38	0.13

water intrusion. This could mean that the heavy $\delta^{18}O$ signatures of Group B are due to low height of recharge.

In the uplands of Mt. Arachnaio we find Groups G and H. Group H is represented by two sealed large manmade rain tanks and their isotopic composition approximates the mean annual stable isotopic values, which are the lowest in the studied area. At the same time, the tritium content shows the highest values and defines the mean tritium composition of the precipitation. In the vicinity of these rain tanks Group G is located, which is a shallow well and the $\delta^{18}O$ measurements show a slight difference from those of the rain tanks. A probable cause could be the evaporation effect [2], which increases the stable isotopic concentration during summer. On the other hand, tritium in this site lies within the value range of the rain tanks, enhancing the assumption that the shallow groundwater in the well is replenished mainly from the precipitation in Mt. Arachnaio.

The Groups D and F present different stable isotopic values, with Group F values being more depleted than those from Group D, indicating again the influence of altitude effect [5]. However, the samples of Group D do not show similar tritium content, since site 7 contains tritium which oscillates between 1.0–5.1 TU, while site 9 ranges between 6.3–8.1 TU indicating that the groundwater residence time of the former is probably longer than the latter. Tritium content of Group D is not comparable to the one from Group F that ranges between 4.2–8.7 TU.

Group A has the most positive stable isotopic content in the area, in contrast to the expected values based on the morphological structure of the surrounding environment. This effect in sampling site 11 can be attributed to local recharge, while in shallow well 8, it could be due to the evaporation effect. The tritium value range of site 11 could be attributed to the modern recharge, while this from site 8 reflects a mixture between old groundwater component and modern precipitation. The well is regularly pumped and the water is mainly used for the supply of local agricultural activities, especially

TABLE 3. MEAN CHEMICAL COMPOSITION OF GROUNDWATER AND RAINWATER SAMPLES FROM ARGOLIS PENINSULA.

No.	pH	EC[1]	Ca^{2+}*	Mg^{2+}*	Na^{+}*	K^{+}*	HCO_3^-*	Cl^-*	SO_4^{2-}*	NO_3^-*
1	7.04	726.64	140.00	8.58	13.36	0.55	386.24	14.77	15.91	11.85
2	7.20	733.00	124.90	9.95	16.79	0.89	377.70	19.50	10.82	19.92
3	7.67	663.10	112.74	7.61	22.22	0.64	360.24	22.94	30.89	9.57
4	7.99	499.45	72.17	8.80	26.23	0.16	253.58	21.50	14.80	9.63
5	7.30	840.70	113.67	36.90	20.07	0.63	424.90	21.56	53.44	28.61
6	7.83	677.09	69.74	42.81	28.21	1.24	336.89	32.77	36.91	8.69
7	7.72	653.73	44.53	56.16	12.92	0.44	382.58	15.18	7.09	9.71
8	7.56	934.36	103.78	38.79	52.38	1.06	390.29	82.00	41.73	25.28
9	7.14	852.00	114.08	35.72	17.42	1.44	416.94	19.35	37.50	51.05
10	7.91	597.50	93.71	11.17	23.03	0.65	292.62	34.70	30.80	4.40
11	7.71	790.60	64.24	59.96	24.08	0.78	377.53	39.40	43.00	25.24
12	7.30	784.89	117.79	28.82	13.77	0.50	462.85	9.61	17.22	7.20
13	8.03	445.63	83.30	5.83	6.43	0.39	203.59	7.69	25.38	24.90
14	8.10	172.86	25.77	1.93	5.95	1.85	72.94	8.43	9.36	11.89
15	8.14	143.08	24.25	0.87	4.09	1.88	72.55	4.88	5.00	6.12

[1] Values given in μS/cm
* Values given in mg/L

during summer season, where we observed a decrease in tritium content. It is likely that, due to the intense pumping, there is a significant runoff of stored water in the subterranean reservoir.

Additional information on the isotopic precipitation content are required in order to determine the stable isotopic altitude gradient and to verify the observed tritium levels. Moreover, we consider that supplementary environmental isotopes (i.e. deuterium) are necessary to comprehend more precisely the groundwater flow patterns in the peninsula.

4.2. Hydrochemistry

Water chemistry data (Table 3) were processed using the program code AQUACHEM in order to determine properly the water types of the studied groups and we also constructed the representative Piper graph for January 2007 (Fig. 2).

The majority of samples from the springs and wells/ boreholes contained a high proportion of HCO_3, reflecting mainly the weathering of the surrounding carbonate formations. Groups C, E and G showed a low concentration in magnesium leading to their classification in water type Ca-HCO_3. In Group B, site 5 is classified in water type Ca–Mg–HCO_3, while site 6 in water type Mg–Ca–HCO_3. Therefore, we presume that the borehole in sampling site 6 penetrates a different geological horizon than that of sampling site 5, richer in magnesium.

Sampling sites 10 and 12 belong to the water type Ca–HCO_3, although site 10 was sometimes classified in water type Ca–Mg–HCO_3. Therefore, we can consider the same lithotype for Group F, but with higher magnesium content in water sample 12.

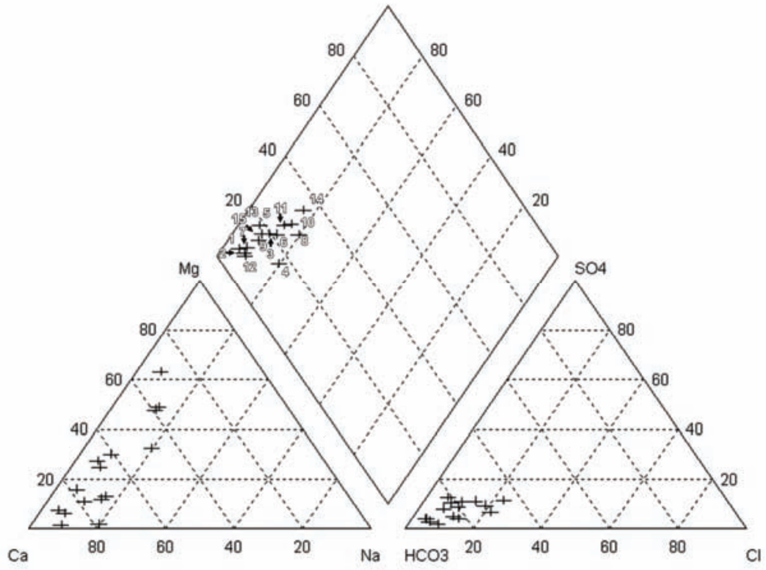

FIG. 2. Representative Piper graph of the Argolis peninsula water sampling sites (January 2007).

The hydrochemistry of Group D is again dissimilar from the sites 7 and 9. The first has increased Mg concentration and low Ca value, while the second shows an increased Ca and a decreased Mg content. Consequently, the water types, Mg–Ca–HCO_3 and Ca–Mg–HCO_3 respectively, suggest a different water-rock interaction, with possible higher contribution of dolomite in the former. Moreover, the source of recharge may not be in the same region. The same goes for sites 8 and 11 of Group A. Groundwater of sample 11 seems to dissolve more magnesium carbonate minerals than sample 8.

5. CONCLUSIONS

In the studied area, half of the springs are likely to be related to carbonate groundwater reservoirs around Arachnaio mountain range. The lack of significant stable isotopic seasonal variations in most of the springs indicates that precipitation flattens the isotopic composition of stored groundwater, while the different stable isotopic signatures between the sampling sites were attributed mainly to the altitude effect and the evaporation effect. Additionaly, the tritium content of the springs outlined a short residence time and a mixture between old groundwater component and modern precipitation.

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CROSS-BORDER GROUNDWATER MANAGEMENT: THE CONTRIBUTION OF DEEP GROUNDWATER TO QUATERNARY BASINS DEDUCED FROM ISOTOPE DATA

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Abstract

In the frame of an EU Interreg IIIa project we investigated to what extent the interregional Upper Jurassic karst aquifer, which underlies parts of southern Germany and the area around Schaffhausen in Switzerland, contributes to the water budget of shallow Quaternary basins on both sides of the border. Because the differentiation between mixing end members based on chemical parameters is ambiguous, isotope tracers were emphasized. Proportion and spatial occurrence of deep karst water were determined based on ^{3}H, ^{85}Kr, ^{39}Ar and ^{14}C. The data were interpreted based on a 3D-hydrogeological setup which was completely re-evaluated using reprocessed seismic profiles. The reviewed scientific results provide the basis for sustainable groundwater protection and resource management overcoming national borders as the groundwater does.

1. INTRODUCTION

For groundwater management, the top priority is to quantify the availability, the flow paths and the origin of resources. Beside classic hydrology methods the use of environmental tracers provides important additional information about flow dynamics, recharge areas and mixing proportions of different water components. For large-scale groundwater systems the range of groundwater residence times is generally wide and the number of potential mixing components is enlarged. Multi-tracer investigations are required to obtain a sound characterisation of the groundwater system. In this study tritium, stable isotopes of the water molecule (^{18}O, ^{2}H), ^{85}Kr, ^{39}Ar, Carbon-isotopes (^{13}C, ^{14}C) as well as strontium isotopes were applied [1]. In this paper we highlight the main scientific strategy and preliminary results of an Interreg IIIa project founded by the European Union and the Canton Schaffhausen (Switzerland) [2]. The main objectives of the project were to establish a sound basis to prevent exploitation of high quality groundwater sources (i), to quantify and qualify the groundwater resources in order to develop a long-term groundwater management for the region (ii) and to encourage bilateral co-ordination in the fields of groundwater monitoring and water concessions (iii).

2. SITE DESCRIPTION AND HYDROGEOLOGY

The area under investigation is located near Lake Constance in Central Europe (Fig. 1). The Northern and Western boundaries are defined by the outcrop area of the Upper Jurassic formation and the river Danube respectively. The Southern and Eastern boundaries are represented by the Rhine which acts as discharge and the Danube-Rhine watershed (Fig. 1). The project area (2400 km^{2}) encloses the recharge and discharge zones of the aquifer systems of interest. The general sequence of geological covering from North to South is described by outcropping limestone in the North, sometimes overlaid by thin Tertiary sedimentary layers. Towards the middle of the project area the limestone formation is sub-ducting under the out-conning Molasse formation. In this zone Quaternary sediments were directly deposited on the limestone formation. Further South the thickness of the Tertiary sediments is generally increasing and Quaternary sediments including coarse gravel layers are found in erosion basins and depressions of the Molasse. Groundwater renewal for the Jurassic aquifer is mainly controlled by Danube infiltration and precipitation in the outcropping regions. Discharge is observed in various Quaternary basins but seems to be mainly controlled by the Rhine, especially around the fault zone of the Rhine cascade [3]. The piezometric head of the Upper Jurassic limestone aquifer was interpolated assuming a continuous aquifer system. The head gradient between the deep karst aquifer and the local shallow aquifer systems indicates an upward flow in most areas.

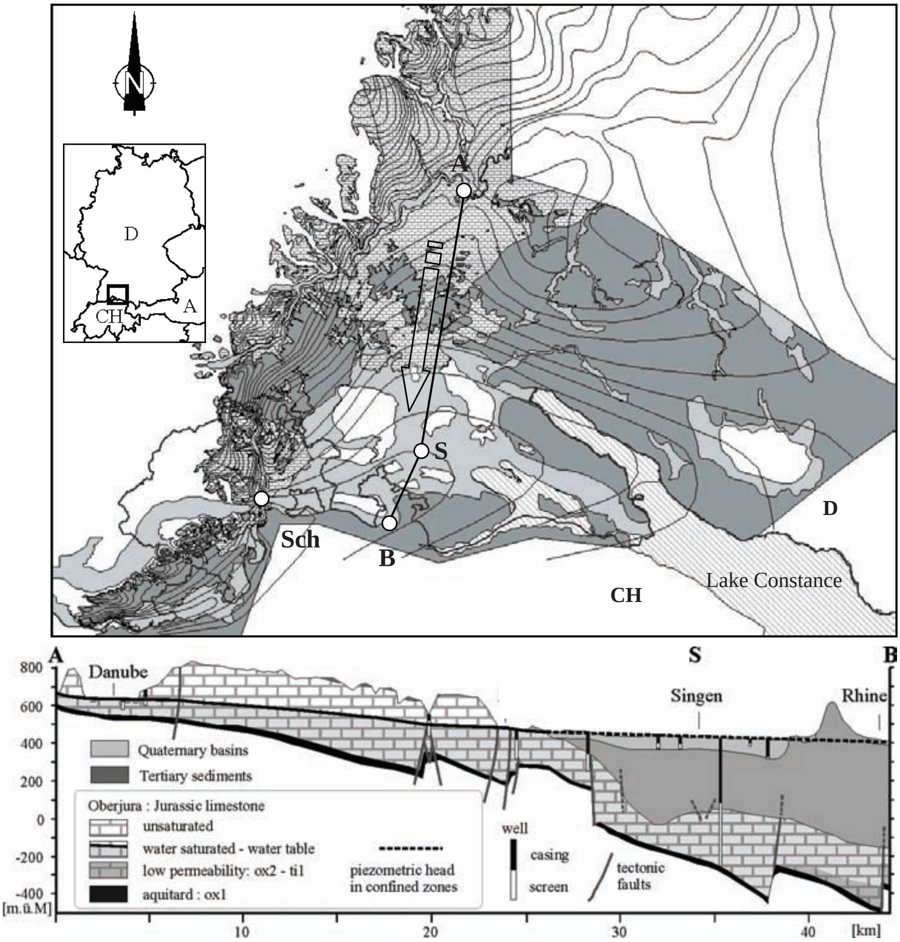

FIG.1. The arrow indicates the direction of groundwater flow in the karst aquifer. The piezometric surface of potential of the sub-ducting Jurassic karst aquifer exceeds the elevation of the Quaternary basins along the selected cross section (A-S-B) as it can be seen out of the lower picture.

3. OBJECTIVES

Former investigations [4, 5] showed that substantial quantities of water originating from the deeper Jurassic limestone aquifer discharge into the Quaternary basins, which are generally exploited by the local water supplies. As new groundwater supplies are planned or already realised in the region to satisfy the increasing demand of high quality water the question arises to which extent future pumping could affect the hydrological situation within the Jurassic limestone aquifer. So far, the high quality water from the karst aquifer ameliorates the quality of shallow groundwater which is commonly affected by human impact. An increased water extraction rate in the shallow basins would also locally increase the head difference to the karst aquifer and thus the inflow of karst water if the extraction rate exceeds the natural renewal rate. As a consequence, this higher (over)-exploitation could reduce the head of the karst water resulting in a reduction of water quantity and quality in the Quaternary basins. Two large urban agglomerations of Singen (D) and Schaffhausen (CH) could be interlinked that way. Thus, the main objective of the present investigations is to quantify the portion of karst water in the shallow systems and the flow dynamic and permeability of the karst system.

4. CONCEPTUAL APPROACH AND METHODS

As most of the wells are situated in the Quaternary gravels little is known about the chemical and isotopic composition of the karst mixing end-member. Due to the shallow screen depths of the extraction wells, which are generally placed within the top 50 m of the Quaternary sediments, locally recharged water will be marked with anthropogenic substances as ^{85}Kr ($T_{1/2}$: 10.76 yr) and Tritium ($T_{1/2}$:12.32 yr). Previous studies in the area indicate that the karst water in the confined Jurassic aquifer is free of these environmental tracers [4, 6] and therefore older than ~50 years. Mean residence times (MRT) and mixing proportions of shallow groundwater were estimated using lumped parameter models [7]. For the ^{85}Kr input function the mean annual concentrations measured at the station Schauinsland (D) [8] were used. Tritium input concentrations in precipitation were reconstructed from data from the weather station in Steisslingen (D) (time period 1992-2006) and correlated and extended with data from the closest IAEA station Constance (D) [9]. ^{85}Kr, ^{39}Ar ($T_{1/2}$: 269 yr) and ^{14}C ($T_{1/2}$: 5730 yr)-activities were measured at UEP Bern by low level counting [10-12]. Tritium concentrations were measured at Hydroisotop GmbH by liquid scintillation counting.

5. ENVIRONMENTAL TRACER RESULTS

5.1. Age structure in Quaternary basins

Thirty nine groundwater samples were analysed for Tritium and ^{85}Kr, most of them in wells equipped in the Quaternary gravels. In Fig. 2a, the measurements are plotted together with calculated ^{85}Kr–^{3}H relation using a combined model with 60% Exponential and 40% Piston-flow (EPM60). Admixture of tracer free water is indicated by a concentration shift towards the origin of the coordinate system. Measurement errors, uncertainties of the tracer input functions and some ambiguity of the model selection result in an overall uncertainty in the estimation of young water fractions of up to 15%. The box-models were selected according to local geological information, e.g. depth of the well screens, distance to geological faults. Three groups of waters can be distinguished in Fig. 2a. Samples plotting near the suspected model curve represent waters from local recharge in the Quaternary basins or the unconfined karst aquifer. The residence times of these waters range up to 20–30 years (group 1). The second group of samples, mainly in the age range 20–25 years and originating essentially from greater depths of the Quaternary basins, become increasingly influenced by the deep karst water (group 2). The third group of samples is dominated by old karst water [4, 5]. The ^{39}Ar-activites of the ^{85}Kr and ^{3}H free waters were now estimated by subtracting the contribution from the young water fraction. As underground production of ^{39}Ar can not be excluded (see also section 5.2 and Fig. 3c) the ^{39}Ar-values of the old water were further conservatively corrected for 30% mod underground equilibrium production (UEP). ^{39}Ar-Piston flow ages for the ^{85}Kr and ^{3}H free water were calculated taking the uncertainties in the young water fraction, measurement errors and UEP into account (Fig. 2b). Most samples fall in the age range of 100-400 years. Previous studies carried out in the region further east [13] resulted in residence times of the karst water of many thousands of years based on ^{14}C data. In our area at least parts of the karst system are much more dynamic.

5.2. Geochemical evolution and water dynamics in the karst aquifer

Water samples containing high amounts of young water portions (>60%) show ^{14}C and δ^{13}C concentrations of 60–90 pMC and –16 to –12‰ δ^{13}C, respectively. For them the scattering of ^{14}C can be explained by admixture of different amounts of ^{14}C from atmospheric nuclear explosions. The mean values of 80 pMC and –14‰ in δ^{13}C can be regarded as a starting point for the geochemical evolution in the limestone aquifer. With decreasing ^{14}C, δ^{13}C increases almost linearly towards the carbon isotope composition of the matrix carbonates [3] (Fig. 3a). With increasing δ^{13}C the $^{87/86}$Sr-signature of the ground water also converges to the Sr-isotope signature of the rock matrix (Benken, formation water: 0.7075 [14]), (Fig. 3b). This trend can either be explained (i) by a progressively increasing portion of karst water, which is in chemical and isotopic equilibrium with the host rock or (ii) represents the kinetics of a geochemical evolution along a hypothetical groundwater flow line in the karst.

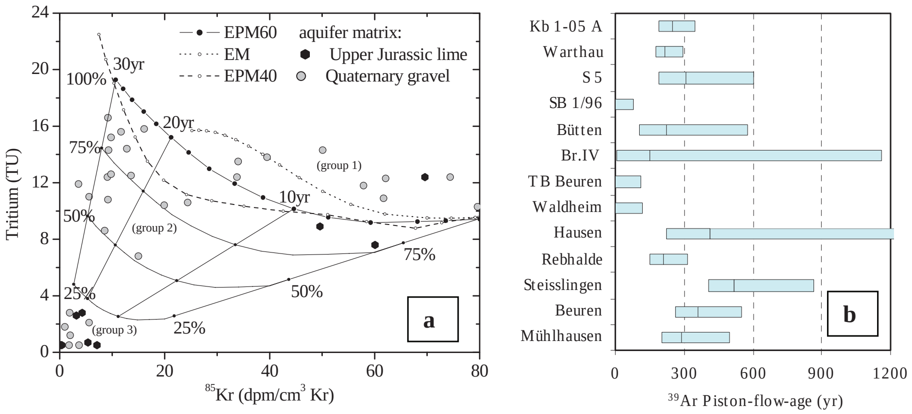

*FIG. 2. **(a)** Measured activities of ^{3}H and ^{85}Kr plotted with calculations applying different lumped parameter models [7]. The model curves are labelled with the MRT and portion of admixed young water and ^{3}H and ^{85}Kr free old water components (EPM60). **(b)** ^{39}Ar-Piston flow ages of ^{85}Kr and ^{3}H free karst water component.*

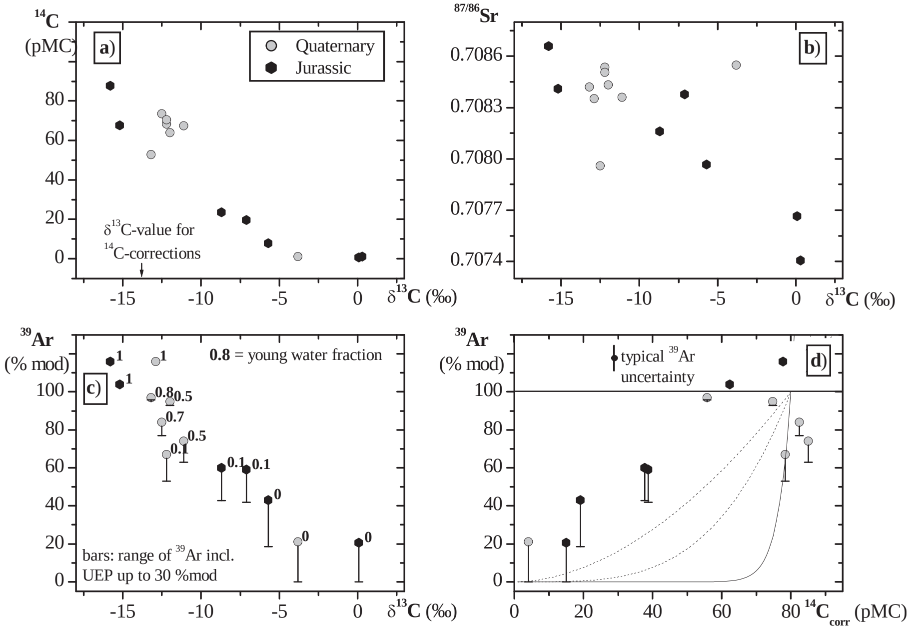

*FIG. 3. **(a)** ^{14}C decrease with increasing δ^{13}C. (b) Water-rock-interaction is supported by the linear relationship of δ^{13}C and $^{87/86}$Sr towards the signature of the aquifer matrix. (c) ^{39}Ar decrease with increasing δ^{13}C; the small numbers indicate the fraction of young water. (d) ^{39}Ar decrease linearly with Carbonate-dissolution corrected ^{14}C (^{14}C$_{corr}$); the bold line represents expected behaviour assuming radioactive decay, by reducing the half life of ^{14}C assuming water-rock interactions, the model curve is approaching the data, the dotted lines indicate effective ^{14}C half lives of 500 and 1000 years. The dash-dotted line represents the mixing line of young water with Pleistocene water.*

TABLE 1. EXPLOITATION OF THE JURASSIC LIMESTONE AQUIFER IN THE PROJECT AREA WITH TERTIARY COVER.

Pumping stations	Model	Age of the young water (yr)	Fraction of old water (%)	Concession (m^3/s)	karst water* (m^3/s)
Br. III Nord Singen	EPM60	22	40	0.111	0.044
Br. II Nord Singen	EPM60	17	0	0.111	0
Br. IV/1959 Münchried	EPM60	18	25	0.048	0.012
Br. VI/1960 Münchried	EPM60	14	0	0.048	0
Br. VII/1960 Münchried	EPM60	22	20	0.048	0.01
TB Gottmadingen I	EPM60	24	50	0.030	0.015
TB Weitenried	EPM60	22	25	0.015	0.004
TB Beuren 1974 (neu)	EPM40	22	20	0.060	0.012
TB Bietingen Neu 96	EPM40	24	20	0.015	0.002
Randegger Ottilienquelle 4	EPM40	15	80	0.010	0.008
Br. Bütten	EPM40	25	30	0.200	0.060
HFB Warthau	EPM40	35	50	0.347	0.17
Rheinhalde	EM	5	0	0.810	0
				Total	0.34

* calc. as old water fraction

Additional temporal information can be obtained from ^{39}Ar-measurements (Fig. 3c, 3d). The two samples which have almost no ^{14}C and are completely equilibrated with the rock carbonates contain still about 20–30% mod ^{39}Ar. 30% mod was therefore assumed as an upper limit of underground production and subtracted from the measured values (vertical bars).

The resulting activities show again an almost linear correlation with the carbon isotopes $\delta^{13}C$ and $^{14}C_{corr,}$ which have been corrected for dilution by "dead" carbon using the procedure of Ingerson and Pearson [15] using an initial $\delta^{13}C$ value of –14‰. The two scenarios described above can be further constrained:

(i) Mixing of a ^{14}C and ^{39}Ar dead (apart from underground equilibrium activity) water component with a younger but ^{3}H and ^{85}Kr free water component. The resulting mixing line is depicted in the Fig 3d. Evidence for the admixture of Pleistocene karst water was derived from depleted $\delta^{18}O$-values for dead ^{14}C samples.

(ii) The linear correlation is related to kinetics of isotopic exchange between dissolved inorganic carbon of groundwater and the matrix. Half-lives for the isotope exchange in karst systems in the range of 3000–5000 years were found in similar systems. This results in an overall combined ^{14}C half-life of 1700–3000 years [16, 17]. In Fig. 3.d modelled ^{39}Ar–^{14}C relations (dotted lines) assuming effective ^{14}C half-lives of 500 and 1000 years are shown respectively. The observed linearity of the $\delta^{13}C$–^{39}Ar and ^{14}C–^{39}Ar relations implies, however, a geochemical exchange time in the order of the half life of ^{39}Ar. Although this cannot be completely excluded, it is believed that the observed relation is a combination of both scenarios. However, both cases imply an interconnected flow system and water components with flow times in the order of hundreds of years, as deduced in the previous chapter (Fig. 2b).

6. CONCLUSION

By multiplying the pumping rate concessions with the fraction of old tracer free water, one obtains an actual estimate for Jurassic limestone aquifer exploitation scenario (Table 1). In reality, water concessions are generally not used up by water supplies. Nevertheless, it is wise to consider water concession limits, as they are legitimated by law. In principle, by comparing real outtake rates with calculated renewal rates, one can make a good estimation for the exploitation rate of the karst aquifer by cross boundary flow. In a first trial we have estimated the total discharge rate for the covered Jurassic limestone aquifer via the Rhine and the Quaternary basins to be 4.4 m^3/s. The exploitation of the Jurassic limestone aquifer via Quaternary basins via the investigated water supplies sums up to 0.34 m^3/s. This number reflects a minimal guess as only ^{85}Kr and ^{3}H free karst water was assumed.

The main conclusion is that approximately 10% of the karst water discharge rate is used to sustain the water supplies in the Quaternary basins.

However, so far it is difficult to predict how local exploitation by water supplies affects the local underlying karst aquifer and its flow dynamics. Especially in Quaternary basins, where new water supplies are built or planned, the response of groundwater withdrawal to the Upper Jurassic aquifer has to be monitored.

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IDENTIFICATION OF GROUNDWATER RECHARGE SOURCES BY USING EXCESS ^{234}U AND ^{34}S FOR THE ARID EJINA-BADAIN JARAN INTERIOR BASIN OF ALXA PLATEAU, INNER MONGOLIA

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Abstract

The Ejina-Badain Jaran depression of the Alxa Plateau of Inner Mongolia covers an area of 81,380 km^2 with annual mean precipitation of about 50 to 80 mm. It is composed of Gobi, Badain Jaran Shamo (Dune Desert) and two grasslands, Gurinai and Wendu Golei. The intermittent Black River ends into lakes in this depression. Precipitation, surface water and groundwater from dug wells, boreholes and springs were sampled. Big variations of U, $^{234}U_{ex}$, $^{34}S_{sulphate}$ and ^{18}O, T, ^{14}C of waters were found especially that of U and $^{234}U_{ex}$ with ranges of 0.06 ppb to 1455 ppb and –0.408 eU to 13.91 eU respectively. It leads to the differentiation of groundwaters into groups as Gobi, Shamo and the grasslands. The $^{34}S_{sulphate}$ was also used for this purpose due to the sulphate in this huge nomads area is mainly the naturally sourced. The recharge sources of groundwaters were identified by using end members with special reference to the Gurinai grassland. Three source waters of its phreatic groundwater are: the local precipitation, the Gobi groundwater and the leakage from deep aquifers. Three source waters of deep groundwater are: the Gobi groundwater, the deep groundwater from Shamo and, the palaeowater. These recharge sources were checked by other isotopic relationships especially that of $^{34}S_{sulphate}$. The Gobi water appears the mixing of local precipitation, deep percolation from the Black River and, the deep groundwater from different areas including that from Mongolia. From data of all the sampling sites distributed in Gurinai, an areal averaged contribution of every source water for both the phreatic and deep groundwaters were estimated by using U and $^{234}U_{ex}$.

1. STUDY AREA

The study area, Ejina–Badian Jaran Depression, is the main part of the Alxa Plateau (Fig. 1). It includes geomorphologically the Badain Jaran Shamo (dune desert) with an area of approximately 49,200 km^2, the Gurinai grassland and Wendu Golei (Guai-Zi) lowland with area of about 3000 km^2 and 800 km^2

situated to the west and north of the Shamo respectively and, the Ejina Basin with Gobi and survived *Populus* forest to its northwest. Megadunes with a relative height of about 200–500 m dominate the Shamo, about 140 lakes distribute within megadunes of its south and southeast part. Sourced from the Qilian Mountains the Black River flows northward into the west part of the study area. It forms the Ejina Basin, the "lady's fan"as described by NASA, and terninates into two lakes near the country border.

1.1. Hydrological and geological settings

The annual mean precipitation of Ejina Gobi is 50 mm averaged from data of 25 years, Wendu is 48 mm from 21 years. No record is available in the sand sea. Precipitation was estimated from records for the lake area outside the Shamo. It varies from about 50–70 mm from north to south.

Geotectonically, this basin is a fault block. Developed on the Cretaceous and Paleogene bedrock inclined from southeast towards northwest, the deposit

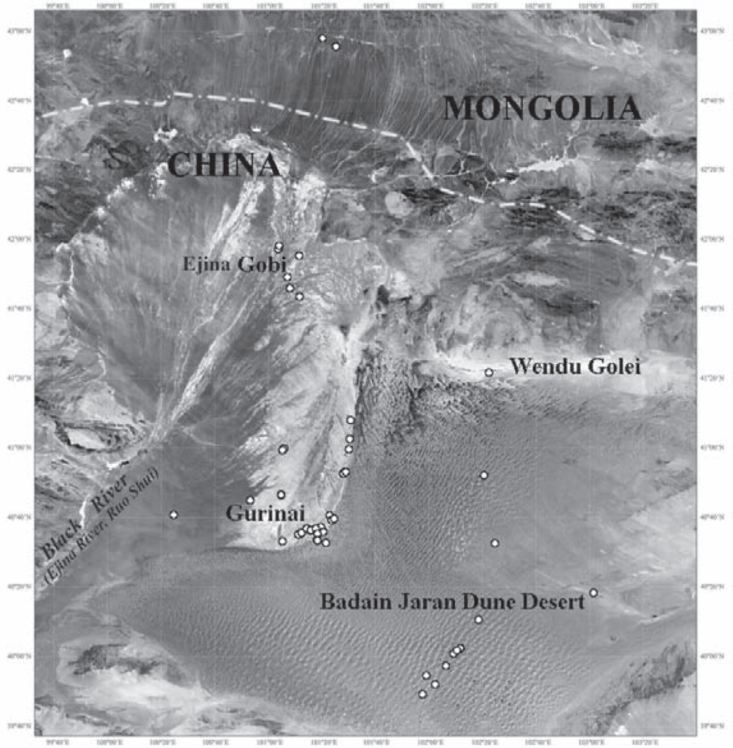

FIG. 1. The study area with sampling sites marked by circles.

thickness of Pleistocene and Holocene with various formations including the alluvial, diluvial, eolian and lacustrine ranges from 200–400 m in the Gurinai area. The Shamo was developed during Pleistocene, the megadunes were formed with inselbergs [1] and maintained by vadose water with confused mechanisms [2]. The geological controls of the hydrogeologial conditions are two latitudinal belts of lifted constructions situated to the north and south of study area and, several longitudinal hidden faults. The porous aquifers are formed following the depositional cycles of the alluvial-diluvial fan during mainly the Holocene.

1.2. Sampling

According to the results from preliminary works [3, 4], 44 sampling sites were designed to cut across three profiles of the study area (Fig. 1), i.e., the east one traverses the Shamo until Wendu lowland, the middle for the Gurinai grassland and, the west one stretches over the Gobi until the South Gobi of Mongolia. The data were collected from 1988 until 2006.

2. THE FUNDAMENTAL RELATIONSHIPS OF URANIUM DISEQUILIBRIUM IN HYDROLOGICAL CYCLE OF STUDY AREA

The uranium concentration U and $^{234}U/^{238}U$ activity ratio (AR) [5] in water cycle is summarized as shown in Fig. 2. The U concentration averaged from all groundwaters reaches a high level of 7.99 ppb if compared with the reported mean value 4 ppb of groundwaters from arid area [6]. The averaged U of the phreatic groundwater of both the Gobi area and that of the Shamo reaches the high level of 22.5 ppb and 16.6 ppb respectively. According to Osmond and Cowart [7], high concentrations above 10 ppb are from the vicinity or ore-bearing aquifers, but the study area is not the area of ore-bearing, the high level of U may be from the original deposit or, the modern anthropogenic sources. The water from saline lakes within the megadunes has a very high U of 1455 ppb with AR of 1.45.

3. IDENTIFICATION OF VARIOUS GROUNDWATER SYSTEMS OF STUDY AREA

3.1. Groundwater systems identified from uranium disequilibrium

Groundwater systems, GB (Gobi), SM (Shamo), GRN (Gurinai) and WDG (Wendu), are identified from uranium disequilibrium, U vs. AR (Fig. 2) as following.

3.1.1. The Gobi groundwater system GB

It is characterized by a mean AR of 2.11, the highest mean value between all groundwater systems of the study area and, a high U of 9.85 ppb in average. The high ARs imply a reducing environment of confined aquifer waters with recoil mobilization of ^{234}U [5]. However its big variation, from 1.29 to 2.92, reveals the existence of a deep circulation. From the relationship of reciprocal U concentration vs. AR (Fig.3), the recharge direction will follow the decreasing of the ^{234}U excess defined as $^{234}U_{ex}$ =U(AR-1), which is the parameter of this relationship.

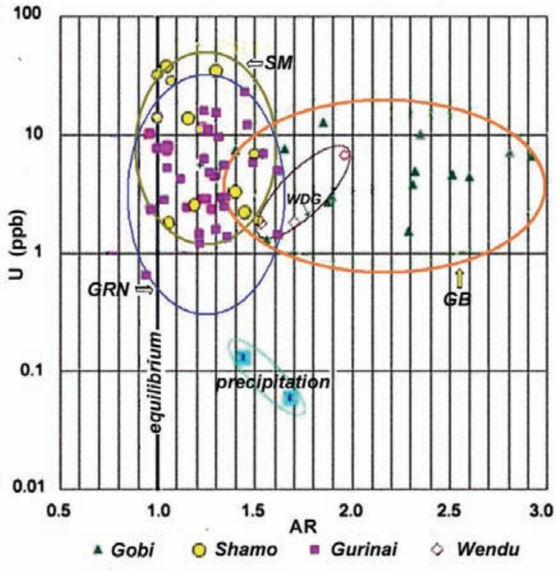

FIG. 2. U vs. AR for the different groundwater systems (lake water with U of 1455 ppb and AR of 1.45 is not included).

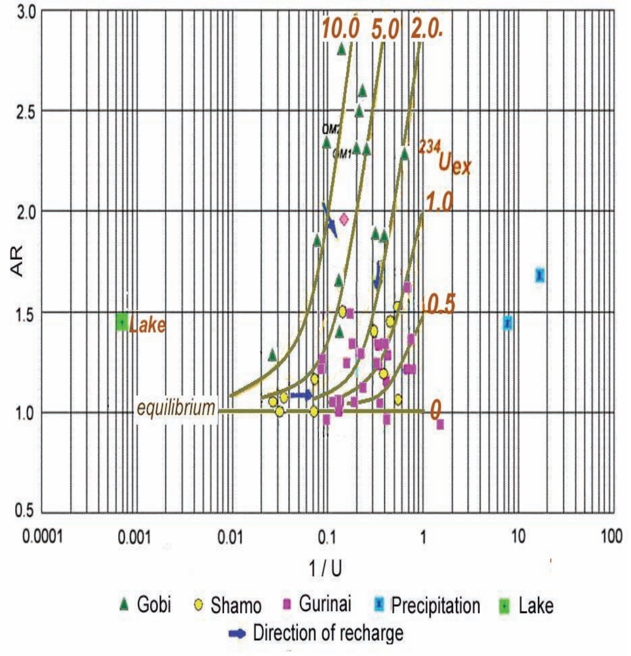

FIG. 3. 1/U vs. AR showing the recharge direction following the decrease of $^{234}U_{ex}$.

3.1.2. The Shamo groundwater system SM

It is characterized by a highest averaged U of 13.07 ppb and, a lowermost averaged AR of 1.22. It shows an active circulation dominated by process of eluviation compared with the exchange between solid-liquid phases. The repeated eluviations make the deficit of ^{234}U of the solid phase and, more ^{238}U being dissolved into the liquid phase, it causes the decrease of AR. The wide variations of both the ARs and U concentrations also imply a recharge direction as shown by $^{234}U_{ex}$ in Fig. 3. Such a recharge direction from Shamo to Gurinai is also found from traditional methods [8]. It is argued that why the Shamo can offer their very limited water to its neighbours, it leads to a study for the source water of that Shamo with some suggestions, e.g., the Shamo gets water from Qilian Mountains [9]. However the evidence for such a conclusion is still not enough even Gu is one of the co-authors of that paper.

3.1.3. The grassland groundwater systems GRN and WDG

The shallow and deep groundwaters of Gurinai grassland and that of Wendu lowland have similar mean ARs and uranium contents even the data of Wendu are not enough. However, it appears that they are very different systems, as shown in Fig. 2 which reveals the different compositions of groundwater recharge sources. In fact, the GRN is the lacustrine deposit but WDG the fluvial facies. There are 4 sites of GRN with unusual AR less than unity of about 0.95 accompanied by both low and high U concentration, e.g., 10.2 ppb of spring TLST with pMC 34.4%, 0.65 ppb of shallow S6 with pMC of 95.3%, the mechanisms for it are still not clear. Compared with GB and SM, GRN is subjected with strong evaporation as shown by its ^{18}O.

3.2. Groundwater systems identified from ^{34}S of sulphate

Different from other area with about 2/3 of anthropogenic sulphate in atmosphric deposit and, that from various pollution sources in groundwater, the sulphate in groundwaters of study area even that of grasslands is dominated by natural processes without any anthropogenic impacts except at very few sites in the Ejina city. The impact from livestocks of nomads can be negelected. So, the variations of $^{34}S_{sulphate}$ in groundwaters of study area are resulted from different compositions of recharge sources and the dynamic and redox environment of groundwaters. Fig. 4 makes identification for groundwater systems, the GB is

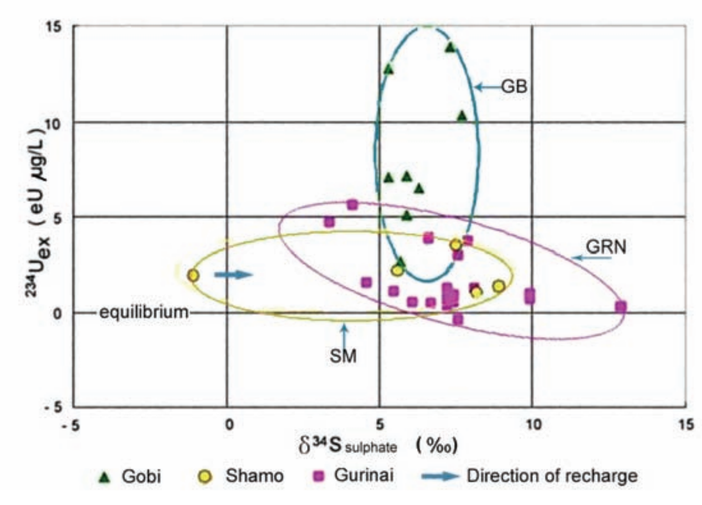

FIG. 4. $\delta^{34}S_{sulphate}$ vs. $^{234}U_{ex}$.

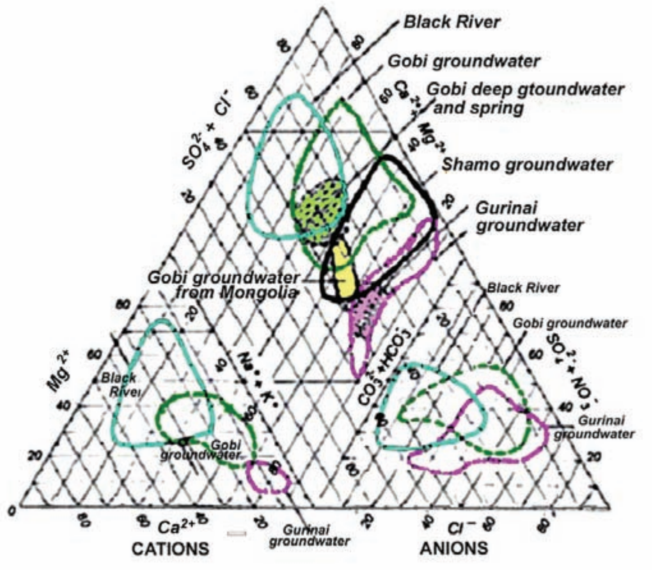

FIG. 5 Groundwater systems grouped on Piper diagram.

characterized with a narrow range of $\delta^{34}S_{sulphate}$ of 5–8 permil which is mostly the atomospheric origin. The wider range of SM and GRN appears the mixing of atmospheric, pedospheric and lithosperic origins [10]. The SM shows that its circulation appears more active than that of GRN which has some contributions from bacterial reduction in aquifers. It shows a recharge direction from SM, too.

3.3. Groundwater systems identified from hydrochemistry

As a crosscheck, from the Piper diagram (Fig. 5), it can be seen the different groundwater systems, their relationships and, the evolution of GRN.

4. SOURCE WATERS AND ITS CONTRIBUTION TO GURINAI GROUNDWATERS

4.1. Recharge sources of the phreatic groundwater

Aimed at the identification of recharge sources, the spices of a triangle in the diagram of U vs. $^{234}U_{ex}$ can be thought as the end-member source waters [11], if all the possible source waters of the area are included. Three source waters of the phreatic groundwater of GRN are identified from Fig. 6. They are: (A) precipitation with U of 0.1 ppb and $^{234}U_{ex}$ of 0; (B) Gobi groundwater with U of 15 ppb and $^{234}U_{ex}$ of 11 and (C) leakage of deep groundwater and/or spring with U of 10 ppb and $^{234}U_{ex}$ of 0.

4.2. Recharge sources of the confined groundwater

Three source waters of the deep groundwater of GRN are identified from Fig.7 as the following: (A) Gobi groundwater with U of 20 ppb and $^{234}U_{ex}$ of 11; (B) deep groundwater from Shamo with U of 45 ppb and $^{234}U_{ex}$ of 0 and (C) Palaeowater with U of 1 ppb and $^{234}U_{ex}$ of 0, the ^{14}C age of representative water M37 is 12440 BP. This source water is also checked by using the relationship of ^{3}He vs. $^{234}U_{ex}$. It has the lowermost ^{3}He of about 6 10^{-14} STP cm^3/g [13] with varied $^{234}U_{ex}$.

4.3. Contribution estimation for source waters in Gurinai groundwater

Using the U_A, U_B, U_c and E_A i.e.,$(^{234}U_{ex})_A$, E_B and E_c of identified source waters A, B and C respectively, the contributions of these source waters, α_A, α_B,

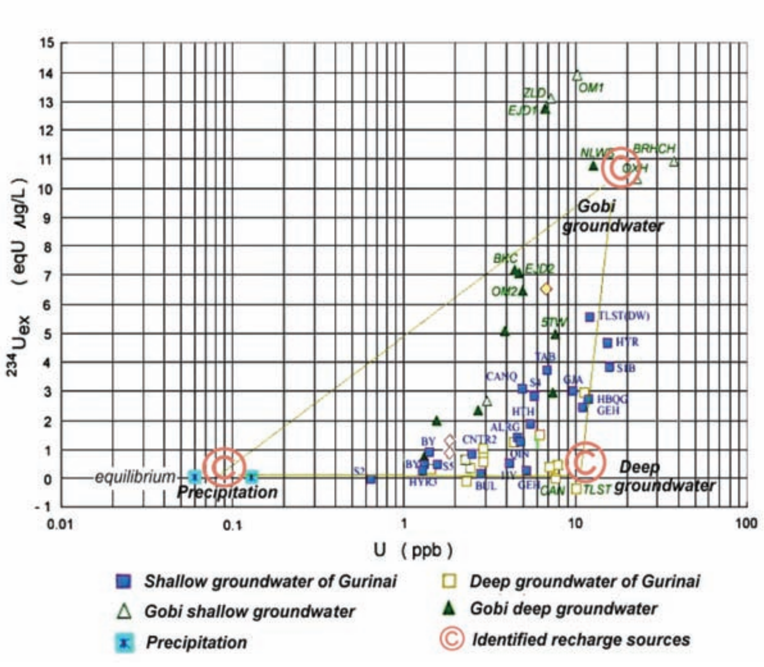

FIG. 6. Three identified recharge sources of shallow groundwater of GRN.

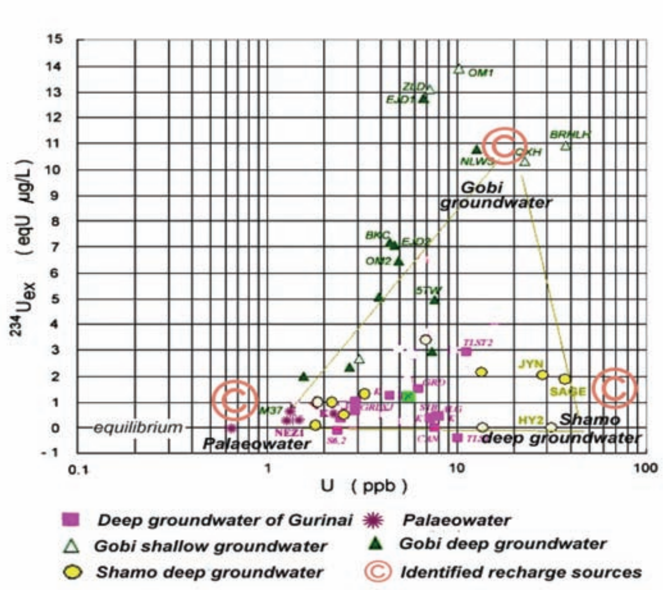

FIG. 7. Three identified recharge sources of deep groundwater of GRN.

α_C, to groundwater at different sites with U_X and E_X respectively can then be estimated from the equations as follows [12].

$$\alpha_A = \frac{(E_B - E_C)(U_X - U_C) - (U_B - U_C)(E_X - E_C)}{(E_B - E_C)(U_A - U_C) - (U_B - U_C)(E_A - E_C)} \tag{1}$$

$$\alpha_B = \frac{(E_A - E_C)(U_X - U_C) - (U_A - U_C)(E_X - E_C)}{(E_A - E_C)(U_B - U_C) - (U_A - U_C)(E_B - E_C)} \tag{2}$$

$$\alpha_C = 1 - \alpha_A - \alpha_B \tag{3}$$

By using above equations, from all the 20 phreatic groundwater sampling sites, the estimated source water contribution is 60.7% from the precipitation, 27.4% from spring or leakage from deep aquifers and 11.9% from Gobi groundwater. For the contribution of precipitation, tritium profiles collected from 1987–1990 and from 1999 are used for the recharge evaluation. A recharge rate of about 1/5 of annual mean precipitation i.e., about 11 mm/year is resulted from peak T depth of 3 m with measured effective porosity of 10% within 27 years since 1963.

Averaged from all 13 confined groundwater/spring sampling sites, the estimated source water contribution is 86.9% from palaeowater, 7.1% from Gobi groundwater and 6.0% from the Shamo.

The formation of Gobi groundwater however is still not clear. Preliminary results show that it is a mixing from the local precipitation, deep percolation of Black River and deep groundwater from other sites including that from Mongolia.

ACKNOWLEDGEMENTS

The authors are grateful to many colleagues from Earthwatch Institute too numerous to name here who have been involved in the 10 years expeditions in the Gobi desert and the sand sea of camel caravan since 1997 for water sampling. Gu also wish to express his gratitude to Mebus Geyh, Dieter Jakel and Klaus Froehlich for their great support over years for the environmental isotopic study in this area since 1985. Many thanks to G. Davaa, Institute of Meteorology and Hydrology of Mongolia for his support during Gu's Expert Mission of IAEA to help for water sampling in South Gobi.

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MONITORING CARBON DIOXIDE INJECTION AND STORAGE IN AQUIFERS AND DEPLETED OILFIELDS USING CARBON AND SULFUR ISOTOPE TECHNIQUES

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Abstract

Fluid and gas monitoring can be used to confirm the security and integrity of geological CO_2 storage. The distinct carbon isotopic composition of CO_2 from many industrial sources that process or combust hydrocarbons allows the use of isotopic and chemical analyses of produced fluids and gases to trace the injected CO_2 and quantify CO_2 storage processes in the subsurface. Our four year monitoring programme at the International Energy Agency Weyburn CO_2 Monitoring and Storage Project in Saskatchewan, Canada, featured frequent chemical and isotopic measurements of produced fluids and gases from around forty wells. Over the four year period, over four million tonnes of CO_2 were injected for storage and enhanced hydrocarbon recovery in the Weyburn oilfield. CO_2 concentration and carbon isotopic measurements of produced fluids and gases trace CO_2, and confirm that the order of magnitude increase in the amount of CO_2 in the subsurface resulted from CO_2 injection. The amount of CO_2 stored as HCO_3^- can be quantified using HCO_3^- concentration and carbon isotopic measurments, while concentration and isotope data for SO_4^{2-} and H_2S indicate that bacterial sulfate reduction was not a major source of HCO_3^-. To allow widespread application of geological CO_2 storage, reliable, cost effective monitoring of storage integrity will be essential. The produced fluid and gas monitoring techniques described here are based on chemical and isotopic techniques that are already widely employed and well understood by environmental isotope hydrologists, and have the potenital to play an essential role in future geological CO_2 storage monitoring programmes.

1. INTRODUCTION

Globally deep saline aquifers and depleted oilfields have a huge capacity for large-scale geological storage of carbon dioxide (CO_2), providing an opportunity to reduce the emissions of this pre-eminent greenhouse gas to the atmosphere [1]. Geological storage is likely to be one of the the most effective technologies for reducing emmissions from large stationary CO_2 sources. Presently, three full scale geological storage projects with CO_2 injection rates of one million tonnes per year or greater are operational, in Canada, Algeria, and Norway. Both the UNFCCC and the European Commission have indicated that emission reduction credits for geological storage may be granted, possibly before current emission targets expire in 2012.

Monitoring of geological storage is essential to confirm the integrity of the storage site, both during injection and following site closure. Monitoring programmes should be designed to trace injected CO_2 and quantify the amount of CO_2 stored by the different trapping mechanisms. A number of techniques for monitoring geological storage are available, including surface seismic surveys, borehole geophysical tools, and fluid and gas sampling. Our ongoing monitoring programme at the International Energy Agency Greenhouse Gas Weyburn-Midale CO_2 Monitoring and Storage Project in Saskatchewan includes frequent sampling of produced fluids and gases from over forty production wells. At Weyburn geological CO_2 storage is combined with enhanced hydrocarbon recovery from a depleted billion barrel oilfield [2]. As the majority of the pore space in the Weyburn field is filled with high salinity aqueous fluids (TDS ~80,000 mg/L), the CO_2 storage processes at Weyburn are similar to those that would take place in deep saline aquifers.

The objective of this study was to demonstrate how chemical and isotopic data can be used to monitor the fate of injected CO_2, including storage as HCO_3^- and molecular CO_2, while differentiating other sources of HCO_3^- e.g. bacterial sulfate reduction.

2. BACKGROUND

2.1. Principles of CO_2 storage – trapping mechanisms

Carbon dioxide injected at high pressure in the subsurface can be stored by a range of physical and chemical trapping mechanisms that vary in both the time intakes for the CO_2 to become immobilized and the long term security of the storage [3, 5]. Short term trapping mechanisms include solubility trapping of dissolved molecular CO_2 in aqueous or hydrocarbon fluids (e.g. equation 1), and ionic trapping; dissolution of CO_2 in brine followed by dissociation to form HCO_3^- (equation 2), and trapping of free phase CO_2 in pore volume.

$$CO_{2(gas)} + H_2O \Rightarrow CO_{2(aq)} \quad (1)$$

$$CO_{2(aq)} + H_2O \Rightarrow H_2CO_3 \Rightarrow H^+ + HCO_3^- \quad (2)$$

Free phase CO_2 storage security is dependant on seal integrity. Solubility and ionic trapping take place rapidly, within days to months; as long as the reservoir fluids remain in the storage site these trapping mechanisms are considered effective. Carbon isotopic and concentration data from selected Weyburn wells have been used to demonstrate that it is possible to quantify ionic trapping [6], and these data suggest that there is a limited contribution of HCO_3^- from carbonate mineral dissolution as a result of injected CO_2 producing carbonic acid (equation 3).

$$CO_2 + H_2O \Rightarrow H_2CO_3 \qquad H_2CO_3 + CaCO_3 \Rightarrow Ca^{2+} + 2HCO_3^- \quad (3)$$

Longer term trapping mechanisms include reactions with reservoir minerals that lead to mineral storage of injected CO_2. Reactions between CO_2 and reservoir minerals take place more slowly than the dissolution and dissociation reactions. While carbonate mineral precipitation could be relatively rapid, silicate reaction kinetics are sluggish in the geological CO_2 storage environment, taking 100 s to 1000 s of years to reach completion [4, 3].

Concentration and sulfur isotopic measurements of sulfate (SO_4^{2-}) and hydrogen sulfide (H_2S) can be used to trace the origin and evolution of sulfur species in subsurface environments [7, 8]. In the presence of organic carbon and dissolved sulfate, numerous members of the *Desulfovibrio* genus acquire energy via the oxidation of organic carbon and the dissimilatory reduction of sulfate (equation 4). The end products of bacterial sulfate reduction (BSR) are H_2S and oxidised organic carbon (HCO_3^-). At numerous oilfields in western Canada and throughout the world, H_2S concentrations are elevated (up to a few %) as a result of BSR [8]. HCO_3^- produced by BSR (equation 4) needs to be accounted for when quantifying the amount of injected CO_2 stored by ionic trapping (equation 2) in geological storage projects.

$$SO_4^{2-} + 2CH_2O \Rightarrow 2HCO_3^- + H_2S \quad (4)$$

2.2. Weyburn background

The International Energy Agency (IEA) Greenhouse Gas Weyburn CO_2 Monitoring and Storage Project was created to advance understanding of all aspects of geological CO_2 storage: economic, scientific and regulatory. The Weyburn field covers around 180 km^2 and produces medium gravity crude oil from Carboniferous shallow water carbonates at a depth of 1450 m. Following 50 years of production, oil wells now produce around ten times more water than oil, indicating that much of the reservoir is dominated by aqueous fluids. Enhanced hydrocarbon recovery at Weyburn currently involves the injection of around 5000 tonnes of supercritical CO_2 per day at over 15 MPa via 31 horizontal and vertical injection wells. The CO_2 injected at Weyburn is produced by coal gasification and transported via a 300 km pipeline from a synfuel plant in North Dakota, USA. Preliminary studies suggest that the Weyburn field may have a total storage capacity for around 25 million tonnes of CO_2 [2]. The project is now being expanded to include a CO_2 storage and EOR project in the adjacent Midale field.

3. METHODS

In August 2000, before CO_2 injection began at Weyburn, fluids and gases were collected from approximately forty producing wells in and surrounding the area of CO_2 injection. Sample collection continued (at three to four month intervals) for the following four years. Samples were also taken from the CO_2 pipeline. Gas samples were taken from the well casing within a metre of the wellhead pump while fluid samples were taken directly from the production tubing a few metres downstream of the pump. Sampling took place at surface temperature and pressure according to procedures published by the United States Geological Survey [10].

The geochemical parameters measured on fluids and gases collected from each wellhead include the determination of the concentration of 15 dissolved species including SO_4^{2-} and H_2S, field measurement of both alkalinity and pH, and isotopic compositions of sulfur in H_2S and SO_4^{2-}, and carbon in CO_2 and HCO_3^-. HCO_3^- concentrations were derived from standard titration alkalinity measurements conducted immediately (within an hour) in the field and then corrected to reservoir conditions using oil and gas compositional data, oil and water production data, and measurements of other species that contribute to alkalinity (i.e. H_2S and organic acids) using the computer program SOLMINEQ-88 [11]. Unacidified, filtered samples were analysed for anion concentrations (SO_4^{2-}, Cl^-) on a Waters ion liquid chromatograph using an

Alltech Allsep A-2 anion column. Dissolved sulfide (H_2S as S^{2-}) concentrations were determined using Orion sulfide specific and double junction electrodes. Repeated analysis of samples suggests analytical errors of less than ±10% for SO_4^{2-} concentration measurements, while for H_2S concentrations, though the sulfide anti-oxidant buffer was added immediately in the field, sulfide loss via oxidation as the samples adjust to surface conditions resulted in estimated errors of ±15%. Cumulative errors in calculated HCO_3^- concentration are approximately ±10%, and are mainly due to uncertainties in oil, water, and gas volumes, and H_2S measurements and the resulting contribution of H_2S to total alkalinity. CO_2 concentration in casing gas samples were measured on a Varian 3600 portable gas chromatograph from samples collected in tedlar bags. Measurement uncertainties on mole% CO_2 are less than ±5%.

Carbon isotope ratios of CO_2 were measured from gas samples collected via bubbling wellhead casing gas through water and collecting gas in upturned glass jars. Samples of filtered produced brine were injected into vacutainers containing 2 mL of ammoniacal strontium chloride solution (NH_4OH saturated with $SrCl_2$) to precipitate $SrCO_3$ for carbon isotopic analysis of HCO_3^- . Excess cadmium acetate ($CdCH_3COOH$) was added to precipitate dissolved sulfide as CdS for sulfur isotopic analysis, Subsequently the CdS solid was recovered by filtration and converted to Ag_2S. The dissolved sulfate was precipitated from the remaining aqueous fluid as $BaSO_4$ using an excess of $BaCl_2$. Sulfur isotopic ratios of H_2S and SO_4^{2-} and carbon isotope ratios of HCO_3^- were determined by isotope ratio mass spectrometry (e.g. [12]). Sulfur isotope ratios are reported in the usual δ-notation in ‰ relative to the internationally accepted standard Canyon Diablo Troilite (CDT), while carbon isotope ratios are also expressed using the δ-notation in ‰ relative to the Vienna Pee Dee Belemnite (V-PDB) standard. Sulfur isotope measurements were normalized using the sulfate reference materials IAEA S05, S06, and NBS 127 with assigned $\delta^{34}S$ values of 0.5 ±0.2‰, –34.1 ±0.2‰, 21.1 ±0.4‰ and the sulfide reference materials IAEA S1, S2, S3, with values; –0.3‰, 22.7 ±0.2‰, –32.6 ±0.2‰. Carbon isotopic measurements for HCO_3^- were normalized to the NBS 18, NBS 19, IAEA CO-1, CO-8, and CO-9 reference materials with $\delta^{13}C$ values of –5.1‰ ± 0.1, 1.95, 2.5 ±0.1‰, –5.8 ±0.1‰ –47.3 ±0.2‰ , while for CO_2, NBS 18 and 19 were used along with Messer CO2I and CO2II (values –0.29 ±0.20‰ and –40.13 ±0.17‰ respectively). Analytical uncertainties for $\delta^{34}S$ values of H_2S and SO_4^{2-} are both around ±0.4‰ and for $\delta^{13}C$ values of HCO_3^- and CO_2 are approximately ±0.2‰ and ±0.5‰.

TABLE 1. CHEMICAL AND ISOTOPIC DATA: RANGE, MEAN AND STANDARD DEVIATIONS FROM BASELINE SURVEY AND FOLLOWING FOUR YEARS AND FOUR MILLION TONNES OF CO_2 INJECTION.

	Injected CO_2	Baseline			Four years and four million tonnes CO_2 injection		
	Mean	Range	Mean	Stdev	Range	Mean	Stdev
		chemical abundance					
CO_2 (mole%)	98	0.4 to 9.7	4.0	0.02	0.4 to 80	27	28
HCO_3^- (mg/L)	–	46 to 535	268	97	63 to 1788	728	458
SO_4^{2-} (mg/L)	–	2895 to 3850	3464	240	3026 to 4250	3703	313
H_2S (ppm)	–	13 to 686	126	120	12 to 372	103	84
		isotopic composition					
$\delta^{13}C_{CO2}$ (‰)	–20.4 ± 0.4	–20.2 to –6.5	–12.6	3.5	–22.7 to –12.0	–18.2	2.4
$\delta^{13}CH_{CO3-}$ (‰)	–	–10.0 to +1.7	–2.7	3.1	–15.5 to 1.8	–5.73	5.9
$\delta^{34}S_{sulfate}$ (‰)	–	+17.0 to +31.6	+23.0	2.8	+17.4 to +30.3	+24.1	3.1
$\delta^{34}S_{H2S}$ (‰)	–	–2.7 to +10.9	+1.3	3.3	–2.6 to +9.7	+2.8	3.4

4. RESULTS

Table 1 summarizes ranges of chemical and isotopic compositions and mean values for CO_2, HCO_3^- , SO_4^{2-} and H_2S in fluids from circa 40 wells from baseline sampling and for circa 40 samples collected and analysed after four years and four million tonnes of CO_2 injection, along with data for injected CO_2.

5. DISCUSSION

At baseline carbon isotopic compositions of CO_2 and HCO_3^- with mean $\delta^{13}C$ values of –12.6‰ and –2.7‰ respectively, reflect two different carbon sources in the subsurface at Weyburn. Dissolution of ^{13}C enriched reservoir carbonate minerals provides the main carbon source with a smaller contribution from ^{13}C depleted organic carbon [6]. High sulfate concentrations (~3500 mg/L) with $\delta^{34}S$ values around +23‰ indicate that dissolution of reservoir anhydrite minerals was the major sulfate source.

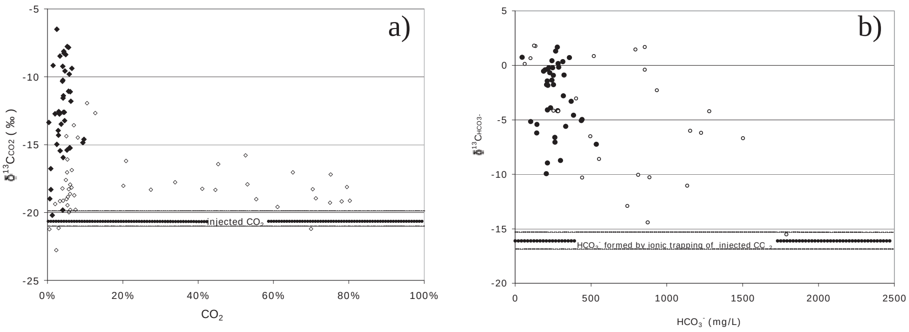

FIG. 1. a). Mole % CO_2 versus $\delta^{13}C_{CO2}$ for circa 40 wells from baseline pre CO_2 injection (filled diamonds), and following forty months and four million tonnes of CO_2 injection (open diamonds). b). HCO_3^- concentration versus $\delta^{13}C_{HCO3}$- from circa 40 wells for baseline pre CO_2 injection (filled circles), and following forty months and four million tonnes of CO_2 injection (open circles).

Mean H_2S concentrations at baseline of 126 ppm, with $\delta^{34}S_{H2S}$ values approximatley 20‰ lower than those of sulfate, provide strong evidence that bacterial (dissimilatory) sulfate reduction (BSR) has taken place in the reservoir. BSR produces CO_2 and HCO_3^- with a $\delta^{13}C$ values of circa –30‰ and is likely to be the ^{13}C depleted oxidised organic carbon source at baseline.

The most striking changes in the carbon species chemical and isotopic data over the four years of CO_2 injection are the decrease in the $\delta^{13}C$ values for CO_2 and HCO_3^- and the increase in the concentrations of CO_2 and HCO_3^- observed in many of the sampled wells. Fig. 1a and Fig. 1b demonstrate that the increases in CO_2 and HCO_3^- concentrations are combined with a change in their $\delta^{13}C$ values towards the $\delta^{13}C$ value of injected CO_2 (~ –20.4‰), and the $\delta^{13}C$ value for HCO_3^- formed via dissolution and dissociation (ionic trapping) of injected CO_2. The dissolution and dissociation of injected CO_2 under equilibrium conditions at the Weyburn reservoir temperature of ~ 60°C is associated with a carbon isotope fractionation of +4.5 ±0.2‰ [13], resulting in HCO_3^- from injected CO_2 ($\delta^{13}C_{CO2}$ ~ –20.4‰) having a $\delta^{13}C$ value of ~ –16‰. Thus the trends of increasing molecular CO_2 and HCO_3^- with decreasing carbon isotope ratios towards values of –20‰ for CO_2 and –16‰ for HCO_3^- (Fig. 1a and b) clearly indicate that injected CO_2 is retained via solubility and ionic trapping.

The carbon isotopic and chemical data for CO_2 and HCO_3^- demonstrate that significant amounts of injected CO_2 are stored as molecular CO_2 and HCO_3^- in the Weyburn reservoir. Mass and isotope balance calculations for four selected Weyburn wells [6] demonstrated that around 1000 mg of injected CO_2 was stored in each litre of reservoir brine as HCO_3^- (ionic trapping). A similar approach for assessing the amount of injected CO_2 stored as molecular CO_2 in the reservoir is currently underway.

Following four years of CO_2 injection, mean H_2S contents decreased slighly from 126 ppm at baseline to 103 ppm and the difference between the $\delta^{34}S_{sulfate}$ and $\delta^{34}S_{H2S}$ values remained constant around 20‰ (Table 1). This suggests that bacterial (dissimilatory) sulfate reduction has not been enhanced by the CO_2 injection. Hence HCO_3^- generation via bacterial sulfate reduction is not expected to have increased compared to baseline conditions, confirming that dissolution and dissociation of injected CO_2 (equation 2) rather than BSR (equation 4) has led to the increase in HCO_3^- concentrations. For a minority of wells a contribution of HCO_3^- from carbonate mineral dissolution is indicated by HCO_3^- concentration increases at $\delta^{13}C_{HCO3-}$ values ~ 0‰ (Fig. 1b) and increases in Ca^{2+} and Mg^{2+} concentrations.

6. CONCLUSIONS

Chemical and isotopic data for fluids and gases from around forty wells in the Weyburn field indicate that, after four years and four million tonnes of CO_2 injection, significant amounts of injected CO_2 are stored in the reservoir as CO_2 and HCO_3^- . Carbon isotopic compositions of CO_2 and HCO_3^- combined with chemical data reliably trace injected CO_2 and have the potential to quantify CO_2 storage as molecular CO_2 (solubility trapping) and HCO_3^- (ionic trapping). CO_2 carbon isotopic measurements confirm that the order of magnitude increase in the amount of CO_2 measured in subsurface gas samples results from injection of CO_2, while the amount of CO_2 stored as HCO_3^- can be quantified using HCO_3^- concentration and carbon isotopic measurments, with supporting evidence provided by sulfur species concentration and sulfur isotopic data. Isotopic and concentration measurements of sulfur species indicate that H_2S was generated via bacterial sulfate reduction (BSR) and confirm that there has been no significant increase in the contribution of HCO_3^- from BSR during the four years of CO_2 injection.

ACKNOWLEDGEMENTS

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$\delta^{18}O$ ISOTOPE MAP-GENERATION OF EUROPEAN MINERAL WATERS, APPLICATIONS AND LIMITS[1]

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Abstract

There is an increasing demand for independent analytical methods which can control the geographical origin of food. The EU project TRACE was started with the aim to develop a general understanding of the relation between the geo-bio-climatic environment and the isotope and elemental signature in food commodities. Beside mineral water the agricultural products wheat, honey, olive oil and lamb meat are investigated. As one part of the study a detailed $\delta^{18}O$ map for groundwater will be generated by the isotope results of 600 samples of European mineral waters. These isotope groundwater maps provide a multitude of applications not only for authenticity of food, but for groundwater recharge and climate studies, criminal forensics as well as archaeology.

1. TRACE PROJECT

The EU funded TRACE project will develop commodity specific traceability systems that will enable the analytical verification of the origin of food. Natural tracers such as trace elements, ratios of isotopes and genetic markers will be used to determine geographical, species and production origin. Geo and bioclimatic mapping is undertaken to extrapolate geographical origin and reduce the need for costly, time-consuming and laborious commodity specific data bases. The projects focus is on meat, cereals, honey, olive oil and mineral water.

Mineral water has not only been chosen accidentally but as a special link between geology, soil, climate effects (precipitation) and also as a very uninfluenced food product in comparison to other food.

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[1] Work performed within the 6th framework of the European Commission.

By EU law mineral water production has very limited possibility of anthropogenic treatment and production processes. Mineral water at all means originates from groundwater with limited influence of surface waters. Therefore any small-scale climatic effects on water content both isotopic and hydrochemical are flattened by the "mixing" of year around precipitation and long-term weather episodes. The groundwater of certain regions reflects very effectively the regional climate by its isotope signature of the oxygen-18 and deuterium.

Therefore the investigation of mineral water will provide not only a traceability system for mineral water based on climate and geology, but will also be used as a general groundwater map.

The spatial information of groundwater itself is the basis for a predictability of the isotope signature not only for groundwater but also for other food commodities as any food is linked to the local isotope signature of water.

2. SAMPLING AND METHODS

As one of the investigated food commodities 600 samples of mineral water have been collected all over Europe. As several countries of Europe have quite different drinking cultures and mineral water markets not every country provides the same spatial distribution of mineral waters. Additionally not every region is ready to provide groundwater readily for mineral water concerning quality and population's preference. For example the EU listing of officially noted mineral waters gives more than 800 mineral water brands in Germany but only three brands in Ireland. To enlarge the amount of samples in certain regions also some other bottled groundwaters such as spring, spa and table waters have been collected.

The measurement of the stable isotopes oxygen-18 and deuterium were only carried out in the lab of Hydroisotop, Germany using IRMS.

The geographical positions of the wells and springs where the groundwaters are pumped have been identified using the quoted bottling locality on the bottle. The bottling locality is in most cases provided as a city's name. The longitude and latitude was identified using a route mapping software. It is assumed that the locality is not correct in a range of about 15 km which is negligible in European scale.

For quality control a selection of samples have been sampled which are of the same brand, but bottled at different dates, which are added with different CO_2 contents (3 g/L CO_2 or 7 g/L CO_2), which are bottled in different bottles such as glass and polyethylene and which are sold under different labels respectively different selling companies.

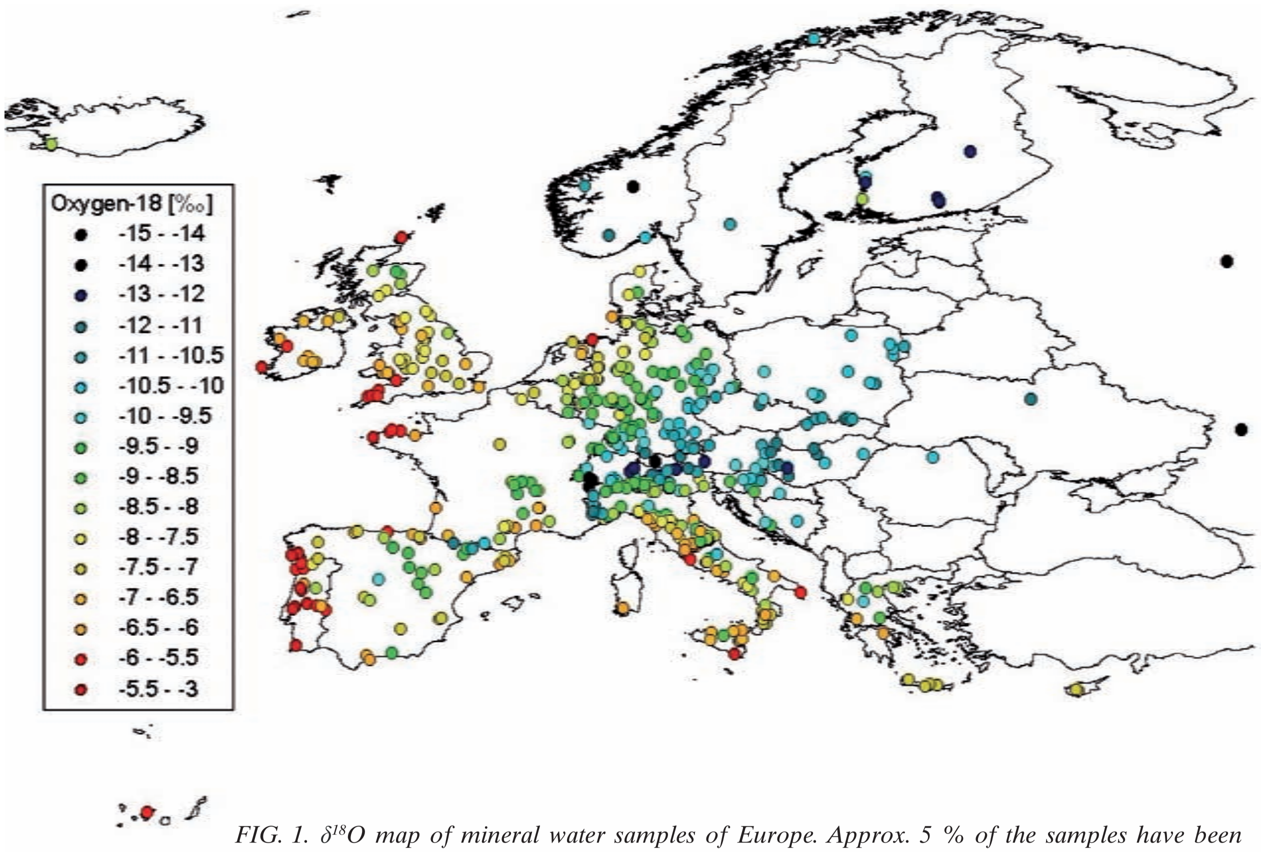

FIG. 1. $\delta^{18}O$ map of mineral water samples of Europe. Approx. 5 % of the samples have been excluded from the data set for mapping because they show major influence by either palaeowaters or brines. Values are given in relation to the standard VSMOW. Analytical precision is ±0,15 ‰.

3. RESULTS, GEOGRAPHICAL RELATION AND SPECIAL ISSUES

The results of the oxygen-18 measurement have been mapped (Fig. 1). The climatic effects are clearly visible. The effects are either dominated by the distance to coast, by the latitude (e.g. higher evaporation in the Mediterranean regions), by wind direction and by altitude.

All samples have been investigated towards special issues which are known to influence the contents of $\delta^{18}O$ and $\delta^{2}H$ of groundwater. Surprisingly only approx. 5% of all mineral water samples were identified to show visible effects of either natural CO_2 contents or technical CO_2 addition, of palaeo-waters such as groundwater recharge during Pleistocene climate (identified by tritium and carbon-14 analyses) of seasonal variability of very young groundwater, of river infiltrates (identified by repeated sampling) or of brines (identified by ion content, detailed hydrological knowledge of the sampling sites).

4. POSSIBLE APPLICATIONS

The measured values as well as data of precipitation and climate will be used for a spatial modeling of oxygen-18 and also of deuterium and/or of deuterium excess. Samples with deviating isotope signature of typical “young meteoric water” will be excluded.

Because of the relative irregular localisation of the samples the map quality will not be very precise. To improve the map quality the usage of additional information that may explain the change of the values and that are available at a higher resolution are necessary. For $\delta^{18}O$ there are indicators for climate as latitude, altitude, temperature and rain amount. Results of this investigation will be published soon.

These modeled groundwater maps will provide immense usage for the authenticity of foods especially for fruits and vegetables but also for honey, oil, meat and wine because they are marked by the isotope signature of the local groundwater and local climate.

The same way as authenticity analyses works these methods are used for criminal forensics and migration studies of human culture and animals such as birds in archaeology and biology.

Because all samples have been collected, which means have been bottled, in 2006, the dataset provides a clear “snapshot” of groundwater. Because all samples have been measured for tritium content as well the mean residence time of the water can be roughly estimated. The dataset can therefore provide a valuable snapshot for climate change studies in the near future.

5. LIMITS OF GENERATION

The generation of a European wide oxygen-18 map is limited both by hydro-geological and cultural issues. The partly irregular localisation of the samples will produce a groundwater map with different accuracies for the different locations in dependence of the number of samples per region and climatic zones.

The usage of the groundwater map for a prediction of isotopic values in food still needs comprehending investigations over factors influencing the final signature in fruits and vegetables e.g. seasonal water uptake, transpiration of plants, etc..

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GEOCHEMICAL AND ISOTOPIC CHARACTERIZATION OF GROUNDWATER RESOURCES IN MAIDERE BASIN (SOUTHERN PART OF MOROCCO)

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Abstract

Integration of geochemical and isotopes techniques in water resources investigations has contributed considerably to a better understanding of the aquifer hydrodynamic functioning in complex structural areas. Maidere Basin, located in south Morocco, is extending over 13,000 km² and limited by some orographical chains of the Anti-Atlas. Lithological formations outcropping in the basin are divided into compartments by major faults of NE–SW direction. This fault network helped to generate aquifers compartments with lateral hydraulic discontinuity. Five aquifers constitute the multilayer system: Precambrian, Lower Cambrian, Middle Cambrian, Ordovician and Quaternary units. Ordovician outcrops are a large spread and constitute the more important aquifer in the basin. Furthermore, a smell gas like carbon dioxide is observed in some bores sampled from different aquifers. Geochemical and isotopic study has been undertaken in Maidere Basin in order to better understanding the hydrodynamic functioning of the aquifers units and to determinate the CO_2 gas origin. Correlations between saturation index of calcite and the partial pressure of CO_2, have

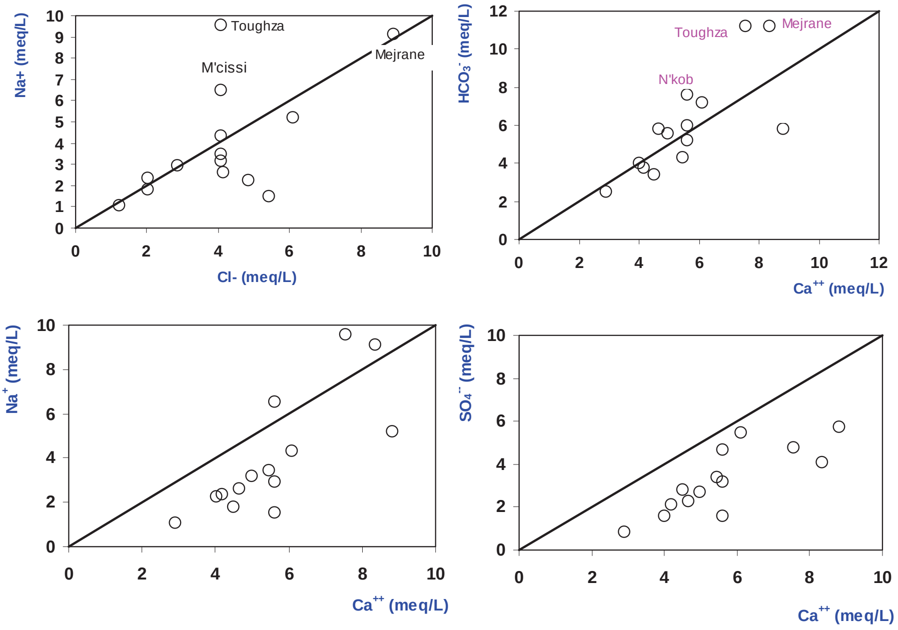

FIG. 1. Mineralization sources of the water sampled in the Maider Basin: correlations between the ionic species.

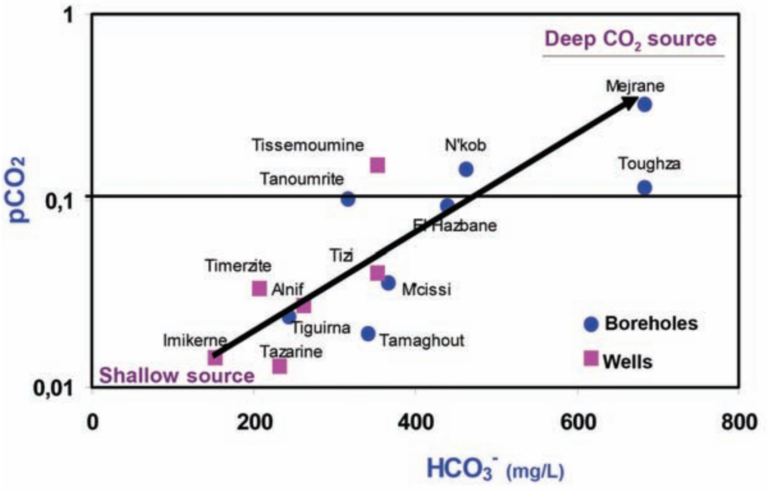

FIG. 2. Correlation between log pressure of CO_2 and bicarbonate contents.

allowed distinguishing undersaturated water with a lower pCO_2 sampled from all of wells and oversaturated water with high values of pCO_2 sampled in boreholes. Radiocarbon analyses showed the presence of old water in the boreholes with high values of pCO_2. Carbon dioxide seems to come from deep levels and circulate through the deep faults network. The relationship between $\delta^{13}C$ and pMC (percent modern carbon) oppose the modern groundwater and impoverished in $\delta^{13}C$ (that keep the pedological marking of the carbon at the time of their infiltration) to paleowaters (<16 pMC) and having exchanged the carbon with an impoverished matrix and/or having dissolved a carbon dioxide of deep origin.

1. HYDROLOGICAL SETTING

Maidere basin, located in south Morocco, is extending over 13,000 km² and limited by some orographical chains of the Anti-Atlas. It’s limited by Jebels Sarhro-Ougnate in the North, by the plain of Tafilalt in the East, by Jebel Bani in the West and in the South and South-East by Hamada Cretaceous rocks of Kem-Kem. The Maidere basin is characterized by an arid and semi-arid climate with a mean annual rainfall of about 80 mm/a, a mean air temperature in the range 40–15°C, and very high evapotranspiration.

Lithological formations outcropping in the basin are divided into compartments by major faults of NE–SW direction. This fault network helped to generate aquifer units with lateral hydraulic discontinuity. Five aquifers

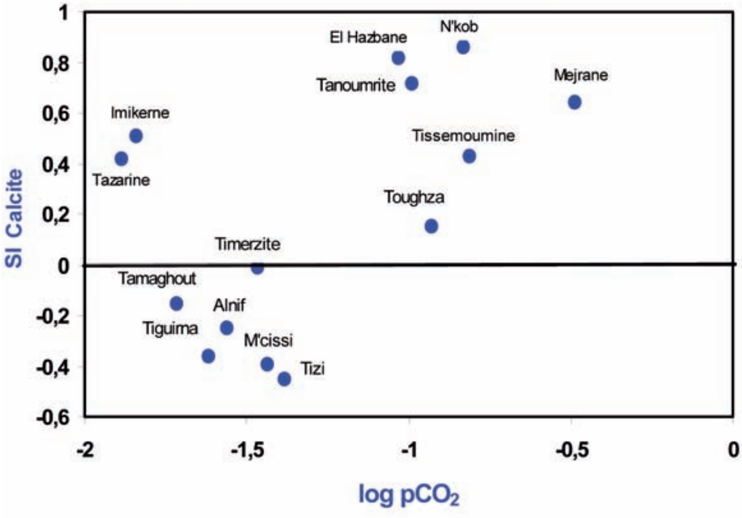

FIG. 3. Correlation between log pressure of CO_2 and saturation index of calcite.

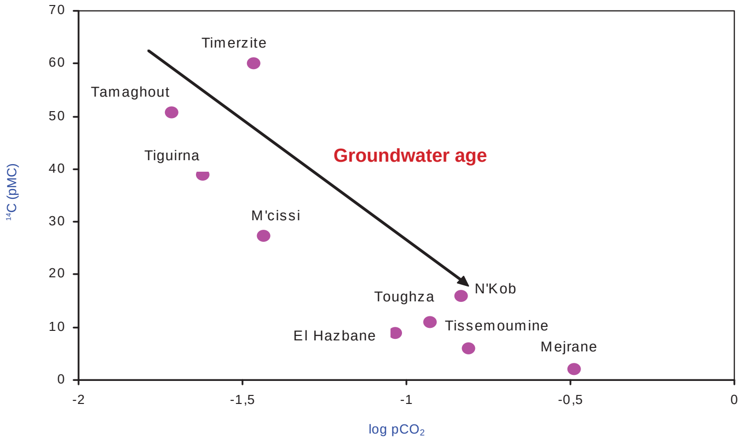

FIG. 4. Radiocarbon activity (pMC) versus log pressure of the CO_2.

constitute the multilayer system: Precambrian, Lower Cambrian, Middle Cambrian, Ordovician and Quaternary units. Ordovician outcrops are common and constitute the more important aquifer in the basin [1]. Furthermore, presence of gas was observed in some bores, when sampling different aquifers.

Lithological formations outcropping in the basin are divided into compartments by major faults of NE-SW direction. This fault network helped to generate aquifer units with lateral hydraulic discontinuity [2–3], which makes very difficult the application of the methods based on the measurements of piezometric levels. Geochemical and isotopic study has been undertaken in Maidere basin in order to better understand the hydrodynamic functioning of the aquifer units and to determine the CO_2 gas origin. Fourteen samples were collected for geochemical and isotopic analysis.

The geochemical study of the water inventored in the Maïdere basin shows that these waters present an intermediate chemical facies. The spatial distribution of salinity does not obey any gradient, making it possible to highlight the zones upstream and downstream of the aquifer system.

The correlation between total salinity and the major elements reveal the importance of bicarbonate and chloride for the anions and calcium then sodium for the cations in the acquisition of mineralization. In the same way, the correlationbetween the ionic species (Fig. 1) show that the mineralization is governed mainly by the dissolution of carbonates, halite, and the bases exchange with clays, also in some samples, by probable contribution of deep CO_2.

The pCO_2–HCO_3^- correlation shows a linear trend between not very deep water and the one having undergone a probable contribution of deep CO_2

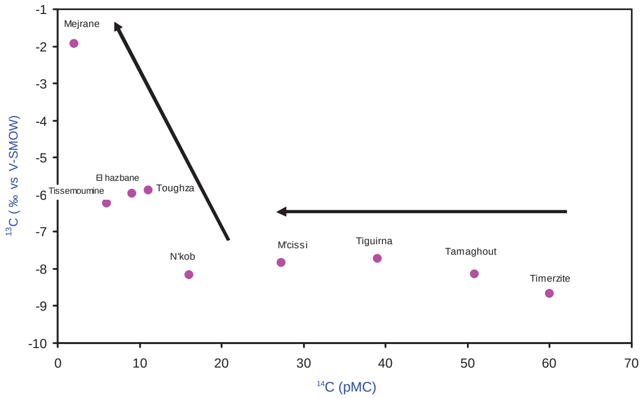

FIG. 5. Carbon-13 versus radiocarbon activity (pMC).

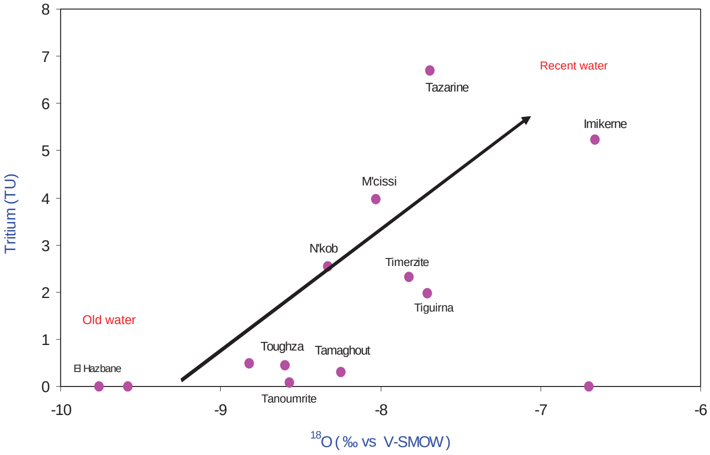

FIG. 6. Relation between tritium and oxygen-18.

(Fig. 2). The saturation index of calcite was calculated from calco-carbonic contents of the waters. These saturation indicies versus the partial pressure of CO_2 graph (Fig. 3) show two groups with decreasing level of evolution. The first group contains all wells with unsaturated water and lower pCO_2 waters. This group contains water with a short residence time. These waters can still dissolve carbonates. The second group contains the majority of wells with oversaturated waters that have been stored for a long time in the aquifer. These waters had time to dissolve deep CO_2 and carbonates.

Radiocarbon versus log pCO_2 relationship (Fig. 4) shows that the calco-carbonic mineralizations depend on time. A water type with low pCO_2 and high ^{14}C content is opposed to old and mineral-bearing water (El hazbane, Tissemoumine, Mejrane, N'kob and Toughza) which undoubtedly dissolved a deep carbon dioxide.

Carbon-13 versus ^{14}C content relationship (Fig. 5) presents water with short residence time, depleted in carbon-13 (which keeps the pedological marking of carbon at the time of their infiltration) at some samples (El Hazbane, Tissemoumine, El Mejrane and Toughza) with waters with a long residence time (<16 pMC) and having exchanged carbon with depleted matrix and/or having dissolved a deep carbon dioxide.

The isotope analyses present variations in ^{18}O from –6.66 to –9.76‰ vs SMOW with an average of about –8.29‰ vs SMOW and deuterium from –42.20 to –65.75‰ vs SMOW with an average of about –54.16‰ vs SMOW. Deuterium excess of the majority of the water samples ranges between +10 and +14‰.

Results of these analyses show tritium values ranging from 0 ± 0.12 to 6.70 ± 0.360 TU with an average of 2.16 ± 0.24 TU. Values over 5 TU are obtained on both sides of the Tazarine-Taghbalt synclinal (Imikerne and Tazarine wells, Mejrane drilling).

The relation between tritium and oxygen-18 (Fig. 6) allows to appreciate the palaeoclimatic effect on the recharge process. Indeed, the majority of the samples show a gradual arid tendency of the climate, between waters with low tritium values existing in the centre of the basin (Tissemoumine, el Hazbane) and water enriched in oxygen-18 and tritium existing in Jebel Bani Piedmont (Imikerne) or in the synclinal of Taghbalt (Tazzarine).

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ASSESSING THE APPLICABILITY OF GLOBAL CFC AND SF_6 INPUT FUNCTIONS TO GROUNDWATER DATING IN BRITAIN

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Abstract

Chlorofluorocarbons (CFCs) and sulphur hexafluoride (SF_6) are increasingly being used to date groundwaters. While these trace gases are generally well-mixed in the atmosphere, local atmospheric excesses (LAEs) have been found in some parts of the world, thereby affecting the interpretation of data from groundwater studies. To investigate the possibility of LAEs in Britain, mixing ratios of CFC-11, CFC-12 and SF_6 were measured in soil gases from two large conurbations (London and Birmingham) and a smaller urban area, Bristol. Most mixing ratios for CFC-12 and SF_6 were <10% above the current northern hemisphere atmospheric mixing ratio (NH-AMR) values. CFC-11 was more variable, but usually <20% above the NH-AMR value. Given the errors associated with trace-gas groundwater dating, there is little justification for factoring in the minor LAEs found in this study to urban groundwater investigations, and accordingly the use of CFC and SF_6 input functions based on the NH-AMR curves appears justified for Britain.

1. INTRODUCTION

Chlorofluorocarbons (CFCs) and sulphur hexafluoride (SF_6) are increasingly being used to date recent groundwater components [1–4]. Their use in this role depends critically on the input function, i.e. the atmospheric mixing ratio over time for the individual gases [5]. Observations by the worldwide network of atmospheric monitoring stations indicate that the gases are well-mixed in the atmosphere [6], and therefore a single input function for each gas should in theory suffice for groundwater investigations worldwide.

However, local atmospheric excesses (LAEs) due presumably to urbanization and its associated industrial activity have been observed by some researchers. For example, Oster et al. [3] and Ho et al. [7] found CFC excesses in south-west Germany and the New York metropolitan area respectively, while SF_6 excesses have since been measured in the same areas [8, 9]. On the basis of these measurements, the use of input functions raised by up to 60%

above the global average has been proposed. Clearly, then, it is important for groundwater dating studies in the more-populated areas of the world to be aware of this possibility, and if possible to address it. The work reported here is concerned with the situation in southern Britain, an area with a relatively high population density where CFCs and SF_6 are increasingly being used for groundwater dating [10–12].

2. BACKGROUND

2.1. The importance of assessing local atmospheric mixing ratios

The effects of LAEs on water dating vary with each of the gases, but can have a major impact. Fig. 1 shows plots of the groundwater concentrations calculated from the northern hemisphere atmospheric mixing ratio (NH-AMR) curves (http://water.usgs.gov/lab/software/air_curve/), and a 50% increase from the beginning of emissions. Both assume a recharge temperature of 10°C, which is close to the annual average air temperature for the whole of lowland Britain

It is clear that while age differences are very small in waters recharged around 50 years ago, in recent waters they are large. Taking the highest point on each of the NH-AMR curves, the same groundwater concentration would be indicating differences of about 9 yr (SF_6), 12 yr (CFC-11), and 20 yr (CFC-12). Thus if an LAE is present in an area, it must be taken into consideration for groundwater dating purposes. Not only can it help to correct the water age, but can also be used to extract useful information from waters that would be regarded as 'over-modern' (i.e. contaminated) using the NH-AMR.

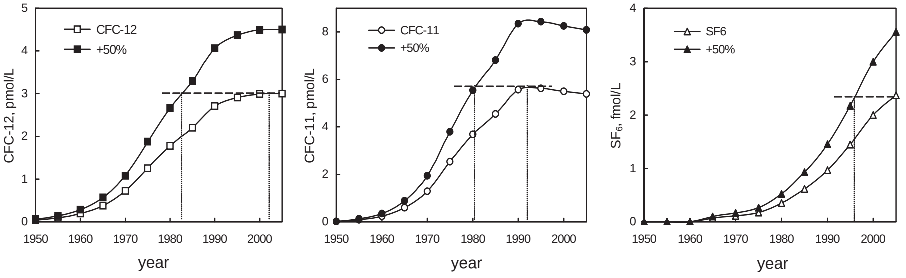

FIG. 1. Plots showing the concentration of CFC-12, CFC-11 and SF_6 in air-equilibrated water at 10ºC, based on the respective NH-AMR (northern hemisphere atmospheric mixing ratio) curves over the past half-century. Also shown is the concentration curve for a 50% local atmospheric excess, and the resulting maximum difference in interpretation of water age.

The intensive long-term atmospheric monitoring which would otherwise be required to determine the magnitude of an LAE can be avoided by sampling soil air. Studies have shown that the soil acts as a low-pass filter for variations in atmospheric gas mixing ratios [3, 9, 13], typically integrating over timescales in excess of one month.

2.2. Approach of the present study

Southern Britain contains the UK's two largest cities, London (population 7 million for Greater London) and Birmingham (1 million, though the remainder of the West Midlands Conurbation extending mainly to the north west of the city contributes a further 4 million people). As such, they are obvious areas to seek evidence of atmospheric excesses. A third city, Bristol (0.4 million) was chosen for comparison. The location of each city is shown in Fig. 2. While there are some variations in topography across each city, none of the areas is in a pronounced basin where stagnant atmospheric conditions might prevail. The predominant wind direction for each of the urban areas is SW to WSW [14]. This means that Bristol is most 'upwind', while Birmingham and London are at comparable 'effective distances' from the ocean of approximately 200 km. In neither case are there major industrial areas supervening.

3. SAMPLING AND ANALYSIS

3.1. Sampling

Grassed parkland areas were chosen as being least likely to have suffered from contaminating industrial activities. A stainless steel tube of approximately 8 mm o.d. and 4 mm i.d. was fitted with a disposable tip and driven into the ground by a sliding hammer to a depth where significant resistance was encountered (this varied with the nature of the soil conditions). The tube was then extracted by 20–30 mm to create a small void into which soil gas could diffuse. After purging atmospheric air from the steel tube and the connecting flexible tubing with a hand vacuum pump, the soil gas was sampled into a pre-evacuated 300 mL glass bulb. At each site two or more tubes were driven in 1–2 m apart to assess how representative the individual samplings might be. Atmospheric spot samples were also taken at most sites. Locations of the sampled sites are shown in Fig. 2.

FIG. 2. Map of southern Britain showing the location of the sampling sites in relation to urban boundaries in Bristol (left), Birmingham (centre) and London (right). W–BGS Wallingford.

3.2. Analysis

Soil gas samples were analysed for CFCs and SF_6 by cryotrapping onto porous-polymer-packed sample loops followed by quantification by gas chromatography using an electron capture detector (ECD). The method used was based largely on the approach of Bullister and Weiss [15]. To check how representative the samples were of the soil atmosphere, CO_2 concentrations were measured by gas chromatography using a thermal conductivity detector (TCD), and $\delta^{13}C_{CO2}$ values were determined by isotope ratio mass spectrometry. Both CFC and SF_6 analyses were calibrated back to an air standard collected at the Mace Head Atmospheric Research Station of NUI Galway, Ireland.

4. RESULTS

4.1. Atmospheric gases

Results for atmospheric gases are given in Table 1, together with the end-2005 NH-AMR values (see also Fig. 3). All the CFC-12 values lie between 100

TABLE 1. RESULTS OF SOIL GAS SAMPLING AT THE STUDIED SITES, INCLUDING ANALYSES OF CFC-12, CFC-11, SF_6, CO_2 AND $\delta^{13}C_{CO2}$. ALSO INCLUDED ARE VALUES FOR THE CFCS AND SF_6 FROM ATMOSPHERIC SPOT SAMPLES.

Site	Site code	Date	Atmosphere			Soil sample					
			CFC-12 pptv	CFC-11 pptv	SF_6 pptv	Depth mbl	CFC-12 pptv	CFC-11 pptv	SF_6 pptv	CO_2 % vol	$\delta^{13}C_{CO2}$ ‰ PDB
LONDON											
Chislehurst	LN-PW	15 Mar 06	550	253	6.58	0.60	539	251	6.25	0.39	–26.5
						0.65	532	242	6.13	0.71	–27.2
Epping Forest	LN-EF	15 Mar 06	550	253	6.87	0.25	570	342	6.36	0.62	27.8
						0.30	547	335	7.14	0.07	–
Harrow-on-the-Hill	LN-HH	10 Mar 06	–	–	–	0.70	577	350	6.21	0.82	–27.5
						0.70	584	309	6.16	0.70	–27.1
Hyde Park	LN-HP	10 Mar 06	539	254	6.40	0.70	546	269	6.07	0.62	–27.8
						0.70	555	261	6.21	0.78	–25.3
						0.70	571	271	6.08	0.83	–25.0
Richmond Park	LN-RP	15 Mar 06	544	267	8.34	0.80	548	232	6.93	1.94	–27.1
						0.75	552	254	6.37	2.03	–26.5
BIRMINGHAM											
Edgbaston	BM-ER	28 Mar 06	557	269	6.35	0.65	574	279	6.02	2.50	–25.9
						0.50	577	287	6.63	2.49	–26.5
Kingshurst	BM-KL	28 Mar 06	594	548	15.72	0.65	577	304	6.17	4.15	–29.2
						0.35	584	301	5.96	3.98	–29.1

Sandwell	BM-SP	28 Mar 06	562	297	6.09	0.30	561	349	6.68	3.28	–30.2
						0.35	566	330	6.24	0.47	–29.1
Shirley	BM-NR	28 Mar 06	581	477	6.61	0.65	562	276	6.39	0.89	–28.1
						0.50	567	252	6.45	0.51	–28.9
						0.75	553	254	6.46	0.41	–27.6
BRISTOL											
Clifton Down	BL-CD	23 Mar 06	611	281	5.89	0.35	598	275	6.07	0.45	–25.2
						0.45	587	257	6.03	0.51	–25.2
Fishponds	BL-OP	23 Mar 06	602	253	6.04	0.35	585	220	6.03	3.16	–28.5
						0.50	578	235	5.97	1.14	–28.2
Hanham Common	BL-HC	23 Mar 06	614	289	6.28	0.55	570	285	5.73	1.92	–26.4
						0.70	587	292	5.80	0.38	–24.6
Southmead	BL-TP	23 Mar 06	596	252	6.11	0.55	735	2251	6.43	5.28	–29.3
						0.65	692	458	6.20	2.67	–29.3
WALLINGFORD											
CEH Met Site	W	06 Feb 06	547	262	6.41	0.70	538	249	6.76	0.60	–26.7
						0.70	548	260	6.29	0.68	-26.6
NH-AMR end-2005		31 Dec 05	539	250	6.11						

and 114% of the NH-AMR value of 539 pptv (parts per trillion by volume). Most CFC-11 values fall in the range 101–119%, but two Birmingham sites (BM-KL and BM-NR) are about twice as high as the NH-AMR value of 250 pptv. Most SF_6 values are between 96 and 112% of the NH-AMR value of 6.1 pptv, but two sites exceed this by one-third (LN-RP) and one-and-a-half times (BM-KL). The BM-KL atmospheric sample was therefore the only site where two of the three trace gases were significantly elevated above NH-AMR values.

4.2. Soil gases

The results of the soil gas sampling are given in Table 1. The CO_2 concentrations (0.4 to 5.3%) and $\delta^{13}C$ values (–25 to –30 ‰) indicate that in all cases except one, LN-EF (ii), the gas extracted consists predominantly of soil air rather than a mixture with inadvertent atmospheric contamination (CO_2 <0.04%, $\delta^{13}C$ ~8 ‰).

Intra-site trace gas measurements were generally in good agreement. For CFC-12, 13 out of 14 sites yielded measurements within 5%, the exception being BL-TP (6.2%). For CFC-11, seven out of 14 sites were within 5%, and a further 5 within 10%. One of the two remaining sites was within 13% (LN-HH), though BL-TP was very poor. For SF_6, nine out of 14 sites were within 5%, a further three sites within 10%, and one site (LN-EF) at 11%.

The measured values for CFC-12, CFC-11 and SF_6 are shown in graphic form in Fig. 3. As a result of the usually good intra-site agreement, results from each site have been averaged and are shown in relation to the end-2005 NH-AMR. On each plot the +10% value is also shown, with an additional +20% for CFC-11 only. For CFC-12, one site is just below atmospheric, 12 out of 14 sites lie within the +10% band, and one is elevated at +33% (BL-TP). For CFC-11, two sites are just below atmospheric, six sites are within +10%, and another three within about +20%. A further three sites are elevated by approximately one-third, while there is an extreme enrichment of over four times for BL-TP. For SF_6, 13 out of 14 sites are within ±10% of atmospheric, the remaining site (LN-EF) being just in excess at +10.5%.

5. DISCUSSION AND CONCLUSIONS

The atmospheric gas samples, though necessarily only a ‘snapshot’ of conditions on the day of sampling, were for the most part close to the current NH-AMR figures. On each of the sampling days there were breezy or windy conditions, which would tend to dilute and disperse any plumes containing elevated proportions of one or more of the three trace gases. It is noteworthy

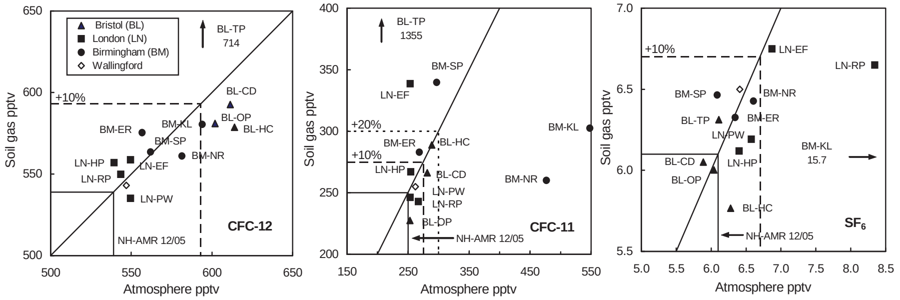

FIG. 3. CFC and SF_6 compositions of soil gas samples plotted versus atmospheric samples from the studied sites. Also shown are the NH-AMR values for the end of 2005, with 10% and 20% additions as appropriate. Site codes as in Table 1.

therefore that the Birmingham site BM-KL had CFC-11 and SF_6 values more than twice as high as the NH-AMR values.

The soil gases were generally consistent, particularly for CFC-12 and SF_6 where nearly all values were within 10% of the current NH-AMR value. CFC-11 was more wayward but there was only one very high value, from BL-TP, also the only site with significantly raised CFC-12, suggesting that in this single instance the site selection was flawed, e.g. there may have been landfilling or creation of made ground in the vicinity which has contributed to the elevated CFCs. There was little or no evidence from the BM-KL site for the elevated values found in the atmosphere.

Consideration of prevailing wind direction and industrial history leads to the empirical prediction that LAEs should be developed least in Bristol and most in Birmingham. As Fig. 3 shows, for CFC-12, London is least enriched and Bristol the most. For CFC-11, the picture is less clear but London shows the least excesses in atmospheric or soil gas. For SF_6 Bristol is lowest, while London is highest in soil gases. Thus no overall pattern emerges; the data in Table I suggest no pattern either within the individual cities, although the sampling density clearly cannot be definitive in this regard. The semi-rural control site (Wallingford) as might be expected gives results close to the NH-AMR values for the CFCs, with SF_6 being only slightly elevated by comparison.

Studies of urban and peri-urban groundwaters have not infrequently encountered 'over-modern' concentrations of the CFCs [12, 16, 17] and, as mentioned in the introduction, some researchers have justified using the LAE concept to extract dates from waters which they regard as otherwise uncontaminated, for example [3] and [8]. While there may be many regions of the world where this is a valid approach, the results reported here lead to the conclusion that it is not currently justified in Britain, because given the errors associated with trace-gas groundwater dating (e.g. precision of measurement, assumptions about recharge temperature, excess air, contamination or degradation in the subsurface [5]), there is little or no justification for factoring in the minor LAEs found in this study to urban or peri-urban groundwater investigations. The alternative interpretation, that CFC excesses are the results of variable point-source contamination, inevitably hinders the understanding of urban groundwater systems in terms of 'true' residence time. Nevertheless the CFCs still have some value as environmental tracers, and because SF_6 tends to suffer very much less from contamination, it remains a potential dating agent.

A caveat to the above view is that more-significant LAEs may have existed in the past when the use of CFCs was uncontrolled, as considered by Oster et al. [3] and Ho et al. [7]. However, in the absence of any historical data for the cities in the present study, this can only be speculative.

ACKNOWLEDGMENTS

We thank our colleague David Jones (BGS Keyworth) for assistance with equipment and advice on soil gas sampling.

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THE USE OF OXYGEN-18 AND DEUTERIUM IN THE WATER DYNAMICS ASSESSMENT OF TWO LAKES IN THE VOLCANIC STRUCTURE OF MOUNT VULTURE, SOUTHERN ITALY

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Abstract

Two small volcanic lakes in the Quaternary structure of Mount Vulture, Southern Italy, exhibit different isotopic and physico-chemical features. Lake Piccolo is permanently stratified, with a water temperature increasing and δ-values decreasing from the pycnocline to the bottom. This indicates a recharge of denser groundwater from the lake bottom, which does not mix with the shallow water. A slight increase of recent ^{18}O values with respect to old ones may reflect the current climatic change. The other lake, Lake Grande, has a 'normal' behaviour.

1. INTRODUCTION

The volcanic area of Mount Vulture (Basilicata, Southern Italy) has been widely studied for the geological features of the volcanic edifice, as well as for the hydrologic, hydrogeologic and environmental aspects of the two crater lakes (Lake Piccolo and Lake Grande) present in the area. The groundwater issued by numerous springs is largely exploited by bottling companies because of its CO_2 and salt content.

The research reported here is a follow-up of a study published three decades ago [1]. During such first survey, spanning over a full year, a permanent thermal and isotopic water stratification was observed in Lake Piccolo, where the water temperature increases and the heavy isotope content decreases from the pycnocline to the bottom. These effects, repeatedly confirmed in investigations carried out during the nineties of last century [2, 3], were attributed to groundwater gushing at the lake bottom. An almost homogeneous isotopic composition of water can be occasionally observed in winter, which is due to the seasonal variations of surface inflow, and does not indicate vertical mixing. The aims of the present investigation is to assess if the water stratification has been maintained in Lake Piccolo, and improve our understanding of the water recharge dynamics of the two crater lakes by means of water stable isotope dat emistry.

2. GEOGRAPHICAL, GEOLOGICAL AND HYDROGEOLOGICAL SETTINGS

Our hydrological investigation is focused on the volcanic area of Mount Vulture, which is the highest remnant (1326 m asl) of a crater rim of a Pleistocene stratovolcano. The edifice is constituted by a succession of lava flows and pyroclastic deposits produced by eruptive activity occurred between 730 and 130 kyr BP [4, 5]. Mount Vulture is characterized by an abnormally high content of high-S feldspathoid (instead of leucite) and a K_2O/Na_2O ratio close to the HKS magma series [6, 7, 8]. Its last (of many) phreato-magmatic eruption generated a crater in the south-western flank that now hosts two small lakes: Lake Piccolo and Lake Grande. The first lake, at an altitude of 658 masl, has a surface area of 0.14 km^2 and a maximum depth of 38 m. The second lake, with an altitude of 656 msl, a surface area of 0.42 km^2 and a depth of 36 m, is located down-stream of the first. The excess water (about 0.05 m^3 s^{-1} on the average) flows from Lake Piccolo to Lake Grande through a channel and it is removed from Lake Grande by an emissary. A lake balance estimate indicates a water deficit, so implying a groundwater contribution especially to Lake Piccolo, being the Lake Grande bottom impervious owing to clay deposits [7].

Despite the alternation of more permeable fissured lavas, and less permeable tuffs, paleosoil and fine-grained pyroclastic deposits, an overall hydraulic continuity exists between the formations, and thus the Vulture relief can be considered to host a multilayered aquifer [7]. Faults, however, may locally hamper the groundwater horizontal movement but at the same time provide paths for the ascent of water, deep fluids and gases. Several springs are related to these tectonic discontinuities, while some others are located at

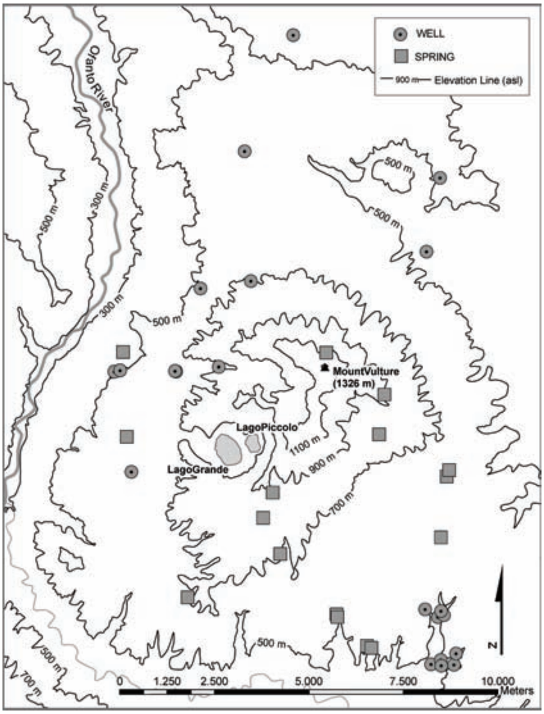


FIG. 1. Sampling site location map.

the edges of the volcanic edifice, or scattered at various elevations and possibly fed by perched aquifers. The springs, in spite of their modest discharge (up to 0.01 $m^3 s^{-1}$), have a permanent regime.

3. SAMPLING AND ANALYSES PERFORMED

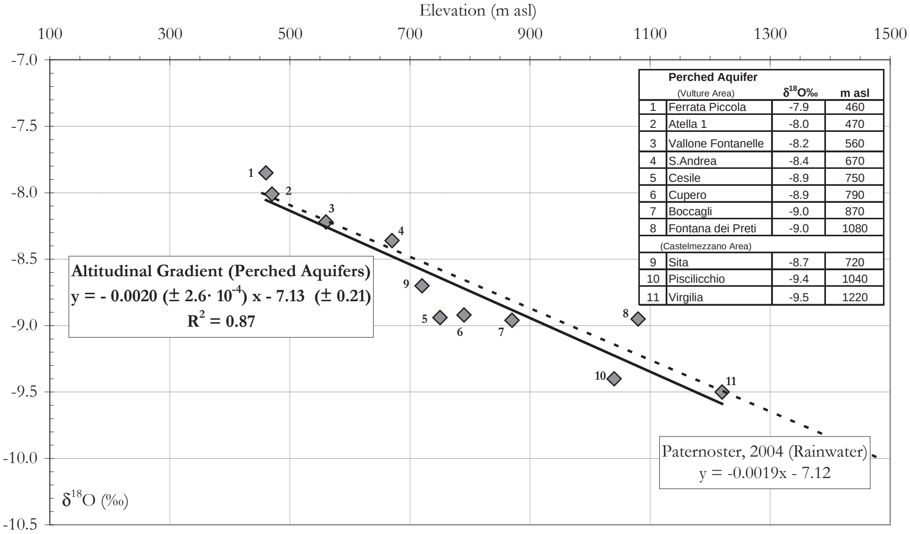
The two lakes of the Vulture volcanic area were sampled at different depths along vertical profiles in August and September 2006, together with twenty-three springs and twenty-one wells. Few more springs were collected in January 2007. Field measurements of physico-chemical parameters included temperature, pH, electrical conductivity (EC), and dissolved oxygen (DO). The isotopic analyses (oxygen-18 and deuterium) were performed in the Geokarst Engineering laboratories (Trieste, Italy).

Some springs scattered along the volcano slopes and in the nearby mountain area of Castelmezzano (50 km south), fed by small perched aquifers, were sampled in order to determine the isotope altitudinal gradient of the prevailing orographic precipitations [9]. The altitudinal gradient is needed to estimate the mean recharge elevation of the main aquifer, which feeds the springs located at the outcrop of the underlying, less permeable flysch at the edges of the volcanic edifice, or where tectonic features (mainly normal faults) allow the groundwater ascent. The location of sampling sites is shown in Fig. 1.

4. RESULTS

4.1. Springs and wells

The basal and perched springs show a wide variety of water types. While pH values are uniformly scattered from neutral to acidic, two different groups can be identified on the basis of EC and DO. The first group includes low-mineralized springs with high-DO values, possibly related to shallow groundwater. The second group includes springs with high-mineralization (about 1100 μS·cm^{-1}, with a few exceeding 5000 μS·cm^{-1}) and low-DO (<3 mg/L) indicating a deeper origin of groundwater. The $\delta^{18}O$ of spring water varies between –8 and –10‰, and the δ^2H between –51 and –63‰. As a whole, spring data reflect, with a certain degree of dispersion, the mean weighted values of the local meteoric water, which are $\delta^{18}O$ = –8.3‰ and δ^2H = –48‰ at the Melfi station [10]. The same conclusion applies to



	Perched Aquifer (Vulture Area)	$\delta^{18}O$‰	m asl
1	Ferrata Piccola	-7.9	460
2	Atella 1	-8.0	470
3	Vallone Fontanelle	-8.2	560
4	S.Andrea	-8.4	670
5	Cesile	-8.9	750
6	Cupero	-8.9	790
7	Boccagli	-9.0	870
8	Fontana dei Preti	-9.0	1080
	(Castelmezzano Area)		
9	Sita	-8.7	720
10	Piscilicchio	-9.4	1040
11	Virgilia	-9.5	1220

FIG. 2. $\delta^{18}O$ altitudinal gradient from perched aquifer data.

wells, whose salt content ranges from 350 to 2300 µS·cm^{-1} and pH from slightly acidic to neutral (from 5.6 to 7).

The δ^{18}O altitudinal gradient derived from the 11 perched springs at various elevations (450 to 1200 m asl) is shown in Fig. 2. Its value, –0.20‰/100 m, is very close to that of –0.19‰/100 m reported by other authors [10, 11].

4.2. Lakes

In summer, with a well-developed thermocline, the physico-chemical data of shallow water differ from those of deep water in both lakes (Fig. 3 & 4). As predictable, temperature, DO and δ-values are higher in epilimnion than in hypolimnion water. The Lake Piccolo vertical profile, however, shows peculiar features: the salt increase at depth is significantly high (EC from 350 to above 1000 µS·cm^{-1}); the temperature first decreases to a minimum of 6°C at a depth of 13 m, and then increases towards the bottom to about 9°C; and the pH decreases from neutrality to 6.1 at the bottom. The heavy isotope enrichment of surface water is obviously due to evaporation, while the isotopic characterization of bottom water (–8.4‰ δ^{18}O and –54.5‰ δ^2H) is consistent with that of local precipitation [10]. The vertical variations of the same parameters are much smaller for Lake Grande, as shown in Fig. 3 and 4. All these data are in substantial agreement with the previous findings [1, 2].

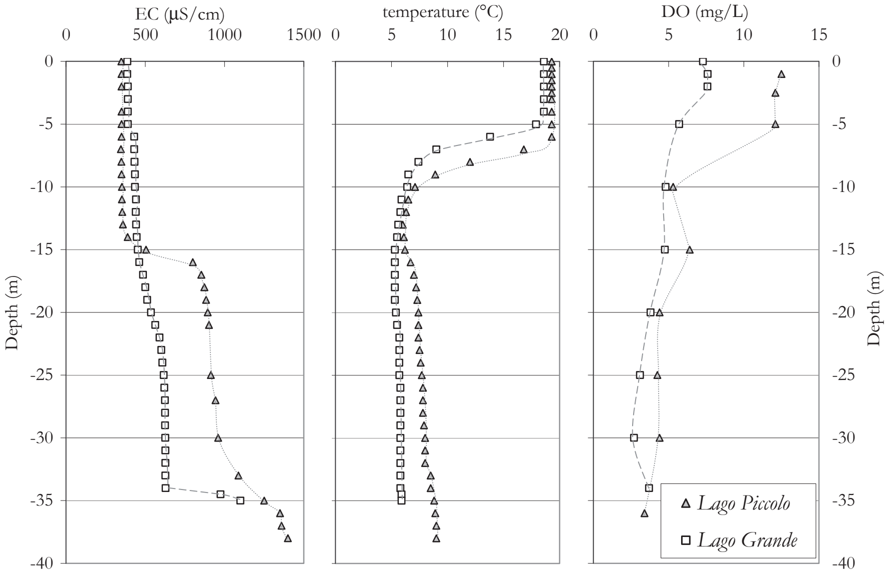


FIG. 3. Vertical profiles of EC, temperature and DO in Lake Piccolo and Lake Grande.

5. DISCUSSION

While the isotopic composition of Lake Piccolo bottom water is alike that of groundwater (springs and wells), the deep water of Lake Grande exhibits a heavy isotope enrichment similar to that of surface water, including the usual deviation from the meteoric water line. The evaporation line of lake waters is $\delta^2H = 5.1 \times \delta^{18}O - 11.7$, close to that previously reported [1]: $\delta^2H = 5.2 \times \delta^{18}O - 8.3$ (Fig. 5).

Thus, the isotopic and physico-chemical data of Lake Piccolo indicate a permanent stratification, maintained by groundwater gushing from the bottom and whose salt content and density are higher than that of precipitation and surface water recharge. A hydraulic equilibrium is reached, in which the groundwater inflow is counterbalanced by the hydrostatic pressure of over-floating shallow waters, whose excess is evacuated to Lake Grande through the channel connecting the two lakes. This equilibrium seems quite stable, and even occasional vertical mixing appears unlikely; however, seasonal oscillations of the surface water-groundwater interface level can be expected.

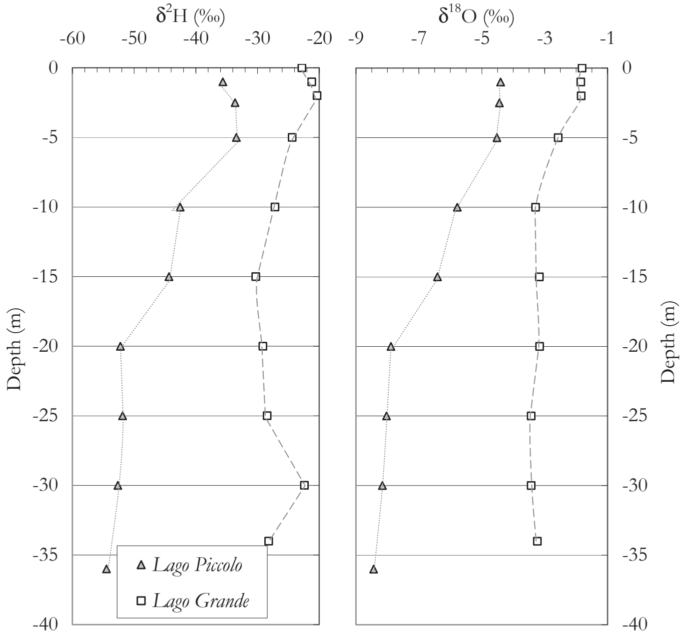


FIG. 4. Deuterium and oxygen-18 vertical profiles for Lake Piccolo and Lake Grande.

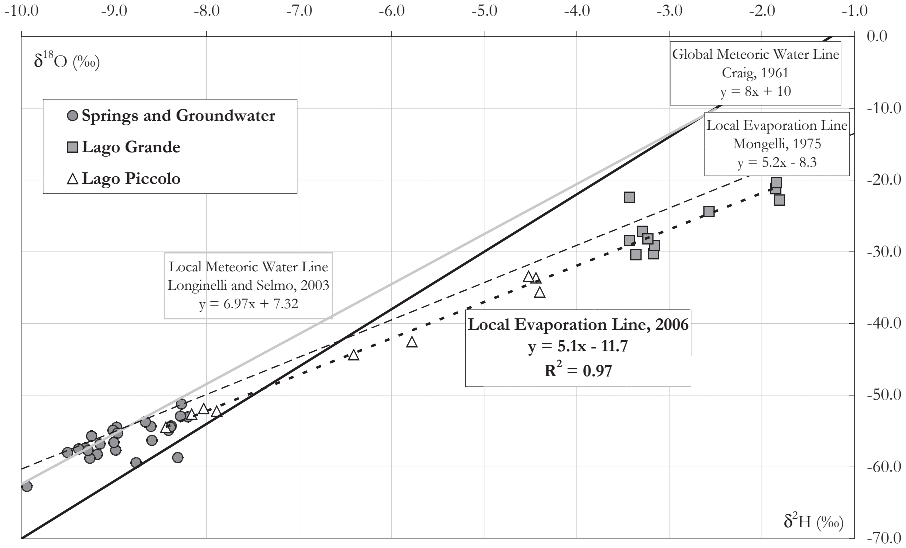


FIG. 5. Oxygen-18 vs deuterium for spring, lake and groundwater.

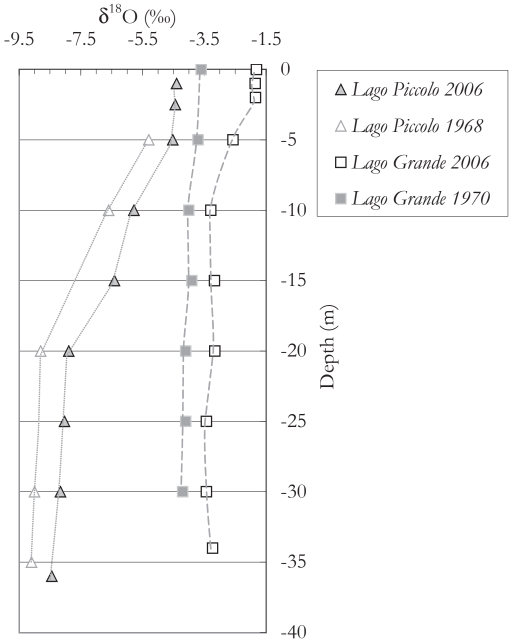


FIG. 6. Comparison between past and present oxygen-18 data for Lake Piccolo and Lake Grande.

Lake Grande, on the contrary, has a ‘normal’ behaviour. An important fraction of its water supply derives from the Lake Piccolo overflow, and this is reflected by the increased heavy water enrichment. There is no evidence of any significant groundwater recharge.

The isotopic composition of groundwater gushing from the Lake Piccolo bottom, indicates a mean altitude of recharge of about 600 m asl, close to the lake altitude. However, the basal springs at the same or lower elevation, show a more negative isotopic signature, which reflects a recharge from higher altitudes. Therefore, the deep aquifer does not seem to contribute to the Lake Piccolo recharge.

A comparison of the isotopic vertical profiles of both Lake Piccolo and Lake Grande obtained by us in September 2006 with those reported for the same season in 1965–66 and 1969–70 [1], shows that the previous $\delta^{18}O$ data are consistently more negative by about 0.5‰ than the recent ones (Fig. 6). Although a poor intercalibration of measurements performed more than three decades apart by different laboratories cannot be excluded, it is possible that the observed isotopic shift is true and reflects the current climatic change and mean temperature increase. Such an effect would be consistent with the variation of the isotopic composition of precipitation reported in ref. [12] and also with the observed decrease of precipitation over Italy [13].

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HYDROCHEMICAL AND ISOTOPIC EVOLUTION IN A DEEP CARBONATE AQUIFER IN NORTHERN ANDALUSIA, SPAIN

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Abstract

The Loma de Ubeda aquifer is formed by Jurassic carbonates with a mean thickness of about 80 m. The carbonate sequence is covered in the southern part of the study area by a thick sequence of Miocene sediments, and groundwater becomes confined. Groundwater samples in the phreatic zone contain tritium activities similar to present-day precipitation, as well as high nitrate contents, indicating the relevance of recent recharge. Further down-gradient, in the confined part of the aquifer, tritium contents become null. $\delta^{18}O$ values in most groudnwater samples are similar to those of present-day recharge. The uncorrected ^{14}C-DIC “ages” increase from recent up to 20–25 ka in the deepest part of the aquifer. Carbon-13 values in the confined part become progressively depleted (up to -21‰,) indicating the presence of a source of organic carbon in the aquifer. The $\delta^{34}S$ values in dissolved sulphate and the high concentrations of H_2S reflect the importance of sulphate reduction. Geochemical models suggest that the residence time of groundwater in the deepest part is up to 10,000 years younger than the uncorrected ^{14}C-DIC ages.

1. INTRODUCTION

Spain is the first world producer of olive oil, representing about 34 % of recent global olive oil production. Most of the oil production in Spain is concentrated in Andalusia, accounting for about 65–80 % of the national output [1]. The area with the highest olive oil production is located in the Jaen province, where the olive oil industry constitutes the main economic activity. The Loma de Ubeda aquifer is located in this province and its exploitation has played a very important economic role in recent years, due to the continuous increase in the production of olive oil in this area.

Despite the severe drought period from 1992 to 1995 in Spain, the olive oil production in the Loma de Ubeda area increased, mainly due to the intensive exploitation of groundwater of the Loma de Ubeda aquifer [2]. Since the discovery of this deep confined aquifer in the early 1990s, groundwater exploitation has regularly increased, mainly due to the improvement of the drilling techniques, which can easily set up boreholes for irrigation to a depth beyond 800 m. The cost on borehole drilling by local farmers in the area was estimated to be about 180 M€ [3]. On the other hand, the use of conventional hydrogeological techniques did not provide all hydrological information required for the proper management of this deep aquifer. Hydrochemical and isotope techniques were used to assess the origin, hydrochemical evolution and groundwater dynamics of the Loma de Ubeda aquifer. This paper presents the last results obtained as part of the hydrochemical and isotopic study jointly conducted by the Instituto Geológico y Minero de España (IGME) and Centro de Estudios y Experimentacion de Obras Públicas (CEDEX).

2. HYDROGEOLOGICAL SETTING

The Loma de Ubeda aquifer is located in the headwaters of the Guadalquivir Basin (Fig. 1). The study area is crossed from east to west by the rivers Guadalimar and Guadalquivir rivers. The northern limit of Loma de Ubeda aquifer is formed by detritic Triassic sediments cropping out extensively in the northern sector of Guadalimar catchment area. Overlaying the Triassic sediments, the stratigraphic column shows the Jurassic dolostone and limestone layers, that constitute the main aquifer units. The geological structure is relatively simple; with carbonate beds outcropping in the Guadalimar Valley, with a mean dip of 2–3º towards the south.

The mean thickness of the Jurassic carbonates is about 80 m, forming two different units: a lower unit, with a thickness of about 20 m, formed by laminated limestones, and a second unit formed by carbonatic breccias with a thickness of about 50–60 m [3]. Towards the south, the Jurassic layers become confined at about 1–2 km distance from the outcrop. The depth of the limestone layers regularly increases towards the south, reaching about 700-800 m in the deepest drilled areas. Seismic studies have shown the presence of large transversal geological faults, leading to net slips of about 100 m. Overlaying the Jurassic

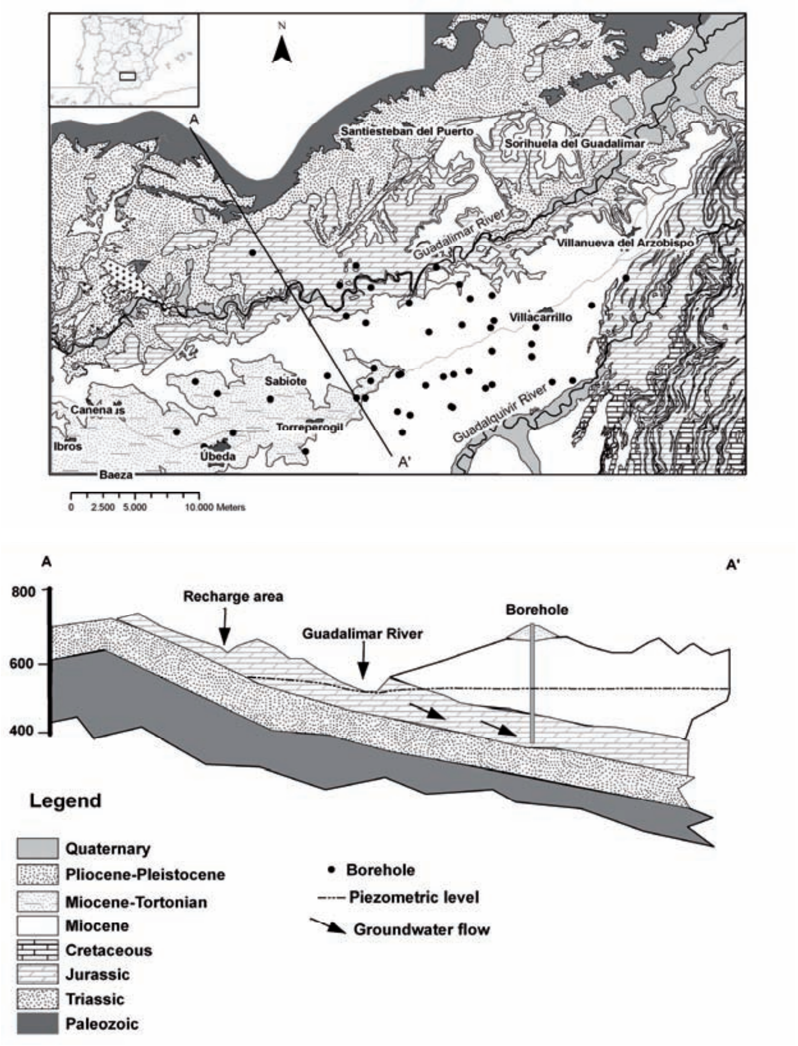

FIG. 1. Geological map and schematic cross section of the Loma de aquifer, Andalusia, Spain.

sediments, Miocene sediments are constituted by marls, silts and clays, with a thickness ranging from 200–600 m (Fig. 1) [4]. The potentiometric surface in the Ubeda aquifer is very difficult to draw, due to the morphology of the aquifer, and the fact that most wells collect groundwater from several aquifer units, producing mixing of several groundwater types.

The main springs in the Loma de Ubeda area are located in the phreatic part of the aquifer in the northern sector of the Guadalimar River. These groundwaters represent perched aquifers within the phreatic Jurassic aquifer [3]. Due to intensive pumping, groundwater levels in the phreatic part of the aquifer, even in south of the Guadalimar river, have dropped to the level of the Guadalimar river. Further down-gradient the aquifer becomes confined (Fig. 1), but groundwater exploitation extentd now to depths up to 800 m.

Groundwater recharge from precipitation takes place in the phreatic part of the aquifer over the entire Jurassic outcrop, which extends over 252 km^2. The confined part of the aquifers extends over 600 km^2. Under natural conditions, the pheatic part of the aquifer discharged directly into the Gudalimar river while the confined sector would discharge through fault towards the Guadalquivir river. Under present conditions of intensive groundwater exploitation, the aquifer shows a progressive lowering of the water table in both the phreatic and the confined sectors.

The analysis of available data from five meteorological stations, located at the same altitude of the phreatic sector of the aquifer, allowed to estimate the present potential recharge rate to the aquifer. Mean annual amount of precipitation over the recharge area is about 530 mm/a [5], and the vegetation cover over the Jurassic layers is scarce. The different models used provided estimates of annual recharge over the phreatic sector of the aquifer of about 30 Mm^3 [5], significantly less than the actual rate of extraction over the whole aquifer [3].

3. RESULTS AND DISCUSSION

Groundwater samples were collected for isotope and chemical analyses in two field campaigns carried out during 2005 and 2006. Fig. 2 summarizes the changes of the most relevant hydrogeochemical parameters along the main flow-path (from the recharge area in the north towards the confined sectors in the south) as indicators of the processes and evolution of groundwater within the aquifer.

In the phreatic part of the Jurassic aquifer, wells drilled for irrigation and water supply to some towns reach depths up to 140 m. Electrycal conductivity of these groundwaters ranges from 0.7 to 1 mS/cm. The important hydraulic gradients in these sector lead to fast groundwater circulation, as shown by the tritium levels found in this area. Typical tritium contents range from 4.5 to 7.0 TU, similar to the values found in present-day precipitation in central Spain. Groundwater in the recharge area also presents oxidizing conditions,

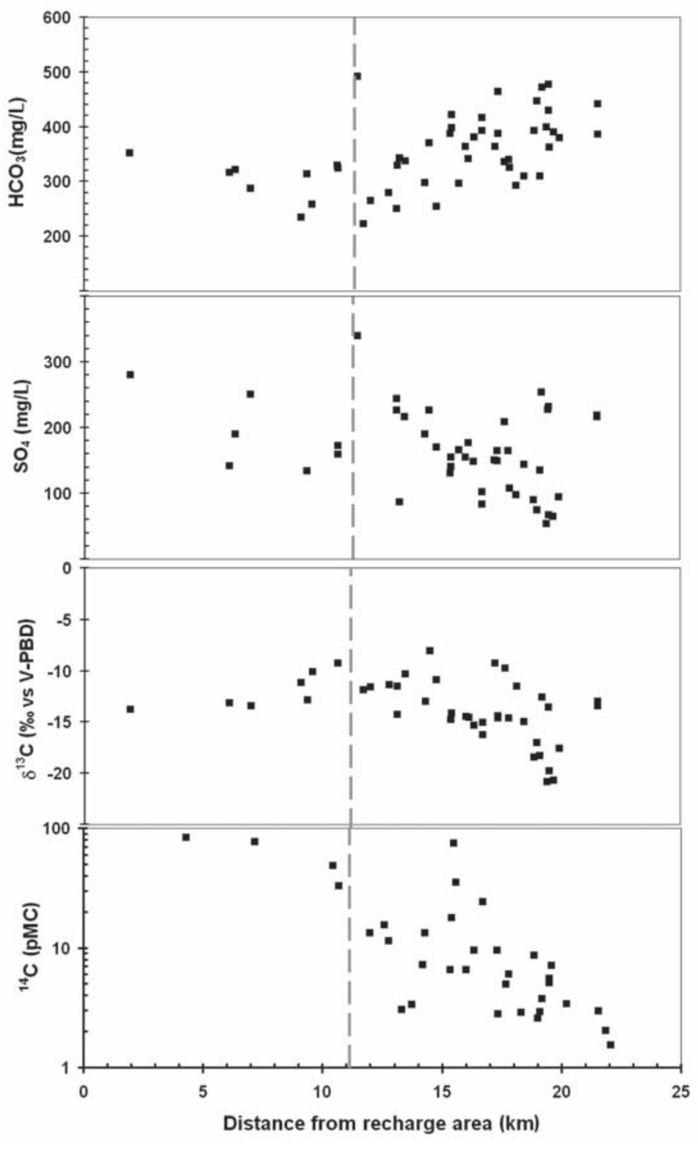

FIG. 2. Evolution of selected hydrochemical and isotope parameters along a characteristic flow-path of the Loma de Ubeda aquifer.

with relatively high levels of nitrate (up to 70 mg/L), and mostly are of calcium-bicarbonate or calcium-sulphate type. Some groundwater samples were collected in this sector for $\delta^{34}S$ analysis. $\delta^{34}S$ values around +12.5‰ vs VCDT and +11‰ of $\delta^{18}O_{SO4,}$ i.e. typical values for dissolved sulphur derived from Triassic and Jurassic gypsum minerals [7]. The ^{14}C activity in the phreatic aquifer ranges from 68–85 pMC, confirming the short transit time of groundwater in this part of the aquifer.

Groundwater samples collected in the central and southern sectors of the aquifer, (south of the Guadalimar river), show a regular increase in salinity, although a decreasing trend in the nitrate contents. This trend is maintained in the first part of the confined section. In this sector, dissolved oxygen is totally consumed, leading to reducing conditions, and therefore to the denitrification along the main flow path (Fig. 2). Tritium contents in this central section range from 0.5 and 3.0 TU, mainly as a result of aging of groundwater and mixing of groundwaters of different origins and residence times.

In the deepest, confined part of the aquifer, groundwaters are extracted from greater depths, reaching temperatures of 55–60ºC, and total salinity, expressed as TDS of 2 to 3.5 g/L. Groundwater change to sodium-chloride type, with a marked increase in these two ions and in alkalinity (Fig.2).

The strong reducing conditions in the deepest part of the aquifer lead to high H_2S and ammonia concentrations and the ecorresponding decrease in sulfate (Fig. 2). In this deeper zone, tritium contents become null and there is a marked decrease in the ^{14}C activity (Fig. 2). Most groundwater samples show an activity between 0–10 pMC, corresponding to a radiometric uncorrected "age" of about 25,000 a BP. However the high contents of H_2S, high alkalinity and positive shift of $\delta^{34}S_{SO4+H2S,}$ with a values close to +2 ‰ clearly indicates the importance of sulphate reduction, mainly through oxidation of organic matter $2CH2O + SO_4^{2-} \rightarrow 2HCO_3^- + H_2S$ [8]. In fact, sulphate concentration decrease from about 200–300 mg/L to values as low as 20 mg/L. This reaction with organic matter affects the carbon isotope contents, producing lower ^{14}C activities and depleted $\delta^{13}C$ (from –15 ‰ in phreatic zone, decreasing to ~ –21 ‰ in the deepest part of the aquifer as shown in Fig. 2).

The stable isotope composition of groundwater shows a relatively large range of $\delta^{18}O$ and δ^2H values (Fig. 3). Present-day recharge, as determined by monitoring the isotope composition of a number of spring in the phreatic part of the aquifer is characterized by $\delta^{18}O$ values around –5.5‰, as most of the points cluster just below the GMWL (Fig. 3). On the other hand, most boreholes in the intermediate part of the Loma de Ubeda aquifer are isotopically depleted in stable isotopes, and most of them are well below the GMWL, most negative $\delta^{18}O$ values are found in the deepest boreholes (Fig. 3), which also present the lowest ^{14}C activities (less than 2 pMC). However, it is not clear cause of the observed depletion as the clustering of most groundwater points along a line with a slope

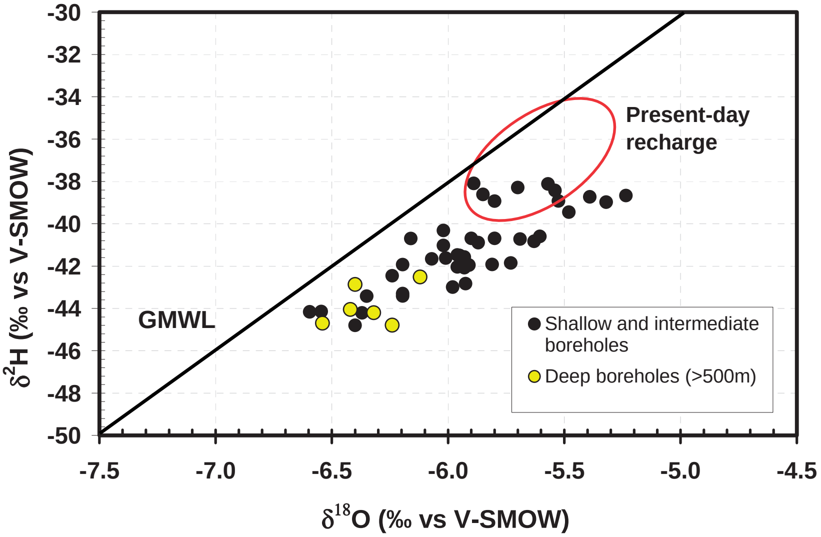

FIG. 3 Distribution of isotopic contents of the Loma de Ubeda carbonate aquifer.

lower than 8. The importance of irrigation return has been pointed out as a possible mechanisms to explain the observed distribution in the δ^{18}O vs δ^2H.

4. PRELIMINARY CONCLUSIONS

The preliminary geochemical and isotope results of the study of the Loma de Ubeda aquifer are as follows:

(a) The phreatic aquifer part of the Loma de Ubeda aquifer is characterized by the rapid circulation of groundwater.

(b) Recently recharged groundwaters present a calcium bicarbonate facies, high levels of nitrate and sulfate, as well as tritium contents similar to present-day precipitation.

(c) In intermediate-depth boreholes, south of the Guadalimar river, mixing of different water types and progressive “aging” of groundwater leads to a wide range of oxygen-18 and deuterium values, as well as lower tritium and nitrate levels.

(d) Deeper groundwater in the intermediate zone shows the effects of a progressive geochemical evolution of groundwater towards a sodium-chloride type.

(e) Further downgradient, a marked redox front is found, leading to a pronounced reduction of the sulphate and nitrate ions.
(f) Groundwater dating of deep groundwater (>500 m) by radiocarbon requires the use of complex geochemical modelling. Uncorrected radiocarbon ages in the order of 25,000 a BP, turn significantly younger (~ 10,000 a BP) when all geochemcial corrections are applied.

ACKNOWLEDGEMENTS

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CHARACTERIZATION OF THE AQUIFERS OF THE ESSAOUIRA SYNCLINAL BASIN (MOROCCO) BY USING ^{2}H, ^{3}H, ^{14}C AND ^{18}O ISOTOPES

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Abstract

The study of characterizing the principal aquifer of the Eassouira Coast zone, was carried out with the principal objective of dating of undergrounds waters of the region and that are used to supply drinkable water to the city and neighbouring villages. Different water samples have been collected from drillings, rivers and wells belonging to the plioquaternary and turonian aquifers of the studied region. Water samples were collected for ^{18}O, ^{2}H and ^{3}H determinations. A meteoric local line was determined and compared to the world meteoric line. The apparent radiocarbon ages of the studied aquifers were evaluated. The recharge of the main aquifers of the studied region was investigated. It has been shown by this study that the recharge rate of the deep turonian aquifer is too low. This may cause a shortage of water supply to the Essaouira city and its surrounding region. Among the concerned aquiferious, the turonian that provides for more than 50% drinkable water for Essaouira city and rural villages must be the object of rational and durable exploitation.

1. INTRODUCTION

Due to the scarcity of surface waters, people exploit mainly underground water reservoirs. Hence, it is necessary to study and characterize these water reservoirs to avoid any excess exploitation. All waters have fingerprints of naturally occurring isotopes that provide information about their origin. Among the most powerful fingerprinting tools are the ratios of stable isotopes of hydrogen-deuterium to hydrogen ($^2H/^1H$) and of oxygen 18 to oxygen 16 ($^{18}O/^{16}O$) [1, 2].

The Essaouira synclinal zone is one of the Moroccan semi-arid areas with mean annual rainfall not exceeding 300 mm per year [3]. The mean temperature is about 20°C; the temperature gap between January and August may reach 17°C. With a surface area of about 300 km², it is bordered by the Ksob River in the north, Tidzi River in the south, Tidzi diapir in the east and Atlantic Ocean in the west (Fig. 1). In this region, underground water resources are contained in two main reservoirs: the plioquaternary and turonian aquifers. The plioquaternary aquifer hosted by grey limestone marl rocks shows a primary hydraulic conductivity by porosity and contains an important free water table with a wall formed in the syncline structure, by the senonian marls. This aquifer is exploited for irrigation and potable water supply. The turonian

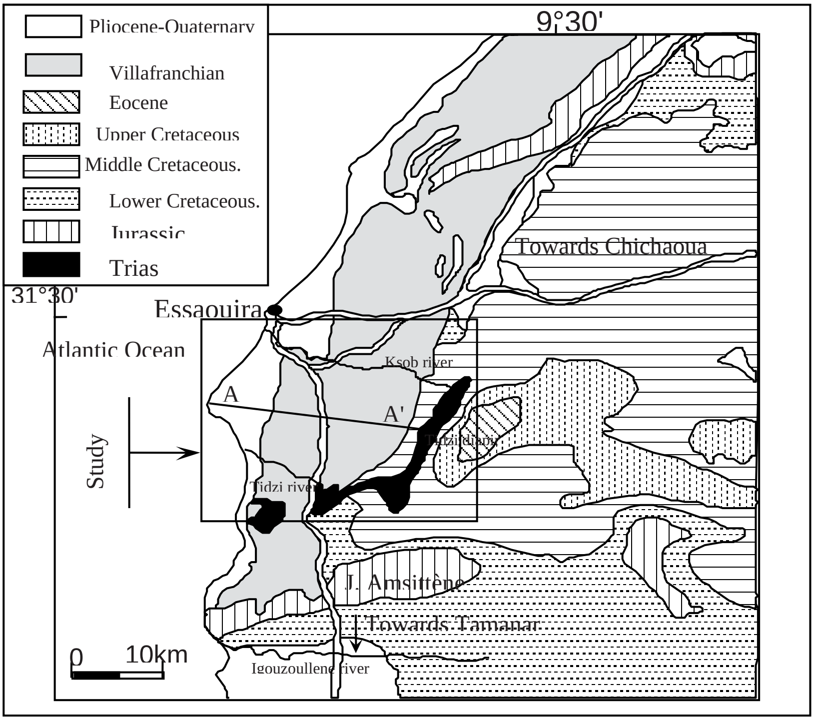

Fig.1. Map showing the study area.

contains a rapidly captive aquifer confined under the senonian marls in the synclinal structure and likely in direct contact with the plioquaternary on the edges of this structure, near the Ksob River in the north, the hidden diapir of Essaouira in the west and the Tidzi diapir in the south and east. Many deep drillings have been done in this aquifer during the eighties of the twentieth century in order to supply drinking water to the city of Essaouira and some neighbouring towns. The piezometric level is at 180 m altitude upstream where the hydraulic gradient is strong, about 2%, due to the high tilting of the aquifer wall and the rising of the Tidzi diapir. Different gauging, realized during the 1990–1991 hydrologic cycle and confirmed in 2004, permitted to assess that waters are infiltered from the Ksob River to the plioquaternary aquifer with a flow rate of 42 L/s [4]. The passage of this river in canyons, where it outcrops the turonian aquifer, causes water losses of 64 L/s in favour of this aquifer.

2. METHODS AND RESULTS

A water sampling from thirty wells, drillings and sources belonging to the plioquaternary and turonian aquifers was realised. The electric conductivity and temperature were measured on the ground. Waters belonging to the plioquaternary aquifer present very variable electric conductivities from 1590 µS/cm to 6940 µS/cm. In spite of this variability, they form the same family and are characterized by sodium-chloride facies. There exists, however, a good correlation between the electric conductivity and chloride and sodium contents.

Unlike the plioquaternary aquifer, turonian waters show homogeneous electric conductivities ranging between 2000 µS/cm and 2500 µS/cm. Waters from the turonian aquifer present the same sodium-chloride chemical profile as that of the plioquaternary waters. It is then difficult to distinguish between the turonian and plioquaternary waters according to only the mineralisation.

Results obtained for the oxygen-18 (^{18}O) and deuterium (^{2}H) are shown in Table 1. ^{18}O isotopic concentration of the plioquaternary waters ranged from –2.52‰ to –4.86‰. It is to be noticed that sample belonging to well 11/51 situated in the ocean borders is affected by marine intrusion. Water samples collected from well Part/51 situated near the IddaouGard town and well 272/51 supplying potable water to the city of Essaouira, respectively, show values of ^{18}O varying from –2.52‰ to –2.85‰ close to those of the upstream Ksob river with a value of –3.06‰ confirming that these wells are supplied by that river. Values of ^{18}O for the turonian waters fall between –4‰ and –4.5‰ and most of them are situated around –4.5‰, showing by this a higher recharge, especially on the Tidzi diapir outcrops (Table 2). Data obtained for the deuterium analysis

TABLE 1. ISOTOPIC DATA OBTAINED FOR THE PLIOCENE-QUATERNARY AQUIFER (2004 CAMPAIGN) AND UPSTREAM AND DOWNSTREAM OF THE KSOB RIVER.

Water sample	$\delta^{18}O$ (‰)	$\delta^{2}H$ (‰)
149/51	–3.68	–21.9
132/51	–3.70	–17.6
M98	–4.03	–23.7
15/51	–3.84	–16.9
11/51	–3.43	–17.0
21/51	–4.53	–23.8
327/51	–4.00	–20.7
27/51	–4.86	–28.2
M24	–4.47	–24.9
28/51	–4.85	–24.4
140/51	–4.63	–.29.0
148/51	–4.06	–23.6
389/51	–3.28	–22.0
134/51	–4.29	–23.6
53/51	–3.69	–27.9
93/51	–4,35	–25.7
Part/51	–2,52	–24.4
272/51	–2,85	–23.4
Upstream river	–3.06	–12.4
Downstream river	–2.17	–24.0

permitted to determine the ^{18}O –^{2}H correlation with a meteoric local line of equation: $\delta^{2}H = 8.26 \times \delta^{18}O + 10.5$ (n = 11, r = 0.97) close to the world meteoric water line (WML) of a slope of 8 with a deuterium excess close to 10 [5] (Fig. 2). This meteoric local line characterizes oceanic precipitations. The equation of this meteoric local line was determined without taking into account the three water points (65/51, 272/51 and Ksob River), which are identified as evaporated because they are placed below the meteoric line. The other water samples

TABLE 2. ISOTOPIC DATA OBTAINED FOR THE TURONIAN AQUIFER.

N°IRE	X	Y	Z(m)	N.P(m)	H(m)	CE(µS/cm)	T°C	pH	Aquifer	$\delta^{18}O$(‰)
386/51	92	98.65	105	30	75	2240	17.3	7.66	Turonian	–4.03
363/51	89.75	88.2	150	60	90	2410	19.9	7.71	Turonian	–4.46
157/51	86.55	105.3	30		source	1950	23.8	7.42	Turonian	–4.49
390/51	97	100	105.5	26.2	79.3	1820	27.5	7.15	Turonian	–4.07
346/51	97.25	100.7	105	26	79	1950	26.5	7.16	Turonian.	–4.20

TABLE.3. DATA OBTAINED FOR THE PHYSICAL PARAMETERS AND RADIOISOTOPE CONCENTRATIONS FOR THE UNDERGROUND WATERS OF THE COASTAL ZONE OF ESSAOUIRA (NOVEMBER 1996).

^{14}C	Nature	Origin	Altitude	Depth (m)	T(°C)	C.E (µS/cm)	pH	Alk. (méq/L)	^{3}H (TU)	^{14}C (pMC)	^{13}C (‰)
272/51	Well	Plio-Quat	105.5	38.4	20.6	1660	7.65	3.30	3.9 ± 0.5		
21/51	Well	Plio-Quat	135	29	21.7	5170	7.13	2.80	2.0 ± 0.5		
327/51	Well	Plio-Quat	130		22.2	3880	7.23	4.03	3.2 ± 0.4		
65/51	Well	Turon	15	20.3	22.5	2870	7.48	4.64	2.8 ± 0.5	88.9 ± 0.5	–9.8
390/51	Drilling	Turon	95	200	26.7	1995	7.35	4.94	<2	32.5 ± 0.4	–9.4
386/51	Drilling	Turon	105	100	23.2	1828	7.56	4.26	4.2 ± 0.5	84.8 ± 0.6	–10.3
380/51	Drilling	Turon	135	194	26.1	2280	7.54	4.67	<2	3.0 ± 0.5	–9.0

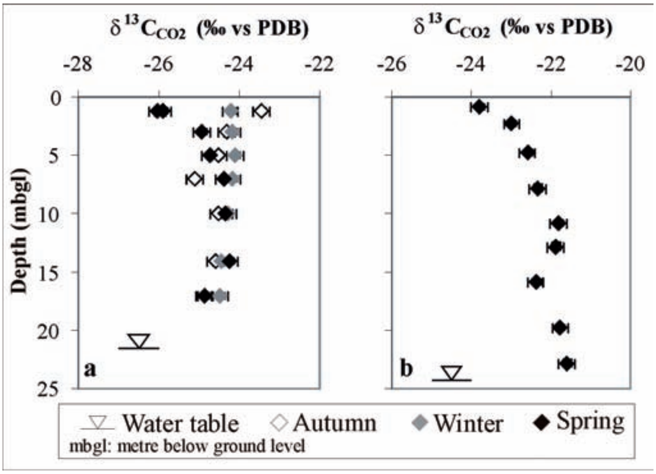

Fig. 2. The ^{18}O–^{2}H line obtained for the Essaouira basin (2004).

TABLE 4. DATA OBTAINED FOR TRITIUM DATING OF THE MAIN WATER POINTS WHICH SUPPLY POTABLE WATERS TO THE CITY OF ESSAOUIRA (MAY 2004 CAMPAIGN).

No. IRE	X	Y	Z (m)	N.P (m)	H (m)	CE (µS/cm)	T°C	pH	Aquifer	Tritium (TU)
261/51	96.42	99.25	124	46	88	1900	23.2	7.40	Plio-Quat.	1.4 ± 0.6
390/51	97	100	105.5	26.2	79.3	1890	25.9	7.15	Turon.	2.0 ± 0.6
386/51	92	98.65	105	30.7	74.30	2260	18.5	7.70	Turon.	2.5 ± 0.7
272/51	97.17	100.76	105.5	36	69.5	1917	20.9	7.42	Plio-Quat.	4.2 ± 0.7
6/51	86.1	105.4	25	25		2780	23.4	7.01	Turon..	1.4 ± 0.7
346/51	97.25	100.7	105	26	79	1830	26.5	7.24	Turon.	1.5 ± 0.6
363/51	89.75	88.2	150	60	90	2600	24.5	7.14	Turon.	1.2 ± 0.8
380/51	89.35	91.8	135	55	80	2180	21.10	8.26	Turon	0.9 ± 0.7
M98	89	100	125	80	45	2460	21.5	7.47	Plio-Quat	1.1 ± 0.6
149/51	85.1	105.8	40	36.2	3.8	2800	23.3	7.83	Plio-Quat	0.2 ± 0.8

TABLE 5. DATA OBTAINED FOR THE INITIAL ACTIVITY OF ^{14}C AND RADIOCARBON AGES OF THE UNDERGROUND WATERS OF THE ESSAOUIRA COASTAL ZONE.

Water point	Tamers		Pearson		Fontes Garnier		AIEA		Evans	
	Age (a)	A_0 (pMC)	Age (a)	A_0 (pMC)	Age (a)	A_0 (pMC)	Age (a)	A_0 (pMC)	Age (a)	A_0 (pMC)
65/51	present	53.6	present	46.7	present	46.4	present	76.5	present	44.6
390/51	4267	54.5	2646	44.8	2558	44.3	6445	70 .9	2128	42.0
386/51	present	53.0	present	49.0	present	48.9	present	79.9	present	47.0
380/51	23739	53.0	21984	42.9	21891	42.4	25829	68.2	21443	40.1
M98	present	52.8	present	44.3	present	44.0	present	72.9	present	42.2

analysed are situated on the meteoric line showing that these two aquifers and more specifically the turonian one are rapidly supplied without evaporation. For the tritium analysis (November 1996, Table 3), we notice from results that recent waters of the Essaouira coastal zone present tritium concentrations between 2 and 4 TU. It is notably the case of 65/51, 272/51, 327/51 and 386/51 water points, confirmed by higher ^{14}C activities for some of them. Water having tritium concentrations smaller or equal to 2 TU are considered as being old such as those belonging to the 21/51, 380/51, 390/5. ^{14}C was analysed in some of these waters to confirm or show up the weakness of this hypothesis. Tritium was analysed in May 2004 in water samples belonging to water points supplied by the main aquifers used for supplying potable water to the Essaouira city (Table 4), confirming the former results. To assess initial ^{14}C activities of underground waters of the coastal zone of Essaouira many models were tested (Table 5).

These different models may take into account the ^{14}C chemical dilution, isotopic exchanges and isotopic mixtures with isotopic exchange. From the analysis of data given in Table 3, 4 and 5 one can deduce that: two water points, among those studied presenting significant tritium concentrations and ^{14}C percentage larger than 85% should be considered as recent. Among these two water points one can notice well number 65/51 situated downstream of the Ksob river which supplies potable water to the Essaouira city with a flow rate of 6 L/s (5% of the total water supply). The second water point consists of the 386/51 drilling, impounded by the turonian aquifer waters and supplying potable waters to the aerodrome of Essaouira. The M98 drilling which has no detectable tritium and has a ^{14}C concentration of 80%, has been supplied before the 1952–1963 nuclear tests and its radiocarbon age does not exceed some hundred years independently of the model utilized. The 390/51 drilling impounded by the turonian aquifer waters, supplies the Essaouira city with a flow rate 60 L/s representing 50% of the water needs. This drilling has a radiocarbon age of about 6,500 years according to the IAEA model, a little lower but still always of several thousand years according to the other models. The 380/51 drilling impounded by the turonian aquifer which supplies potable water to the Si Ahmad ou Hmad town (5,000 inhabitants), is also overexploited. It has a radiocarbon age greater than 20,000 years independent of the model utilized indicating a low recovery rate of the turonian aquifer.

4. CONCLUSION

It has been shown by this study that the recharge rate of the deep turonian aquifer is too low, finally dating of the turonian aquifer waters which are ancient, must be taken into account in managing water resources for future development projects in this region.

The plioquaternary aquifer is less deep, and sensitive to drought episodes, which are more frequent in Morocco; the most severe one happened in 1995. This may cause a lack of water for supplying the Essaouira city and its region.

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A PRACTICAL APPROACH TO RADIOCARBON DATING OF GROUNDWATER

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Abstract

Radiocarbon dating of groundwater is widely used, but the calculated ages are often difficult to interpret for two reasons. Firstly, the ^{14}C age is ambiguous in that it depends on the sampling depth, sampling interval and flow system behaviour. Second, the age is in reality a ‘carbon age’ and the plethora of correction schemes that produce model water ‘ages’ are confusing to many practicing hydrogeologists. To simplify the process, I suggest that using relative ‘ages’ within a hydrostratigraphic context with minimal correction (with a nominal starting point of say 85% MC) is more practical. For confined aquifers, the approximation of age difference along a transect or inferred flow lines may be used to estimate horizontal flow velocities. For unconfined aquifers, one would plot the ‘age’ as a function of depth incorporating the length of the screened interval to estimate recharge rates. The advantages are that it makes the data internally consistent and minimizes the large apparent errors inherent in the estimates of ‘absolute’ ages. The results have more meaning for those people requiring information to make groundwater management decisions.

1. INTRODUCTION

Radiocarbon dating of groundwaters began in earnest in the 1960s when application of ^{14}C to environmental problems was in its infancy [1–4]. ^{14}C is now a widely used isotope in groundwater studies because of its half-life of 5,730 years covers a critical time scale of ~500 to 30,000 years, which is ideal for use on dating of regional and intermediate scale flow systems. Dissolved inorganic carbon (DIC) is ubiquitous in all but the most acidic groundwater and ^{14}C can now be measured by a variety of well established methods.

Dating of groundwater in its simplest form assumes that (i) the isotope in question moves with the water molecule as they flow along the hydraulic gradient and (ii) that only radioactive decay alters the activity or concentration of the relevant radionuclide during transit within the aquifer.

Calculation of groundwater ages usually involve the basic decay equation:

$$A = A_o e^{-\lambda t} \qquad (1)$$

where A = activity of measured ^{14}C in the water sample, A_o = initial actvity of ^{14}C, λ = decay constant for ^{14}C and t = time.

Rearranging Eq. 1 and taking the log of both sides yields:

$$t = \ln [A/A_o] \ln 2/\lambda \qquad (2)$$

In such situations one must estimate the initial concentration of ^{14}C (A_o) at the time when the soil water enters the water table. In the commonly adopted units of percent modern carbon (% MC) where 100 %mc is equivalent to pre-1890 level of ^{14}C in the atmosphere, the "age" can be calculated from Eq. 2.

There are two important factors to consider for the interpretation of ^{14}C ages. Firstly, the age is in reality a "carbon age". Converting to "water age" involves using one of a plethora of correction schemes (see below) that correct for the incorporation of ^{14}C-free carbon derived from dissolution of organic or inorganic carbon within the soil zone or aquifer matrix. Secondly, the ^{14}C age is ambiguous in that it depends on the the sampling depth, sampling interval and flow system behaviour. The aim of this paper is to emphasize the importance of the latter in extracting as much hydrological information from ^{14}C data, and that assigning an absolute ^{14}C age is of lesser significance.

2. GROUNDWATER 'AGE' AND ^{14}C CORRECTION SCHEMES

2.1. Model ages (chemical)

Groundwater age determined from ^{14}C dating is the mean dissolved inorganic carbon age and not strictly a water age. The calculated water 'age' is a function of the estimated initial ^{14}C in the groundwater immediately at the time of recharge ($^{14}C_0$) and any modification of the DIC during transport within the aquifer. To relate the carbon age to a water age involves correcting the carbon age through a series of isotopic and geochemical correction schemes to yield a 'model' age. The correction schemes deal with the interaction between $CO_{2(g)}$, $CO_{2(aq)}$, HCO_3^-, CO_3^{2-}, and ^{14}C-free carbonate minerals and organic matter in the unsaturated zone [5–8]. Some correction schemes are termed open-system and others are closed-system with respect to CO_2 in the unsaturated zone, which are in effect dependent on the size of the CO_2 reservoir in the unsaturated zone: the former requires minimal ^{14}C correction, whereas the latter requires substantial correction if there is a significant amount of carbonate minerals. There is also an aquifer mass balance approach [9–10] which also considers incongruent dissolution of carbonate minerals during transit through the aquifer. This in effect dilutes the ^{14}C, resulting in an overestimation of the groundwater 'age' if taken at face-value.

Most models require measured data on the water chemistry and/or the isotopic composition (both $\delta^{13}C$ and ^{14}C) of the groundwater. They also require measured or estimated input parameters of the ^{14}C and $\delta^{13}C$ of both soil CO_2 and soil carbonate minerals. In some cases there are further complications such as methane oxidation, incongruent dissolution in the unsaturated zone, oxidation of 'old' organic matter, that also modify the ^{14}C of soil-water HCO_3^-. In short, while this can be a geochemist paradise, but completely bewildering to hydrolgeologists who need information that is meaningful and useful to estimate long-term mean water fluxes. As the $\delta^{13}C$ for groundwater becomes more positive, the number of possible model scenarios increases as does the uncertainty in age [11]. Fig. 1 shows that one can produce a wide range of ^{14}C groundwater 'ages' for a single set of data but using different modelling approaches. Note that all models produce 'ages' that are younger than the uncorrected age, and that several models produce apparent negative ages. The negative values are produced for two reasons; either the sample contains some fraction of 'bomb' radiocarbon produced by the atmospheric nuclear weapons tests of the 1950s and 60s, or that there is an over correction due to underestimate of the true A_0. For the most part the model age trends are parallel to each other indicating that relative ages between different groundwater samples do not differ from one model to another.

The sheer variety of model schemes can be confusing to many hydrogeologists, especially so because a wide array of outputs are now easy to generate within the geochemical inverse modelling codes such as NETPATH [13] or PHREEQC2 [14]. The required ancillary data to properly apply these models (eg., ^{14}C and $\delta^{13}C$ of soil CO_2 and soil carbonate minerals) are rarely if ever collected in most field campaigns. Propagating the uncertainties in model parameters through any one of the models can also yield errors in the 'age' of a factor of two [11].

Some schemes are open system and others are closed system with respect to CO_2 in the unsaturated zone. They are in effect dependent on the size of the CO_2 reservoir in the unsaturated zone and the soil characteristsics. The open-system (soil gas CO_2 reservoir >> carbonate mineral content) requires no or minimal ^{14}C correction whereas the closed-system (soil gas CO_2 reservoir << carbonate mineral content) requires substantial correction. In general, a porous soil zone with high pCO_2 overlying a non-carbonate aquifer requires

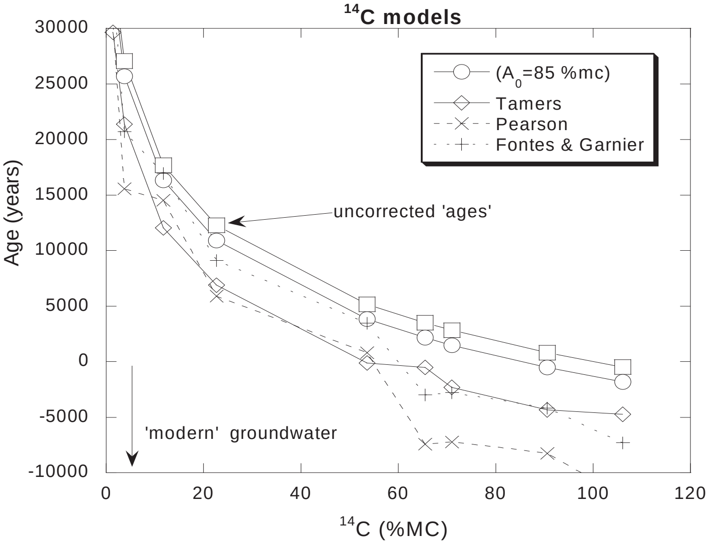

FIG. 1. Estimates of groundwater ages a function of ^{14}C concentration using one of the following: no correction (A_0=100 %MC), A_0=85%MC, or Tamers [12], Pearson [2], Fontes and Garnier [5] correction schemes.

no correction while low porosity soils that have carbonate minerals in the soil or aquifer may require substantial correction [15] This is helpful in that it implies that corrections are needed less often than may be thought. In fact, because quasi open-system behaviour exists in many situations, particularly in arid and semi-arid environments where recharge fluxes are relatively low, the uncorrected age is often closer to the true age than using many correction schemes.

Although the age limit for dating of groundwaters is often quoted as 30,000 years or greater, in practical terms this is generally much less. While the analytical (counting errors, background, standards) might suggest that >30,000 yrs is achievable, the true limit is the ability to distinguish a sample from the lower limit of detection incorporating the errors asociated with sample preparation and reproducibility (rarely are duplicates collected for ^{14}C analysis). Furthermore, the corrected age involves additional uncertainties in the chemical, δ^{13}C and ^{14}C content of soil CO_2 and carbonate minerals (see above) leading to a practical age limit of ~25,000 years. At the opposite end of the age range the limitation is the ability to distinguish estimated values of A_0 from measured ^{14}C in sample making ages younger than ~1,000 years indistinguishable from modern values.

2.2. Hydrogeological ^{14}C 'ages'

A simpler approach for application of ^{14}C data to groundwater problems is to reduce the emphasis on applying chemical correction to obtain absolute ages, but rather use the relative ages within the context of an appropriate hydrogeological conceptual model. In confined aquifers, where horizontal piston flow may be reasonably assumed, the use of correction of ^{14}C data to obtain model 'ages' may be redundant. In such cases, the age increases along the hydraulic gradient, and the horizontal velocity can be calculated along a transect by dividing the distance between boreholes by the age difference [16–17]. Because the age difference is largely independent of the choice of model, the errors inherent in estimating absolute ages will cancel out and there is likely to be little difference in estimated horizontal flow rates from one set of corrected or uncorrected 'ages' to another. Furthermore, the information provides a direct link to the water balance, which is what the data is meant to provide, rather than groundwater ages which have little meaning. While one could incorporate mass balance models [17] such an approach may add complexity that is unwarrantaed, and collecting data on a very well defined flow path may not always be feasible.

In the case of unconfined aquifers, one cannot assume horizontal piston flow. Converting ^{14}C data to a water age can be misleading, because variation in screen depth and screen length integrates flow paths of different scale, especially for boreholes with long screens and low recharge rates. For example, a borehole with a short screen just below the water table would represent just a local flow

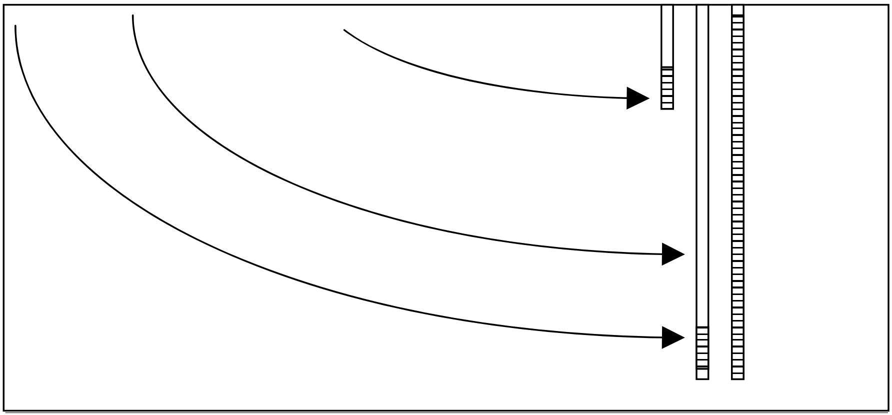

FIG. 2. Schematic diagram of an unconfined aquifer showing boreholes with different screen intervals (horizontal lines) and flow systems. ^{14}C 'ages' would be very different for the three sampling intervals.

system, and likely provide a young ^{14}C age, whereas a deeper borehole, or one that is open to a large vertical portion of the aquifer will represent multiple flow paths, from short to long, and the ‘age’ of the groundwater is an average age (Fig. 2). Thereore, at a given point one get get widely disparate ages depending on the borehole construction alone. One must use a hydrostratigraphic context to incorporate screen depth and screen length.in unconfined systems which can then be converted to recharge rate. Such an approach was articulated more than 40 years ago [3] and suprisingly only adopted by few workers [e.g., 18–21].

For unconfined aquifers, one would plot the age as a function of depth, incorporating the length and depth of the screened interval to estimate recharge rates (Fig. 3). From a practical point of view, sampling from different screen depths or screen intervals introduces yield a range of apparent ages because of different flow systems that are integrated within the well screen. Although the corrected (to 85% MC) ages are used in Fig. 3, the absolute values are not important and the results are most sensitive to hydraulic parameter uncertainity such as porosity.

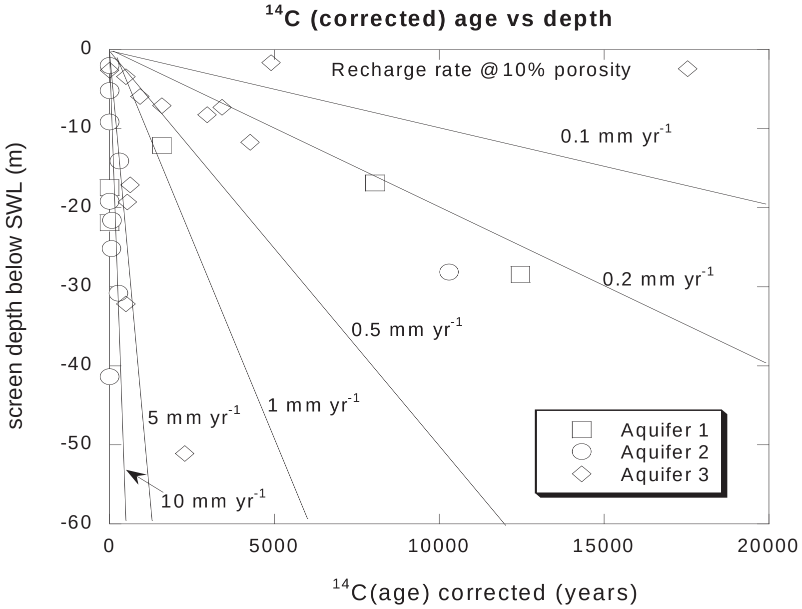

FIG. 3. ^{14}C groundwater ‘ages’ (corrected using A_0=85%MC as a function of depth below the water table to the mid point of the screen interval. The lines represent recharge rates assuming a uniform porosity of 10%. In this case, there are two modes of recharge to the respective aquifers of ~0.2 mm yr-1 and 5-10 mm yr-1.

For hydrological systems that have recharge and flow velocities on a time scale where ^{14}C may be required, one can dispense with the models and use the simple decay equation with a nominal starting point of 85%MC to calculate 'apparent' ages. While the selection of an initial value less than 100 %MC may seem arbitrary, it does allow for dilution of ^{14}C by processes within the unsaturated zone to obtain realistic (i.e., non negative) ^{14}C ages. Similarly although there are problems with diffusion at very low recharge rates [22], and possibly heterogeneities that might make the hydraulic assumptions appear overly simplistic, this approach at least can offer a quantitative base that can be tested with more elaborate numerical models.

3. CONCLUSIONS

While groundwater dating using ^{14}C has been used widely over the last serveral decades, I suggest that better use of the data are made within a hydrogeological framework instead of seeking to produce absolute water 'ages'. Although the suggested approach requires dispensing with the notion of dating as an end in itself, it does provide a more useful and meaningful framework for timescales of the important water fluxes, such as recharge, horizontal flow rates and discharge, that are needed in most groundwater studies. The results, though subject to some simplifications and uncertainties, would have more meaning for groundwater management. Complex correction schemes, while of some value, frequently give widely varying results that often alienate the ultimate users of the information.

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RE-WATERING OF WITWATERSRAND MINING BASINS, SOUTH AFRICA – TRACED BY STABLE LIGHT AND STABLE RADIOGENIC ISOTOPE SYSTEMS

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Abstract

The relative proportions of discharge from underground mine water from abandoned and working gold and coal mines in the classical Witwatersrand goldfields were assessed by a variety of isotope systems. $\delta^{18}O$ and δD values show that direct ingress of surface water contributes only 30% to 40% to water in underground mine workings. Between 60% and 70% or more of mine water is derived from ground and/or fissure water sources. Owing to profound interaction with oxidative weathered Witwatersrand sulphides, S isotopes reveal a “Witwatersrand signature” with $\delta^{34}S$ values between 2‰ and 5‰ in mine water underground and/or emanating at the surface. A component/water mixing curve deduced from the relation of $^{87}Sr/^{86}Sr$ ratios to $\delta^{34}S$ values points to water-rock interaction leaching Witwatersrand sediments. Component mixing is substantiated by $^{208}Pb/^{207}Pb$ vs. $^{206}Pb/^{207}Pb$ ratios with a negative trend representing a mixing relationship between mine void water and ground water and/or surface water. — A multiple isotopic label has great potential in tracing water in abandoned and / or active mine workings and can be used to apportion and quantify possible sources of such water.

1. INTRODUCTION

Approaching the end of the era of mining in the classical Witwatersrand goldfields, many long-established gold mines are already closed or face closure due to reserve exhaustion or becoming uneconomic. Abandoned mines naturally fill up with water and measures for preventing the ingress of water into subsurface workings of the mining basins are needed. Two major problems arise from such underground water:

1. Remaining active gold mines experience ever larger amounts of water reporting underground which have to be pumped from great depth at considerable cost.
2. Mine water which resurfaces from abandoned and working gold and coal mines can cause severe environmental problems due to acid rock (mine) drainage.

The present project was initiated in July 2003 by the Department of Mineral and Energy Affairs (DME) in Pretoria and the study area is shown in Fig. 2. Decanting of polluted mine water was already happening and will occur at more sites in the future, making it necessary to understand the future decanting scenario. Of particular interest for this study was the proportion of surface water entering underground mine workings in order to assist in developing a hydrological model that accounts for the volumes of such water, which have to be pumped or will possibly decant.

In this study light stable isotopes and stable radiogenic isotopes are employed to trace and quantify different water components reaching underground mine workings. Oxygen/hydrogen, sulphur, strontium and lead isotopic systems have been employed to investigate their suitability for the purpose of mine water tracing on the basis of their different characteristics.

Water samples were secured from all over the Witwatersrand mining basins from dams, pans, rivers, canals, boreholes and underground. Not all samples could be analysed for all isotopic systems mentioned above and the following discussion will therefore focus on examples where relevant information emerged from particular isotopic systems.

2. RESULTS AND DISCUSSION

2.1. H and O isotopes

In the Eastern Witwatersrand Mining Basin, surface water from the Blesbokspruit Wetland and underground water from Grootvlei Mine (Fig. 2) have been analysed for D/H and $^{18}O/^{16}O$ isotope ratios. A generalised view

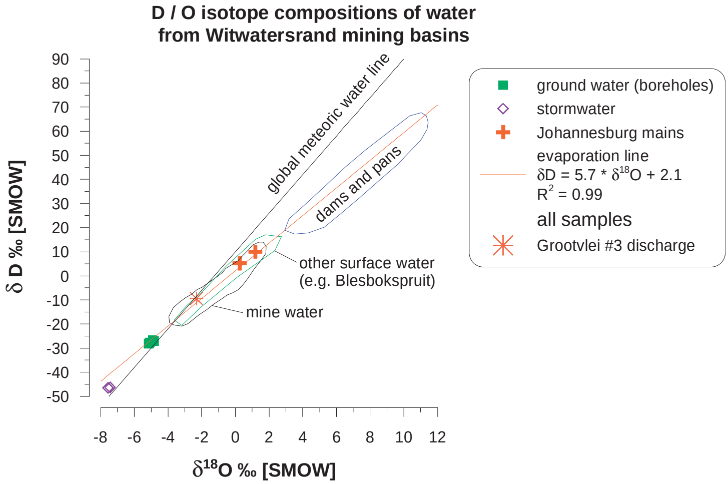

FIG. 1. General $^{18}O/^{16}O$ and D/H isotopic composition of the main sample categories relative to the Global Meteoric Water Line [2]. All samples plot along an evaporation line, but there is a clear distinction between surface dams and pans and mine water and water from the Blesboksspruit. Typical Highveld storm water samples are included for comparison as well as isotopic compositions of Johannesburg mains water [1].

of the results is given in Fig. 1. Different evaporative signatures can be distinguished for surface water from dams and pans, the Blesbokspruit, mine water and groundwater. Added are two points of Johannesburg mains water isotopic composition[1] [1], which may contribute to the Blesbokspruit water. A typical Highveld storm water isotopic composition is shown for comparison.

Water from pans and dams shows, as expected, the highest evaporation with positive δ–values for both hydrogen and oxygen. Mine water and fissure water, sampled underground, has depleted δ–values, i.e. around zero and negative. Far less evaporation is, therefore, indicated here and water from the main discharge point at Grootvlei Mine (shaft #3, Fig. 1) plots among the lower part of this plot with a negative δD and $\delta^{18}O$.

Surface water plotting in the lower half of the evaporation line appears to reflect larger rainfall events with rapid recharge of ground water, providing more depleted isotopic signatures. Dam water with an isotopic composition of the same range is diluted by rain and/or storm water during the wet season.

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[1] The values shown were relevant to the period of study. This signature can be variable over time.

Most of the mine water samples plot at an intermediate position between the dam and surface water and the ground water. Mixing of surface (dam) and ground water is therefore suggested with mine water representing a mixture of 43% surface water and 57% groundwater. A further, unknown proportion of Johannesburg reticulation (mains) water [1] may contribute to the mine water composition.

An observed intimate association of the isotopic composition of mine water from Grootvlei shafts with the Blesbokspruit water would lead to the conclusion that a substantial amount of Blesbokspruit water is entering the mine shafts, at least at shallower levels. For example, δD/δ^{18}O values from No. 1 to 7 level still plot among those of Blesbokspruit water whereas water from the deeper No. 9 level lies close to the "general discharge" at No. 3 shaft (Fig. 1). Likewise, water collected from piezometers at slimes dams around Grootvlei is less evaporated than Blesbokspruit water. Seepage from these slimes dams possibly constitutes another water component entering Grootvlei shafts at shallow levels.

It would appear, as a general model, that surface water influence in mine water decreases with increasing shaft depth (level). This interpretation can be applied similarly to the Central Mining Basin where at ERPM (Fig. 2) mine

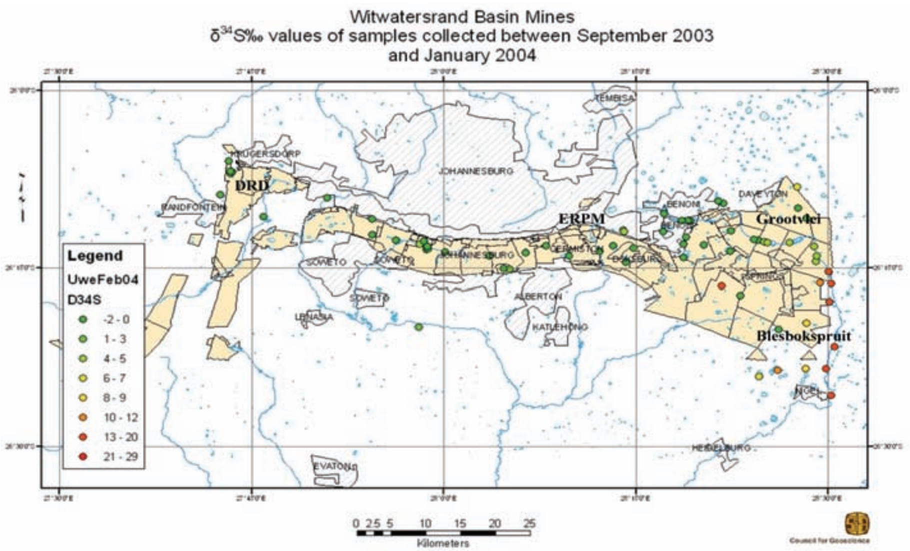

FIG. 2. Study area with distribution of sulphur isotopic composition of surface water samples as δ^{34}S ‰ (CDT). Variation in S isotopes can be attributed to water/rock interaction at water sources and/or anthropogenic or mining induced contamination. DRD: Durban Roodepoort Deep, ERPM: East Rand Proprietary Mines.

water consisting of 20%–30% surface water and 70%–80% groundwater was found.

2.2. S isotopes

Sulphur isotopes of dissolved sulphate (SO_4^{2-}) show four broad ranges of composition, i.e. δ–values from –2‰ to 3‰ (group 1), from 4‰ to 5‰ (group 2), from 6‰ to 9‰ (group 3) and from 10‰ to 29‰ (group 4) as shown in Fig. 2. The lower δ–values (groups 1 and 2) occur in the northern and western part of the project area, with only a few exceptions. Group 3 and 4 sulphur isotopic compositions are observed almost exclusively in the Blesbokspruit area east of Springs (Fig. 2), with only one exception.

Although this subdivision of $\delta^{34}S$ values is rather arbitrary, the S isotopic composition can be attributed to provenances and/or origins of the samples. $\delta^{34}S$ values around 2‰ to 5‰ indicate water that leached sulphides from Witwatersrand sediments, due to profound water/rock interaction with e.g. oxidative weathered pyrites. Lower values (incorporated in group 1) point to different provenances such as coal fired power stations or other anthropogenic influences. Most of the higher isotope values of groups 3 and 4 in the east outline the Blesbokspruit River and wetland. Water with such differing isotopic composition must have an alternative origin, e.g. from interaction with dolomitic sediments of the Transvaal Supergroup. The $\delta^{34}S$ values of groups 3 and 4 are well in agreement with those reported for SO_4^{2-} in fresh water systems world-wide, which lie generally between +5‰ and +15‰ (e.g. [3, 4]). It is difficult to decide at present whether water with $\delta^{34}SO_4^{2-}$ values of 10‰ and higher (group 4) acquired its S isotopic composition from interaction with bedrock in their source area and/or received anthropogenic input from municipal or industrial water. At least locally, mixing of water is indicated by S isotopes, possibly pointing to different degrees of water / rock interaction of mine water with Witwatersrand sedimentary sulphides.

2.3. Sr isotopes

The $^{87}Sr/^{86}Sr$ ratio in relation to the inverse Sr concentration is illustrated in Fig. 3. A linear trend emerges, indicating a two component mixing for samples which, on the basis of their S isotopic composition, can be regarded as Witwatersrand rock leachates. The increasing trend of radiogenic Sr (higher $^{87}Sr/^{86}Sr$ values) with Sr concentration points to a higher residence time of samples with more ^{87}Sr. More time was available for chemical reactions and/or leaching to take place and this water would become enriched in Sr, if suitable rocks/soils are leached. Its $^{87}Sr/^{86}Sr$ values are likely to increase as well.

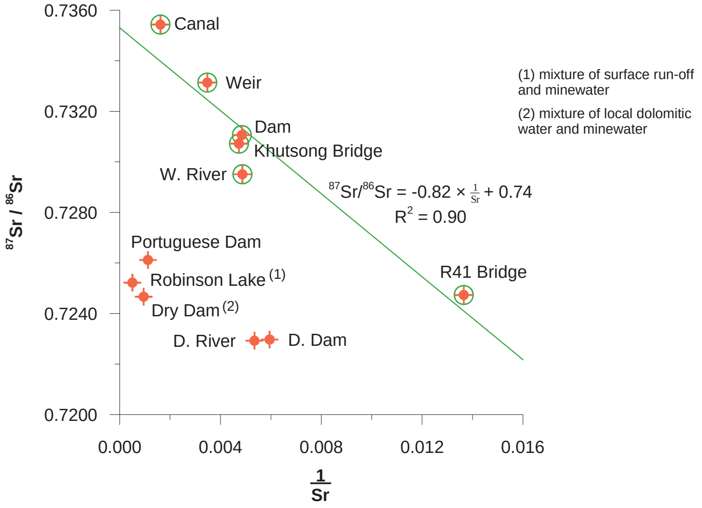

FIG. 3. ^{87}Sr/^{86}Sr ratio vs. inverse Sr concentration (ppb). Two-component mixing is indicted for samples forming a reverse trend (circled). Samples off this trend suggest hydrologically different conditions involving as yet unknown end-members.

Another and more likely interpretation of the Sr concentration and isotope patterns is two component mixing between mine effluent and water originating from or having flown through a dolomite area. Owing to its trace element character and its high Damköhler number in a given system [5, 6], Sr exchanges readily with the surrounding rock in an aquifer and thus reflects possible water–rock interactions of a given water body. Mixing of surface run–off and (Witwatersrand sediments leaching) mine water may lower the Sr isotopic composition and admixture of local dolomitic water would reflect the less radiogenic signature of Transvaal Dolomite. Sr isotopes, therefore, point to mixing of Witwatersrand sediment and Transvaal Dolomite components in water sampled particularly in the Western Mining Basin. This is substantiated by the linear trend of ^{87}Sr/^{86}Sr ratios vs. the inverse Sr concentration (1/Sr, Fig. 3). Although no end members have been identified, samples with a low Sr concentration represent less contaminated water. Mine effluent is gradually admixed increasing the Sr content. The inverse curve in Fig. 3 can thus be explained as a mixing line between "dolomite water" and mine effluent. Samples falling off this trend (Fig. 3) probably belong to locally different hydrological systems with as yet unknown end-members.

2.4. Pb isotopes

The Witwatersrand gold/uranium ores are characterised by high (up to several hundred ppm) uranium concentrations. Furthermore they are approximately 3 billion years old. These two factors combine to produce highly uranogenic lead isotope ratios (enriched in ^{206}Pb and ^{207}Pb and observed as elevated ^{206}Pb/^{207}Pb ratios. The relatively low thorium concentrations have not produced a similar enrichment in ^{208}Pb. Eglington et al. [6] describe the use of the lead isotopes, along with other isotopic systems in the quantification of different sources of water in acid mine drainage scenarios. A small portion of the project area was sampled to determine the applicability of this method to the identification of mine water sources and the tracing of possible mine effluents in the environment.

The data describe a linear trend, with a reverse gradient, due to the enrichment in ^{206}Pb. The negative trend relative to the x-axis is produced by the enrichment in ^{207}Pb, relative to ^{208}Pb. This trend suggests that lead in the samples represents a mixing relationship between the void water, sampled at the vent shaft (Fig. 4) and an environmental background value. This value has not been determined, however, and it is likely to be close to the Stacey-

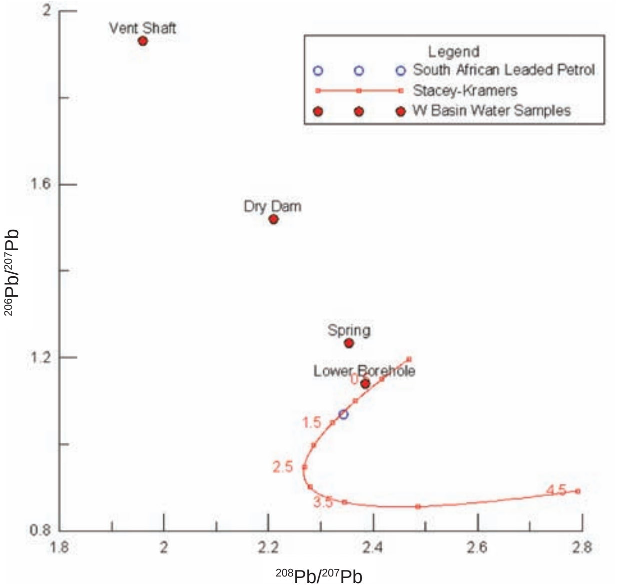

FIG. 4. Results of lead isotope analyses for the Western Basin decant area. Labels on the Stacey-Kramers [7] curve represent different stages of crustal evolution, in 10^9 years before present.

Kramers [7] curve and similar to the value recorded for the lower scavenging borehole (Fig. 4).

The lower ^{206}Pb/^{207}Pb ratio measured on water from the lower scavenging borehole (Fig. 4) suggests that the scavenging boreholes are drawing down the local water table and allowing the inflow of less contaminated or uncontaminated water from the surrounding dolomitic aquifer. The lead isotope ratio determined does not, however represent that of either the Witwatersrand crust (~3 billion years) or the Transvaal age crust (~2.5 billion years) as would be expected from the local geology or the ratio of modern South African leaded petrol, generally thought to be a major source of environmental lead in South African urban areas.

3. CONCLUSIONS

The isotopic characterisation of surface and underground water throughout the study area provided fundamental information about water components entering active and/or abandoned mine workings. In many instances H and O isotopes allow for the quantification of surface and groundwater proportions of underground resident or decanting mine water.

The wide spread of S isotope values of dissolved SO_4^{2} points to water sources ranging from leaching of Witwatersrand sediments to possible industrial sources. A “Witwatersrand signature” of δ^{34}S between 2‰–5‰ was found in most samples and helps tracing water components on the basis of their water/rock interaction.

The composition of Sr and S isotopes reveals two component mixtures of water most probably originating from dolomite areas with mine effluents. Plots of the strontium isotopic composition (^{87}Sr/^{86}Sr) vs. the inverse Sr concentration show a correlation that is interpreted as a mixing line between the said two components. Although no clear–cut end members can be established, a gradual mixing between water of most probably dolomitic provenance and mine effluent is indicated.

Lead isotopes have shown that contaminated water, which has interacted with Witwatersrand sediments, is entering the ground water and surface water systems. Other sources of groundwater do exist in the study area and have been intercepted in the lower scavenging borehole (Fig. 4). Mixing relationships between void water and an environmental background value are represented by the isotopic composition of lead.

The combination of naturally occurring isotopic tracers of water components provides a valuable tool for the identification and quantification of Witwatersrand-sourced contaminations in ground and surface water. There is a strong indication that water reporting underground can be characterised and eventually apportioned by isotope ratio analysis.

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INTERACTIONS BETWEEN RIVER AND GROUNDWATER IN AN ALLUVIAL AQUIFER IN CENTRAL ITALY ASSESSED BY MEANS OF CLASSIC HYDROGEOLOGICAL METHODS AND NATURAL TRACERS (^{222}RN AND WATER CHEMISTRY)

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Abstract

The seasonal changes of river-groundwater interactions in an alluvial aquifer in Central Italy have been investigated by ^{222}Rn and major ions measurements in river and groundwater. Stream discharge at various locations and water table levels all over the plain were also measured. The surveys carried out throughout the hydrologic year evidenced an area of groundwater inflow into the stream. Groundwater inflow to the stream was determined by means of ^{222}Rn data, corrected for the degassing, and stream discharge measurements used together in a two components mixing model. ^{222}Rn measurements in the stream were effective to determine fractions of groundwater inflow to the total discharge and to identify sections of flow-through condition. The integration of different approaches gave the best results in the investigation of such complex interactions.

1. INTRODUCTION

Surface water and groundwater interact in many different ways in a large variety of landscapes, from alpine to coastal, to riverine systems. The characterization of the exchange of groundwater with a river is usually carried out (i) measuring water levels in wells, piezometers and nests of piezometers placed within the alluvial plain, the streambanks and the streambed; (ii) performing stream discharge measurements at several cross sections in a short time period; (iii) comparing groundwater and stream geochemistry; and (iv) applying one-dimensional transport modelling [1]. In the last years, the combination of classical hydrogeological techniques with tracer techniques is becoming a widespread approach in order to gain a much complete overview of these, sometimes very complex, processes. Among geochemical tracers, chloride is one of the most used, giving information about the mixing of different reservoirs or tracing water movements [2], as well as the radioactive noble gas ^{222}Rn (radon) has been largely used to quantify groundwater inflow contributions to river discharge, applying a two-component mixing model [3]. The main aim of this research was to test the noble gas ^{222}Rn as a tracer of groundwater inflow to a stream in the Castel di Sangro alluvial plain in Central Italy. Additional geochemical and classical hydrogeologic methodologies were applied simultaneously in order to gain as much as a complete description of the processes occurring.

2. THE STUDY AREA

The Castel di Sangro alluvial plain (UTM33 N4625000 E425000E) is located in the Abruzzo Region (Central Italy) at the boundary between the carbonate units of Monte Greco – Monte Genzana and the siliciclastic deposits of the Molisan Basin with a N30°E striking regional strike-slip fault [4]. Two rivers flow in the plain, the Sangro and the Zittola rivers, along the north-western and the south-eastern margins, respectively. The Sangro river, as enters within the plain, flows in a cemented channel, which minimizes the interaction

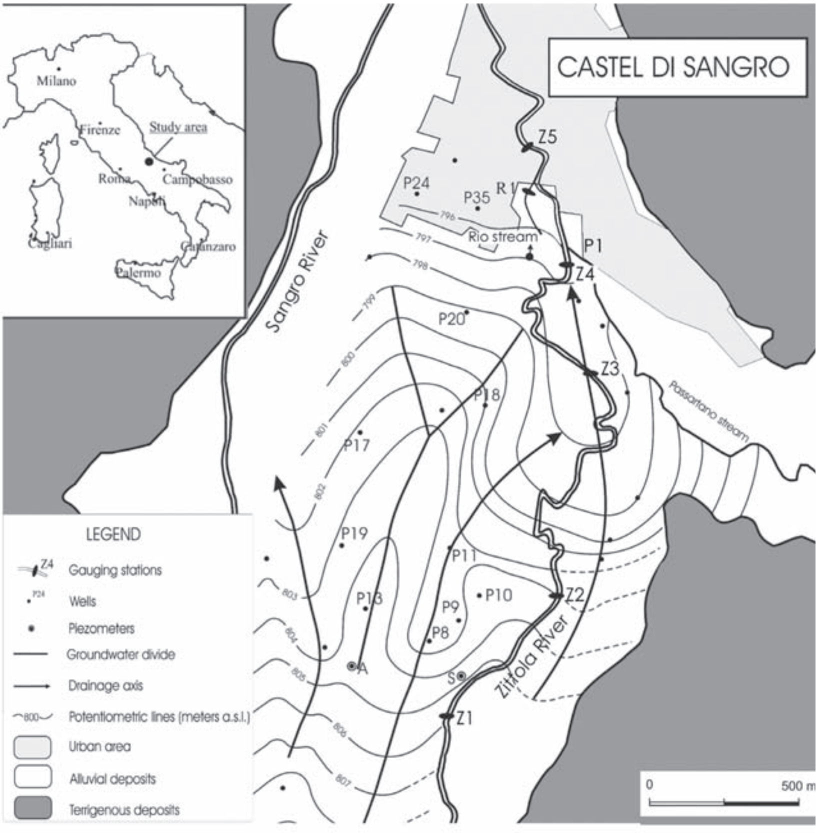

FIG. 1. Field site map. The reported water table map is referred to the survey of April '04.

with groundwater, while the course of the Zittola river is natural and presents meanders before entering the town of Castel di Sangro in the northern part of the plain. Moreover, in this portion of the plain the Rio stream flows for a few hundred of meters, from the Rio spring to the Zittola river in a cemented channel. In the same area, from the hydrographic right the Passartano stream, which has a seasonal flow regime, joins the Zittola river (Fig. 1).

Groundwater flows within an aquifer which is predominantly made of present-day alluvial deposits (Holocene), distributed along the rivers, and terraced alluvial deposits (Upper Pleistocene). The saturated zone is mainly made of gravels and sands, except the northern part of the plain where the groundwater flows predominantly within the silt deposits (zone of wells P24 and P35 in Fig. 1). In the study area the recharge phase usually goes from

November to May, while the recession phase coincides with later spring and summer (from June to October). The discharge of the Zittola river, monitored hourly at gauge station Z1, from January 1995 to December 2000, ranges from an average value of 0.25 $m^3 \cdot s^{-1}$ in the recession phase (minimum value 0.1 $m^3 \cdot s^{-1}$) to about 4.0 $m^3 \cdot s^{-1}$ in the recharge phase (maximum value 8.3 $m^3 \cdot s^{-1}$) (data from Servizio Idrografico e Mareografico Nazionale di Pescara).

3. METHODS AND MATERIALS

3.1. Field survey

Nine sampling campaigns were carried out from October 2003 to July 2004 (7–14/7, 27–28/10, 25–26/11, 16–17/12 in 2003, 10–11/2, 31/3–2/4, 27–28/4, 18–20/5, 15–16/6, 6–7/7 in 2004; dates are given in day/month) during which 1 spring, 26 wells and river water were sampled to determine chemical-physical parameters (T, pH and alkalinity), major ions concentrations and radon activity. The discharges of the Zittola river and of the Rio and the Passartano streams were monitored at the sections Z2, Z3, Z4, Z5 and R1 by means of a current meter (Fig. 1). A reconstruction of the water table surface was made monitoring the groundwater level by using a water level meter monthly in 26 wells, having a diameter of about 1 m and a screened depth of 11 to 21 m, and continuously in 2 piezometers by means of pressure tansducers (Fig. 1), from October 2003 to July 2004. All water table measurements were carried out in a single day during each sampling campaign.

3.2. Sampling and analytical techniques

Groundwater samples for ^{222}Rn determinations were taken after purging the well till stable values of pH and T were measured by a WTW multiparametric probe, according to the procedure described by Ref. [5]. Surface water was sampled by syringe directly into the stream at a mean depth from the water surface of 15 cm; the samples were taken always in the middle of the river or where the main flow was supposed to run. Three replicates at each observation point were collected and analyzed by means of a low-background Wallac Quantulus 1220 liquid scintillation counter, at least three hours after the sampling to allow ^{222}Rn to reach the equilibrium with its daughters. Counting time was 15 minutes. Lower level detectable was 0.5 $Bq \cdot L^{-1}$. At each observation point T, pH and alkalinity were measured. For major ions determinations 50 mL polyethylene bottles were filled; samples for cation determination were acidified at pH < 3 with concentrated HNO_3, and stored at 4°C. Major ions concentrations, after filtering the samples at 0.45 μm, were analyzed by ion chromatography (IC) with chemical suppression for Cl^-, NO_3^- and SO_4^{2-} and without suppression for Na^+, NH_4^+, K^+, Ca^{++} and Mg^{++}.

3.3. ^{222}Rn tracer method

The use of ^{222}Rn (a naturally occurring radioactive isotope, product of the ^{238}U natural decay chain and a direct product of α–disintegration of ^{226}Ra, it has a half-life of 3.8 days) as a hydrogeologic tracer is based on the fact that usually river water has a very low radon concentration because of degassing, while groundwater accumulates it flowing into the aquifer rocks. The influx of groundwater (Q_{gw}) to total stream discharge (Q_r) in a stream reach is quantified applying a two-components mixing model:

$$Q_{gw}/Q_r = (Rn_r - Rn_d)/(Rn_{gw} - Rn_d) \quad (1)$$

where Rn_r and Rn_{gw} are the radon concentrations ($Bq \cdot L^{-1}$) measured in stream and groundwater, respectively; Rn_d is the radon concentration downstream the considered stream reach estimated by Eq. (2), assuming no groundwater inflow between the upstream and the downstream sections:

$$Rn_d = Rn_u \times \exp\{- [(D \times v)^{1/2}/(h^{3/2})] \times x/v - \lambda \times x/v\} \quad (2)$$

where Rn_u is measured radon concentration at the upstream section ($Bq \cdot L^{-1}$), D is the radon molecular diffusivity (1.2×10^{-9} $m^2 \cdot s^{-1}$ at 23°C [3]), h is the average stream depth (m), v is the stream water velocity ($m \cdot s^{-1}$) and x is the distance between the upstream and the downstream sampling locations (m); λ is the ^{222}Rn decay constant (2.08×10^{-6} s^{-1}). The gas exchange is described by a turbulent flow model (surface renewal theory, [6]), applied mainly when the streamflow is turbulent (Reynolds number >2000). The difference between predicted (Rn_d) and observed (Rn_r) radon concentrations in the stream at a given location will be proportional to the amount of groundwater entering the river upstream that location. The average radon concentration of groundwater in the basin, Rn_{gw}, can be determined by sampling springs and wells; it can be considered constant, owing to the secular equilibrium occurring between the parent, ^{226}Ra, and the daughter nuclide, ^{222}Rn, if radon is lost only by radioactive decay and the aquifer has homogeneous ^{226}Ra content, porosity and emanating power.

4. RESULTS AND DISCUSSION

4.1. Groundwater flow scheme and river discharge measurements

Throughout the hydrologic year 2003/2004 the water table surface reconstruction (see a representative example in Fig. 1) always evidenced a groundwater divide in the central part of the plain, located on the crest of the impermeable bottom of the aquifer, and a main drainage axis, flowing within the paleovalley, between the divide mentioned above and the central segment of the Zittola river, and joining, in the northern part of the plain, a main drainage axis which extends along the northern segment of the same river. From section Z2 to section Z5 of the Zittola river, Ygroundwater is likely to recharge the river, according to the groundwater flow scheme and to the monitored groundwater heads. Direct stream discharge measurements (Table 1) confirm that from downstream of the section Z2 there is a diffuse groundwater inflow to the Zittola river. In summer the diffuse groundwater inflow is not significant between sections Z4 and Z5 and the increase in discharge into the river is mainly generated by the tributary Rio. The seasonal Passartano stream discharge was in the range of 0.005 to 0.01 $\mathrm{m^3 \cdot s^{-1}}$ during the hydrogeological surveys and for this reason was considered as a not significant contribution to the Zittola discharge.

TABLE 1. DISCHARGE MEASUREMENTS ($\mathrm{m^3 \cdot s^{-1}}$) AND IN BRACKETS ^{222}RN CONCENTRATIONS ($\mathrm{Bq \cdot L^{-1}}$) MEASURED IN THE ZITTOLA RIVER AND THE RIO STREAM.

River section	distance (km)	Nov. 2003	Dec. 2003	Feb. 2004	Mar. 2004	Apr. 2004	May 2004	Jun. 2004	Jul. 2004
Z2	0	– (0.3)	0.54	0.76	0.79	1.65 (1.7)	1.05 (1.9)	0.410 (1.3)	0.13 (0.5)
Z3	1.16	–	–	–	–	– (1.6)	– (2.6)	0.403 (2.6)	0.41 (3.0)
Z4	1.70	–	–	–	0.92 (4.5)	1.11 (3.5)	– (3.6)	0.86 (5.4)	0.49 (5.4)
Z5	2.43	0.83 (3.1)	1.09 (2.9)	0.65 (3.6)	1.33 (4.6)	1.70 (7.3)	1.50 (3.3)	0.99 (4.8)	0.62 (7.1)
Rio	–	–	–	0.13	0.16 (10.5)	0.19 (12.5)	0.16 (10.5)	0.15 (11.1)	0.19 (9.2)

4.2. Hydrochemistry

Among the determined ions, Mg^{++}, Ca^{++} and SO_4^{2-} are the most sensitive to spatial and temporal variations of river and groundwater chemical composition. When the ratio Mg^{++}/Ca^{++} is plotted against SO_4^{2-} (Fig. 2) a summary view of the temporal and spatial variations occurring in our system can be obtained. River water is characterised by the lowest values of both the indexes (from 0.08 to 0.25 meq·L^{-1} for the sulphate and from 0.02 to 0.2 for the Mg^{++}/Ca^{++} ionic ratio), while groundwater is characterised by sulphate values ranging from 0.07 to 0.40 meq·L^{-1} and a cationic ratio of about 0.3; Rio spring concentrations are reported in the group of groundwater.

River water samples follow a trend; in fact, the lowest values of both the indexes are from the river stations and the spring in the southern part of the plain, while the highest values are found in the river flowing in the northern part of the plain, where a recharge from groundwater occurs, according to the groundwater circulation scheme and discharge measurements (see Table 1). In the area of groundwater inflow (downstream Z2), river water samples in the drainage phase have solutes concentrations closer to those of groundwater than in the recharge phase. This behaviour is justified by the lower discharge of the Zittola river during the recession period (Table I) causing an enhancement

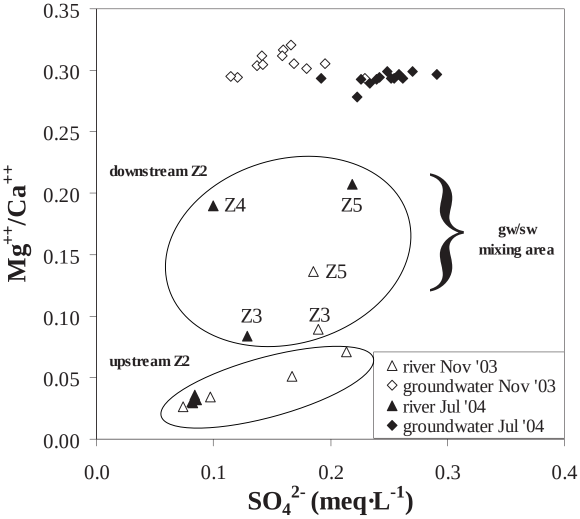

FIG. 2. Mg^{++}/Ca^{++} vs SO_4^{2-} concentration measured in river water and groundwater samples collected in the Castel di Sangro alluvial plain in the recharge (November '03) and in the recession (July '04) phases. Measurement uncertainties are in the order of 1%.

of groundwater contribution to the baseflow. In Figure 2 is also evidenced a seasonal pattern: the bigger scattering of Mg^{++}/Ca^{++} ratios in the recharge phase is likely due to the mixing with rain water, which changes the equilibrium between groundwater and rock matrix composition; the saturation indexes, monthly averaged on all the wells in the plain, vary from a maximum of 0.65 ± 0.14 in November ‘03 to a minimum of 0.12 ± 0.14 in July ’04 and from a maximum of 0.33 ± 0.08 in November ’03 to a minimum of 0.08 ± 0.08 in July ‘04, for dolomite and calcite respectively, supporting the previous hypothesis.

4.3. Groundwater contribution to river discharge: ^{222}Rn mixing model

^{222}Rn measurements in river water show throughout the hydrologic year an increase along the stream water path between the section Z2 and the section Z5 (see Table I). This hypothesis is supported by discharge measurements (Table 1), which show an increase from upstream gauge (Z2) to downstream station (Z5) in agreement with the groundwater flow scheme and the water chemistry. Between stations Z2 and Z5, the river receives a diffuse groundwater seepage and a discrete inflow by the Rio stream (Fig. 1). ^{222}Rn activity concentration in the Rio ranges from 9.2 to 12.5 $Bq\cdot L^{-1}$ (mean: 10.8 ± 1.2 $Bq\cdot L^{-1}$). In the reach Z2-Z4 the stream receives diffuse supplies mainly from groundwater draining an area characterised by an average annual ^{222}Rn concentration of 6.3 ± 0.8 $Bq\cdot L^{-1}$ (calculated from the values of the well P18); while, in the reach Z4-Z5, besides the punctual inflow of the Rio, the stream receives a diffuse groundwater inflow with an average annual ^{222}Rn concentration of 12.1 ± 0.7 $Bq\cdot L^{-1}$ (calculated from the values of the wells P24 and P35). The consideration is supported by ^{222}Rn measurements performed in the wells located in the northern area of the plain and by the groundwater flow scheme, which shows the highest values of the hydraulic gradient in this area, where the groundwater mainly flows within the silt deposits. The groundwater inflow (%) calculated by the application of Equation (1) is reported in Table 2. A comparison between the fraction of groundwater inflow to the total stream flow in the different reaches determined by direct stream discharge measurements and by the ^{222}Rn mixing model, considering the two different groundwater contribution signatures, has been performed. The calculation has been made in the months of June and July 2004, when the available set of data is the most complete (Table 2). In the reach Z4-Z5, the two methods agreed almost perfectly (Table 2). In the reach between Z3 and Z4 both methods yielded the highest contributions by groundwater to the total discharge. Nevertheless, the percentage of groundwater inflow given by ^{222}Rn data is always from 1.5 to about 5 times greater than that obtained from stream gauging measurements, probably because in the stream reaches between Z2 and Z4, the river water is influent and effluent at the same time;

TABLE 2. PERCENT OF GROUNDWATER INFLOW AND GROUNDWATER DISCHARGE MEASURED BETWEEN THE INDICATED STREAM REACHES BY MEANS OF STREAM DISCHARGE MEASUREMENTS (ERROR: ±10%) AND BY ^{222}RN DETERMINATIONS (*) (ERROR: ±20%).

	June 2004				July 2004			
stream reaches	% gw	Q_{gw} ($m^3 \cdot s^{-1}$)	% gw*	Q_{gw}* ($m^3 \cdot s^{-1}$)	% gw	Q_{gw} ($m^3 \cdot s^{-1}$)	% gw*	Q_{gw}* ($m^3 \cdot s^{-1}$)
Z1-Z2	–	–	12	0.05	–	–	6	0.01
Z2-Z3	–2	0	30	0.12	67	0.28	44	0.18
Z3-Z4	53	0.46	79	0.68	16	0.08	77	0.38
Z4-Z5	12	0.12	12	0.12	22	0.13	19	0.12

only in July 2004 for the reach Z2-Z3 the opposite feature is found. This consideration is justified by the meandering morphology of the river and by the groundwater flow scheme which evidences flow-through conditions (see Fig. 1), which are difficult to detect only by differential discharge measurements.

5. CONCLUSIONS

An annual monitoring of ^{222}Rn and water chemistry in the alluvial aquifer of Castel di Sangro, Central Italy, has been carried out in order to study stream water-groundwater interactions. Detailed analysis of a large set of data allowed to conclude that ^{222}Rn is a very sensitive hydrogeologic tracer of groundwater recharge to river [7]. Differential stream discharge measurements, water table surface reconstructions and chemical and radioactive (^{222}Rn) analyses confirmed that the Zittola river is significantly fed by the groundwater in the final part of its course, before it enters the Sangro river, identifying stream reaches characterised by conditions of influent and effluent river (flow-through).

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HYDRO-ISOTOPE MIXING CELL MODEL FOR ASSESSING FLUXES IN COMPLEX AQUIFERS UNDERGOING TRANSIENT HYDROCHEMICAL AND ISOTOPIC EVOLUTION

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Abstract

The aim of this study was to develop a flow model that will enable identification of the hydraulic parameters and quantitative calculation of groundwater fluxes in a complex and transient hydrogeological system in which the piezometric heads and the spatial distribution of solutes varies with time. In such a system the boundaries and hydrological conditions along the boundaries are not sufficiently clear or distinct, and there is a lack of hydrogeological and hydrochemical information. Thus it is difficult to construct, solve and calibrate a hydrological model based on the continuity equation. The algorithm proposed in this study is therefore based on a more simplistic approach in which the flow domain is subdivided into pseudo-homogeneous flow cells forming a multi-compartmental flow model. The creation of the multi-compartmental structure is based on spatial distribution of dissolved ions and isotopes in a transient hydrological system.

1. OBJECTIVES

The objectives of the present study were as follows:

(a) To build a conceptual model of transient groundwater flow in a complex hydrogeological system in the form of a non-steady multi-compartmental model;
(b) To develop a suitable inverse mathematical algorithm for solving the nonsteady multi-compartmental model presented: i.e. one that allows identification of the hydraulic parameters of the aquifer and enables a

quantitative solution of the flow components — including calculation of water and solute balances;

(c) To demonstrate the use of the mathematical algorithm for a quantitative solution of the hydrological system in the Central Arava Valley, Israel, including calculation of all the contributing components from external sources (recharge, connected neighboring aquifers) to each of the aquifers, and calculation of the quantities of water flowing from one aquifer to another.

2. TRANSIENT MIXING-CELL MODEL

In a newly developed hydrological basin combined of several sub-aquifers with various water-bearing units prevailing different groundwater qualities, long term water extraction will be followed by temporal variations of groundwater quality. Therefore, the magnitude and the spatial distribution of dissolved minerals and environmental isotopes vary with time and space. This results in continuous variations of the location and the boundaries of the “pseudo-homogeneous” sub aquifer units (or compartments) that vary with time and space imposing a non-steady Mixing-Cell modeling approach [1].

The flow model was constructed according to the principle of division into mixing cells, related to a Lumped Parameter model (henceforth known as “compartmental model,” [2] or when there is more than one compartment: “multi-compartmental model” [3]). The underlying goal of sub-division of the aquifers into discrete sub-hydrological systems was to create hydrological units, in which each of the compartments has relatively homogeneous and fixed values for the parameters (the hydrological properties) and variables (the concentrations and hydraulic heads). In this way we attain a situation (stemming from the definition of “compartment” in the multi-compartmental model) in which there is no gradient of hydraulic heads or concentrations of solutes in each compartment. On the other hand, there may be differences between one compartment and another, which enable flow and transience in each cell. In other words, the continuous variation of the parameter or the property is approximated, and therefore replaced, by a sort of “step function” imposed on the cell’s boundaries. The model assumes mixing of solutes in the compartments of the system, due to the presence of water from various sources with differing solute compositions. As a result, the different sources of water are mixed, and a new solute composition is created which is considered unique to the water in the cell at that specific point in time.

Based on this model, a set of balance equations was formulated to describe the water and solute balances in the compartments [4]. The Water balance for each cell *n* for transient flow system has the following expression:

$$\sum_{i=1}^{I} q_{in} - \sum_{i=1}^{J} q_{nj} + \sum_{r-1}^{R} Q_{rn} - W_n = s_n^* \frac{dh}{dt} \tag{1}$$

where q_{in}, q_{nj}, and Q_{rn} represent influx *i*, outflux *j* and various point sources *r*, respectively (L^3/t), W_n is the known rate of water abstraction (pumping rate) from cell *n*, and *S*

$$S_n^* = \rho\, g V_n \frac{d\varphi_n}{dp_n}$$

is the storage capacity of cell n (L^2). As each source and groundwater flux components has a unique mineral and isotopic composition, in view of (1) the mass balance expression for every *k* dissolved species and and/or isotope (k=1,2,3,...,K_n) has the following form:

$$\sum_{i=1}^{I}(c_{ik}q_{in}) - \sum_{j=1}^{J}(c_{nk}q_{nj}) + \sum_{r=1}^{R} c_{rk}Q_{rn} - c_{nk}W_n = S_n^* c_{nk}\frac{d_{hn}}{dt} + V_n^* \frac{dc_{nk}}{dt} \tag{2}$$

Where C_{ik}, C_{rk}, are the isotopic composition or the concentrations (m/L^3) of the *k* isotopic or chemical species associated with influxes and sources into cell n, respectively. C_{nk} is the (already mixed) concentration of the *k* constituent in cell *n*, and $V_n^* = V_n \Phi_n$ is the water volume occupied in cell *n* having a volume V_n with a porosity Φ_n. Therefore, for every cell *n* one ends with K_n+1 balance equations, far beyond the number of unknown fluxes associated with this cell. In a finite difference form for space and time equations (1) and (2) are written as:

$$\sum_{i=1}^{I} q_{in} - \sum_{j=1}^{J} q_{nj} + Q_{rn} - W_n = S^{**} \frac{h_n^{t=2} - h_n^{t=1}}{\Delta t} \tag{3}$$

$$\sum_{i=1}^{I}(c_{ik}q_{in}) - \sum_{j=1}^{J}(c_{nk}q_{nj}) + \sum_{r=1}^{R} c_{rk}Q_{rn} - c_{nk}W_n = V_n^* \frac{c_{nk}^{t=2} - c_{nk}^{t=1}}{\Delta t} +$$

$$+ S_n^* c_{nk}^{t=2} \frac{h_n^{t=2} - h_n^{t=1}}{\Delta t} \tag{4}$$

The set of equations that was created constitutes a set of constraints, under which, in order to identify the hydraulic parameters and flow components in the aquifer, it was necessary to solve the so-called "Inverse Problem" by making use of large quantities of water and hydro-chemical chemical balance equations.

The problem as presented is solved using a process of optimization, in which a range of possible solutions is defined, from which the optimal (most suitable) solution is chosen, according to predetermined criteria (target function). Solution by optimization is necessary due to the Inverse Problem (e.g. [5]), and because the model is intended to help identify the structure of the flow system, which is not known in advance. In other words, while running the model it is necessary not only to calculate the values of unknown fluxes, whose existence is highly probable, but also to try to identify and locate those unknown fluxes. In order to do this, at the data collection stage and when constructing equations for the model it is necessary to include a large number of all potential unknown fluxes (groundwater fluxes between compartments of the system and discharge of external contributors to the compartments), about which there is uncertainty whether they are really active within the flow domain. However, they all must be hydrologically feasible [1, 3, 4]. As a result, a large number of equations are required in order to include all the possible flow components of the system in the model, even those flow components which are in-active and will eventually receive the value of zero in the solution, and accordingly will be classed as nonexistent.

In order to conduct the calculations that would enable us to receive a quantitative solution for the unknown groundwater fluxes, we were required to make use of a mathematical algorithm with specific properties, which enables the simultaneous solution — by optimization — of a large number of balance equations, capable to accommodate several orders of magnitude differences among the unknown parameters while limiting the solution to only positive values of water fluxes. The algorithm based on the Least Squares (LS) method was the most effective for solving the compartmental model investigated. The advantages of this algorithm are primarily expressed in complex yet vague, hydrological systems, which include a range of hydrological and hydrochemical data, and in which the hydrological conditions change both in time and space [1, 3].

3. FINDINGS AND RESULTS

A preliminary examination of the algorithm was conducted on a synthetic data system, which describes a non steady flow system (the concentrations of the chemical components, like the piezometric head in the compartments, vary over time). Figure 1 shows a simplistic compartmental flow model with 8 cells, 12 external unknown fluxes ($q_1 - q_{16}$) and 7 in-between cells fluxes [4]. In a system of this type, there are additional parameters, which do not exist in a steady state system – and which must be calculated in the course of the solution:

the *volume of water* in the compartment (V^*) and the *water storage capacity* of the compartment (S^*) which add two additional unknown parameters to each cell, all together 35 unknowns. The assigned (synthetic) values are posted next to each parameter in Figure 1.

In the attempts made to solve complex non-steady state systems, it was found that it is not possible to obtain sufficiently precise results using a direct-forward solution method [6]. Accordingly, a special procedure was established, which enables us to deal with complex flow problems, by the addition of "external" information such as a preliminary assessment of V_n^* by using of graphic tools [7]. It is assumed that the variations with time in the *storage capacity* (S^*) and the *water volume* (V^*) parameters for every Cell n are several orders of magnitude smaller than the variations in pumping rates and the expected changes in fluxes. Under the above-mentioned assumptions,

$$\frac{S_n^*}{V_n^*} = \rho g \alpha \frac{1-\varphi}{\varphi}$$

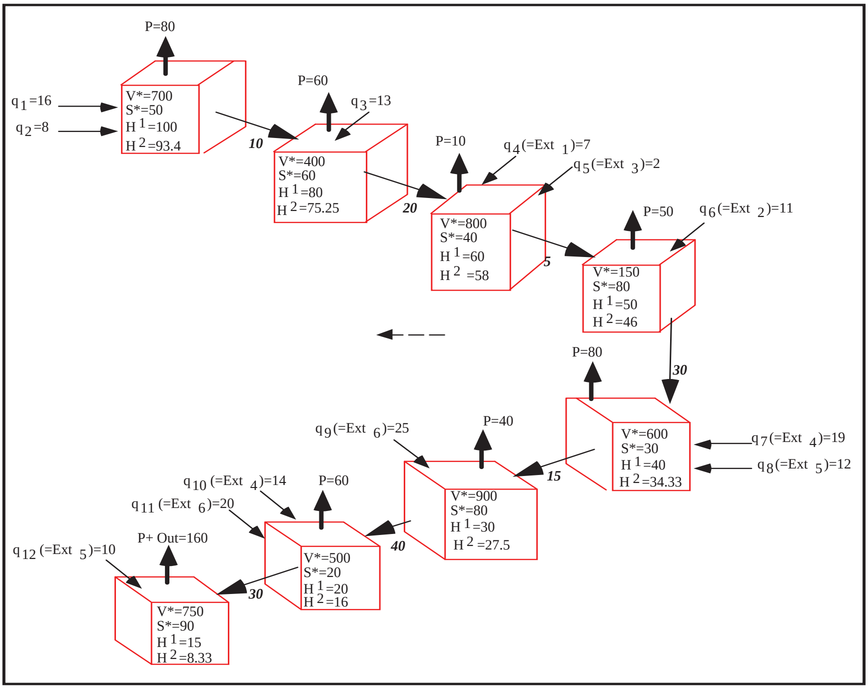

FIG. 1. Synthetic compartmental flow system with assigned fluxes, cell's volume, storage capacity and pumping rates for one time step between t^1 and t^2 during which the hydraulic heads were changed from H^1 to H^2.

TABLE 1. OPTIMIZED RESULTS OBTAINED WITH THE LS ALGORITHM FOR 35 UNKNOWNS ILLUSTRATED IN FIGURE 1.

Unknown parameter	Given value	LS results	Deviation (%)	Unknown parameter	Given value	LS results	Deviation (%)
q_1	16	15.50	3.1	$q_{vii\text{-}viii}$	30	28.00	6.7
q_2	8	7.85	1.9	S^*_i	50	50.49	1.0
q_3	13	12.00	7.7	S^*_{ii}	60	60.74	1.2
q_4	7	7.37	5.3	S^*_{iii}	40	42.00	5.0
q_5	2	1.5	25.0	S^*_{iv}	80	80.21	0.3
q_6	11	10.25	6.8	S^*_v	30	29.96	0.1
q_7	19	18.02	5.2	S^*_{vi}	80	80.65	0.8
q_8	12	12.73	6.1	S^*_{vii}	20	21.00	5.0
q_9	25	24.38	2.5	S^*_{viii}	90	91.91	2.1
q_{10}	14	13.21	5.6	V^*_i	700	670.00	4.3
q_{11}	20	19.76	1.2	V^*_{ii}	400	376.08	6.0
q_{12}	10	9.43	5.7	V^*_{iii}	800	770.63	3.7
$q_{i\text{-}ii}$	10	10.15	1.5	V^*_{iv}	150	140.00	6.7
$q_{ii\text{-}iii}$	20	19.29	3.6	V^*_v	600	580.00	3.3
$q_{iii\text{-}iv}$	5	4.68	6.4	V^*_{vi}	900	850.98	5.4
$q_{iv\text{-}v}$	30	29.09	3.0	V^*_{vii}	500	478.24	4.4
$q_{v\text{-}vi}$	15	14.00	6.7	V^*_{viii}	750	703.41	6.2
$q_{vi\text{-}vii}$	40	38.38	4.0				

can be assessed from measured and/or estimated parameters. A special subroutine was established in which wide range of suggested random V_i^* values are imposed for each iteration "*i*" in the model, from which the S_i^* parameters are obtained. The most feasible (representative) V_n^* is obtained from S_i^*/V_i^* versus V_i^* for the above calculated S_n^*/V_n^* [7]. Using this procedure the algorithm obtained a solution with very high precision as presented in Table 1.

The need to develop a multi-compartmental hydrological model arose after the conditions of the complex hydrological system of the Central Arava Valley, Israel, were studied, in which the piezometric heads and spatial distribution of solutes vary over time due to the dynamics of continuous groundwater pumping during the last 50 years, reflecting a progressive development of the local aquifer units.

Each one of the water bearing units comprises mixed water from various sources, characterized with different chemical and isotopic compositions. This water penetrates the aquifer units both as recharge – from flood flows along the alluvial fans (wadis) and from infiltration and percolation over the alluvium – and from underground contributions from deeper hydrological units, through areas of massive geological faults.

In order to construct the compartmental system (Figure 2) and characterize the hydraulic links between compartments, environmental

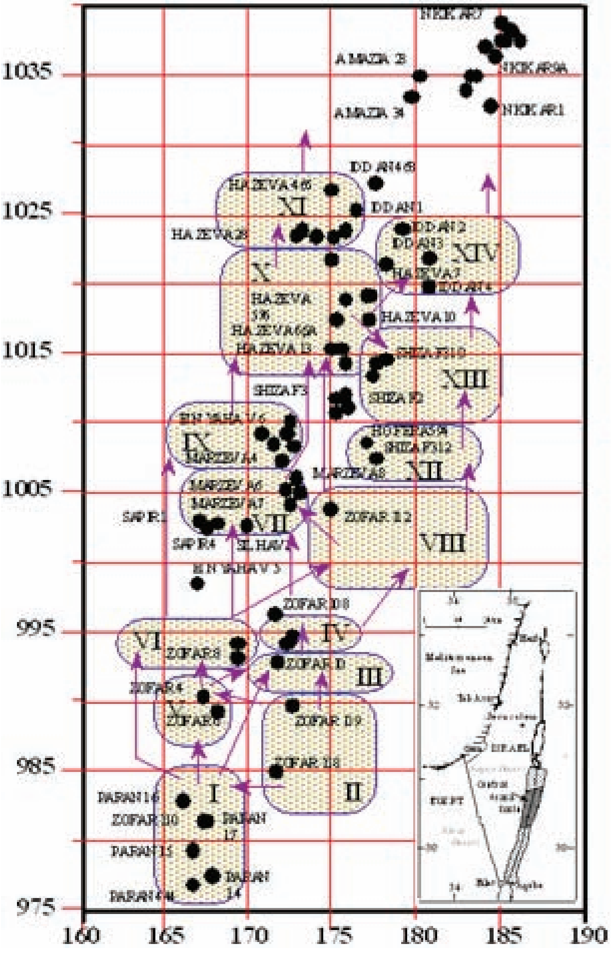

FIG. 2. Compartmental structure of the Arava aquifer.

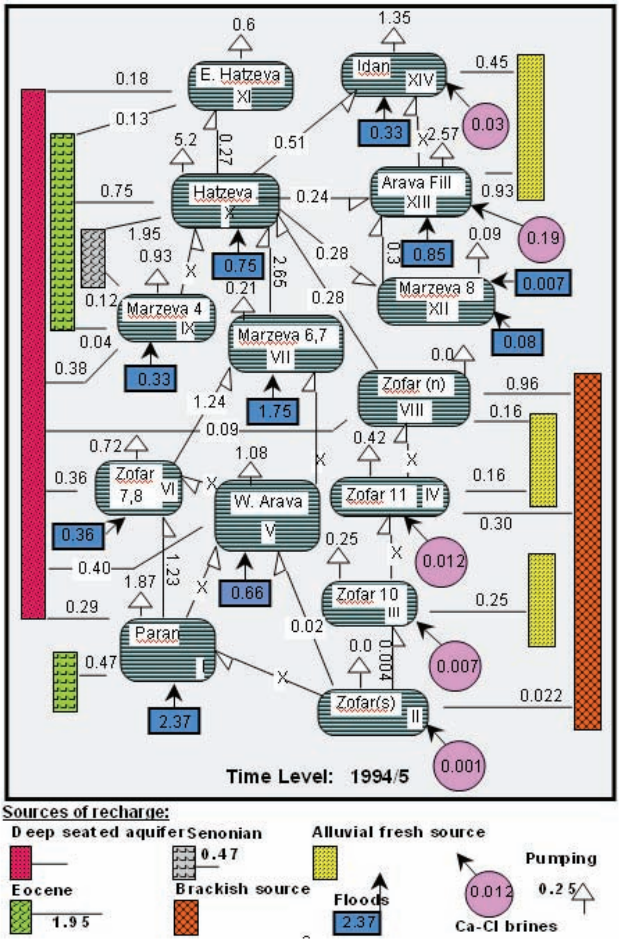

FIG. 3. Calculated fluxes into the Central Arava aquifer (M·m^3/5 years).

isotopes, hydrochemical, geological and geographical data were used. The system was divided according to the principle of division into compartments [7], in which each compartment has spatial homogeneity of parameters (hydraulic characteristics) and variables (concentrations and hydraulic heads). At the first stage of construction, a statistical cluster analysis was conducted, which uses the data of the concentrations of the various chemical components in the water, and which creates a division into clusters or subgroups according to criteria of maximal similarity in all the components (multi-variable cluster analyses). Each subgroup was characterized by its unique chemical and isotopic composition, which is different from other subgroups, and is defined as a compartment in the compartmental model.

After construction and testing of the mathematical tools required for solution, the mathematical algorithm was applied to provide a quantitative solution to the hydrological system of the Central Arava Valley, while using data taken from wells of the Alluvial Fill aquifer [7]. The solution for the last time step (1995) is presented in Figure 3.

4. SUMMARY AND CONCLUSIONS

Following application of the model to the Central Arava Valley aquifer system, and after examination of the results obtained, the following conclusions were reached:

- For extremely complex hydrogeological system with wide range in magnitude of the unknown parameters, it was necessary to pre-assess at least one parameter in each cell and assigned it with a fixed known value. That was the only way to guarantee a unique LS global optimized solution.
- The changes in time: Over the years, and particularly during the period prior to the development of settlement in the area and the increase in groundwater exploitation, the main reason for the non-steadiness of the hydrological system (namely: the fluctuations in the groundwater level and in the concentrations of the chemical components) was related to the varying character of flood flows due to the construction of attenuating reservoirs, which serve as the most important recharge sources for the groundwater. Recently, pumping regimes, which vary in time, have also contributed to this, as have salinization processes related to the penetration of brackish and salty water from external sources.
- In the analysis of the quantities of water flowing through and between the compartments of the system, it is possible to identify and pinpoint situations of underground hydraulic discontinuities, as well as regions of hydraulic connections between various hydraulic units [8].
- In an analysis of the external sources contributing to the aquifer system of the Central Arava Valley, it is possible to estimate the total water contribution from external sources, the internal fluxed among sub-aquifer units, and also to distinguish between the relative contributions of different sources to the various regions in the hydrological system.

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ISOTOPE INVESTIGATION OF INTERRELATION BETWEEN DELAY ACTION DAMS AND GROUNDWATER IN THE ARID REGION OF BALOCHISTAN, PAKISTAN

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Abstract

Isotope techniques (^{2}H, ^{18}O, ^{3}H) were applied to investigate interrelationship between delay action dams and groundwater in Ziarat Valley of Balochistan. These reservoirs are meant to collect water in rainy season and supplement groundwater recharge in dry season. The data indicate that the mean values of $\delta^{2}H$, $\delta^{18}O$ and tritium of precipitation are: –6.4‰, –37‰ and 9 TU respectively. Ranges of $\delta^{18}O$ and $\delta^{2}H$ values of the groundwater samples (wells and karezes/kanats) are –6.8 to –1.2 ‰ and –42.5 to –0.7 ‰ respectively. The $\delta^{18}O$ and $\delta^{2}H$ of dam reservoirs range from –6.9 to +15.6 ‰ and –42.6 to +86 ‰ respectively and they follow evaporation lines in the $\delta^{18}O$–$\delta^{2}H$ plots. Isotope data indicate that there is no significant groundwater recharge from the Pechi Dam reservoir. Uchki Dam has some contribution in groundwater recharge. Results of tritium suggest that the residence time of groundwater is quite short (fresh water).

1. INTRODUCTION

Baluchistan, the biggest province of Pakistan, is mostly arid with meager precipitation and high evaporation. Karezes have long been used for irrigation purposes. A kareze (also called kanat) is a subsurface water channels emerging on the ground surface after receiving groundwater through open wells. In the arid area of Balochistan thousands of such karezes were used for groundwater explotation. Installation of tube-wells to get water for various purposes has lowered water table so much so that flow in karezes has been adversely affected. As a result, many karezes have gone completely dry while the flow of others reduced drastically [1]. In order to combat the situation, more than 150 storage dams, called delay action dams were constructed on the alluvial fans in different areas to collect the flow of hilly streams, and allow water to percolate and supplement the flow in the karezes. The ability of delay action dams to recharge groundwater regime is crucially controlled by the rate of silt deposition in the reservoir. As the siltation of dams progresses, the percolation of water diminishes and may stop altogether at some later stage. A study was undertaken to investigate the effectiveness of few dams in Ziarat valley. Environmental isotopes and water chemistry were used.

The rocks of Ziarat area have been deformed into mega-anticlines/synclines. Numerous local fold and fault systems have developed into the area. Ziarat Nallah itself has made its way along a big fault system which ultimately has developed into a valley. The rocks of the area have been involved in the constitution of Sulaiman Fold Belt. The rocks have deposited in the Lower Indus Basin during Jurassic, Cretaceous, Tertiary and Quaternary geologic time. The rocks of Oligocene period are missing in the area showing that either they have not been deposited or have been eroded due to emergence of the area above sea level. Ziarat village is perched over the rocks of Paleocene period. Different workers have classified the rocks of the area into different formations/groups depending upon their lithology and age. Terrace gravel and fan deposits of Quaternary age are found deposited near Ziarat and in the syncline extending northwest and southeast. Talus and scree deposits are mainly found in the south of the area. Other Quaternary sediments consist of cultivated silts, colluviam deposits and stream deposits. Lithological logs of three boreholes drilled by Water and Power Development Authority show that the upstream area of Pechi Dam is underlain by alluvium containing gravel and boulders along with some sand and reddish silty clay up the varying depth from 8 to 14 m. Bed rock of fractured limestone is found below the alluvium up to the maximum drilled depth of 205 m. A layer of shale of light grey colour, 4.3 m thick with minor pieces of limestone was also encountered in the well drilled in Ziarat Town [2].

The climate is characterized by cold winters and warm and dry summers. June-August are the hottest months during which mean maximum temperature reaches to 30°C. Snow fall occurs during cold months of December–February when minimum temperature goes several degrees below the freezing point. Rainfall is scanty. According to the rainfall record of the nearby Meteorological Observatory at Ziarat, the mean annual precipitation is 356 mm. The wettest months are July and August while significant amount of rain also falls during January to April. Snowfall occurs in winter. Mean annual evaporation is 3638 mm [1].

2. MATERIALS AND METHODS

Water samples were collected periodically (monthly/quarterly) from Pechi Dam and downstream karezes during October 1990 to October 1993 and Uchki Dam and downstream wells during August 1995 to February 1998. Sample locations are given in Fig. 1. Important physico-chemical parameters like pH and electrical conductivity (EC) were measured in the field using portable pH and EC meters. Filtration and acidification of samples was carried out in the field if required. Rain and snow samples were collected from Ziarat Valley.

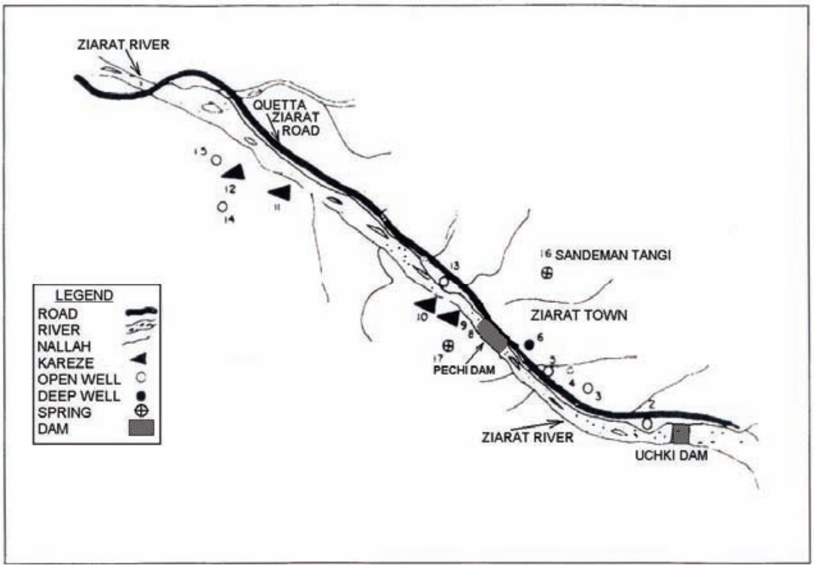

FIG. 1. Location map of sampling point (dams, karezes and wells).

The $\delta^{18}O$ was measured by the CO_2 equilibration method [3]. Water samples were reduced to hydrogen gas by zinc shots for δ^2H measurement [4]. Measurement uncertainties for $\delta^{18}O$ and δ^2H are 0.1‰ and 1.0‰ respectively. Tritium content of the samples was determined by liquid scintillation counting after electrolytic enrichment [5]. The standard error of measurement is of the order of ±1 TU.

3. RESULTS AND DISCUSSION

3.1. Isotopic indices of precipitation and local meteoric water line

Rainfall and snow samples collected from Ziarat Valley during June 1996 to October 1999 give wide ranges of $\delta^{18}O$, δ^2H and ^3H and with the mean values of –6.4‰, –37‰ and 9 TU respectively. Weighted averages were not calculated because the exact amounts of individual events are not known. For $\delta^{18}O$ and δ^2H, the available rain data of the same locality from March 1991 to September 1993 were also combined. After excluding the very enriched $\delta^{18}O$ and δ^2H values (normally positive $\delta^{18}O$), the local meteoric water line: $\delta^2H = (7.8 \pm 0.2)\,\delta^{18}O + (12.6 \pm 1.3)$, $n = 58$, $r^2 = 0.965$ was determined by taking the simple regression of the data.

TABLE 1. ISOTOPIC VALUES OF DAM RESERVOIRS.

Isotope		Uchki Dam	D/S Wells	Pechi Dam	Karezes
	Min.	–4.9	–5.6	–6.9	–6.8
$\delta^{18}O$ (‰)	Max.	+15.6	–1.2	+10.8	–5.2
	Mean	+3.5	–4.1	–1.0	–6.1
	Min.	–25.0	–32.2	–42.6	–42.5
δ^2H (‰)	Max.	+86.0	–0.7	+59.1	–28.9
	Mean	18.0	–23.1	–4.8	–36.1
	Min.	8	11	5.7	7
^3H (TU)	Max.	27	14	16.3	14
	Mean	17	12	11.9	10

3.2. Isotopic character of dam reservoirs and groundwater

The minimum, maximum and mean values of $\delta^{18}O$, $\delta^{2}H$ and tritium for dam reservoirs, groundwater (karezes and wells) are shown in Table 1. The $\delta^{18}O$ values for dam reservoirs show wide variations starting from –6.9 to +15.6‰ indicating very high enrichment. Similarly $\delta^{2}H$ show high enrichment from –42 to +86‰. Such enrichment could be expected in the reservoirs/ponds undergoing high evaporation in the dry environment.

3.3. Pechi Dam and downstream karezes

The $\delta^{18}O$ and $\delta^{2}H$ values for Pechi Dam reservoir show wide variations whereas those of the downstream karezes exhibit small fluctuations. In the $\delta^{18}O$ vs. $\delta^{2}H$ plot (Fig. 2) the data points pertaining to the dam reservoir are scattered along a line: $\delta^{2}H = 5.7 \times \delta^{18}O + 0.3$. The slope (5.7) of the trend line clearly indicates the dominance of the evaporation process [6]. All the data points relating to the karezes are clustered on the LMWL around the precipitation index indicating precipitation as the main source of recharge. Had the dam reservoir significant contribution to the groundwater recharge the data points of the downstream karezes would have plotted on the evaporation line (mixing line). Therefore, it seems that the dam reservoir does not recharge the groundwater.

The temporal variation of $\delta^{18}O$ of karezes and the dam reservoir has been given in Fig. 3. The value of $\delta^{18}O$ of karezes is almost uniform with small fluctuations. However, the reservoir water shows large variations in $\delta^{18}O$ (–6.9 to +10.8‰) with most enriched values during October 1991. The $\delta^{18}O$ values of reservoir water during August to October 1992 matches with those of the downstream karezes. It was due to the fact that the sample was taken from the reservoir after major rain events during the monsoon period when the reserevoir was full there was no significant evaporation effect. So, the $\delta^{18}O$ of the reservoir remained similar to that of karezes. After the rainy season (from November 1992 to October 1993), $\delta^{18}O$ of the reservoir got enriched up to +4.9‰ but the downstream groundwater did not reflect any significant contribution of isotopically enriched water during the whole period.

3.4. Uchki Dam and downstream wells

Ranges of $\delta^{18}O$ and $\delta^{2}H$ of the wells downstream of Vouch Ghouski Dam reservoir are –5.6 to –1.2‰ and –32.2 to –0.7‰ respectively, which are generally more enriched than the precipitation water. These data clearly indicate that the isotope indices of groundwater in the vicinity of the dam are

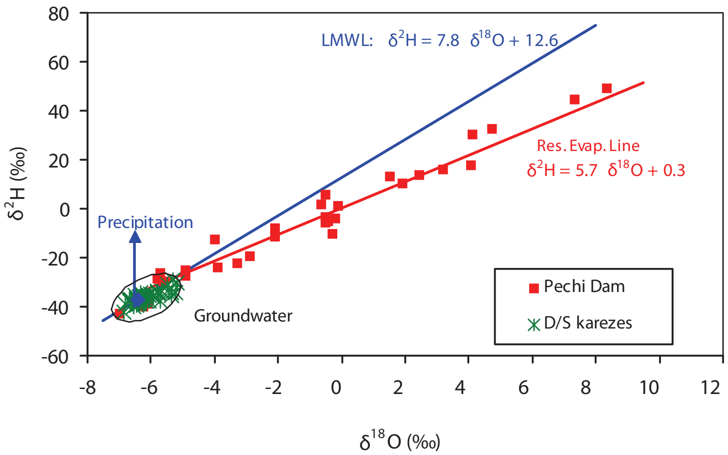

FIG. 2. $\delta^{18}O$ vs. δ^2H diagram of Pechi Reservoir and downstream karezes.

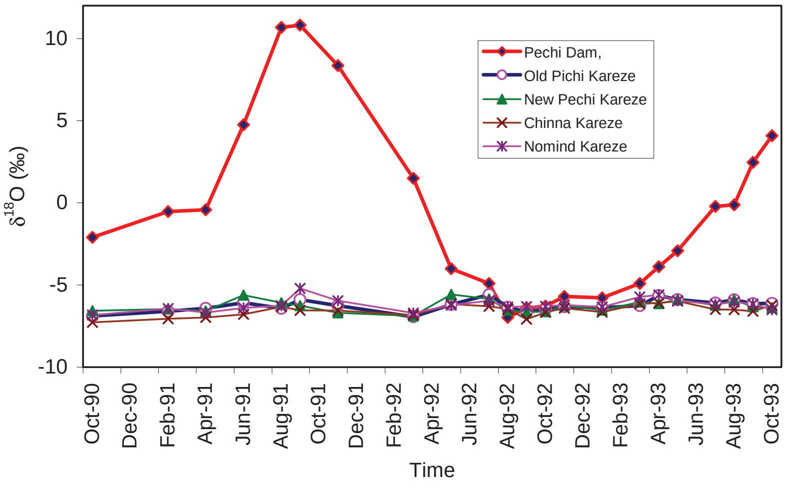

FIG. 3. Temporal variation of $\delta^{18}O$ of Pechi Dam and downstream karezes.

modified due to some contribution of highly evaporated water in the delay action dam having enriched isotopic values. In the $\delta^{18}O$ vs. δ^2H plot (Fig. 4) the data points pertaining to the dam reservoir are scattered along a line: $\delta^2H = 5.5 \times \delta^{18}O + 0.8$. The data points of the downstream wells are scattered on the same line extended up to precipitation index showing some contribution of evaporated water from the dam reservoir in the groundwater recharged by precipitation.

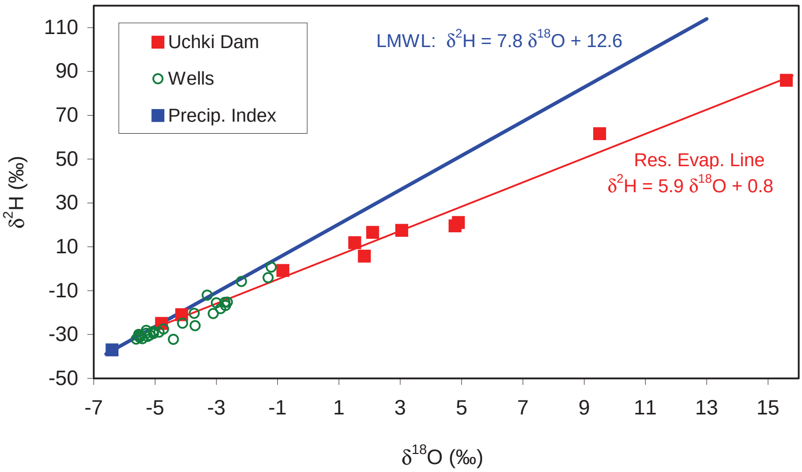

FIG. 4. $\delta^{18}O$ vs. $\delta^{2}H$ of Uchki Dam and down stream wells.

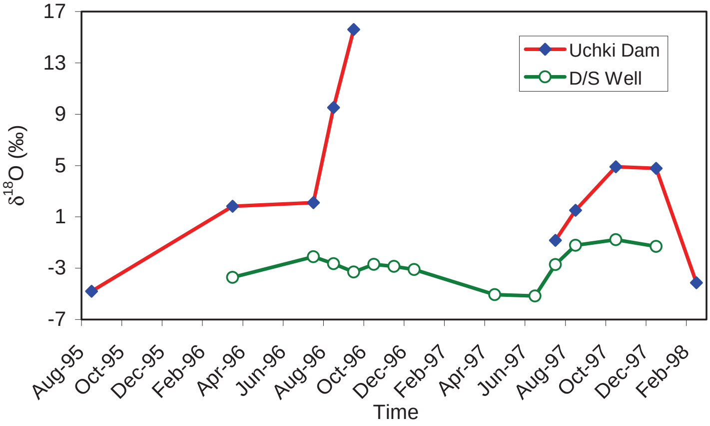

FIG. 5. Temporal variation of $\delta^{18}O$ of Uchki Dam and downstream and well.

Temporal variation of $\delta^{18}O$ in the downstream well (Fig. 5) also reflect the effect of the Dam. The reservoir after having the most enriched $\delta^{18}O$ during September 1996 (must be of very small quantity of water) remained completely dry up to July 1997. During this period $\delta^{18}O$ of the well was found decreasing because of absence of the recharge component from the reservoir. But when the reservoir had water again and its $\delta^{18}O$ was increasing due to evaporation during the period from July 1997 to February 1998, water samples of the well also reflected enriched δ^{18}O. It clearly indicates that Uchki Dam recharges the groundwater body.

3.5. Groundwater dating

Mean tritium concentration of the groundwater samples (open wells, springs and karezes) fall in the range of 7–13 TU indicating the residence time from 2 to 10 years. Considering most of the tritium values of groundwater in the range of 9 to 13 TU, mean residence time can be refined to only few years. Slightly higher value of tritium (17 TU) for Uchki and Pechi dams is due to enrichment by evaporation.

4. CONCLUSIONS

Recharge source of the groundwater is meteoric water recharged mainly by precipitation directly/ through runoff. Hydraulic connection does not seem to exist between Pechi Dam reservoir and groundwater (downstream karezes). Under the prevailing conditions, the dam has lost is effectiveness to recharge the groundwater. The reservoir water seems to be lost through evaporation. Uchki Dam has some contribution to the recharge of the groundwater. Transit time of the groundwater is very short (few years).

ACKNOWLEDGEMENTS

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GROUNDWATER SUSTAINABILITY

ISOTOPE HYDROLOGY APPLICATION IN CUBA FOR ASSESSMENT OF WATER RESOURCE MANAGEMENT IN THE MOST IMPORTANT BASIN OF HAVANA CITY

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Abstract

The paper shows the results obtained during the investigations carried out in two research and development projects; a national project (2002–2005) and an international collaboration project jointly carried out between Cuba and Argentina (2005–2006). Isotope hydrology tools are applied to the assessment the “Almendares-Vento” karstic basin, which is the main water supply system to the Cuban capital. The basin is affected by the overexploitation of its water resources and discharges of industrial and urban wastewaters. Additionally, an extensive period of drought, justify the necessity of carrying out an integral characterization of the basin for a better management. Using a monitoring network of groundwater and surface waters, a preliminary isotopic study (^{3}H, ^{18}O and ^{2}H) including rainfall analysis in the basin was accomplished. Also, a detailed geochemistry characterization, including the integral geologic study, the determination of the major anions and cations (HCO_3^-, Cl^-, SO_4^{2-} Ca^{2+}, Mg^{2+}, Na^+, K^+), and physico-chemical parameters (electrical conductivity, pH, TDS) was achieved. The isotope composition indicates their meteoric origin. Groundwater and surface water fit on an evaporation line, but not all samples follow an evaporation pattern. The isotope variations respond to processes such as selective infiltration or direct infiltration through preferential channels through the karst. The used models show good water mixing and the aquifer receives fresh recharge annually, but not in the whole extension. The aquifer is overexploited in the main water extraction point of the basin. The vulnerable zones associated to the contamination by saline water intrusion and the human activities in the urban areas are observed in the basin west side. Also were clarified some geologic and hydrogeology uncertainties of the basin. The utility of the isotope hydrology to assess the water resources management was established.

1. INTRODUCTION

The Almendares–Vento Basin is one of the most important in Cuba, because it is the main water supply for the Cuban capital (La Havana). The water resources of this basin are affected by overexploitation, depletion of the supply sources and risk of contamination by anthropogenic action. Additionally, an extensive period of drought made it necessary to carry out an integral basin characterization for a better water resources management.

The paper summarizes two research stages, a first period from 2003–2005, developed in the framework of the Cuban Nuclear Project and a second period 2005–2006, supported by an International Collaboration Project between Cuba (CPHR) and Argentina (INGEIS). In the first project, the ^3H concentrations were used as natural tracer and also the physical-chemical characterization of the waters was obtained. In the second study, using stable isotopes (^{18}O and ^2H) and physical-chemical analysis, were used to supplement the previous results and the uncertainties were clarified.

2. HYDROLOGY AND HYDROGEOLOGY OF THE ALMENDARES-VENTO BASIN

The Almendares–Vento Basin has great importance for the Cuban capital in terms of economic, social, health, cultural, recreational and urban aspects. The “Ejército Rebelde” Dam, located on the basin, is an efficient recharge system (Fig. 1). The studied basin extends over an area of about 40 202 km^2 and is occupied by more than half a million inhabitants.

The basin is classified as a closed basin and is extended in the longitudinal direction. This basin constitutes the surface drainage of the Almendares river. Great part of the runoff infiltrates in the karstic plain, in which the basin is formed. The exploitable resources of the basin are estimated in 287 million m^3/a. This basin provides about 47% of the total water volume used in the capital.

3. MATERIALS AND METHODS

Fig. 1 shows a 3 D model of the basin including the sampling points and the Almendares river.

Water sampling was carried out using an optimized monitoring network [1]. The first sampling was carried out monthly during one year (2003–2004) at 11 points (9 wells, 1 dam and 1 point at a water pumping site). The major components, the physical-chemical parameters and the ^{3}H concentrations were determined in all waters and in precipitation. The second sampling was carried out in December 2005, in 14 points (2 points in the river and 1 point in another dam were added). In this sampling, the stable isotope contents (^{2}H and ^{18}O) in surface water, groundwater and precipitation from November, 2005 were included. Also the surface and groundwater physical-chemical parameters were determined. In order to fulfil the sample collection and level measurement, a bathometer and electric level meter were used. The samples were always taken

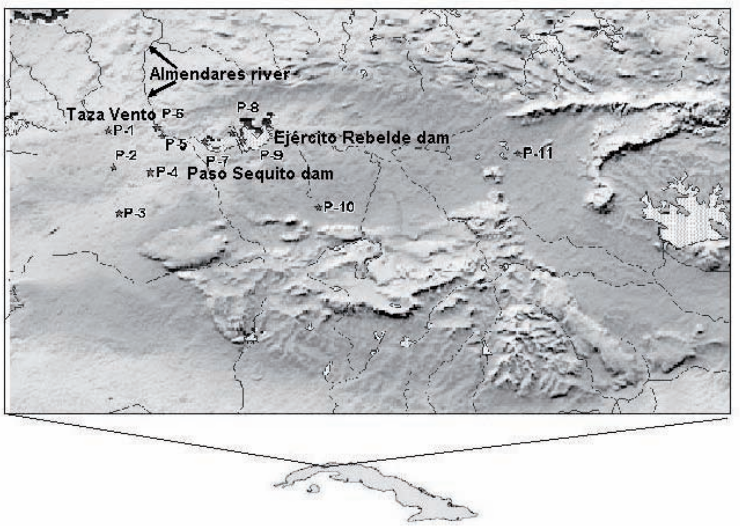

FIG. 1. 3 D model of the "Almendares Vento" basin, sampling points and "Almendares" river.

1.5 m below the water level. For the classification and evaluation of possible waters mixtures in the Basin, Stiff and Pipper graphics were used, obtained by the AQUACHEM V-4 software [2]. Isotope analyses (^{2}H and ^{18}O) were carried out at the INGEIS Laboratories (Argentina). Samples were treated following established techniques [3, 4] and measured with a mass spectrometer of triple collector, multiple introduction system, Finnigan MAT Delta S. The results are expressed as δ like $\delta = 1000\ (R_s/R_P - 1)$‰, where: isotope deviation in ‰; S: sample; P: international reference; R: isotope ratio (^{2}H/^{1}H, ^{18}O/^{16}O). The reference is Vienna Standard Mean Ocean Water (V-SMOW) [5]. The uncertainties are ±0, 2‰ for ^{18}O and ±1,0‰ for ^{2}H.

The tritium analyses were carried out at the Environmental Radiological Surveillance Laboratory (LVRA) at the CPHR (Cuba). Tritium was concentrated by electrolytic enrichment and later was measured by liquid scintillation. The ^{3}H concentrations are expressed as tritium units (1 TU = 1 atom ^{3}H/10^{18} atoms ^{1}H). The ^{3}H uncertainties were calculated using the Krantgen method [6]. The uncertainty range was 0.14–1.02 for a range of ^{3}H concentrations (0–2.79) TU [7]. In order to evaluate the system input function was used the "The Quebrada" Meteorological Station (CPHR) and Global Network Isotopes in Precipitation (GNIP) [8].

Chemical analyses for the 2003–2004 campaign were carried out by the Center of Hydrology and Waters Quality (CENHICA) in Cuba and were determined major components, electric conductivity (CE) and pH. For the second sampling campaign chemical analyses were carried out at INGEIS Laboratories (Argentina).

As a base for the tracer modelling and the hydrodynamic interpretation of the results, the following conceptual model was adopted: The basin is a system of karstic regional flow, with diffuse and free flow, which has vertical stratification. The flow field is homogeneous anisotrope at regional scale and the regional transport is governed by the Darcy Law. The flow field is totally surrounded by impermeable borders. Therefore, recharge occurs inside the limits of the system, through the unsaturated zone. The total discharge of the basin takes place at point 6 (Taza de Vento). Transport occurs by total mixing with two peaks, one of them at the end of the dry period (draining older waters) and another in the rainy period (draining youngest waters).

The tritium measurement in precipitation of the "La Quebrada" Station was used as input data. The model is deterministic and it is based on the application of the expression: $a_0 = a_t / \exp(-0.056t)$, where ($a_0$) is the ^{3}H monthly registered in the reference station and (a_t) is the concentration measured in each groundwater sampling station. The model is exponential by nature and the theoretical decay curves for every month of observation were extrapolated until the date of groundwater measurement.

4. RESULTS AND DISCUSSION

4.1. Geochemistry characterization

The behaviour of Ca^{2+} concentration values was similar to the CE and HCO_3^- pattern.The observed behaviour, corresponds with the flow direction of the groundwater in the basin which is East to West, so low values of CE for the sampling point 11 and high values in the point 1 are appreciated. The values in the sampling point 1 could be associated to the high mineralization in this zone. Due to the proximity of the shoreline to the sampling points 1, 2 and 3 and the effect of tillage variations, a temporal saline water intrusion could take place. Relatively high values of pH were observed in point 9 (Ejército Rebelde dam). These values should be related to water pollution. According to the international Drinking Water Standards [9] (the Cuban standards have not regulated these parameters), the total dissolved solid (TDS) values were above of the permissible limits (500 mg/L) at sampling points 1 and 2. These results show the probable water contamination due to uncontrolled exploitation or the pollutants incorporated to the wells through pumping.

As shown in the Stiff (left) and Piper (right) diagrams, the majority of waters are calcium bicarbonate type (Figs 2 and 3). Nevertheless, it was observed some deviations in anions and cations patterns at the sampling points (points 7, 8, 9 and 11). Fig. 3 summarizes groundwater, surface water and rainfall results for the December 2005 sampling period. Sample point 11 shows higher chloride and magnesium content. Rainfall shows higher contents of chloride and sodium. The results obtained in the second sampling campaign, corroborated the conclusions obtained in the first period of sampling.

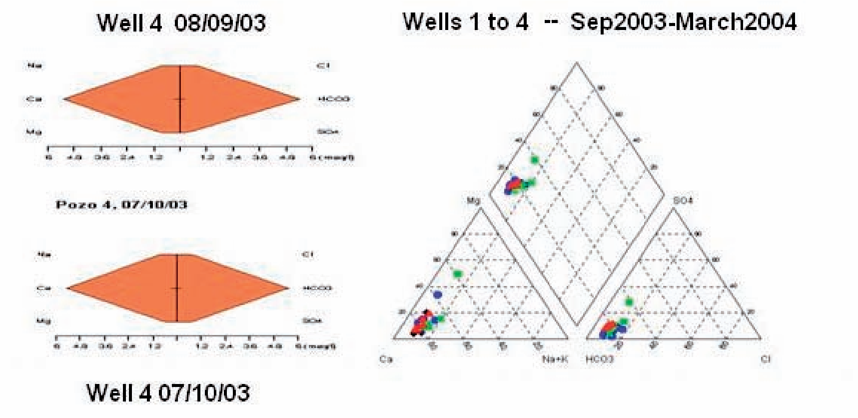

FIG. 2. *Stiff and Piper graphics. Sampling campaign 2003–2004.*

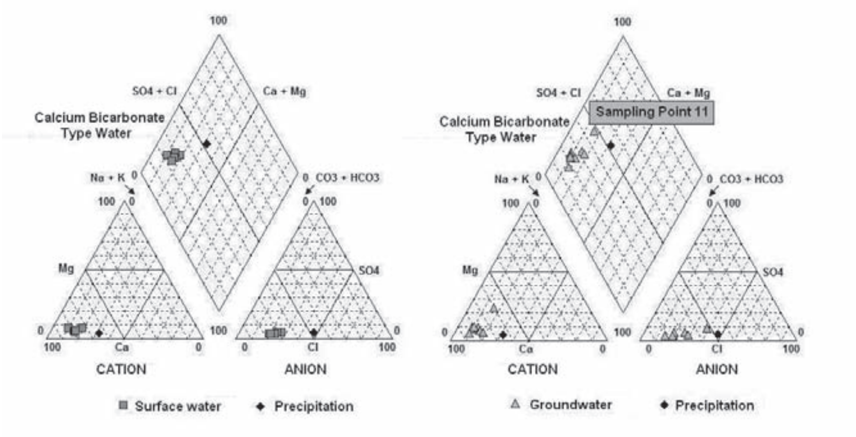

FIG. 3. Piper diagrams. Sampling campaign of December 2005.

4.2. Estimation of the residence times according to the known input mode

The ^{3}H measured values in the surface water, groundwater and rainfall, ranged between (0 and 1, 5) TU and (0 and 3) TU respectively [10].

According to the result obtained using this model, the major recharge events occurred in the rainy period (May to October). The system receives fresh water annually but not in all sampling points and this behaviour means that the renovation of groundwater not always takes place in the year. These results are in good agreement with other geostatistical studies [11].

A few recharge events at the sampling point 6 (Taza de Vento) were identified. Probably this behaviour is related to the distance of the recharge zones to this sampling point 6. The model behaviour in the sampling point 9 shows the presence of groundwater or, at least, water mixing with minor contribution of surface water. The losses of groundwater by evaporation take place at sampling point 9 during several months. These results disagree with the accepted role for the “Ejército Rebelde” dam as source of fresh water recharge to the basin.

Other zones with less active recharge are related to the sampling points 1, 2 and 3 and the more active recharge are associated to sampling points 7, 10 and 11. The last three mentioned points should be protected because they are effective water recharge source for the aquifer and for this reason, this zone is vulnerable to contamination.

4.3. Stable isotopes

The stable isotope data from groundwater and surface water samples were plotted on conventional diagrams δ ^{2}H *vs.* δ^{18}O with the global meteoric water line (δ^{2}H = 8 × δ^{18}O + 10‰) [12], the weighted average rains for 1990 and 2002, the individual rains of the same years and November, 2005 precipitation (Fig. 4). The water isotopic composition shows its meteoric origin [13]. Groundwater and surface water fit on an evaporation line, i.e. δ^{2}H = 4,6 × δ^{18}O – 6.2‰. However, not all samples fulfil the evaporation pattern probably due to several processes such as: selective infiltration, evaporation prior to infiltration, direct infiltration through preferential channels in the karst and mixing mechanisms.

The residence time of the rainfall in the soil depends on the permeability of surface materials and the evaporation processes are more effective when the soil permeability is low. In this region, they are two dams (“Ejercito Rebelde” (point 9) and “Paso Sequito” (point 13)) with the main objective of recharging the aquifer. These open surfaces undergo evaporation so water infiltrated is more enriched [14].

Sample 11 has a dissimilar isotope composition, suggesting different process as selective infiltration or possibly recharge in another zone. A longer record of isotope composition (^{2}H and ^{18}O) of precipitation and periodic sampling of groundwater will improve the hypotheses about the recharge mechanisms and the groundwater residence time.

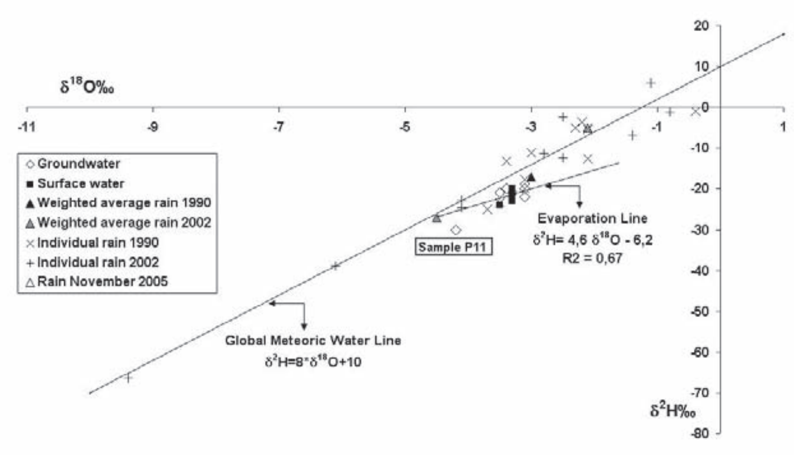

FIG. 4 δ^{2}H vs. δ^{18}O, Global meteoric water line, individuals rains from 1990 and 2002, weighted average rain 1990 and 2002, rain November 2005 and analysed samples.

5. Conclusions

According to the geochemical characterization, groundwater of the “Almendares Vento” Basin classifies as calcium bicarbonate type and a temporal saline water intrusion was found in the west zone of the basin.

(1) The accepted role for the “Ejército Rebelde” Dam as source of fresh water recharge to the basin was rejected, taking into account the presence of groundwater in this sampling point.
(2) Water mixtures were observed only in the sampling points near to surface water (“Almendares” river and “Ejército Rebelde” Dam), showing a possible confined geology for the Almendares-Vento Basin.
(3) The applied model showed that recharge and renovation of the groundwater not always take place in the year.
(4) The less active recharge zones were related to the sampling points 1, 2, 3, and 6 (Taza Vento), these zones have been identified as vulnerable. For the sampling station 6, it was confirmed the presence of aquifer overexploitation.
(5) The active recharge zones of the aquifer were associated to the sampling points 7, 10 and 11 which are vulnerable zones to pollution and they should be protected.
(6) The effectiveness of the isotope hydrology for the assessment of water resources management was confirmed.

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ISOTOPE COMPOSITIONS OF MEKONG RIVER FLOW WATER IN THE SOUTH OF VIETNAM

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Abstract

As a part of the Research Contract No. VIE/12569, isotope composition of Mekong river flow water in the South of Vietnam has been monitored to provide information on water origin and residence times, surface-groundwater exchange in the monitoring area. According to the primary results obtained, a seasonal variation as well as the dependence on local precipitation and on the river water level of isotopic composition of two distributaries of Mekong river water have been observed. At the same time a slight seasonal change of tritium in river water and the difference between tritium content in local rainy water and river water have been recorded.

1. INTRODUCTION

Mekong is a long river in Asia. Originating from high mountains area in the north-west of China, Mekong river flows over Myanmar, Thailand, Laos, Cambodia and divides into two distributaries before flowing into the South of Vietnam. In Vietnam the two distributaries are named Hau river with a flow rate of 20% and Tien river, with average flow rate of about 80%. The length of each distributary in Vietnam is about 450 km and both flow into the East Sea through nine estuaries.

Extending from 35° to 9° north latitude with a basin area of about 810 000 km^2, Mekong river drains water from different climatic areas. Therefore the isotope compositions of river water could reflect the cumulative influence of hydrological processes from precipitation to discharge, including the influence of snow, melting glaciers, dams, lakes, karst terrain, altitude, arid zone evaporation, snow melt events and tributaries and can provide information on water origin and residence times, surface-groundwater exchange, precipitation variability, and climate/land use changes because its importance in river systems of the world.

Previous studies on the origin and groundwater dynamic in Nambo plain (South of Vietnam) applying isotope techniques show that there is a quite difference between the isotope composition of Mekong river water and those of local precipitation, groundwater and surface water in the area. The seasonal variation in stable isotope compositions of Mekong river water was observed especially in its small tributaries. These differences are a good index for hydrogeological studies in the area, such as the origin of groundwater, interaction between surface water and groundwater, recharge mechanism as well as the changes in water quality. For these purposes, a project to monitor the isotopic composition of Mekong river water was set up in 2003. This paper presents the primary results obtained from Sep. 2003 to Sep. 2005.

2. RIVER WATER SAMPLING AND ANALYSIS

The part of the basin in the South of Vietnam accounts for 8% of the total river basin and the average water flow is about 11% of the total Mekong flow-rate. Each distributary, from the Cambodia–Vietnamese border to the East Sea, has a length of about 450 km. All these distributaries are regulated by Tonlesap lake in Cambodia (source: vnmc.gov.vn). Based on the topographic and hydrogeological characteristics of the monitoring area, a network of 5 sampling points: MK01, MK03 and MK04 along Tien river; MK09 and MK11 on Hau rivers was set up for observing the isotope compositions of river flow water (Fig. 1).

Sampling campaigns were carried out for collecting river water samples

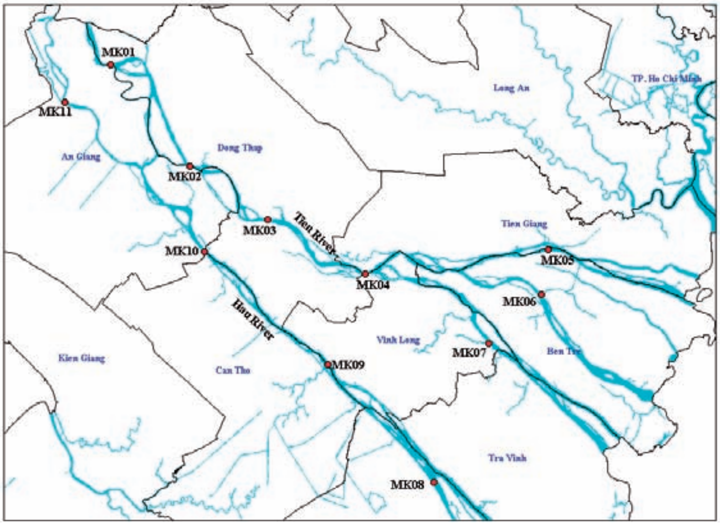

FIG.1. Sampling sites for river water.

from Sep. 2003 to Sep. 2005. For rivers, water is sampled in midstream at the depth of 3 meters under surface water by a submerged pump. River water was sampled monthly for stable isotopes analysis and for tritium analysis every 2 months. Local rainy water was sampled at a meteoric station locating in the center of the monitoring area.

All water samples were analyzed for stable isotopic compositions (^{18}O and ^{2}H) and for tritium. Stable isotopes is analyzed at the Institute of Nuclear Sciences and Technology in Hanoi, while tritium analyses are performed at the Center for Nuclear Techniques in Ho chi minh City.

3. ASSESSING THE PRIMARY RESULTS OBTAINED

Isotopic composition of river water collected, from Sep. 2003 to Sep. 2005, along Tien and Hau rivers is shown in Fig. 2. Water samples cluster in two groups. One group more enriched in heavy isotopes, includes river water samples collected in dry season and the other more depleted in heavy isotopes, involve water samples taken in rainy season. A clear seasonal variation could be defined.

The variation of ^{18}O and ^{2}H over time of all river water samples is demonstrated in the Fig. 3 and Fig. 4 below.

In general heavy isotopes in river water are enriched in the dry season (Nov. to Apr.), especially in January and become depleted during the rainy season. It seems that ^{2}H and ^{18}O isotopes are more enrich along the river course.

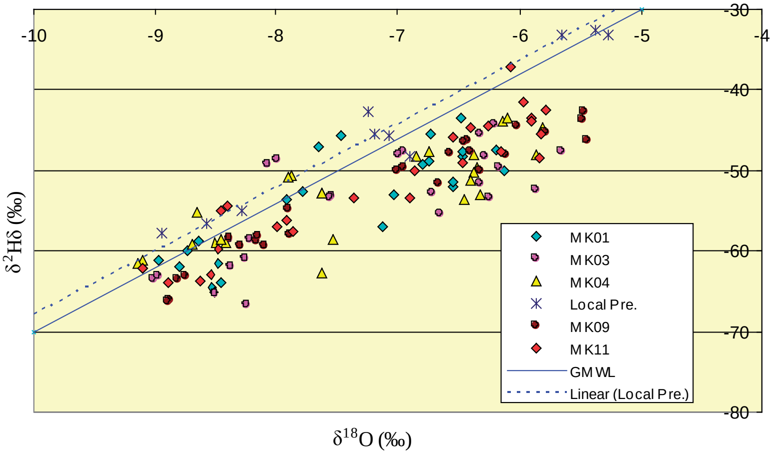

FIG.2. Relationship between ^{2}H and ^{18}O of rivers waters.

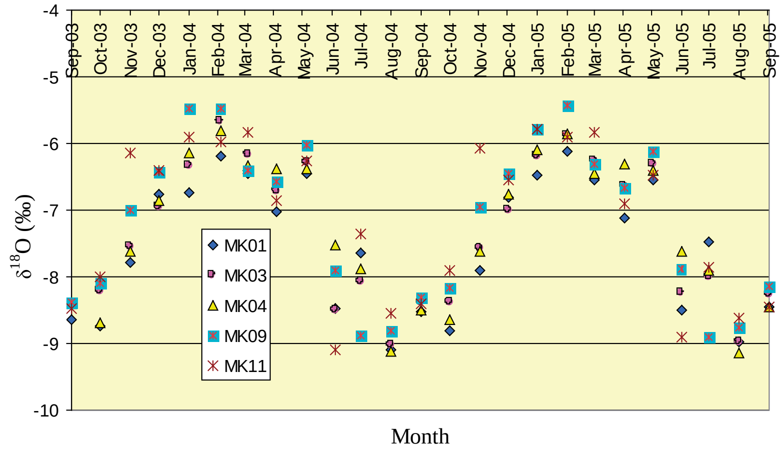

FIG. 3. Variation of ^{18}O on time of river water.

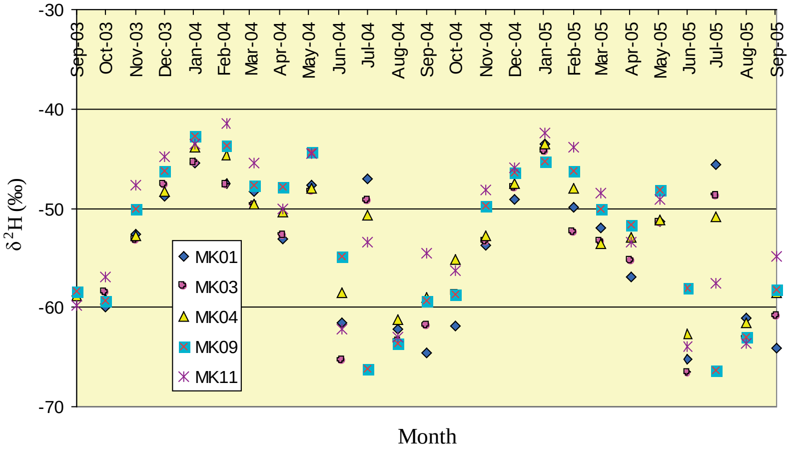

FIG. 4. Variation of ^{2}H on time of river water.

It could be caused by the evaporation effect due to the high temperature in the monitoring area.

For both rivers, stable heavy isotopes are enriched in July while they have to be depleted. It could be explained by the fact that precipitation observed in July in the monitoring area, is usually lower than other months during the rainy season.

Fig. 5 shows the dependence of ^{18}O concentration on local precipitation. The enrichment of ^{18}O (as well as of ^{2}H) in July shows the importance of local

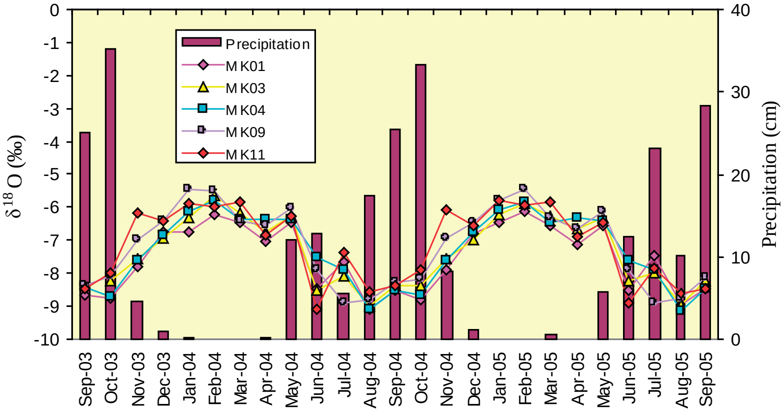

FIG. 5. Variation of ^{18}O on local precipitation and on time, Tien and Hau river.

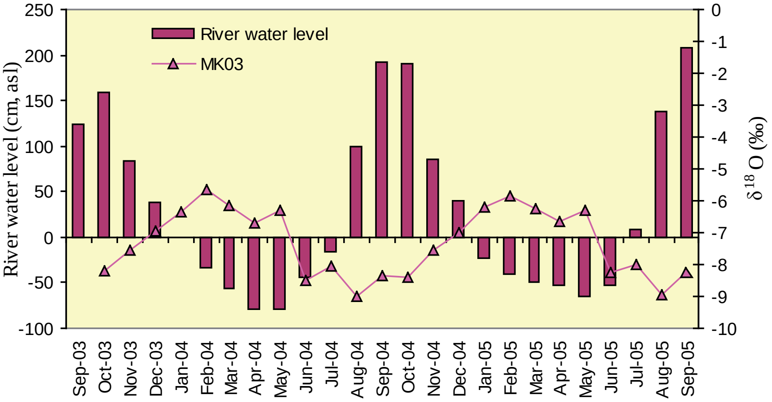

FIG. 6. Variation of ^{18}O on river water level and on time, Tien river.

precipitation in Tien river water. The enrichment in heavy isotopes of river water samples collected in July is observed in Hau river too, but it is not so much as in Tien river. It could be caused by the difference in flow rate of two rivers as described in Figs 6, 7 and 8.

For Tien river, ^{18}O (and ^{2}H) in water is enriched during the dry season but ^{18}O reaches maximum value in February, while deuterium gets maximum value in January.

At MK11 station, upstream of the Hau river (Fig. 8) and at MK09 downstream (Fig. 7) the variation of ^{18}O (and ^{2}H) seems to be the same. But

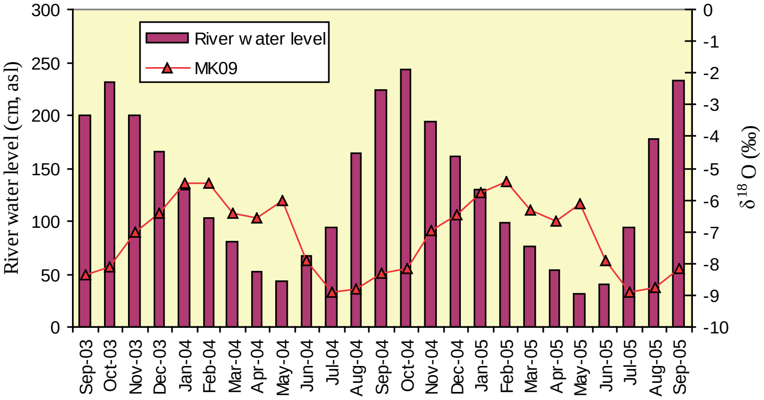

Fig.7. Variation of ^{18}*O on river water level and on time, Hau river*

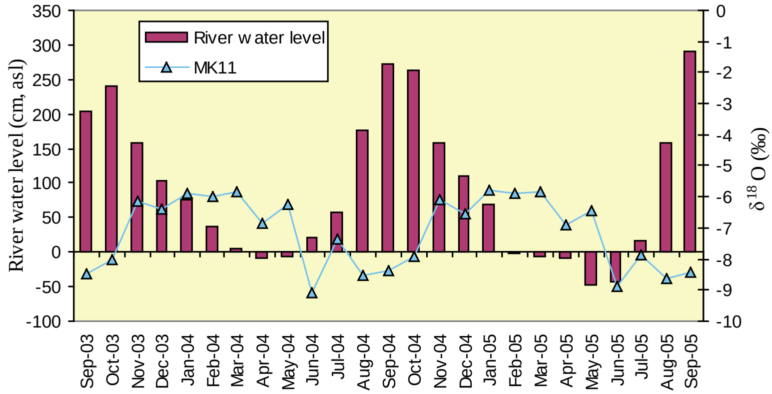

Fig.8. Variation of deuterium on river water level and on time, Hau river

at MK11 station, stable isotopes reach maximum in February while at MK09, river water is most enriched in February. This fact could be used for evaluation the discharge of groundwater to river.

For Hau river, there is a significant difference in the isotope composition between dry and rainy season for both ^{2}H and ^{18}O. In the rainy season, especially after August, heavy isotopes in river water are strongly depleted with respect to high precipitation. This means that Hau river receives a significant fraction of water from local rain.

Evaporation effect can be found in waters from both Tien and Hau rivers. It is supported by the fact that the isotopic composition of river water becomes

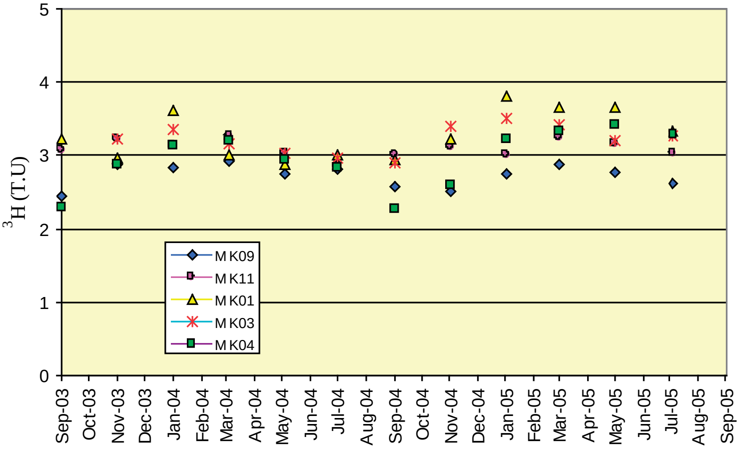

Fig.9. Tritium content in water of Tien river

more enriched during the dry season (see Fig. 2) but water of Hau river is not influenced so much by this effect as water from Tien river. This could be explained by the higher flow rate of Hau river when compared to that of the Tien river, as presented above.

The tritium content observed in river water over time shows a seasonal change (Fig. 9); higher in the dry season when water coming from high latitude area with high tritium dominates in rivers at monitoring site. At the same time tritium content of river water is always higher than that of local rain water (less than 2 TU). The changing of tritium on season needs to be monitored for longer time.

4. CONCLUSION

In general, for both two distributaries (Tien and Hau) of Mekong river, the stable isotope data show that the heavy isotopes are more enriched during the dry season months (from November to April) and become depleted during the rainy season. A small divergent in May was observed because of seasonal changing while enrichment in heavy isotopes was recorded in July (rainy season) when the local precipitation strongly diminishes.

The dependence on river water level and season of the heavy isotope content shows the influence of the evaporation effect over monitoring area.

The variation of isotopic composition on the local precipitation shows the importance of local precipitation in river waters.

Tritium content of river water shows a seasonal change. This needs to be monitored for a longer time. At the same time, tritium content in river water is always higher than those in local precipitation. For this the regional circulation regime of air moisture could be the cause as shown in Ref. [4] by P.K. Aggawal et al. in 2004.

It is necessary to monitor continuously the isotopic composition in river water, groundwater and local precipitation in the part of Mekong basin in Vietnam area. The obtained data is useful not only for hydrological processes in Vietnam but also in other Asian rivers.

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GEOCHEMISTRY AND ISOTOPE EVOLUTION OF GROUNDWATER AND RECHARGE MECHANISMS AT A URANIUM PRODUCTION CENTRE IN THE SEMI-ARID REGION OF CAETITÉ-BA, BRAZIL: IMPLICATIONS FOR GROUNDWATER MANAGEMENT

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Abstract

The semi-arid region of the northeast of Brazil is characterized by a lack of superficial waters due to low precipitation and high evaporation rates. Due to these adverse climatic conditions, intense pressure is being put on the use of groundwater resources. However, there is still insufficient knowledge about the aquifer system which is causing an overexploitation of the water resources. Groundwater is pumped from a fractured, crystalline aquifer of low productivity, where wells show generally yield rates lower than 3 $m^3 \cdot h^{-1}$. The study was carried out in a semi-arid area located in the centre-south region of Bahia State at an elevation of 900 m a.s.l., where were discovered several radioactive anomalies by aerogeophysical surveys performed during the 1970s, that give origin to the uranium province named Lagoa Real. The research approach included isotopic and geochemical analysis of groundwater sampled from 25 wells placed in crystalline rock areas (granite or gneiss) covered by thin layers of residual soil or alluvial sediments. Groundwater is Na–HCO_3 type water and relative high concentrations of Cl and SO_4^- are observed in some groundwater. The stable isotope data (δ^2H and $\delta^{18}O$)

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showed that evaporation plays a role in the salinization of groundwater. The radiocarbon ages, corrected by carbonate dissolution (through $\delta^{13}C$ and DIC), showed very young waters that were recently recharged, perhaps during the last few decades These data discard the possibility that groundwater salinization was caused by discharge of deeper saline groundwater through faults associated to a regional groundwater flow system. The presence of an active shallow groundwater flow system offers better possibility for substainable use of the groundwater resources in this semi-arid region of Brazil.

1. INTRODUCTION

Groundwater quality depends on many factors including water-rock interaction and groundwater residence time in the aquifer. Thus, its quality can change not only as consequence of human actions, but also due to geochemical evolution caused by weathering along the groundwater flow path, which is constrained by the groundwater residence time. Groundwater salinization can be link to recharge mechanisms and the groundwater flow system (local vs regional). Discharge of old, more saline groundwater through deep faults could cause salinization of shallow groundwater. However, evaporation of groundwater or transpiration during infiltration in recharge zones could also cause salinization that it is not related to residence time.

The study area is the newest Brazilian uranium mining and milling facility located in the semi-arid region of northern Brazil. The crystalline rocks aquifer is the main water resource available for the uranium plant and also for rural properties near the plant. Consequently, impacts into the groundwater may be of primary concern, since aquifers are the only source of water for the local communities. Data from a monitoring program carried out by the mining operator revealed that increase in uranium concentration in groundwater at the area influence by the open pit is already being observed. Besides the influence of mining activities in groundwater, there are other problems related to their relative high salinity. The aquifer, which is composed of fracture crystalline rocks, is of low productivity where wells show generally yield rates lower than $3\ m^3 \cdot h^{-1}$. In recharge areas where vegetation cover is scarce like the Caatinga and infiltration is mainly controlled by evaporation process, soil salinization and low recharge rates often could produce hyper saline waters. Salinization is a recurring process in the study are due to the condition of climate and local hydrogeology, which makes groundwater not adequate for human consumption in the majority of the monitored wells. Hydrogeochemical characterization combined with use of environmental isotopes provides useful information to understand and model the groundwater flow system and its geochemical evolution and eventually understand the origin of salinization.

2. METHODS

Groundwater samples were collected from 25 wells for isotopic and geochemical analysis. The wells are placed in crystalline rocks (granite or gneiss) covered by thin layers of residual soil or alluvial sediments. The stable isotope analyses, δ^2H, $\delta^{18}O$ (‰ VSMOW) and $\delta^{13}C$ (‰ VPDB), were performed by mass spectrometry and the radiocarbon (^{14}C) analyses reported as percentage modern carbon (pMC) were performed by AMS. Major anions and trace metals in groundwater were also measured by inductively coupled plasma–mass spectrometry (ICP–MS). The samples, after acidulation and filtration, were dissolved with 65% nitric acid (Merck Suprapur). After 72 h of digestion, the samples were then diluted (1:20) with ultrapure water with a specific resistivity of 18 MΩ cm obtained by filtering double-distilled water through a Milli-Q (Millipore). Indium and thallium were added as internal standards to all samples, blank samples and standard solutions, in such way as to produce a final solution containing 20 $ng \cdot mL^{-1}$ of each one. The analyses were performed by inductively coupled plasma–mass spectrometry (ICP–MS) on a Perkin–Elmer SCIEX ELAN 6000 instrument equipped with the standard spray chamber and cross-flow nebulizer, applying the quantitative method and using 1, 5, 10, 15 and 20 $ng \cdot mL^{-1}$ solutions of the Perkin–Elmer standard solutions.

3. RESULTS AND DISCUSSION

3.1. Groundwater salinization and geochemical evolution

The study area was divided in cross-sections based on the groundwater flow system determined by available hydrogeological data (Fig. 1). The hydrogeochemical characterization shows the predominance of HCO_3^- and Na^+ íons, which is common in fractured aquifers in geological settings formed by metamorphic rocks with granite or gnaissic composition [2, 3]. The geochemical evolution of these waters is clearly marked with Ca^+ being replaced early by Na^+ along the groundwater flow path (Fig. 2). The source of the Na is albite, which is the dominant plagioclase in the rocks. Cl^- and SO_4^{2-} are also present in relative high concentrations in some groundwaters. These anions came mostly from atmospheric sources in minor concentrations; their relative high concentration could be associated with evaporation in the recharge areas (recharge mechanisms) and/or discharge of older, more saline, deep groundwaters. It seems that shallow groundwater (shallow fractures zones) is more saline than groundwater coming from deeper fracture zones (Fig.

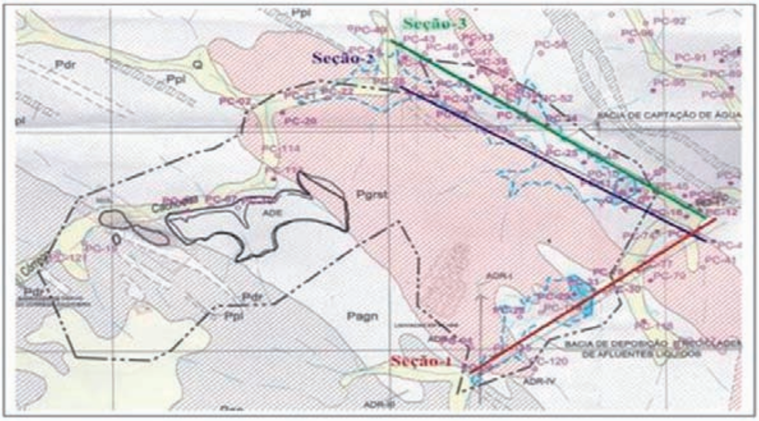

FIG. 1. Hydrogeological cross-sections of the study area with the following geological units: Pgrst — granite with leucodiorite pegmatic; Pagn — amphibole-quartz plagioclase/ microcline.

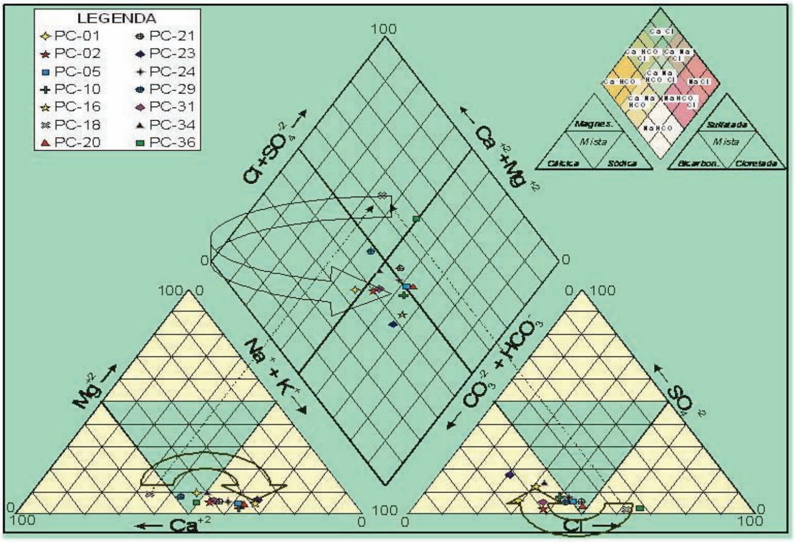

FIG. 2. Piper diagram showing the changes of hydrogeochemical composition along the flow path.

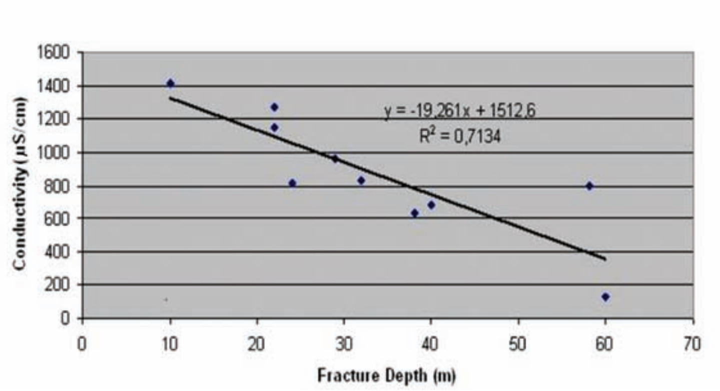

FIG. 3. Relationship between fracture depth and salinity (conductivity) of groundwater samples.

3) implying that residence time is not the main factor causing groundwater salinization and it should be associated to processes such as evaporation in the recharge areas. It is important to highlight that shallow wells are located near alluvial sediments present in the dry river bed. It is posible that salinization occurred due to the accumulation of salts in these sediments during the dry periods. The rivers only flow during intense rains. Then, the accumulated salts are transported into the aquifer during subsequent recharge events. In case of the deeper wells, it possible that recharge is a fast process through faults. The water is then not affected by evaporation. The stable isotopes and ^{14}C data provide more information for testing the proposed model for groundwater salinization.

3.2. Isotopic evolution of groundwater

The $\delta^{18}O$ vs $\delta^{2}H$ relationship allows us to understand how the isotopic signal from the precipitation is transferred to groundwater and to evaluate the role of evaporation during recharge events.. Groundwater can be lost by evaporation or transpiration from runoff or during infiltration in the unsaturated zone. Both evaporation and transpiration are possible causes for groundwater salinization, but only the first process causes a shift in the isotope composition of water [4].

During summer storms, convective rains can suffer strong evaporation during flow over the hot landscape. The slope of these evaporative enrichments for semi-arid regions is usually between 3 and 5, defining a local evaporation line [5] that is different than the Local Meteoric Water Line (LMWL). For

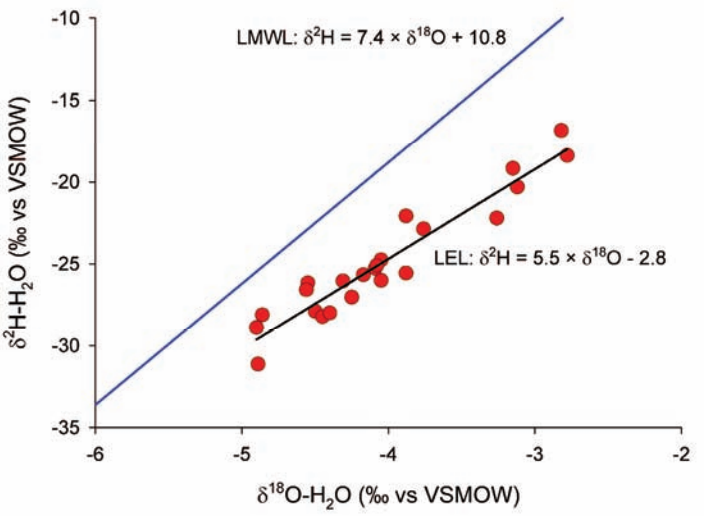

FIG. 4. Stable isotope data.

this study, due to the lack of on-site data, the isotope precipitation data [6] from Salvador (Fig. 4), located 800 km away from the study area, was used to construct the meteoric water line. However, it is possible that precipitation in Caetité has a lower slope than El Salvador (s = 7.4) and a greater deuterium excess due to evaporation affecting the rains. The groundwater data showed clearly an evaporative enrichment pattern with slope equal to 5.5, defining a local evaporation line (Fig. 4). The average evaporative loss was calculated to be around 22%. These data showed that evaporation is playing a role in the salinization of groundwater.

3.3. Groundwater dating and aquifer recharge

Two sources of dissolved inorganic carbon (DIC) dominate in recharge environments: the ^{14}C-active component from soil CO_2, used for groundwater dating and a ^{14}C-free carbonate which dilutes the first source. This dilution is characteristic of sandy and carbonate aquifers as well as aquifers in crystalline rocks where fracture calcite could be present. There are several methods described in the literature to apply corrections for carbonate dissolution [7]. In this work, we used the ^{13}C correction method that allows for incorporation of ^{14}C-active during carbonate dissolution under open system conditions, and following ^{14}C dilution under closed conditions [8]. The only correction was

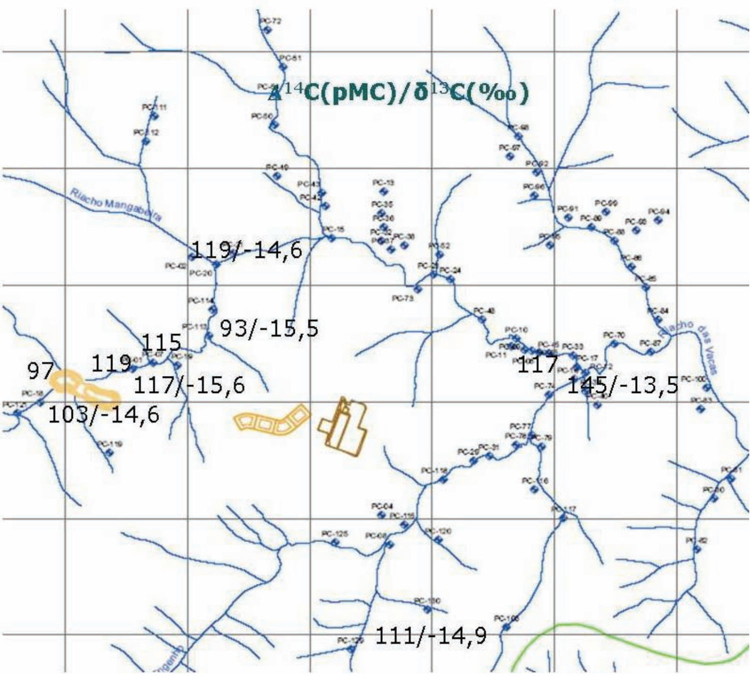

FIG. 5. Map of percentage modern carbon (pMC) and δ^{13}C (‰ VPDB) distribution in the uranium plant along the hydrological flow path.

carried out for samples with ^{14}C values less than 80 pMC. Any correction apply to dates over 85 pMC will produce values over 100 pMC.

Fig. 5 shows the distribution of radiocarbon dates and δ^{13}C (‰) data from wells located up-gradient and down-gradient from the mine. The ^{13}C data showed a range of values between –13.5 and –15.6 ‰ implying that some carbonate dissolution is taking place in the aquifer. δ^{13}C values in the range of –22 to –18‰ is expected for soil CO_2 in this semi-arid region. Most groundwaters showed ^{14}C values over 90 pMC implying they are of recent origin, reflecting a relatively fast infiltration through soils and alluvium that are part of the recharge areas. The wells located at the end of flow path are those presenting highest content of modern carbon, probably due to their location in an alluvium recharge zone [9]. Besides, there are only two wells with percent modern carbon lower than 100%, which are located in sites with more developed soils, increasing the length of infiltration into vadose zone, rendering then ages slightly older (several decades). The ^{14}C data discard the possibility that groundwater salinization could be due to groundwater discharge of old, more saline groundwater through a deep fault system. Thus, groundwater seems to be part of an active groundwater flow system and an evaluation of recharge rates is required to better manage the present and future demand for groundwater resource, by the mining and rural population.

4. CONCLUSIONS

The environmental isotope data showed that the salinization of groundwater is not due to groundwater discharge associated to a regional groundwater flow system. It seems that salinization is due to evaporation taking place during the infiltration in the vadose zone, mainly controlled by the soil permeability. Due to the climatic conditions of the study area, rivers only flow during periods of intense short rains, which are intercalated with dry periods. After rain events, water is affected by evaporation in the fine alluvial sediments that are part of the river bed. This caused an increase in salinity in the pore water that eventually will reach the aquifer during later rain events. In terms of quantity, it is necessary to evaluate the actual recharge rates. However the fact that the groundwater flow system is more active than previously expected for this semi-arid fractured aquifer, it seems that groundwater supply should pose no risk of resource mining to accommodate the actual groundwater demand. However, there are several limitations to groundwater use due to its poor quality, in most cases related to high level of hardness, caused by the salinization process. Therefore, some sort of water treatment is needed for human consumption, e.g. water desalination by reverse osmosis. However, this type of technology is expensive and not substainable in the rural communities. The lack of water resources, amongst other reasons, contributes to the fact that areas with the lowest human development pattern are located in the semi-arid region of Brazil. Therefore, the technological challenge for the Brazilian semi arid areas is the development and implementation of environmental management strategies arising from consistent investigation works that include the relevant social-economical aspects.

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CONTRIBUTION OF ISOTOPIC INDICATORS TO GROUNDWATER ASSESSMENT AND MANAGEMENT IN GROMBALIA PLAIN (NORTHEASTERN TUNISIA)

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Abstract

Grombalia Plain, situated in the Northeast of Tunisia, contains a very important multilayered aquifer. However, the exploitation rate of shallow groundwater resources reaches 170% in order to answer the increasing needs for socio-economic development and specially the agricultural sector. Irregular climate conditions combined with increasing human constraints have lead, as main consequences, to the lowering of the water level and to the salinisation of groundwater along the coast, enhancing the risk of marine intrusion. Multidisciplinary studies have been conducted on this aquifer for the assessment of groundwater resources. Hydrochemical results indicate that shallow and deep groundwaters show similar type of water facies, highlighting vertical hydraulic communication between these different levels. Isotopic tracers (^{18}O, ^{2}H, ^{3}H, ^{14}C) confirm the existence of groundwater mixing between different depths and levels. On the other hand, shallow groundwater presents high ^{14}C activity, indicating a direct infiltration of rainfall.

1. INTRODUCTION

Grombalia Plain is located in Cap-Bon region in Northeast of Tunisia. It is a coastal plain limited to the north by the Gulf of Tunis (Fig. 1). Grombalia is a post-Pliocene rift valley (graben) mainly covered by continental Quaternary deposits with some incorporated marine formations, probably paleosebkha deposits. The plain is formed by a three-layered aquifer system underlying

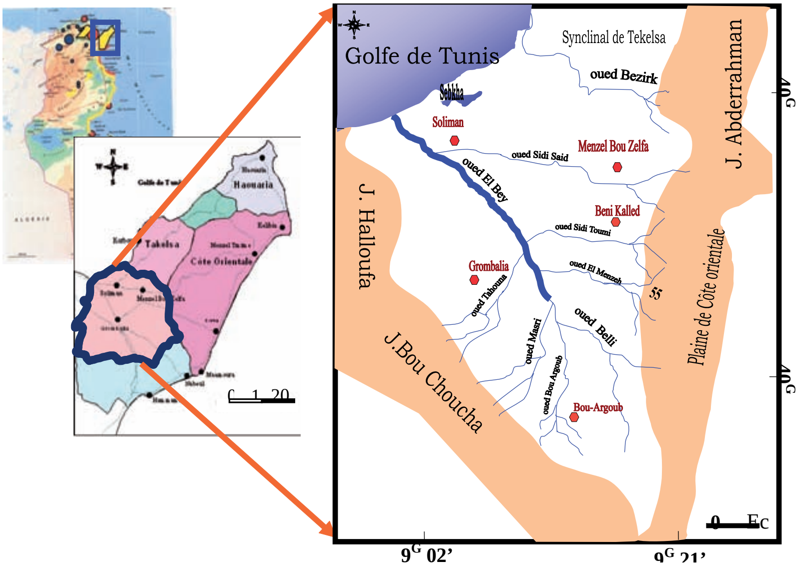

FIG.1. Location map and hydrographic network.

a surface area of approximatively 407 km² and constituted by a shallow, an intermediate and a deep aquifer.

Underground water resources of the Grombalia Plain are regarded as the most important of north-eastern Tunisia and are exploited to supply agriculture and domestic needs. Due to the increase of population and the development of the irrigated agriculture practices, groundwaters are submitted to severe anthropic pressure, therefore their potential has to be updated to ensure their sutainability.

This work aim to improve the hydrodynamic understanding of the system by using geochemical and isotopic technics The chemical analyses and radiocarbon dating were carried out at the Laboratory of Radio-Analysis and Environment of the National School of Engineers of Sfax while isotopic analysis were carried out at the IAEA Isotope Hydrology Laboratory in Vienna.

2. SITE DESCRIPTION

2.1. Climate and geological issues

The Plain of Grombalia is under a typical semi-arid Mediterranean climate type with very irregular annual rainfall, ranging around 500 mm/y. The region is characterized by a soft and rainy winter, with a mean air temperature of 8.2°C and a hot and dry summer with a mean temperature of 30.6°C. Maximum values of evapotranspiration are recorded during the summer season related to high temperature. Mean annual evapotranspiration reaches 1200 mm.

The Plain of Grombalia is a collapsed basin with a depression of the Vindobonian subtratum that is over 500 m. Upper levels of Quaternary series are mainly sandy. However, at a depth of 130 m, Quaternary deposits become marly, gypsifrous and saliferous. Geological outcrops show that old Quaternary terraces are located in the southern part of the plain, while recent terraces outcrop at the northern part. On the other hand, from south to north, deposits become increasingly of littoral type indicating the transition from continental to coastal environment [1].

Two major normal faults of NNW-SSE and NNE-SSW directions have contributed to the depression of the Plain of Grombalia and constitute the natural limits of the zone of study.

2.2. Surface waters

The Plain of Grombalia is crossed by the wadi El Bey with a total hydrographic catchment of 411 km^2 collecting approximately 10 Mm^3. This catchment is located between 14 m and 64 m of altitude and is characterized by a great topographic asymmetry. The natural outlet of the basin is on the Gulf of Tunis, between Hamman-Beach and sebkha El Melah. The catchment of wadi El Bey shows a compacity index of 1.38. Main tributaries of wadi El Bey are

TABLE 1. CHARACTERISTICS OF WADI'S CATCHMENTS

Bassin versant	Surface (km^2)	Compacity index	Surface water (Mm^3)
Wadi Bou Argoub	135	1.64	3.3
Wadi Sidi Saïd	82	1.49	2.0
Wadi El Menzeh	72	1.39	1.8
Wadi Toumi	65	1.53	1.6
Wadi Tahouna	57	1.54	1.3

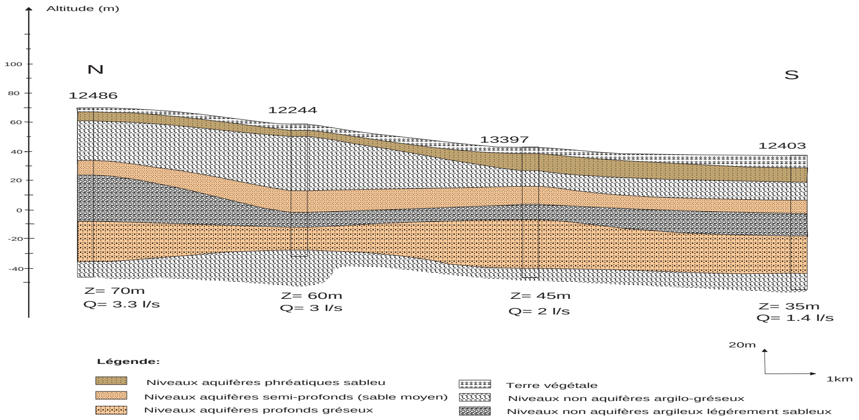

FIG. 2. Schematic cross section of the Grombalia basin.

wadi Sidi Said, wadi Belli, wadi ElMasri, wadi ElMenzeh and wadi Tahouna (Table 1).

2.3. Hydrogeologic aspects

According to lithostratigraphic correlations established from borehole data (Fig. 2), Quaternary deposits are present as alternations of sandy permeable levels with clayey impermeable screens, forming superimposed aquifer layers that communicate with each other. In fact, the system can be considered as a multilayered system in which the upper level forms the shallow aquifer [2].

2.4. Piezometric study

According to the piezometric levels mapped with data of September 2005 (Fig. 3), the flow direction is from south to north following topographic variations, decreasing between approximately 66 m at the southern part of the plain and 5 m in the northern part. The underground flow direction originates in the surrounding reliefs towards the depression of Sebkha El Malah and the Gulf of Tunis, which represent the natural discharge of the aquifer for the wadi El Bey. The main flow is of SE-NW direction on all basins. This fact shows that recharge zones are mainly at the south east of the plain, area of Bou Argoub, and in the North-East in Piedmont de Djebel Abderrahman.

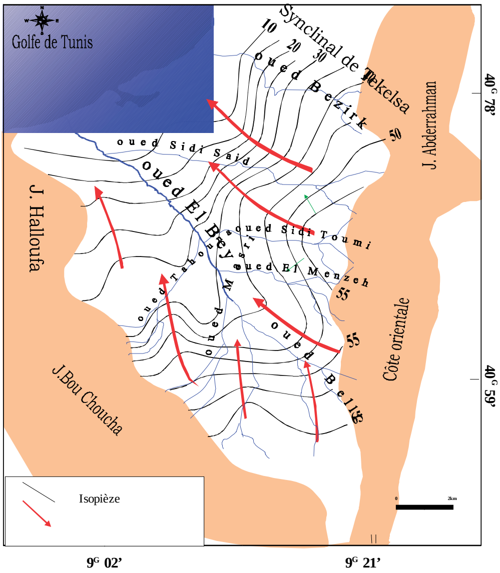

FIG. 3. Potentiometric map of the aquifer system of the Grombalia Plain (September 2005).

3. Exploitation of Grombalia groundwaters

The aquifer system of Grombalia in the sandy Quaternary levels extends over a surface of 407 km^2, it is exploited by approximatively 11000 wells among which 8367 are motorised. Given that the average thickness of the shallow aquifer is about 15 m with a porosity value of 20%, groundwater storage can be evaluated to 1.2 Mm^3 [3].

The exploitation of water resources tapped from the shallow aquifer during the last twenty years enabled us to draw the following remarks:

- Before 1985, groundwater of Grombalia were estimated at 170 Mm^3 which is slightly exceeding the exploited quantity evaluated at 158 Mm^3 per year.
- Since 1990, the exploitation rate underwent a remarkable increase directly related to the decrease of rainfall amounts that can explain the increasing number of wells.
- In 2005, the volume of exploited water was estimated at 250 Mm^3 against an evaluated exploitable reserve of 198 Mm^3 per year what led to a deficit of more than 52 Mm^3. This exploitation rate rwhich represents about 130% of the recharge generates a lowering of 0.6 m per year of the water table.

These remarks have to be considered regarding the socio-economic strategy adopted by policy-makers based on development of the agriculture sector, particularly market-garden products even if this sector is known to need large amount of water resources.

4. HYDROCHEMICAL RESULTS

The hydrochemical characterization of Grombalia groundwaters highlighted a great chemical homogeneity of water sampled from the sandy Quaternary level with a sodium-chloride facies.

4.1. Mineralization

The total mineralisation of the shallow aquifer is characterized by a spatially variable distribution. Indeed, it varies from 0.5 g/L upstream the basin to 5.41 g/L downstream. This spatial distribution enabled us to distinguish three different areas: a first zone, located at south-west and north-east of the plain, which is characterized by low values of salinity (0.5 and 2 g/L), a second zone, located on the western part of the plain, is characterized by an intermediate

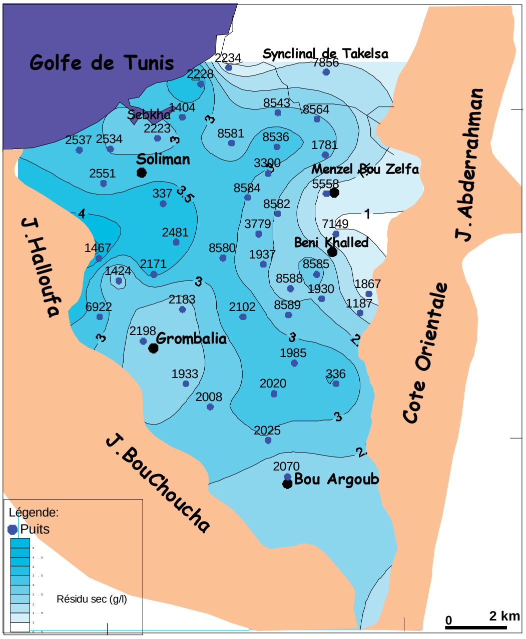

FIG.4. Salinity map of the shallow level of the Grombalia plain aquifer.

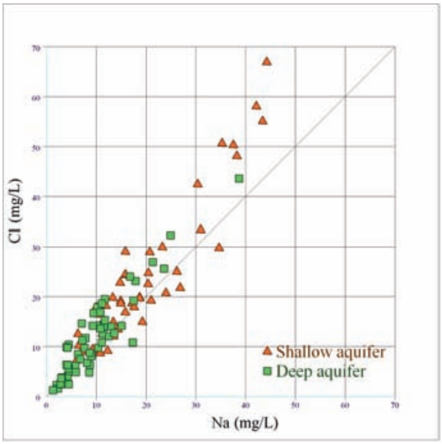

FIG. 5. Na vs Cl

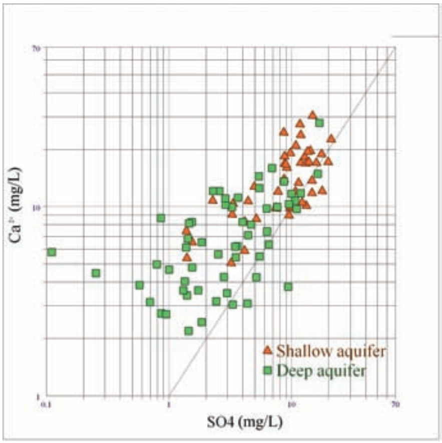

FIG. 6. SO_4^{2-} vs Ca^{2+}

value of salinity ranging between 2 and 3 g/L, and the third zone located at the center of the plain with salinities that exceed 3 g/L (FIG.4).

4.2. Major elements

The majority of Grombalia groundwaters show strong correlation between Na and Cl elements with a correlation coefficient close to 1 (Fig. 5) what indicates a common origin of sodium and chloride. This origin is probably the dissolution of halite (NaCl) during the transit water in the unsaturated zone.

According to the correlation between Ca^{2+} and SO_4^{2-} ions, groundwaters can be classified in two distinct groups (Fig. 6):

- The first group is represented by groundwaters sampled at the central part of the basin and shows Ca^{2+}/SO_4^{2-} ratios close to the unit indicating a common origin of these ions which is probably related dissolution of anhydrite. Ca^{2+} contents are in excess compared to SO_4^{2-} contents which can be explained by basic exchange related to the abundance of clayey minerals in aquifer.
- The second group is constituted by groundwaters sampled in the southern part and along the limits of the basin. The absence of correlation between Ca^{2+} and SO_4^{2-} indicates that the contribution of gypsum and anhydrite dissolution to the mineralisation of these waters is very low and even negligible.

Nitrate contents recorded on the shallow aquifer are higher than the international standards (50 mg/L). Higher values can reach 380 mg/L in the area of Beni Khalled thus evoking pollution degree to the great agricultural activity in this area. However, nitrate contents highlight the significant recent recharge of the aquifer and the contribution of irrigation return to the recharge of the Grombalia system [4].

5. ISOTOPIC RESULTS

Two types of waters have been identified by stable isotopes tracing (Fig. 7):

- A first group plotting along or close to the Global Meteoric Water Line (GMWL) and the Local Meteoric Water Line (LMWL) which indicates a direct infiltration of rainfall water and a low influence of the evaporation phenomenon on groundwaters.
- A second group plotting below the GMWL with a trend to form a straight line of 3 to 5 slope which indicates the effects of evaporation on these groundwaters.

Tritium contents support the two water types identified by stable isotopes. Moreover, using this tracer, a significant recent recharge of the aquifer is highlighted by its values ranging between 2 and 4 TU. This recharge is also deduced from $^{13}C/^{14}C$ results since relatively high activities are measured on groundwater samples.

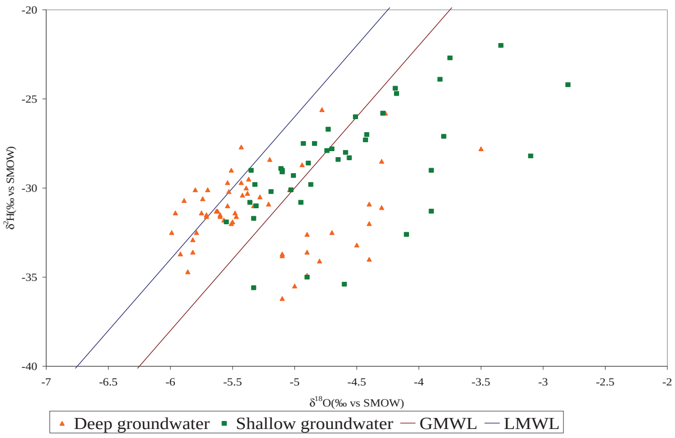

FIG. 7. Isotopic diagram of Grombalia groundwater.

6. CONCLUSION

The first conlusion is given by the salinity of the shallow aquifer which varies from 0.5 g/L upstream the basin to 5.41 g/L downstream. Groundwater with salinities exceeding 3 g/L which is the threshold for human comsumption are located at the center of the plain, indicating a probable contamination by a palaeosebkha.

The second conclusion is the two types of recharge mechanisms highlighted by isotopic tracing of the Grombalia groundwaters: the first recharge mechanism is related to the direct infiltration of actual meteoric water through the outcrops of the formations. This is observed along the relatively high relief bordering the basin and along the wadis network. The second mechanism of recharge is ensured by water that show a high evaporation effect. This type of water probably corresponds to water transferred from Northern Tunisia to the Cap bon area through the “Canal du Nord” to support the agriculture water needs. Further investigations to characterize the isotopic signature of the “Canal du Nord” waters are planned in order to quantify its contribution to the recharge of the Grombalia plain aquifer.

However, we have observed that this recent recharge is followed by a conntamination of groundwater by nitrate due to high agriculture activities and to specific pratices.

ACKNOWLEDGEMENTS

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SURFACE WATER – GROUNDWATER INTERACTIONS IN TRANSITION ENVIRONMENTS: THE EXAMPLE OF THE RIO DE LA PLATA COASTAL PLAIN, ARGENTINA

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Abstract

Environmental isotopes were successfully used to trace surface water - groundwater interactions in a multilayer aquifer system, and to propose a conceptual model for the hydrogeological systems of Rio de la Plata coastal plain. The objective of this work was to identify the surface water contribution to the recharge of the aquifers. A monitoring network of 50 wells for isotopic and geochemical analysis was established, covering different aquifers. According to the results an hydrogeological model has been proposed. The Phreatic aquifer is directly recharged by the Rio de la Plata during level oscillations and indirectly during flooding events by feeding the marshes acting as recharge ponds. Artificial and natural channels act also as recharging lines. The recharge of the semiconfined aquifers occur through lateral flow driven by the induced permanent landward gradients. River acts as a positive barrier, and beyond it there is no possibility

for the depression cones to expand.

1. INTRODUCTION

The study area (Fig. 1), is gently sloped with low relief, situated in the transition zone between the “Pampas” region and the Brazilian shield. Geomorphology is characterized by the presence of two terrace levels [1]. The lower level constitutes a coastal plain with elevations ranging from 0 to 5 metres above sea level and 1.5 to 9 km wide. In this area small differences in elevation lead to the development of marshes that receive direct precipitation, runoff from higher areas and, under certain meteorological circumstances, are partially flooded by the river.

Relationship between geology and hydrogeology allows the identification of three aquifers shown in Fig. 2 (see profile trace in Fig. 3) [2, 3]. The lowermost unit Hipopuelche is a confined aquifer, the middle unit, Puelche is semi-confined, and the uppermost unit, Epipuelche is constituted by phreatic, semi-unconfined aquifers acting as a single one, the top of the active system is placed at the base of the Puelche [4].

Groundwater quality and age is related to geomorphology. While in upper areas is characterized by low chloride ($Cl^- < 50$ ppm) and detectable tritium

FIG. 1. Location of the study area in the Rio de la Plata coastal plain.

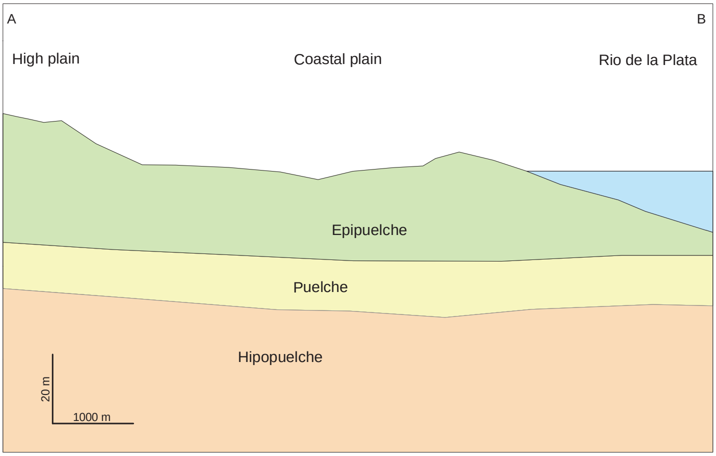

FIG. 2. Schematic cross-section of the aquifer in the study area.

contents, in the coastal plain tritium in negligible and high chloride (>1000 ppm) as the result of a marine transgression *ca.* 7500 years BP [5, 7]. Groundwater flow for the Epipuelche is toward the river with extremely low gradients (0.005) while the Puelche aquifer exploitation in higher areas produced inversion of natural gradients, landward.

2. METHODS

A network of 25 sampling points, was established, covering the semi-confined Puelche and the Epipuelche aquifers. Surface water samples were also taken at two points in the river, marshes and channels to the river. Determination of Alkalinity, pH and Electrical Conductivity (EC) were carried out in the field, major ions were analysed at the Department of Environmental Sciences, Università Ca' Foscari of Venice. Isotopic analyses (^{2}H, ^{18}O, ^{3}H) were performed at Instituto de Geologia y Geocronologia Isotopica (INGEIS). Since contrast in resistivity are likely to occur in areas where groundwater shows variability in EC, vertical electric soundings were also performed to help in the interpretation of geochemical data.

3. RESULTS

Tririum results of the sampling campaign are schematically shown in Fig. 3. Water from the Rio de la Plata shows high Tritium levels far from those explainable by precipitation inputs. These high levels are suspected to be related with nuclear power stations located in the watershed as reported by Panarello et al. [7]. Whithin this study tritium will be used to trace river water contribution to the recharge of the aquifer system.

4. CONCLUSIONS

The hydrogeological model proposed is shown in Fig. 4. According to the results, the high tritium levels found in the Epipuelche and the Puelche aquifers are evidence of active recharge by the river. The sandier facies of the Epipuelche are recharged during tidal oscillation forcing bank storage. Within silty clayey facies, recharge is controlled by topography when exceptional tides cause flooding of the coastal plain and river contribution to the feeding of

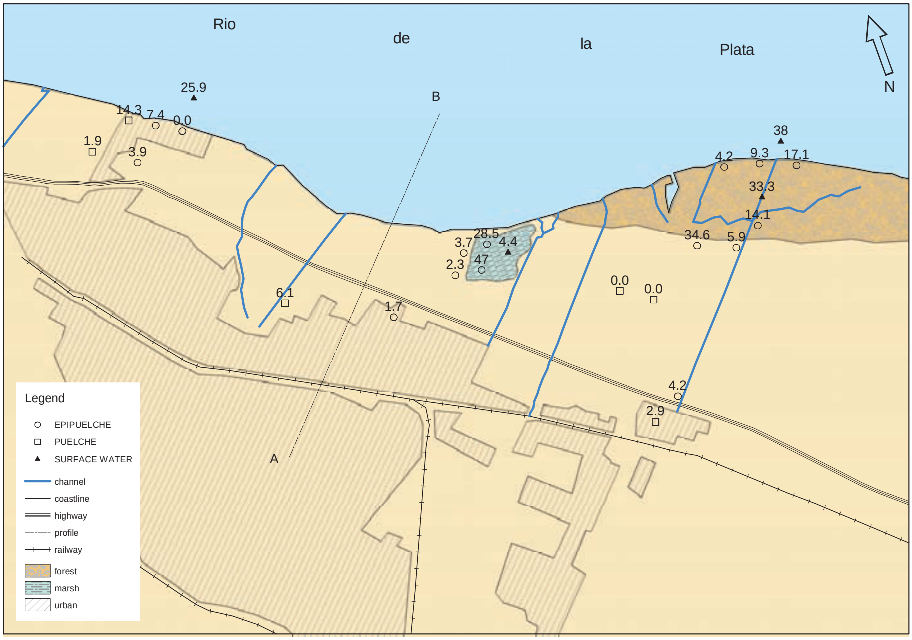

FIG. 3. Tritium contents in the study area.

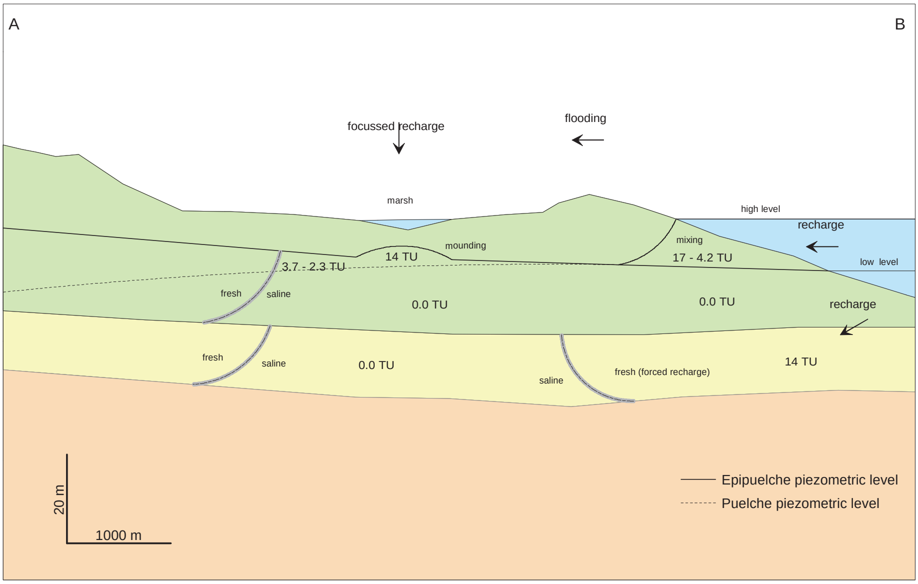

FIG. 4. Cross-section along line A–B in Fig. 3.

marshes acting as seepage ponds. Artificial and natural channels act as well as recharging lines, by means of water loss through the bottom.

For the Puelche aquifer, the high exploitation rates have forced the migration of the saline palaeogroundwater, but also the recharge from the river. The recharge in this case occurs through lateral flow driven by the induced permanent landward gradients.

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ISOTOPE STUDY FOR RELATIONSHIP BETWEEN SURFACE AND GROUNDWATERS UNDER A SEMI-ARID CLIMATE: CASE OF SOUSS-MASSA CATCHMENT (SOUTH-WEST OF MOROCCO)

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Abstract

This study summarizes the application of stable isotopes as tools to infer water sources in the region. Hydrogen and oxygen isotope signatures reveal significant infiltration before evaporation, indicating recent recharge from the Atlas Mountains and infiltration of surface water along the oueds and in the alluvial fans at the margin of the Atlas basins. ^{18}O, ^{2}H and tritium values indicate a mixing between recent and old groundwaters. The old groundwaters encountered in deep wells are not connected to modern recharge, indicating that water followed a long flow path. The slight evaporation recorded by stable isotopes in water from the southern margin close to the Anti-Atlas mountains indicates that these groundwaters are subject to a drier climate, marking the Anti-Atlas Mountains, which form a barrier against the influence of the Sahara. The upstream watershed, which is the place of condensation, shows more characteristic ^{2}H and ^{18}O-depleted waters. This finding can be explained by the altitude and the continental effects. On the other hand, ^{2}H and ^{18}O-enriched waters values towards the ocean, show an evaporation effect near the condensation source or the irrigation returns, especially

in the irrigated zones. The rain isotope values indicate a main recharge from the Atlasic Mountains, whereas the contribution of the local rains is negligible in downstream.

1. INTRODUCTION AND SITE DESCRIPTION

The Souss river flow situated between the high Atlas Mountain in the north and Anti-Atlas in the south (Fig. 1), is closely related to the rain fluctuations and shows inter-annual, and seasonal variation from year to year. The climate is semi-arid to arid, the rainy season extending from November to March and the dry season from April to October. The rainfall and the average runoff vary in time and space, ranging from 200 mm/y in the plains (mean altitude: 460 m a.s.l.) to 600 mm/y in the mountains (altitude >700 m a.s.l.). The long-term mean annual precipitation decreased in 20 years from 343 mm in Aoulouz (700 m a.s.l.) to 232 mm in Taroudant (232 m a.s.l.). The temporary Souss River is the main collector of superficial waters in the basin. The location near mountains (with high rainfall) allows an important inflow by its tributaries especially those coming from the High Atlas Mountain. This flow coming from high altitudes is infiltrated in the piedmont area and in the beds of rivers which contain high permeability conglomerates.

The shallow aquifer of the plain is the main resource for drinking, irrigation and industrial water in the region (Fig. 1). In order to improve the management of these precious resources, several studies, to better understand the hydrological functioning of the aquifer system and define the relationship between surface runoff (rivers and dams) and groundwater, have been carried out during the last years.

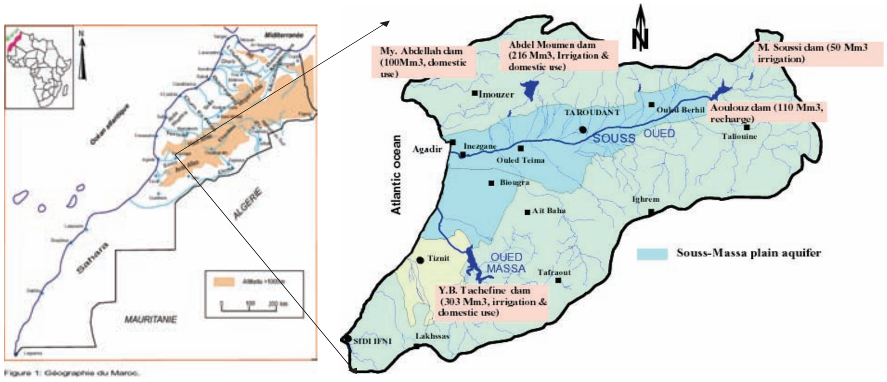

FIG. 1. Location map of Souss-Massa basin.

2. METHOD

In order to improve the management of the water resources in the Souss basin, several studies, to better understand the hydrological functioning of the aquifer system and define the relationship between surface runoff (rivers and dams) and groundwater, have been carried out during the last years.

An investigation of the sources and dynamics of groundwater is being conducted with environmental isotopes including ^{18}O, ^{2}H, ^{3}H. The main objectives of this study during the last 30 years, are:

- Determination of the mechanisms of recharge to the aquifer and the relationship between surface water and groundwater in semi-arid climate.
- Evaluations of the isotopic techniques in the context of large hydrologic systems;
- New guidelines for the optimal use of isotope techniques in water management.

3. RESULTS & INTERPRETATION

This study summarizes the application of isotope hydrological tools to infer water sources of the Souss region. The isotopic contents of waters present a large variation (from –8‰ and to –1‰ for ^{18}O, from –52‰ to –5‰ for ^{2}H). The tritium values show the high values ranging from 0 to 100 TU for ^{3}H for 1970 sampling [1] and low values of 0 to 10 TU for 1998 sampling [2, 3, 4]. The Fig. 2 indicates that all waters are aligned generally along the GMWL [1]. The upstream watershed, which is the place of condensation and the beginning of the Atlas Mountains, shows more characteristic ^{2}H and ^{18}O-depleted waters. This finding can be explained by the altitude and the continental effects. On the other hand, ^{2}H and ^{18}O-enriched waters values towards the ocean, show an evaporation effect near the condensation source or the irrigation returns, especially in the irrigated perimeters. The rain isotope values indicate a main recharge source from the Atlasic Mountains (Fig. 3), whereas the contribution of the local rains is negligible in downstream. The slight evaporation recorded by stable isotopes in some samples can be explained by (i) direct evaporation from dams, rivers, a drier climate, (ii) return irrigation water, (iii) from shallow wells subject to evaporation, particularly in the margin of the Anti-Atlas Mountains, which form a barrier against the influence of the Sahara. Hydrogen and oxygen isotope signatures reveal a significant infiltration of surface water before evaporation, indicating a recent recharge through fractures in crystalline and limestone rocks the Atlas Mountains and infiltration of surface water in

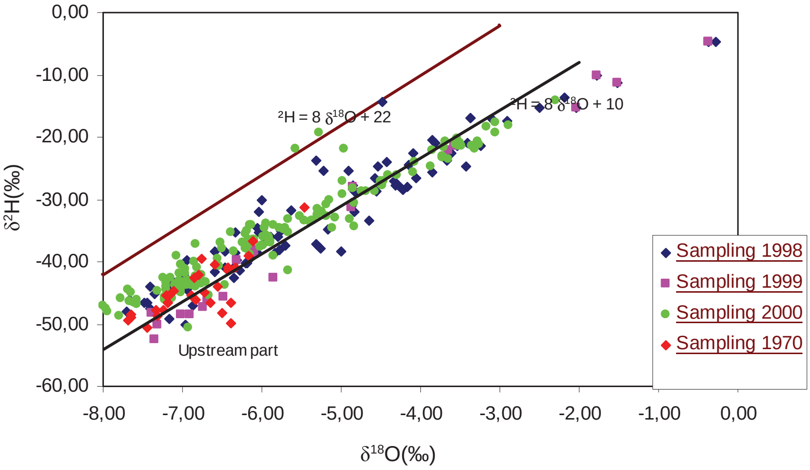

FIG. 2: Relationship between deuterium vs oxygen-18 (‰) in the study area.

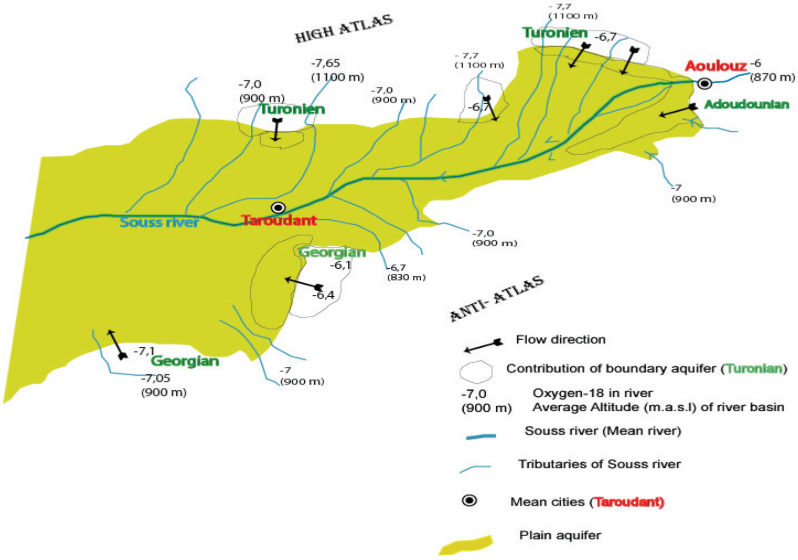

FIG. 3. Main recharge zones of the Souss shallow aquifer.

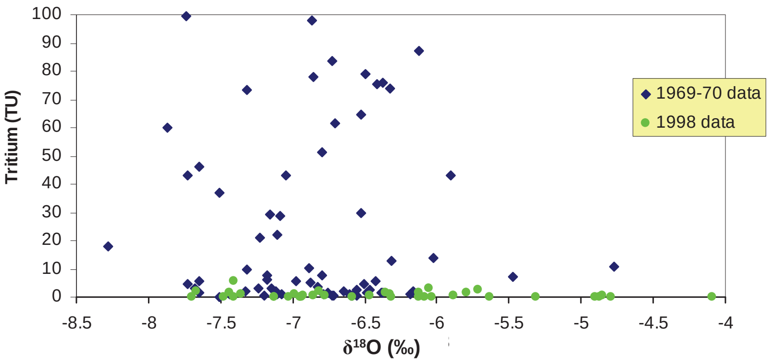

FIG. 4. Relationship Tritium (TU) vs O-18 (permil) for two periods (1969–70 and 1998).

the alluvial fans at the margin of the Atlas basins (Fig. 3). ^{18}O, ^{2}H and tritium values indicate a mixing between recent and old groundwater; the latter were recharged under more humid climatic conditions than that at present. The old groundwater encountered in deep wells are not connected to modern recharge (Fig. 4), indicating that water followed a long flow path. The distinct high tritium values in 1970 sampling, allowed clearly a signature of nuclear bomb effects highlighted between 1960 and 1970 [6].

4. CONCLUSION

This study shows the application of isotopic tools in a semi- arid climate.

- The recharge of the unconfined aquifer in Souss basin is mainly coming from the high Atlas Mountains.
- Two water types were identified: (i) recent water which follows a superficial flow path, (ii) old water which fillows a deep flow path.

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INVESTIGATION OF WATER RESOURCES AND WATER PROTECTION IN THE KARST AREA OF CROATIA USING ISOTOPIC AND GEOCHEMICAL ANALYSES

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Abstract

Hydrogeological investigations using hydrochemical and isotopic methods have been performed to determine the sanitary protection areas of springs in the drainage area of the Vransko Polje near Biograd (North Dalmatia) and main springs in the drainage area of the Gacka River (Lika region). Both regions are situated in the karst area of Croatia. Water samples from springs and precipitation samples at both areas were collected monthly in the period 2005–2006. Hydrochemical results follow the variations caused by the main hydrogeological properties of particular aquifer and recharge conditions during different seasonal hydrologic and vegetation conditions. The mean ^{3}H activity in all main springs in the Gacka River area is similar to that of precipitation, while in the springs of Vransko Polje the mean ^{3}H activity is lower if compared with precipitation due to sea water infiltration. There is no seasonal fluctuation of ^{3}H activity in all springs indicating fast circulation and good mixing of precipitation and ground waters.

1. INTRODUCTION

The investigations presented in this paper were performed in the frame of the IAEA TC Project entitled "Application of isotope techniques in investigation of water resources and water protection in the Karst area of Croatia". Two investigated areas are situated in the Dinaric Karst (Fig. 1) that comprises very important groundwater storage reservoirs in Croatia, but in the same time this area is very sensitive to any kind of pollution. The aim of this investigation was to determine the origin of groundwater discharging at particular springs with respect to its drainage area, recharge conditions and anthropogenic influence. The obtained data can be very useful for determination of sanitary protection zones of several springs in one of the subdrainage areas of the Vransko Polje (important for water supply of the town of Biograd, Middle Dalmatia), and of main springs in the drainage area of the Gacka River (Lika region). We used hydrochemical measurements including *in situ* measurements of temperature, pH, conductivity and oxygen as well as laboratory measurements of Ca, Mg, Na, K, HCO_3^-, SO_4^{2-}, Cl^-, NO_3, NH_3, PO_4^{3-}. For determination of the mean residence time (MRT) of spring waters we used tritium measurements. Spring waters from three main springs and precipitation water at each area were collected monthly in the period 2005–2006.

2. SITE DESCRIPTION

The Atlas Mountain study sites are very important for water supply in these areas. In spite of the fact that both areas are located in the Dinaric Karst, their hydrogeological features are different due to their physiographical and climate conditions. The spring zone of the Gacka River (Fig. 1A) consists of a number of karst springs, which present the strategic reserves of the drinking water by their quantity and quality. Until the construction of a new highway, the whole region was scarcely inhabited, with some small industrial facilities and insignificant agriculture. Today, traffic infrastructure enables increased touristic activities. The climate is typical continental, sometimes under Mediterranean influence. Altitudes vary between 600 to more than 1000 m a.s.l. In the south and west part of the catchment area that is built of well permeable deposits (limestones, dolomites), the structural-tectonic relations have the crucial part in disposition and groundwater flow. Considering the tracing results, it is obvious that groundwaters flow from the specific part of the catchment area towards individual spring or group of springs, connected with an arrangement of structural-tectonic units, structures and tectonic blocks. The spring Pećina gets the water mostly from the western part of the catchment area, where

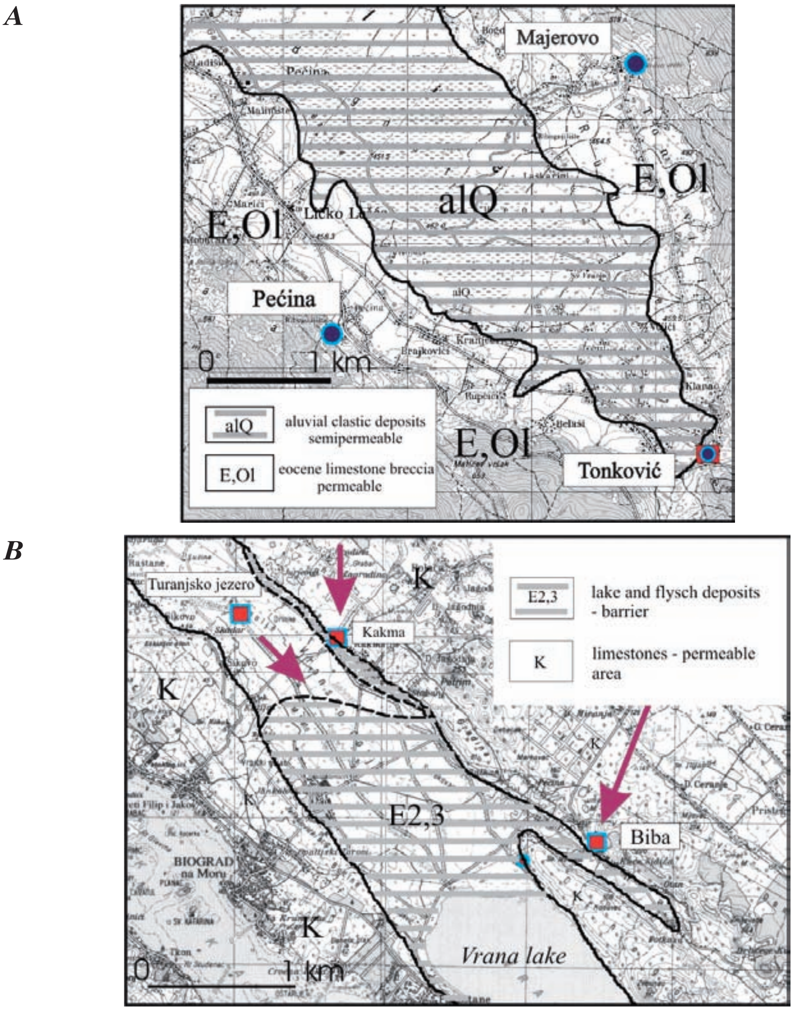

FIG. 1. Recharge area of Gacka River springs (A) [1] and Vransko Polje springs (B) [2]. The main springs that are systematically investigated in both areas are marked. Precipitation samples were collected at Tonkovića vrelo spring (A)and at Kakma spring (B). Arrows indicate prevailing groundwater flow directions.

structures separated by parallel vertical faults prevail. The consequence are strong oscillations of discharge, from dozens of m^3/s in the maximum to only 60 L/s in the minimum (small retention area). The main spring of the River Gacka, Tonkovića vrelo, gets the major part of the water from the structural unit in the immediate hinterland of the spring and in the middle part of the catchment area. This reflects on the hydrogeological properties of the spring: permanency and high discharge, which is connected to a high retention area of the catchment. The groundwater outflow regime on Majerovo vrelo is determined by the existence of open joints and karst channels that enable fast inflow of huge amounts of water [1].

The Vransko Polje (Fig. 1B), situated near the town of Biograd, physiographically and geologically belongs to the outer Dinarides karst region. The climate is typical Mediterranean with an average air temperature of approximately 14.5°C. Altitudes vary between a few meters and 100 m a.s.l. The terrain is composed of Cretaceous and Eocene carbonate rocks, marly deposits of Eocene flysch and Quaternary alluvial and deluvial deposits. From the tectonic point of view, this is a flattened, mildly folded area. The prevailing groundwater flow occurs parallelly to the structural directions, in the NW-SE direction. Along the north edge of Vransko Polje, however, on the barrier of flysch deposits, on several karst springs discharge the waters from the north inland carbonate recharge area. In these parts of the terrain, groundwater flows perpendicularly to the structures. The deep parts of aquifer along the coastal zone and Vransko Polje are partly under sea water influence due to deep seawater intrusion after the last glaciation period. Contribution of fresh water from the inland part formed a fresh water layer with a mixing zone which overlays "aging" seawater. The position of the mixing zone depends on the geometry of impermeable barriers and hydrological conditions. Also, the groundwater of study karst aquifers is strongly affected by agricultural activity, mainly by application of fertilizers. Previous studies established sporadic effects of sea water as well as fertilizers on groundwater quality[3][2].

3. GEOCHEMICAL ANALYSES OF SPRING WATERS

The results of most physico-chemical measurements for 3 main springs in both areas are presented in Fig. 2–6.

Temperatures of spring waters (Fig. 2) are higher in Vransko Polje (B) then in Gacka River area (A) reflecting mean air temperature of each area having the Mediterranean and continental type of climate, respectively. The seasonal fluctuation of temperature is observed in most of the springs due to dominant channel underground flow througout the aquifers what is a consequence of short mean residence time of water. The exception is Tonkovića vrelo (Fig. 2A), where small temperature fluctuation indicates a good homogenization of each new contribution of infiltrated precipitation and longer mean residence time of goundwater.

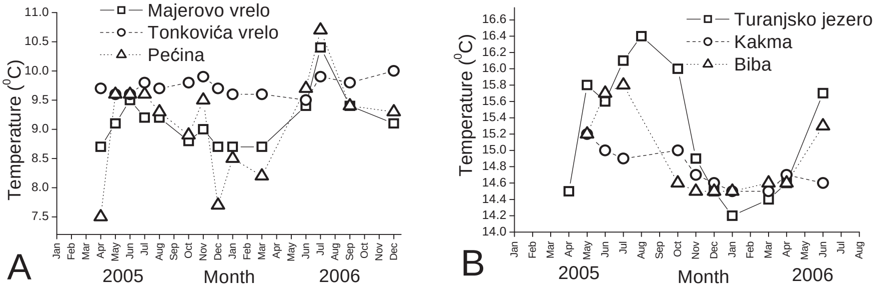

FIG. 2. Temperature of spring waters of Gacka River (A) and Vransko Polje area (B).

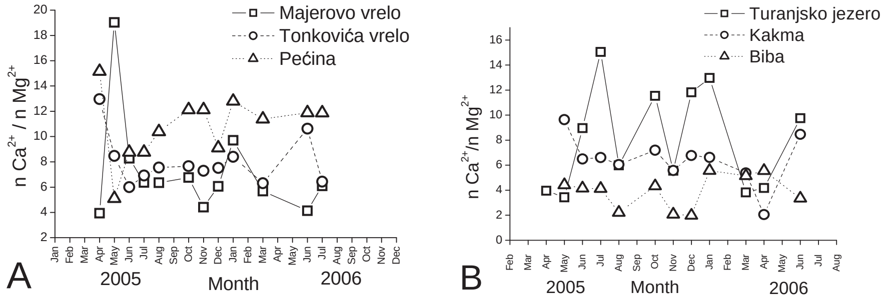

FIG. 3. Molar ratio of calcium and magnesium in spring waters of Gacka River (A) and Vransko Polje area (B).

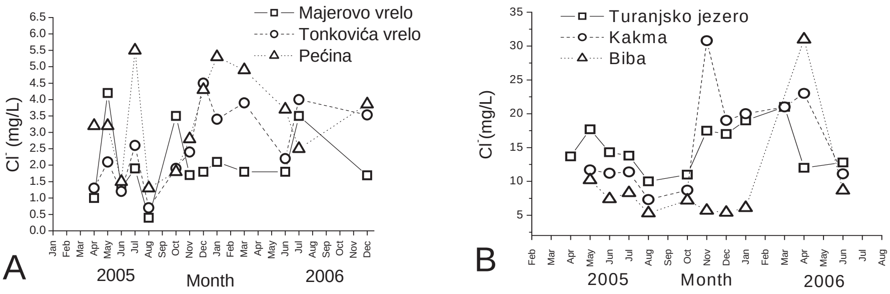

FIG. 4.Concentration of chloride in spring waters of Gacka River (A) and Vransko Polje area (B).

The molar ratios of Ca/Mg are in the similar range for both areas (Fig. 3) typical for the karst hydrogeochemical environment. The lower values of nCa/nMg for Majerovo vrelo and Tonkovića vrelo springs (A) point to limestone with dolomite aquifers while the recharge area of Pećina spring (higher nCa/nMg) is mainly built of limestone. In Vransko Polje (B) the lowest values of nCa/nMg are for Biba spring indicating the presence of dolomites in the recharge area, while for Kakma and Turanjsko jezero springs the higher influence of limestone is observed. The high fluctuation of nCa/nMg in Turanjsko jezero spring can be the consequence of the calcium input from other sources, e.g. leaching from carbonate fraction of flysch or from mineral fertilizers.

The concentration of chloride (Fig. 4) is much higher in spring waters of the Vransko Polje area (B) showing the influence of sea water throughout the mixing zone and of maritime precipitation. In springs of Gacka River (A) with relatively low chloride concentration the slight increase in winter time could be caused by the use of salt on highways.

Concentration of nitrate (Fig. 5) is very low at all springs in the Gacka River area (A). Higher concentration of springs in Vransko Polje (B), particularly during vegetation period, could be the consequence of using the fertilizers (Turanjsko jezero spring) and sewage water from settlements (Kakma spring).

Concentration of sulphate (Fig. 6) is much higher in springs of the Vransko Polje (B) than in the Gacka River springs (A). The increased concentration of sulphate in karst usually originates from the gypsum or anhydrite minerals in the carbonate rocks, sea water contribution or some anthropogenic sources (sanitary landfills, sewage and other waste waters). For example, the highest concentration of sulphate in Kakma spring (Fig. 6B, mean 33 mg/L) with

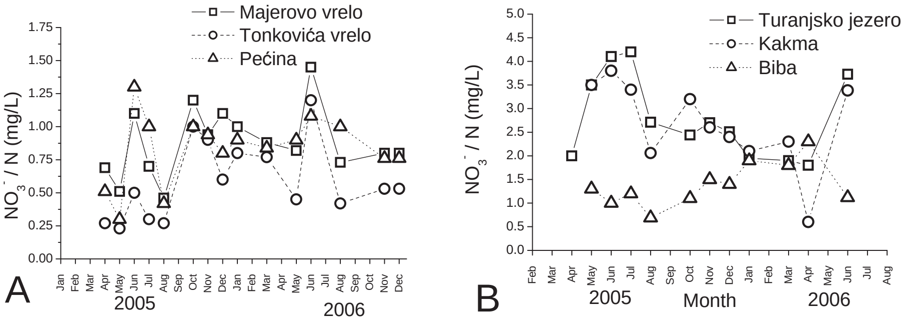

FIG. 5. Concentration of nitrate in spring waters of Gacka River (A) and Vransko Polje area (B).

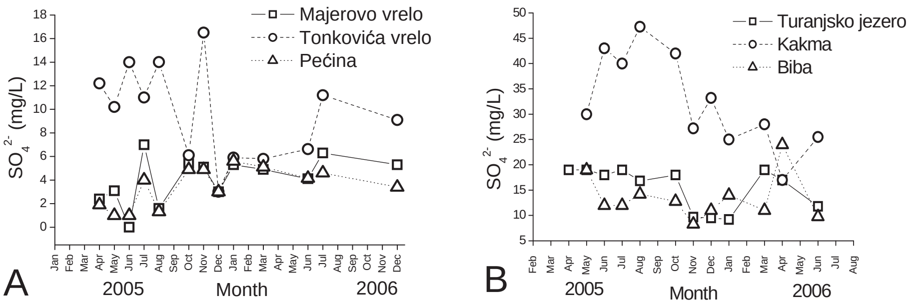

FIG. 6. Concentration of sulphate in spring waters of Gacka River (A) and Vransko Polje area (B).

pronounced seasonal fluctuation (higher in summer) is probably due to the influence of sewage waters from settlements without sewage system.

The concentrations of ammonium and phosphate in all springs (not presented in graphs) are <0.01 mg/L NH_3/N and <0.01 mg/L PO_4^{3-}/P, respectively. Concentrations of sodium are higher in the spring waters of Vransko Polje area (ranged from 5.1 to 9.8 mg/L) than in Gacka River (ranged from 1.0 to 4.9 mg/L) showing again the influence of sea water. Also the alkalinity is higher in Vransko Polje springs (ranged from 302 to 473 mg/L HCO_3^-) than in Gacka River springs (ranged from 265 to 329 mg/L HCO_3^-). Generally, the concentrations of all salts are higher in spring waters of Vransko Polje recharge area that is mainly influenced by sea water infiltration.

4. TRITIUM ANALYSES OF PRECIPITATION AND SPRING WATERS

The seasonal variations of ^{3}H activity in precipitation at both areas (Fig. 7) are observed. The mean ^{3}H activity in precipitation for the Gacka River area is (6.5 ± 3.9) TU, with a maximum of 13.6 TU in June 2006. The mean value for the Vransko Polje area is (6.8 ± 2.5) TU, with a maximum of 10.3 TU in June 2006. The seasonal distribution of ^{3}H in the precipitation in the Gacka River region is well correlated with that in Zagreb (linear correlation coefficient r = 0.9) for the same period since both stations are continental ones, while the correlation is poor between the precipitation in Zagreb and the Vransko Lake area (r = 0.4) (coastal area) (Fig. 8).

Spring waters from both areas show smaller seasonal fluctuations, and also lower maximum ^{3}H activities than the corresponding precipitation. All three main springs in the Gacka River recharge area show similar mean ^{3}H concentrations as that in precipitation (Fig. 7A): Majerovo vrelo

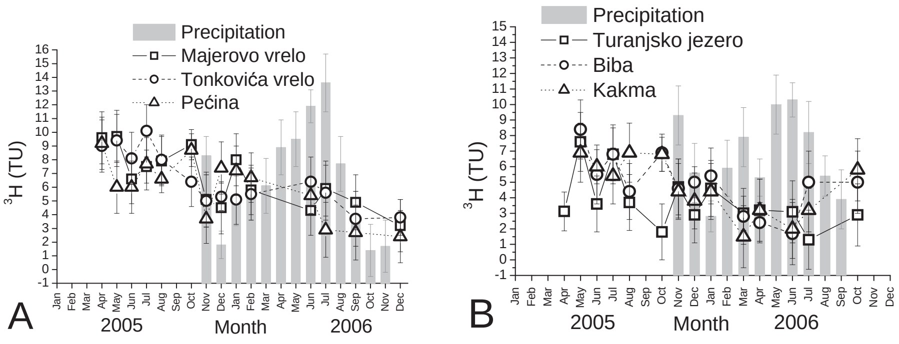

FIG. 7. Tritium activity in spring waters and precipitation in Gacka River (A) and Vransko Polje area (B).

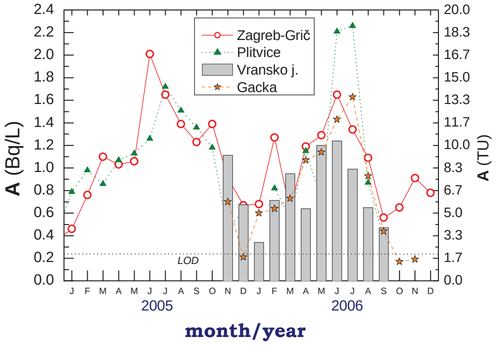

FIG. 8. Comparison of tritium activity in Zagreb and Plitvice precipitation (continental stations) with precipitation in Gacka River and Vransko Polje area.

(6.6 ± 2.1) TU, max 9.7 TU; Tonkovića vrelo (6.5 ± 2.1) TU, max 10.1 TU; Pećina (5.9 ± 2.2) TU, max 9.2 TU. This indicates a short mean residence time and good mixing of infiltrated and ground water. Mean and maximum values of ^{3}H activity for springs of Vransko Polje recharge area (Fig. 7B) are as follows: Turanjsko jezero (3.7 ± 1.7) TU, max 7.6 TU; Biba (4.9 ± 1.8) TU, max 8.4 TU; Kakma (4.6 ± 1.8) TU, max 6.9 TU. Lower ^{3}H activity in springs than in precipitation could indicate recharge preferentially by winter precipitation, but also the influence of sea water infiltration.

5. CONCLUSION

According to the geochemical and isotopic measurements in the main springs of two areas in the Dinaric Karst, namely, Gacka River (continental area) and Vransko Polje (coastal area), we can conclude the following:

The ^{3}H activity of precipitation in both areas shows seasonal fluctuation with lower values in winter (2–5 TU) and higher in spring/summer (10–13 TU). The mean ^{3}H activity in all main springs in the Gacka River area is similar to that of precipitation, while in the springs of Vransko Polje the mean ^{3}H activity is lower compared with precipitation due to sea water infiltration. There is no seasonal fluctuation of the ^{3}H activity in all springs indicating fast circulation and good mixing of precipitation and ground waters. Therefore, both areas are very sensitive to any kind of pollution and the response to the pollution will be very fast.

The chemical composition of spring waters from the Gacka River recharge area shows low concentration of total dissolved salts. Low concentrations of nitrates, amonium and phosphates indicate non-polluted ground waters in this area.

Hydrochemical composition of spring waters in the Vransko Polje recharge area shows seasonal vegetation and hydrological variations (Cl^-, SO_4^{2-}, NO_3^-) closely related with the sea water influence and anthropogenic activities. The sewage waters from settlements and agriculture activity affect the quality of spring waters mainly after a dry season when the precipitation washes out soil and the unsaturated zone of karst aquifers.

ACKNOWLEDGEMENTS

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NATURAL BASELINE QUALITY WITHIN THE LOWER TRIASSIC SANDSTONE OF LORRAINE (FRANCE): STATUS AND EVOLUTION

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Abstract

The Triassic sandstones, that form an important aquifer on the Eastern border of the Paris Basin (France), have been intensively exploited by large scale pumping begun in the seventies that created a significant decrease in head level. Investigations using a combination of geochemical and isotopic methods have been carried out in 1979 and interpreted in terms of residence time of groundwater. This area appeared then of a special interest regarding the groundwater baseline evolution related to over-exploitation and matches the objectives of the EU BaSeLiNe project EVK1-1999-00024 as it allows to establish long term trends in water quality of a deep groundwater system. A new field campaign (major, minor, trace elements and isotopes) was started in 2001 in order to highlight the modifications of the water quality in relation with the modifications of the piezometric levels and the circulation flow paths that occurred after the large scale pumping.

1. INTRODUCTION

The knowledge of the natural baseline quality of groundwaters - depending on aquifer mineralogy, facies change, flow paths and residence time - is an essential prerequisite for understanding pollution and for imposing regulatory limits. However, as groundwater exploitation by means of drilling may penetrate water of different ages and/or quality with increasing depth and then disturb hydrogeological conditions, involving some anthropogenic component in the initial water quality. The EU BaSeLiNe project EVK1-1999-00024 objectives then include the following: (i) establish criteria for the baseline concentrations of a wide range of substances that occur naturally in groundwater, (ii) establish a series of reference aquifers across Europe that can be used to illustrate the ranges in natural groundwater quality as a basis for understanding natural groundwater quality evolution, (iii) establish long term trends in water quality and to interpret these in relation to past changes due to natural geochemical as well as hydrogeological responses or anthropogenic effects, (iv) provide a scientific foundation to underpin EU water quality guideline policy.

The Triassic sandstones, that form an important aquifer on the Eastern border of the Paris Basin, in the eastern France, has been intensively exploited by large scale pumping begun in the seventies that created a significant decrease in head level. Investigations using a combination of geochemical and isotopic methods have been carried out in 1979 [1] and interpreted in terms of residence time of groundwater within the aquifer. Another study carried out by [2] in 2003 focus on the isolating properties of aquitards. This area appeared then of a special interest regarding the groundwater baseline evolution related to over-exploitation, and matches more peculiarly the objective (iii) of the EU BaSeLiNe project as it allows to establish the long term trends in water quality of the Triassic sandstones aquifer. A new field campaign was initiated in 2001 to highlight the modifications of the water quality in relation with evolutions of the piezometric levels and the circulation flow path that occurred after the large scale pumping.

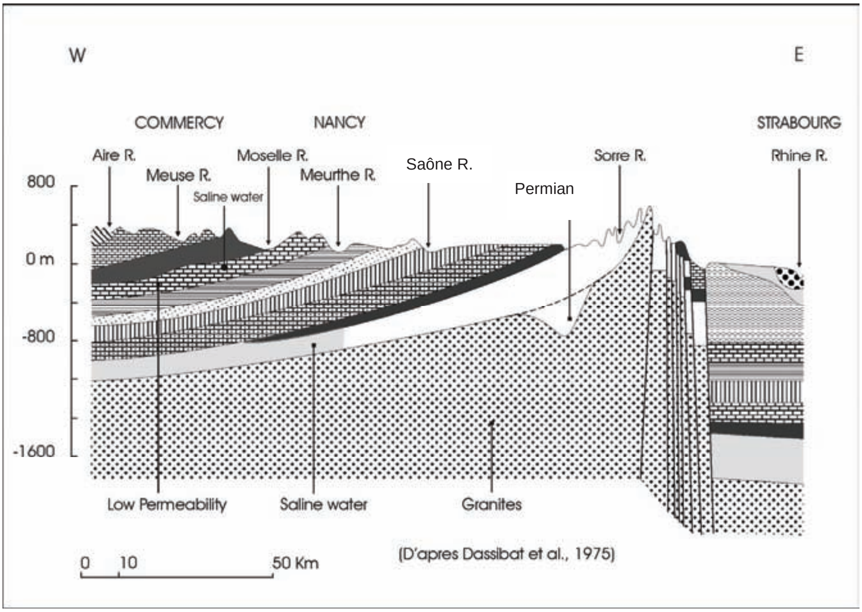
2. ENVIRONMENTAL, GEOLOGICAL AND HYDROGEOLOGICAL SETTINGS

Most of the area is covered by deposits of secondary age (upper Trias and Lias) with low permeability. Recharge of the Triassic Sandstone Aquifer (TSA) occurs in the outcropping zones, providing the groundwater protection from anthropogenic pollution. The current impact could be from diffuse or wide-spread pollution sources from agriculture or industrial activities. This impact could be seen as nitrate concentrations from the excessive use or fertilisers or harmful trace elements.

In Eastern France, the lower Triassic is mainly represented by sandstones and conglomerates. These sandstones crop out along the western border of the Vosges Mountains. Being 500 m thick in the outcrop areas, they become gradually deeper lying and thinner towards the centre of the Paris Basin (Fig. 1). The lower

Triassic sandstones consist of, from the bottom: (1) Annweiler sandstones: red or grey-red fine grained quartzitic and feldspathic sandstones up to 60 m thick that often contain dolomitic nodules and manganese marks, (2) Vosges sandstones; 300 to 400 m thick pink sandstones, locally feldspathic, iron cemented, with an uppermost conglomerate facies, (3) intermediate layers that alternate coarse feldspathic sandstones, red or green clay beds and compact dolomites, (4) Voltzia sandstones: fine grained micaceous and feldspathic sandstones up to 20 m thick that often contain pyrite. These permeable formations are covered by about 600 m thick deposits: (a) succession of shell sandstones, dolomites, marls and calcareous up to 200 m thick from the Muschelkalk, (b) marls and clays that contain evaporitic levels from the Keuper and the lower Lias up to 250 m thick, (c) Dogger: oolithic limestone interbedded with marls. They usually overlie Permian formations consisting of argilleous cemented sandstone and volcanic flows. Locally, evaporitic, and particularly halite deposits have been recognised in the Permian formations [3].

During at least the second half of the Tertiary, the Vosges Massif has been uplifted by Alpine deformation while the central part of the Paris basin was affected by subsidence. This structure is characterised by anticlinal and synclinal folds arranged in the direction of the Variscan orogeny (SW–NE) and is cut by SSE–NNW faults.



(D'apres Dassibat et al., 1975)

FIG.1. Cross section of the Lorraine Basin.

The lower Triassic sandstones form the main aquifer of the Lorraine. They extend from the east outcrop zone to about 150 km westward, where they progressively disappear. South of the line running from Vittel to Epinal, crystalline rocks form the substratum. North of this line sandstones usually overlie Permian formations, with the exception of Sarre-Lorraine anticline crest where they lie over carboniferous provinces. If crystalline and carboniferous rocks act as an aquitard, local connection could exist between Permian and Triassic groundwater. Moreover, the SSE–NNW faults could play a hydrogeological role by connecting the Triassic sandstones aquifer and the overlying Muschelkalk shell sandstones and Dogger oolithic limestones aquifers. It must be noted that the high anisotropy of the reservoir could induce natural groundwater quality stratification.

The aquifer main recharge is provided by the precipitation that occurs in the outcrop zone (Vosges and coal Sarre region). The estimated aquifer capacity is about 30 000 Mm^3 in the unconfined part and 500 000 Mm^3 in the confined part including 150 000 Mm^3 fresh water. The renewal rate is about 0.05% and the abstraction about 130 Mm$^3 \cdot$ y^{-1} and 50 Mm$^3 \cdot$ y^{-1} in the unconfined and confined part of the aquifer respectively.

The aquifer storage coefficient varies from 4.10–4 to 8.10–5 in the confined part of the aquifer to 5.10–2 to 5.10–3 in the outcrop area. The

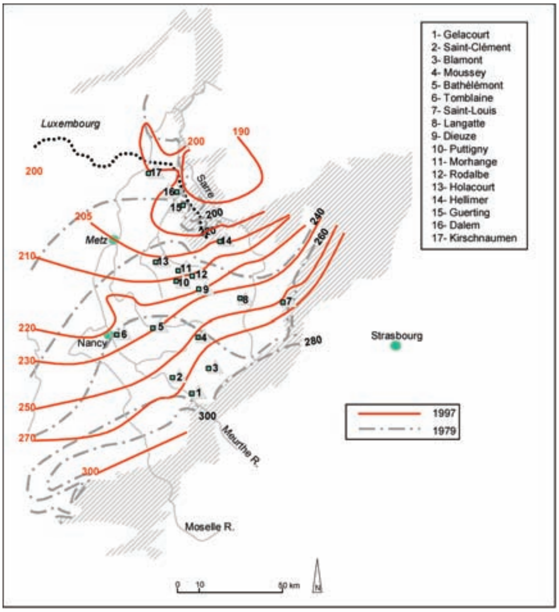


FIG. 2. *Piezometric surface map of the Lower Triassic aquifer.*

associated transmissivity varies from 0.1 to 10–3 m²/s. The effective porosity of the TSA is of 10 to 15%. Since the beginning of the 20th century, potentiometric heads have been deeply modified by the exploitation of coal mines close to the German border and by the development of many water supply boreholes (Fig. 2). The general groundwater flow varies from a north-eastward direction in 1979 [1] to a more uniform northward direction in 1997 [4]. The lowering of the water table has been estimated as follows: 7–8 m in 10 years close to Sarre region, 18–20 m in 30 years close to Vittel, more than 40 m in 75 years close to Nancy, 50–150 m close to the German border. The pressure on the aquifer is nowadays slightly reducing thanks to the closing of coal exploitation and to the progressive drowning of mine galleries.

3. METHODOLOGY

In 1980, a first field campaign was carried out [1]. Using a detailed dataset of chemical and isotopic data, the authors made an evaluation of the palaeohydrological regime of the TSA. The campaign realised in 2001 aimed at highlighting the modifications in the piezometric levels and in the circulation flow path that occurred after a large scale pumping. In this purpose, detailed chemical (major ions and traces) and isotopic study (tritium, radiocarbon, carbon-13, oxygen-18 and deuterium) has been performed on 17 regularly pumped boreholes (Fig. 2). Field parameters including temperature (T°C), specific electrical conductance (SEC), alkalinity, pH, dissolved oxygen (DO), and redox potential (Eh) were measured, as much as possible in anaerobic conditions.

4. RESULTS AND DISCUSSION

Groundwaters in the Vosges to Luxembourg section of the TSA show a wide range of characteristics in terms of physico-chemical parameters and element concentrations.

Groundwater well head temperatures increase from around 10°C in the recharge area to greater than 30°C at depth. There is a good correlation between temperature and well depth, which indicates that the water is derived from the main horizon of the aquifer without leakage from overlying formations. The water electric conductivity varies from 175 to 1289 $\mu S \cdot cm^{-1}$. The reported pH values measured at well head are generally between 6.7 and 8.5 with a median value of 7.3. Many groundwaters contain significant concentration of dissolved oxygen and widely variable Eh values are not always well correlated highlighting the difficulties to measure such parameters. The aquifer seems mostly oxidising with moderately reducing zones without a clear redox boundary; this is probably due to a possible recharge on the two sides of the aquifer.

The results for selected major elements are plotted in a Piper diagram (Fig. 3) for general chemical overview.

The groundwaters in the TSA vary from Ca-HCO$_3$ and Ca-Mg-HCO$_3$ to Na-Cl type. Samples from the northern part (close to Sarre region) are relatively enriched in SO$_4^{2-}$ compared to Cl$^-$ and one of them (Kirschnaumen) is exceptionally of Ca-SO$_4$-HCO$_3$ facies. There is no clear gradual evolution from the outcrop area. A principal component analysis (PCA) was carried out to summarise the relations between chemical variables. The 2 principal axis of PCA explain 69% of the sampling variance. Axis 1 (39%) includes Na$^+$, Cl$^-$, K$^+$, "Distance to recharge area" and temperature to δ^{18}O‰. Axis 2 is defined by Ca^{2+}, SO$_4^{2-}$, HCO$_3^-$ and Mg^{2+}. Two groups of water can be distinguished. Group I have the highest values of the "Distance to recharge area", which suggests a long residence time within the aquifer. These waters have also the highest Na$^+$ and Cl$^-$ contents, which is closely associated with the halite dissolution. Conversely, Group II is characterised by the highest NO$_3^-$ content, which suggest

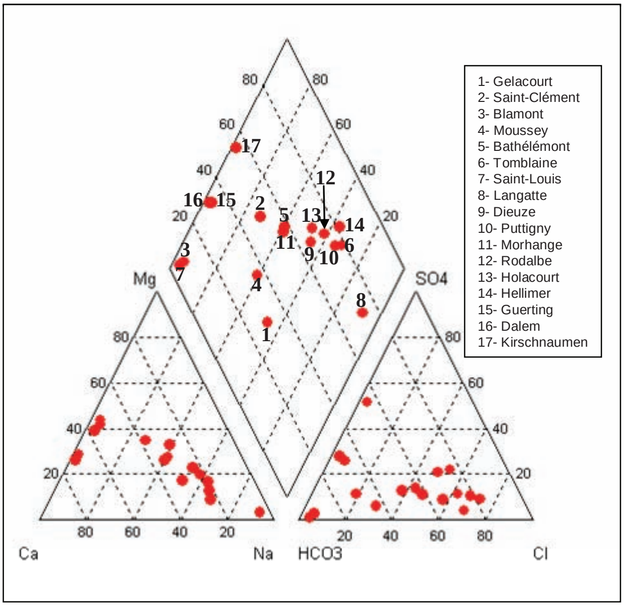


FIG. 3. Piper Diagram for 17 boreholes of the Lower Triassic Sandstones aquifer.

a short residence time within the aquifers and could define an anthropogenic origin. However, Group II also has the highest Ca^{2+}, SO_4^{2-}, HCO_3^- which suggest gypsum dissolution with a possible leakage from the Middle Triassic marls and clays.

Sites have been projected onto a single line following the flow direction from the recharge area in the Vosges Mountains to the Luxembourg border. The well depths or rather the intervals from which the water is derived are between 120 m in the recharge area to over 800 m in the deepest western part of the study area, close to the Nancy-Metz line. The dissolution of calcite and dolomite provide the initial dominant control. Most groundwaters are at or above calcite and dolomite saturation. This may be an effect of the well-head pH measurements not reflecting an equilibrium condition; a decrease of 0.5 pH units due to loss of CO_2 would bring values closer to saturation. The dissolution of gypsum in these waters should also tend to maintain saturation or oversaturation with respect to carbonate minerals. The Mg/Ca ratio is around 0.5 over much of the aquifer with an equilibrium control slightly lower than that expected if both calcite and dolomite are the controls (0.8).

Silica concentrations show a downward gradient. Silica is released rapidly by water-rock interaction with silicate minerals but the upper concentrations are controlled by slower equilibration with silica polymorphs [5]. Groundwaters are all above quartz saturation and exhibit Si concentrations from about 15 to 24 mg/L that are correlated with the distance from the recharge area and thus with residence time. Calculations using PHREEQ-C [6] indicate that all groundwaters are clearly oversaturated with quartz and undersaturated or slightly saturated with chalcedony. This indicates that the formation water temperatures and the prolonged residence times have favoured equilibration with quartz.

Sulphate concentrations are variable, a slight increase from 1 to around 110 mg/L can be noticed from recharge area to Luxembourg. Close to the TSA outcrop area, Kirschnaumen and Dalem boreholes show high sulphate concentrations correlated with high calcium, indicating that preferential gypsum or anhydrite dissolution is taking place particularly in these places. This gypsum or anhydrite dissolution could also occur along the flow line (Rodalbe, Bathélémont). The Guerting sample with high Fe^{2+} concentration, high SO_4^{2-} and low Ca^{2+} shows that pyrite oxidation could also occur. The relatively low pH strengthens this hypothesis.

Chloride may be used as a conservative tracer, representing input concentrations from atmospheric sources (after allowing for evaporative concentration), dissolution of formation evaporates or mixing with entrained formation waters. The Na^+ and Cl^- concentrations range from 1.6 to 301.7 mg/L and from 2.6 to 522 mg/L. These two elements are closely correlated ($R = 0.98$).

This strong correlation can be linked to the halite dissolution. Ca^{2+}, SO_4^{2-}, Cl^- and Na^+ concentrations increase with the distance from the recharge area. This probably implies the participation of evaporitic deposits in the covering formations. In 1980, Salado and Passavy [3] have shown that Permian formations could supply waters enriched in Cl^- and Na^+ with moderate concentrations in Ca^{2+} and SO_4^{2-}. The authors indicated that covering formations supply waters enriched in Na^+, Cl^- but also Ca^{2+} and SO_4^{2-}. Potassium shows a steady increase across the aquifer which takes place in close relation with Cl^- as shown by the K/Cl ratio. The K^+ increase is likely to be linked to Triassic evaporate dissolution as suggested by the Cl–K correlation. The downgradient evolution of several minor and trace elements (Ba, Sr, Li, Rb, Sc, Ce, Mo, Se) suggest that they are indicators of residence time along the main flow line.

Ancient and new isotope data clearly discriminate present and recent water (Group II) from older Pleistocene waters (Group I) as shown on Fig. 4.

Some evolutions can be seen between 1979 and 2001. Boreholes located near the recharge area (Gelacourt, Langatte) supply waters from the upper part of the aquifer and show a decrease of the global mineralization. The other boreholes and especially deeper ones are characterised by an increase of their overall mineralization. This is mainly due to Na^+ and Cl^- and implied dissolution of halite or mixing with more mineralized water. The increase in the residence time is strengthened by the ^{14}C corrected ages calculated by Fontes and Garnier [7] model. The isotopic data show that deep boreholes encounter Pleistocene waters that could circulate in the deeper confined parts of aquifer. The 2001 data analysed for Tomblaine, Puttigny and Morhange, three of the deepest water catchments of the TSA, and show increase of about 20 000 years compared to 1979s values. However, if a global tendency is observed, the

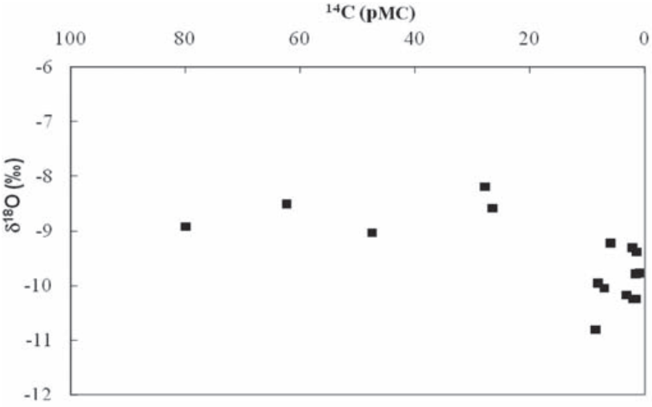


FIG. 4. $\delta^{18}O$ versus radiocarbon activity in the TSA.

ranges of chemical variations are not directly correlated with the water ageing highlighting the role of lithology and structure (closeness of the border layers).

Tritium contents indicate modern recharge in the shallow levels of northern area in good agreement with NO_3^- contents, and some mixing with older water. Due to the combined effects of mixing and possible reduction, nitrates generally decrease from the outcrop area. A few points show low NO_3^- concentrations that can be explained by mixing with middle and upper Triassic levels because of low quality well casing. The comparison between the two field campaigns shows a general increase of the nitrates for most of the boreholes to anthropogenic effects. But, the lack of significant variations in stable isotope composition, show that up to now there is no significant mixing between deep Pleistocene and Holocene and recent groundwaters.

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ASSESSMENT OF GROUNDWATER RESOURCES ON LA DIGUE ISLAND IN THE REPUBLIC OF SEYCHELLES

A study proposal

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Abstract

The objective of the study is to determine the groundwater potential of La Digue Island in the Seychelles Archipelago by mapping out the total extent of the aquifer available for abstraction of fresh water and estimating the recharge to the aquifer, including possible recharge enhancement, thereby estimating the safe yield of the resource. The proposed methodology to achieve the above task is discussed including the use of isotopic signature related to the precipitation inputs and their tracing through the aquifer. Moreover, the previous studies on the same plateau and similar areas are reviewed in order to identify the information gaps and thus, the required additional studies that can be proposed to evaluate the impact of sea water intrusion with or without artificial recharge to the aquifer in relation to various water abstraction scenarios. All possible contamination sources due to the human activities are examined from the available water quality data.

1. INTRODUCTION

The Republic of Seychelles is an archipelago of 116 islands scattered over 1.3 million km^2 of sea in the middle of the Western Indian Ocean, north of Madagascar between latitudes 3° and 11° South and longitudes 46° and 56° East. La Digue is the fourth largest island in the archipelago located at latitude 4° 20’ 60” S and longitude 55° 49’ 60” E. It is the third most populated island, with a population of about 2,500 inhabitants, mostly concentrated around the plateau.

The island has an aerial extent of 14 km^2 and its “Granatic Ridge” extends from North to South (with a maximum elevation of 333 m.a.s.l.). The oval shaped plateau in the West (1.87 km^2) comprises an aquifer consisting of quartz sand and gravels as part of alluvial deposits from six small rivers. The deposits are covered with calcareous sand and a gravel top layer, which is less permeable due to the existence of a clay crust and cementation. The total depth of the aquifer units vary from 12.5 to 17.5 m. The boundaries of the aquifer system are well defined by six streams, connected to the major river which constitutes the eastern boundary of the plateau. The major stream flows to the sea from the south and north ends of the plateau. The area lends itself to proper scientific investigations because it can be hydrogeologically characterized. The unconfined aquifer can be developed as an underground storage reservoir, taking into account risk management measures from possible contamination due to the quality of water from artificial recharge.

The main economic activity is tourism, while domestic agriculture occupies a second place. Much of the plateau is covered by coconut groves while 11.4 ha of land is utilised for the cultivation of vegetables at L’Union Estate in the south. A large swampy area (14 ha) along the western and southern boundaries of the plateau, drains to the sea at the south corner of the plateau. The area bordering this swamp is subject to flooding during the rainy season.

La Digue largely depends on groundwater for its water supply, especially during the dry season. Groundwater and surface water sources are easily polluted by human activities and faulty septic tanks which pose a major health hazard for the island. In the absence of a centralised sewer system, septic tanks are used to contain and treat sewage. The only primary treatment is accomplished within the tanks, and the effluent that is released from the tank undergoes between 30%–40% of BOD removal and 60% suspended solid removal. During the rainy season, when water table rises, many soakways become flooded and overflow of septic tanks is a common occurrence.

The present demand for drinking water in La Digue stands at 800 m^3/day. The present estimated demands for agricultural and livestock are respectively about 815 m^3/day and 10 m^3/day. Until the desalination plant was commissioned in 2003, groundwater was the major source of water supply during the dry season, when surface water resources are considerably depleted. However, a desalination plant is an expensive option and during the few years of its operation the high maintenance and operation costs have raised questions about its long-term sustainability. The projected demand for potable water in La Digue by the year 2025 is about 2000 m^3/day. The agricultural and livestock demand will be reduced to 440 m^3/day, due to the anticipated reduction of cropping land to about 6 ha. If sufficient groundwater resources can be identified, it could be a cost effective solution to meet the increased water demand and could delay the implementation of more technology-intensive solutions such as desalination.

The Public Utilities Corporation (PUC) needs to overcome the following challenges in providing service to the residents. Firstly, it is necessary to quantify and assess the quality of the water resources in La Digue, so that various management options that are economically viable can be pursued. The options include surface water, groundwater including artificial recharge, rainwater harvesting, desalination option of using brackish groundwater instead of seawater and reuse of wastewater for agriculture (L'Union Estate and Farmers). While the supply side management is being pursued, demand side management will also be vigorously explored by PUC, because of the limited amount of freshwater that is available in the Island.

Secondly PUC has to address the water quality issues such as limiting groundwater abstraction to avoid saltwater intrusion, reducing possible contamination due to anthropogenic activities, and addressing other water quality issues related to odour (H_2S as a result of sulphate reduction under reducing conditions, probably to high organic matter content) and hardness (due to the contact of groundwater with calcareous material).

Finally, the aquifer should be developed as an underground reservoir with an integrated perspective that links recharge ponds to tourism activities in the Seychelles. Furthermore, the long term sustainability of these water projects will be given strong emphasis, such as availability of human capacity to run and maintain the infrastructure. A case in point is the proper management and maintenance of the small water treatment plant including the desalination plant and infrastructure by employees from La Digue.

2. PREVIOUS STUDIES, AVAILABLE DATA AND LITERATURE REVIEW

An assessment of available groundwater resources of Seychelles with recommendations for their development was compiled by D.K. Buckley in 1974. Afterwards, groundwater investigations were carried out by the Institute of Hydrology- Wallingford, Oxon UK for the selected plateaus in the Republic of Seychelles. Moreover, the Public Utilities Corporation carried out the water resources evaluation for the La Digue Water Supply Development in 1987.

The physical observation of rock outcrops, soil and excavated ditches, and the review of the literature of previous studies on La Digue Island of Seychelles Archipelago strongly indicated that there are three types of soils and one type of rock in the plateau [1].

Along the coastline, calcareous sand which is often inter-layered with shell fragments and coral pieces is visible. This unit most likely represents the debris washed up and on to the shore by wave and wind action. On the plateau in areas up to altitudes of 5 m, the main type of soil usually found is calcareous, sandy soil. This type of soil is made up of about 80% of coarse sand and is low in chemical fertility and organic matter. It is highly permeable and lacks any structure. Being calcareous, the pH of this type of soil usually ranges from 7.5 to 8.4. This usually leads to low levels of assimilable phosphate, low assimilation of iron by plants leading to chlorosis, and calcium antagonism towards magnesium and potassium.

The second type of the soil which is visible along the granitic boundary of the plateau comprises of quartzite sand and gravel. The minerals present are mainly quartz with some mica and feldspar. This unit is derived from the weathering process of the hill above the plateau and subsequently brought down by the waterways and deposited in the plateau as alluvial sediments.

The third category of soil is decomposed formation of the granitic bed rock which consists of impermeable clay.

Eleven boreholes drilled during the previous investigations provide information about the extent of the fresh water aquifer on the coastal plateau. The aquifer varies in thickness from 12.5 to 17.5 meters and it is an unconfined aquifer that is composed of calcareous sands and gravels.

Pumping tests carried out in 1978 revealed that close to the central region of the plateau, towards the seaward side, transmissivities average 540 m^2/day, and in the hillside average 800 m^2/day. However recorded values in the northern and southern regions are 850 and 1030 m^2/day, respectively. The data are compiled in a published report [2]. An attempt was made to verify the transmisivity values and specific yield by comparing the time lag of peak water level of a borehole with tidal fluctuations.

Furthermore, a pumping test programme was carried out in 1987 for longer duration (more than 1000 min) by PUC and the transmissivities obtained averaged 750, 525 and 300 m^2/day for the northern, central and southern regions, respectively. The highest transmissivities were found in regions with the largest deposits of quartz sand and gravel. The complete data on these tests were also compiled [1]. The estimated specific yield of the unconfined aquifer is 0.1 and this figure agrees with the 1978 study.

However, there is a disparity in the transmissivity values of boreholes in both studies. This disparity could be resolved by using low cost testing techniques, such as the seismic method.

Groundwater quality and the concentration of major ions were measured in 1978. In certain boreholes iron, hydrogen sulphide and fluoride concentrations were marginally higher than the WHO standards. Conductivity profiles were obtained in a number of boreholes to evaluate the aquifer thickness containing potable water and the transition zone from fresh water to saline water. Although the conclusion was made in both studies that the length of the intruded saline wedge is estimated to be between 300–400 m, it is necessary to carry out electricity conductivity (EC), temperature and depth surveys, especially at proposed series of new boreholes about 150 m away from the shoreline.

Apart from the above studies, the "Water and Sewerage Division of the Public Utilities Corporation" which also functions as the National Hydrological Service has maintained the rainfall gauging station at La Digue Pumping Station since 1988. The rain gauge station at La Passe was discontinued in the year 2000. However the rainfall data is available from 1970. The ground water level at the treatment plant is measured twice a day. Moreover the water levels of the other existing boreholes are measured once a week. PUC was planning to setup a compete meteorological station at La Digue. However, the equipments were purchased only to measure precipitation and evaporation.

The last study was carried out in 1987 and it was recommended that groundwater abstraction at L'Union Estate should be limited to 242 m^3/day. The predicted demand for potable water at that time was 400 m^3/day and it was met with the combination of groundwater abstraction and surface water.

During the last twenty years, the situation has changed. The present demand for potable water has increased up to 800 m^3/day and with a further increase of up to 2000 m^3/day by the year 2025 apart from the agricultural needs. Additionally the desalination plant with the maximum capacity of about 300 m^3/day was added to the system and in the absence of proper wastewater treatment system; the quality of groundwater may have degraded. The economic growth of this small island can be attained only through the sustainable management of water resources.

Sophocleus [3] concluded that to turn the principles of sustainable development into achievable policies, solutions must be based on fundamentally sound hydrological analyses and technologies. This entails accurate assessment of research areas for artificial recharge in relation to salt water intrusion under various pumping rate scenarios.

A few mathematical approaches have been developed for solving the combined equations of salt and fresh water flow and transport in aquifers. The most general one considers the fluid as the one of variable density, depending on the salt concentration. The resulting system of equations takes into account Darcy's law, conservation of mass and the transport of salt, salt being the solute. The variable-density approach is one of great numerical complexity, facing difficulties in modelling the transition zone of high concentration gradient. The alternative approach that assumed a sharp interface between the salt wedge and the freshwater lens is simpler to handle numerically. One such solution approach, which is based on the boundary integral method, is presented in [4].

On the other hand, hydrochemical and isotope tools are expected to provide additional information on groundwater origin, dynamics and interconnection processes between different water bodies in the Island. Hydrogen and oxygen isotopes in the water molecules constitute excellent and useful tracers for understanding research on key aspects of groundwater, relevant to its management. The natural isotope fractionation in the water cycle provides invaluable clues about hydrological interaction between precipitation, surface waters, vegetation cover, sub-surface recharge and deeper groundwater [5-6]. Additionally the risk of seawater intrusion or other mechanisms of salinization, due to inadequate distribution of the groundwater extraction points or other causes, will be addressed in the study.

3. METHODOLOGY.

As part of the proposed project, the following hydrogeological studies and activities will be carried out in the next years:

The aquifer geometry will be better defined through out the plateau by using geophysical methods, such as the seismic or resistivity methods. This information will also help to evaluate the extent of the different sedimentary units, their transmissivities and the respective Darcy velocities.

The necessary field equipment will be purchased and the water quality sampling at boreholes will be evaluated to assess the extent of groundwater pollution due to human activities. A surface infiltration study will be carried out to obtain additional information on natural recharge due to the precipitation above the plateau, and a complete meteorological station will be set up at the water treatment plant on La Digue.

New boreholes will be constructed about 150 m away from the shoreline. The electrical conductivity and temperature profiles will be obtained in the new boreholes. This data will be used to assess the position of the seawater-groundwater interface and the extent of seawater intrusion. The tidal fluctuation and the respective time lag will be recorded in those new boreholes in order to estimate transmissivities and the storage coefficient of the coastal sectors of the aquifer.

The pumping data of the previous studies will be reviewed and if required, additional pumping tests will be carried out.

The isotopic signature of precipitation and groundwater recharge will be determined (in shallow boreholes) and their tracing through the aquifer will be used to evaluate the groundwater dynamics, the recharge processes, groundwater flow patterns and other possible characteristic of the unconfined aquifer.

By filling the information gap, the aquifer will be modelled for various pumping rate scenarios and feasible artificial recharge. This will include the possible reuse of treated waste water from the proposed central sewerage scheme for agricultural demand of L'Union Estate and reduction of the operational costs of the desalination plant by using brackish groundwater. If the use of treated waste water is a viable option, the contaminant transport will be modelled at L'Union Estate, ensuring that prominence is given to the protection of the environment.

Moreover, the possible contamination due to the human activities will be accessed and the recommendation will be made to remedy the situation.

PUC staff will be trained as part of the process to ensure the required level of local expertise in managing water resources, use of hydrochemical and isotope tools and continue/upgrade the established groundwater monitoring programme in the La Dingue Island, so that self reliance in terms of capacity building is achieved.

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THE ^{14}C NATURAL ISOTOPE AS A TOOL FOR MONITORING OF GROUNDWATER EXPLOITATION

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Abstract

The ^{14}C natural isotope has been used to monitored exploitation effects within a 10 year interval between 1995 to 2005 in Bontang groundwater basing east Borneo-Indonesia. Exploitation of the groundwater of Bontang basin has occurred since 1981 and at the present the groundwater abstraction for Bontang basin is about 59,000 m^3/day to fulfill the necessity of liquid natural gas and fertilizer industries from more than 20 wells. Isotope investigation of the groundwater Bontang basin have been done through water sources sampling like rivers, cold spring deep wells sea water and rain water in 1995 and 2005. The ^{18}O and D isotope data show that deep groundwater originates from local rain water that infiltrates through the slope of mount Lobang Batik. Along the hilly slope zone, it is layed by the sedimentary Kampung Baru Formation. There is no indication that the Mahakam river water infiltrates and sea water intrusion to the deep groundwater. The ^{14}C of isotope data from deep wells show that the average age of 4 wells with distance 2–3 km located from the outcrop of Kampung Baru in 1995 is about 2300 a. There is a decrease of groundwater age since exploitation to around 500 a. Decreasing of groundwater age is possible due to mixing with recent recharge through the Kampung Baru formation.

1. INTRODUCTION

The groundwater of Bontang basin is the biggest water source in east Borneo. More than 40 wells with depth of 200 m to 300 m drilled 20 ago and have a capacity 30,000 to 50,000 m^3/day. The groundwater abstraction is mainly

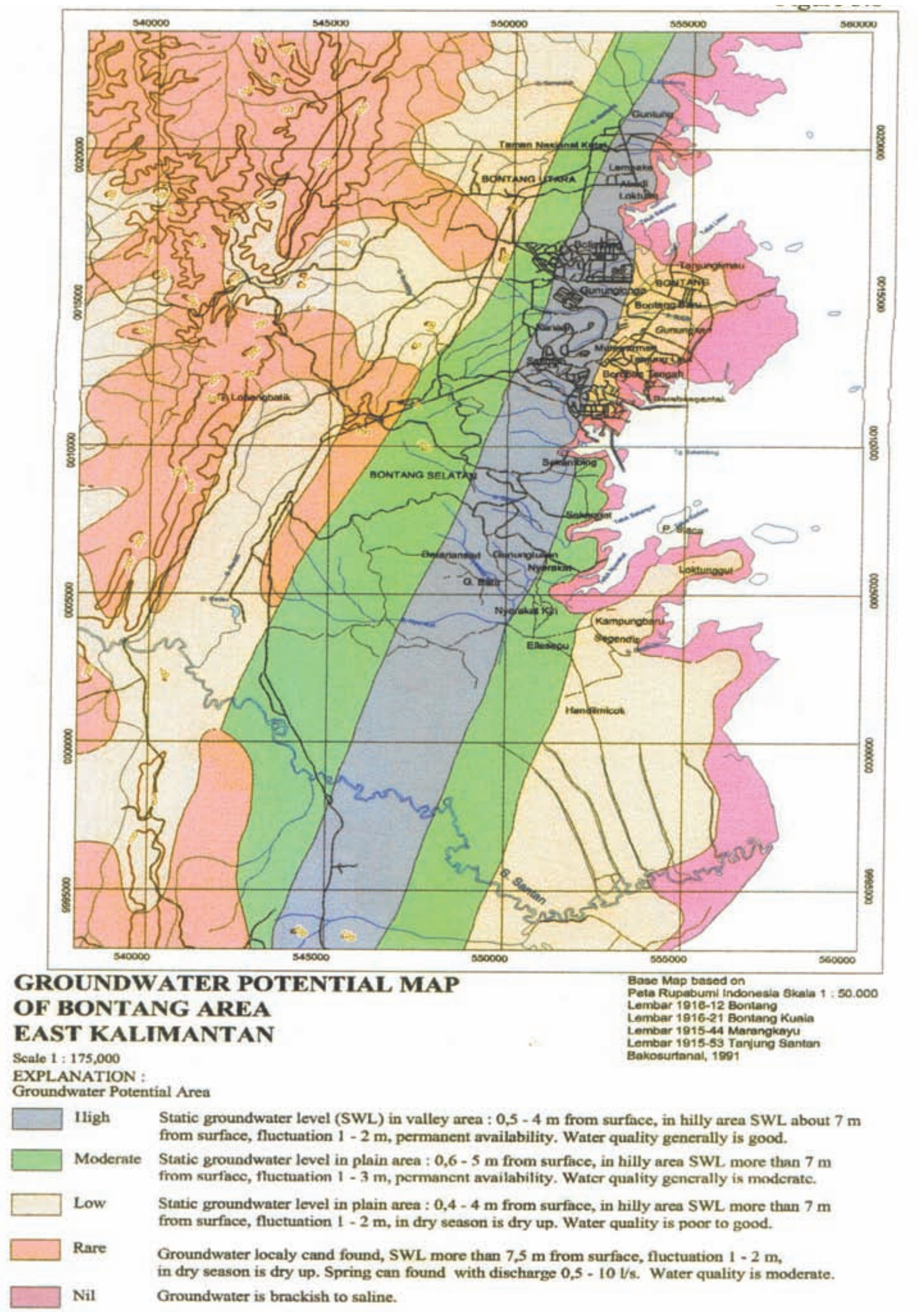

FIG. 1. Hydrogeology map of studied area.

FIG. 2. Sampling location for isotopes analysis in studied area.

used for utilized by petroleum industries (Gas liquefaction and fertilizer) and for municipal drinking water purposes.

Isotope nvestigations during a ten year interval (1995–2005) has been done to determine the origin of water, changes in the water and the effect of intrusion of sea water due to exploitation. Investigation was done by taking samples of various of kinds of water like groundwater, cold spring, river water, rain water and sea water for analysis of isotopes ^{18}O, ^{2}H and ^{14}C in 1995 and 2005. During both investigations analysis of samples were done by the same method, for isotopes ^{18}O and ^{2}H were analyses by equilibrium $CO_2 - H_2O$

and reaction Zn with H_2O. The ^{14}C analyses was done by benzene synthesis. The isotope technique in this investigation will help the decision maker in the region how to manage groundwater exploitation in order to sustain sources for economic development in the future.

2. GEOLOGY AND HYDROGEOLOGY

The geological structure found in the area of investigation is folding structure type that form anticline, syncline, joints and faults. This structure is occurred the beginning to late tertiary age. Based on geology, rock formations in the Bontang basin can be classified in to six types. In terms of stratigrafic sequence starting the oldest to the youngest age is as follows; Pemaluan formation, Bebulu formation, Pulubalang formation, Balikpapan formation, Kampung Baru formation. The youngest is Colluvium and Alluvium sediment. Rainfall to this area directly infiltrates into the outcrop of Kampung Baru formation especially into the sand formation. The sources of groundwater in Bontang consist of three different aquifers, top aquifer having a tickness 10–15 m and a transmitvity (T) of 18.8–180 m^2/day, middle aquifer having tickness 200–300 m and T is 108–1238 m^2/day and bottom aquifer with a tickness of 10–25 m. Hydrogeology map of the Bontang groundwater basin shown in Fig. 1 bellow.

3. METHODS

3.1. Sampling

Sampling strategy in investigation for ^{18}O, D and ^{14}C isotopes analysis is done by sampling various water sources like, well bore, river, sea water and rain water during 1995 and 2005 at the same location. Sampling location is illustrated in Fig 2. below. Water sampling for ^{18}O and D were taken in all kind of water for different and the origin of water in study area.

3.2. Analysis

Isotope ^{18}O and D analysis is done by mass spectrometer through pretreatment chemical reaction equilibrium H_2O and CO_2 gas for ^{18}O analysis and reaction H_2O and Zn (shot) at 450°C in vacuum condition for D analysis. Isotope ^{14}C analysis is done by benzene synthesis method and counting by liquid scintillation counter

4. RESULT AND DISCUSSION

4.1. Origin Recharge Area of Groundwater

Data analysis of ^{18}O, D and ^{14}C isotopes in groundwater of Bontang and its surrounding area is given in table 1. The average concentration of ^{18}O and D isotopes in the groundwater are –9.61 ± 0.086‰ and –51.7 ± 0.76‰, respectively. This reveals that the groundwater in Bontang area are originated from a relatively same recharge area, which is represented by DW-3 in Kanaan

TABLE 1. DATA ANALYSIS OF ^{18}O, D, ^{14}C ISOTOPES AND CHLORIDE.

Location	^{18}O (‰)	D (‰)	Age in 1995 (year)	Age in 2005 (year)	Cl^- (mg/L)
WW–10 (well)	–9.52	–51.4	1681	444	
WW–11 (well)	–9.63	–52.3	2263	2170	
WW–12 (well)	–9.65	–52.1	2698	2600	
WW–15 (well)	–9.72	–52.5	2561	1950	
WW–16 (well)	–9.78	–52.7	–	1170	
BG–33 (well)	–9.53	–51.0	–	–	
BG–34 (well)	–9.6	–51.8	–	2650	
BG–20 (well)	–9.65	–52.6	–	–	
BG–35 (well)	–9.5	–50.8	–	–	
KNA–3 (well)	–9.62	–51.6	–	< 90	
BG–18 (well)	–9.51	–50.3		2055	
BG–24 (well)	–9.63	–51.7	–	500	
Artesian well	–9.71	–53.0	–	550	
Sekambing housing complex	–9.66	–52.4	–	–	
Samarinda (river water)	–10.3	–57.5			45
Delta (river water)	–10.11	–57			89
Andil (river water)	–9.8	–56.2			467
River mouth	–9.1	–52.4			2224
Bontang sea	-1.4	5			15779.5

(owned by PDAM). Its concentrations of ^{18}O and D isotopes were –9.62 ‰ and –51.6 ‰, respectively, which will be used as a benchmark. The value of isotope groundwater concentration in recharge area (Kanaan) is almost the same as the average value for isotope concentration in groundwater of Bontang area. Fig. 3 shows the isotope composition of the water sources in Bontang area.

From point of view of geology and hydrogeology, it is revealed that the recharge area of the groundwater in Bontang (PT. Badak) is located on the west at about 3 to 4 km from well bore location. Isotope data given in Table 1, as mentioned above, consist of more than 12 water wells obtained from the depth of 100–200 m. They have a relatively same concentration of isotopes ^{18}O and D. The contour of isotope ^{14}C as shown in Fig. 4 and 5 reveals that the groundwater is moving from west to east. This movement corresponds to the age of the groundwater showing that the well water in western area is relatively younger than that of eastern area. Therefore, it is clear that the groundwater for Bontang is dominated by water originated from western area (recharge area), which is the outcrop area of Kampungbaru formation.

4.2. Seawater Intrusion

Data analysis of groundwater and seawater isotopes, as shown in Table 1, indicate a significant difference. However, further study is required

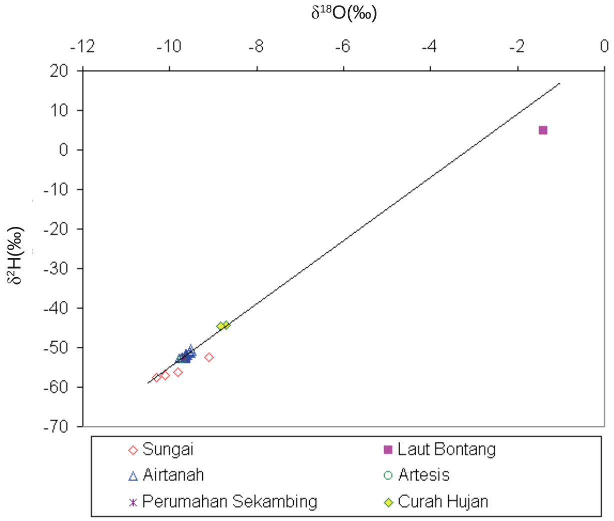

FIG. 3. Data analysis of ^{18}O and D isotopes in the groundwater of Bontang area.

to investigate any probability of seawater intrusion tendency in the aquifer of Bontang area. In general, groundwater exploitation in various places affects to seawater intrusion. For that reason, the data of ^{18}O isotope and chloride can be used to investigate any tendency of seawater intrusion. For example, the tendency of seawater intrusion in Mahakam River can be explained by isotope and ionic chloride data. Seawater in the adjacent area to Bontang, which is used as the reference for seawater isotope and chemical composition, shows an enriched concentration of isotopes ^{18}O and D of –1.4‰ and +5.0 ‰, respectively. Meanwhile, its ionic chloride concentration is about 15,779.5 mg/L. The water of Mahakam River, respectively from its river mouth (estuary) to Samarinda, shows a depleted concentration of isotopes ^{18}O and D. The concentration of ionic chloride is also depleted towards the upstream. The concentration of ionic chloride at Muara Seliki is about 2224 mg/L. To the upstream, the concentrations of ionic chloride are 467, 89, and 45 ppm respectively for Andil, Mahakam Delta, and Samarinda. This condition reveals that seawater intrusion is becoming insignificant at Mahakam Delta to the upstream (on June 2005).The data shows clearly that the groundwater in Bontang (PT. Badak) has been exploited for more than 20 years with no indication of seawater intrusion.

4.3. Groundwater age

Figs. 4 and 5 show the contour of groundwater age in 2005 and 1995. The movement of groundwater given by the contour in 1995 and 2005 show a similar pattern, which is a groundwater movement from west to east. It reveals that the groundwater in the west side is relatively younger than that of the east side. The age of the groundwater given in Fig. 4 and 5 west-east cross section

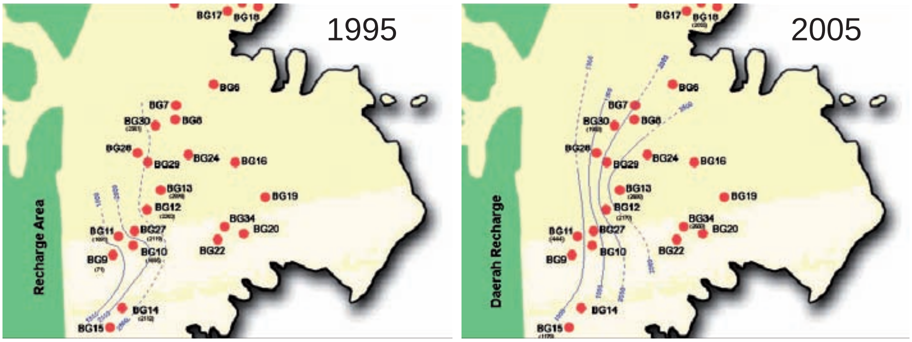

FIG. 4 and 5. Contour of groundwater age in 1995 and 2005.

as represented by WW-10, WW-11, WW-12, and BG-30, shows that WW-10 is located more to the west (in 1995 and also 2005), hence it is relatively younger than WW-11 and WW-12. In the case of WW-7, which has an age of 71 years in 1995 and is predicted to be affected by surface water, an investigation using a bore camera in 2005 reveals that the filter of WW-7 in the depth below 100 m has already clogged. This condition causes a reduced water intake to the well, and the exploited water is dominated by a groundwater originated from a younger groundwater. The similar condition is occurring in WW-10. Data analysis reveals that the age of the groundwater is reduced from 1681 years in 1995 to become 440 years in 2005.

According to the age analysis of groundwater in 1995 and 2005, in general there is no significant age reduction. The reduction of groundwater age is ranging from 50 to 100 years. Except for WW-15 which is currently managed by PDAM, it has age reduction of 500 years and WW10 as mentioned above. Those facts show that the system of groundwater exploitation has not yet interferedwith aquifer in Bontang area.

5. CONCLUSIONS

(1) The age of well water in 2005 tend to be younger compared to the results of 1995 investigation which shows reduced age of groundwater ranging from 200 to 500 years per ten year period. It is predicted that the groundwater deposit will last more than 50 years under the current abstraction in Bontang basin.

(2) The groundwater origin is from meteoric water, there is no mixing with river water and sea water intrusion indication.

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ASSESSMENT OF VIABILITY OF EXPLOITING ARTESIAN AQUIFERS FOR MUNICIPAL WATER SUPPLY IN PARTS OF SOUTH-EAST NIGERIA USING ISOTOPE TECHNIQUES

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Abstract

The steady growth in Nigeria's population, now about 140 million, and the continuing relocation of many citizens from rural to urban areas in pursuit of higher education and employment opportunities have placed considerable stress on social infrastructures particularly water supply in most of the state capitals.

In parts of the Middle Belt and South East, artesian flows have been encountered in boreholes tapping the False bedded Ajali Sandstone and Upper Coal Measures geological formations. The IAEA sponsored TC Project No. NIR/8/007: "Isotope-based Investigation of Groundwater in the Middle-Belt and South East" seeks to evaluate the source, recharge and hydrochemistry of these artesian aquifers through study of their hydro-geological setting, hydraulic and hydro-chemical parameters and isotopic compositions of the source water.

A inventory of most of the existing artesian boreholes has been completed. Thirty-three (33) water samples have been collected from surface and groundwater sources including artesian and non-artesian boreholes at varying depths, for isotopic and hydro-chemical analysis, which results, when available would be interpreted and discussed in a subsequent paper.

This paper reviews the hydro-geology of the project area and outlines the way the project would progress with emphasis on the role isotope hydrology would play in resolving the sustainability question associated with exploitation of the artesian aquifers for municipal water supply schemes.

It is envisaged that integrated interpretation of isotopic and hydrochemical data to be acquired together with baseline data would provide informed advice to water

resources managers and decision-makers on the viability of planning large scale water supply schemes based on these artesian aquifers.

1. INTRODUCTION

Provision of adequate and potable water to city dwellers has been a daunting task for Water Resources Managers in the country over the years. Drilling of boreholes for water supply schemes through individual, community or Government funding within the Anambra-Imo Hydrological basin, South-East, Nigeria has confirmed the existence of a string of artesian (pressure) aquifers in some parts of the basin. The artesian conditions occur where the False bedded Ajali Sandstone or the Upper Coal Measures of the Nsukka Formation is sandwiched/confined between the two Shale formations, the Imo Shale Group and the Mamu formation. Sub-artesian conditions do occur in places depending on the hydrostatic pressure.

Though the basin is situated in a humid tropical environment where there are some perennial rivers/streams, much of the water needs of the people for domestic and industrial activities are met via borehole water schemes which are preferred to surface water schemes because of the high cost of water supply infrastructures, water treatment facilities and consumables including maintenance problems associated with the latter.

Exploitation of groundwater through sinking of boreholes, where feasible, is therefore a common practice in the region and striking an artesian aquifer gives extra joy in view of apparent savings in pumping costs. There is therefore an overriding desire for large scale water supply schemes to target the artesian aquifers. The gigantic Enugu Water Supply Augmentation Project is one such example. The project which commenced in June 2001 and was completed and commissioned on 7th February 2005, involved construction of a battery of eight (8) artesian boreholes in the Oji area, and water conveyed a distance of 32 kilometers to Enugu city and environs to meet the increasing water demand of the area.

This is against the backdrop of incomplete information on the recharge, regional flow system, origin, age and hydrochemistry of the groundwater of the artesian aquifers.

It has therefore become necessary that isotope techniques be applied to evaluate the entire artesian belt in the region in order to proffer informed advice to Water Resources Managers and Decision Makers who might want to replicate the above scheme elsewhere within the basin. This constitutes the basis of the project on “Investigation of Groundwater in the Middle Belt and South East, Using Isotope Techniques”, being implemented by the Federal

Ministry of Water Resources under technical cooperation program with the International Atomic Energy Agency (IAEA).

The project objectives include:

- Establishment of database on the geological structure and hydro-lithological units including hydrological, hydro-chemical and aquifer parameters as well as isotopic compositions of groundwater from the aquifers where the free flows issue.
- Integrated interpretation of the data with a view to facilitating determination of the extent and age of groundwater in the artesian aquifers, its origin, flow rate, rate of recharge, mixing processes (interconnectivity) and assessment of the vulnerability of the groundwater to pollution.
- To proffer informed advice to water resources managers from the research findings, on the viability status of water supply from the artesian aquifers.
- To provide opportunity to further develop local expertise in the application of isotope techniques in the development and management of water resources in Nigeria.

Results of the project would ensure sustainable development and management of the artesian aquifers and consequently ameliorate the problem of water shortage for domestic, agricultural and industrial uses, prevent incidence of water borne diseases, alleviate poverty and improve the socio-economic well being of the people.

2. CLIMATE, GEOLOGY AND HYDROGEOLOGY SETTING

The project area is about 25,000 km^2 and covers parts of the contiguous States of Kogi, Enugu, Anambra and Imo with aggregate population of about 14.653 million. Much of the area is situated within the Anambra River basin which lies approximately between longitudes 6°30′E and 7°30′E and latitudes 6°00′N and 8°00′N. The Anambra River together with its tributaries, the Mama and Adada Rivers constitute the major drainage system and empty their waters into the River Niger which defines the western boundary of the basin. The Udi-Nsukka-Idah escarpment separates the basin from the Cross River Basin to the east.

The climate is hot and humid with two distinct seasons, the wet season which lasts from April to October and the dry season prevails from November to March. The mean annual rainfall ranges from about 1450 mm in the north to 1800 mm to the south of the basin). The vegetation is typically tropical rain forest type with dense vegetation particularly along the banks of rivers and streams, although anthropogenic activities have reduced some of the areas to savanna, thus exposing the soil cover to intense erosion resulting in deeply incised valleys and parched soil in places.

Preliminary investigations of parts of the project area have been undertaken by the Geological Survey of Nigeria [1, 2] and individuals notably [3–7].

The geology of the project area consists in depositional sequence, of the Mamu Formation (Lower Coal Measures), Ajali Sandstone, Nsukka Formation (Upper Coal Measures), Imo Shale, Bende-Ameki Formation (Nanka Sands in places) and Quaternary Alluvium.

The Mamu Formation consists of rapid alteration of fine-medium grained sandstones, shaly sandstones, sand shales, mudstones and carbonaceous shales and coal seams. It has an average thickness of 200 m. The false bedded Sandstone of the Ajali formation which overlies the Mamu consists of thick friable, poorly sorted, medium to coarse grained cross-bedded, highly porous and permeable sandstone. It is the principal water bearing formation and of great area extent with thickness of 400–500 m. It is typically white in colour but sometimes iron-stained.

The Nsukka formation consists of fine-medium grained sandstones, carbonaceous shale, clay, siltstones and bands of impure coal. Eroded remnants of this formation constitute outliers and numerous springs issue out from the flanks of the outliers. Its thickness varies from over 200 m at Aku to a mean of 100 m further south. The basal shale units generally confine the Ajali Sandstone. The Imo Shale Group consists predominantly of thick bluish to grayish shales. It is essentially an aquiclude and boreholes sank over it produce artesian water from the underlying Nsukka formation and the Ajali Sandstone. It is of variable thickness, but could be extremely thick in some places up to 400–1000 m, particularly within the southwestern parts of the Anambra Basin.

The Bende-Ameki formation which overlies the Imo Shale consists of very heterogeneous, fine to coarse sandstones intercalated with calcareous shales and thin shally limestones. The lateral equivalent to the south east is the Nanka Sands which is best developed in Nanka, Agulu, Adazi, Oko and Nnobi areas of Anambra State. It has a thickness of about 300 m and is permeable. Quaternary Alluvial deposits overlie the western parts of the basin close to the River Niger [7].

Under the Enugu Water Supply Augmentation Project, the depth of the 8 artesian boreholes constructed in the Oji area is in the range 110 m–130 m and their total yields is 52,426 m^3/day in December 2004 [8]. Figure 1 shows one of the boreholes discharging freely. The delineation of the string of artesian aquifers within the project area is still a subject of continuing investigation and research.

FIG. 1. An Oji artesian borehole discharging freely.

3. METHODOLOGY

Isotope Hydrology Techniques would be applied complementarily with hydrochemical method in this project. Water samples shall be analyzed for stable isotopes of deuterium (^2H) and oxygen-18 (^{18}O) as well as for radioisotopes of tritium (^3H) and carbon-14 (^{14}C) to provide required information as per the project objectives.

The samples shall be assayed for some of the chemical ions in water namely, sodium (Na), potassium (K), calcium (Ca), magnesium (Mg), iron (Fe), chloride (Cl), flouride (F), sulphate (SO_4), nitrate (NO_3), carbonate (CO_3), bicarbonate (HCO_3). Sampling campaigns shall be conducted on selected water points consisting of boreholes (artesian and non-artesian) and surface water sources. Though preliminary information do not indicate any serious concern for degradation in water quality (except high iron content and low pH reported in some localities), the aim of integrating hydrochemical studies is to provide data for chemical-isotope modeling to enable issues like mixing processes to be determined.

Hydro-chemical data relating to physical parameters of water samples namely temperature (°C), pH, electrical conductivity ($\mu S \cdot cm^{-1}$), total dissolved solids (mg/L), salinity (mg/L) and dissolved oxygen (DO), shall be conducted in-situ during sampling campaigns..

Vital parameters that are missing in the baseline data collected so far would be filled through actual measurements in the field. They include geographical coordinates, total depth of borehole, formations tapped by respective boreholes, static water levels in phreatic aquifers and current discharge rates in both artesian and pumping boreholes.

Surface geophysical survey may also be applied to further define the structural trends and litho-stratigraphic units in the area.

The discharge performance of the 8 boreholes at Oji area being used for the Enugu Water Project would be monitored during the course of this project. In the meantime, the respective discharges of the boreholes between December 2001 and January 2003 have been presented in Figure 2. Long term monitoring is required in order to confirm whether there is progressive reduction in free flow yields and the rate of such decline, if any.

4. CONCLUSION

Considering that baseline data has been collected and missing parameters would be acquired during subsequent field work, the project would progress swiftly as the problem relating to isotope analysis of the samples gets resolved shortly as envisaged.

The project findings would provide invaluable information for sustainable exploitation of the artesian aquifers and further confirm the emergence

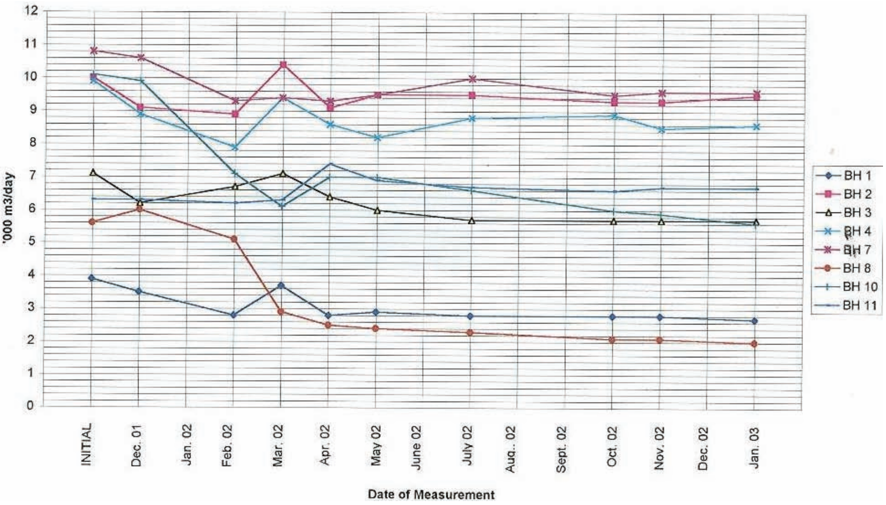

FIG. 2. Borehole yield measurements.

of isotope hydrology techniques as a vital tool in the management of water resources in Nigeria.

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ISOTOPE RESPONSE OF HYDROLOGICAL SYSTEMS TO LONG-TERM EXPLOITATION IN THE SINGEN AQUIFER SYSTEM, GERMANY

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Abstract

This study demonstrates the use of isotope tracers as a tool for monitoring groundwater resources, their depletion and recovery due to a phase of over-exploitation. It is based on spatial hydro-geological data of a Quaternary basin, a three dimensional numerical groundwater flow model and detailed hydraulic, hydro-chemical and isotope records over a period of more than 30 years at selected major production wells.

Hydro-chemical data and tritium values have been used to comprehend the complex flow system throughout this period of exploitation. Tritium values in groundwater samples are influenced by the temporal tritium input function in precipitation, radioactive decay or residence time as well as by the mixing portion of various groundwater components due to exploitation. The mixing portions of groundwater components were dramatically changed by groundwater abstraction, especially during over-exploitation in the late 1960s and early 1970s. The long-term tritium record (1969–2001) demonstrates this change for the central part of the aquifer system where main discharge took and takes place. Various snapshots of calculated mean residence times prove increased flow dynamics in the system during the period of over-exploitation and the recovery of the system due to a more sustainable groundwater management.

The combination of various investigation methods applied here resulted in a profound understanding of the flow and transport conditions within the studied groundwater reservoir under transient flow conditions over a time scale of more than three decades.

The experience of a shallow, fast responding aquifer system, is an encouragement for groundwater managers and experts dealing with (strongly) exploited aquifer systems to use isotope tracer techniques for monitoring purposes and to find adjustment of exploitation to sustainability.

1. INTRODUCTION

The city of Singen at the north-western border of Lake Constance (South Germany, Figure 1), is situated within the water protection area of the city's drinking water supply. The well studied groundwater reservoir has also been tapped by private companies for large quantities of drinking and industrial water (Fig. 2) form the early 20th century to present. Over this period the commercial and industrial use of large areas was competing with the established protective measures for the drinking water supply. Due to the mutual impact of the municipal and private groundwater abstraction facilities and hydrogeological conditions, groundwater quantity and quality was affected by anthropogenic contaminant inputs for several decades. To maintain quality and quantity of this drinking water reservoir, it was recommended to the operators of water supply facilities to conduct geological, hydraulic, hydrochemical and isotope tracer investigation covering the whole aquifer system. The results of these comprehensive and detailed investigations were used to establish a management plan for the water supply and to adjust groundwater abstraction by use of a numerical groundwater flow model.

2. GEOLOGICAL AND HYDROGEOLOGICAL SITUATION

The investigation area is situated in the region of the Pleistocene western Rhine Glacier, which originated in the central Alpine ridge and caused several foreland glaciations. As a result, deep basin structures and channels were eroded into the Tertiary beds. During the latest Quaternary period, these basin structures were filled with sediments. The Singen basin (25.6 km^2) is one of these basins. Significant aquifers exist within the Quaternary sediment layers and in the Jurassic beds underlying the Tertiary Molasse sediments.

Inside the investigation area three aquifers exist within the Quaternary basin sediments. Highly permeable sediments bodies within the basin complex are clustered to three aquifers, confining layers and vertical aquifer connections by hydraulic windows. The resulting information has led to a hydrogeological five-layer-model of the Quaternary basin fill. The five layers differ with respect to their spatial distribution, thickness, petrography, and hydraulic conductivity.

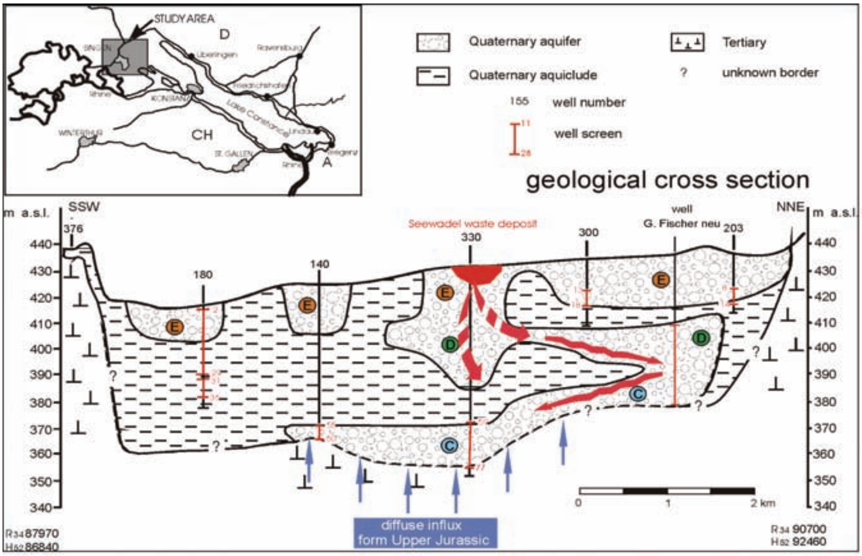

Fig. 1. Map of the study area, geological cross section and flow of seepage waters.

The thickness of the Quaternary sediment fill ranges from 10 to 80 m. Depending on the lithological composition and the results of hydraulic tests representative values for hydraulic conductivity and storage coefficient can be assigned to different types of sediments. Hydraulic conductivity (*kf*) in the gravel beds ranges from 1.0×10^{-4} m/s to 3.0×10^{-3} m/s and in the siltstones, marls, fine sands and diamictons of the aquicludes (Quaternary fines and Tertiary Molasse sediments) from 1.0×10^{-7} m/s to 1.0×10^{-5} m/s.

In areas with a partial absence of the low permeable confining layers, the aquifer are connected vertically by hydraulic windows. Groundwater flow within the individual aquifers is more or less horizontal. Groundwater flow over the hydraulic windows has a decisive impact on water circulation in the system and makes it completely 3-dimensional. Due to large windows between the bottom aquifer C and the central aquifer D their hydraulic heads are equalized and look different from the unconfined water table in the upper aquifer (E). This results in two groundwater storeys (E and CD) in the Quaternary sediments.

The hydraulic connectivity between the two groundwater storeys of the groundwater reservoir can be determined directly from the two contour line maps of hydraulic head (Fig. 2). All hydraulic windows in the western and north-eastern part of the basin show a downward water flux into the deeper storey CD. Only the hydraulic window in the south-eastern part of the basin is

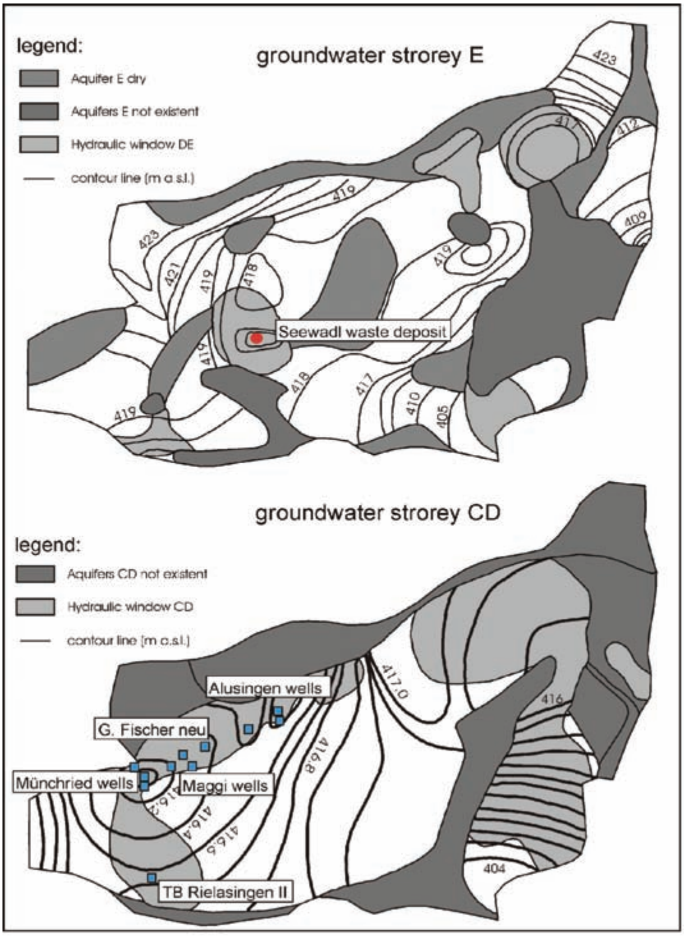

FIG. 2. Contour maps of groundwater storeys E and CD (present situation) location of Seewadel waste disposal site and discharge facilities.

an area of upward water flux feeding the upper aquifer E (Fig. 2). Water table fluctuations lead to dry areas in unconfined aquifer E. Today the thickness of the unconfined aquifer ranges between 0 and 20 m and shows seasonal fluctuations from 0.5 to 1.5 m. The bulk mass of water in the reservoir can be estimated using the saturated aquifer volume times the porosity to a total of 145 million m^3 at present.

Positive balance terms of the groundwater budget are recharge from precipitation, influx from adjacent Molasse ridges and river bank filtration. These components enter the system through aquifer E. Additionally, there

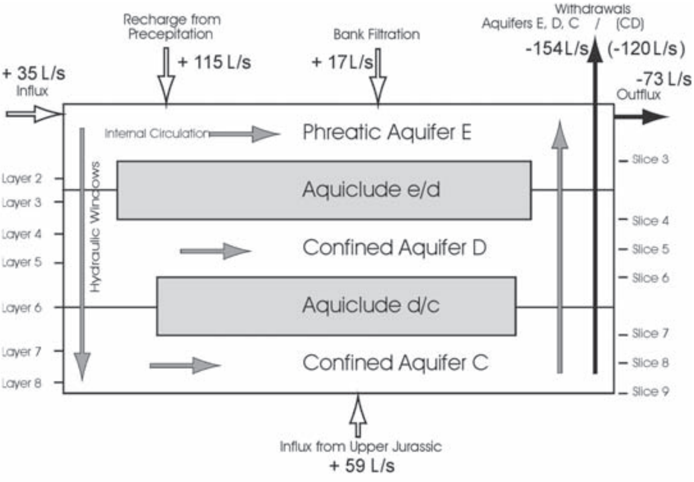

FIG. 3. Basic model of the aquifer systems in Quaternary sediments and mean balance terms of steady-state groundwater budget (present situation).

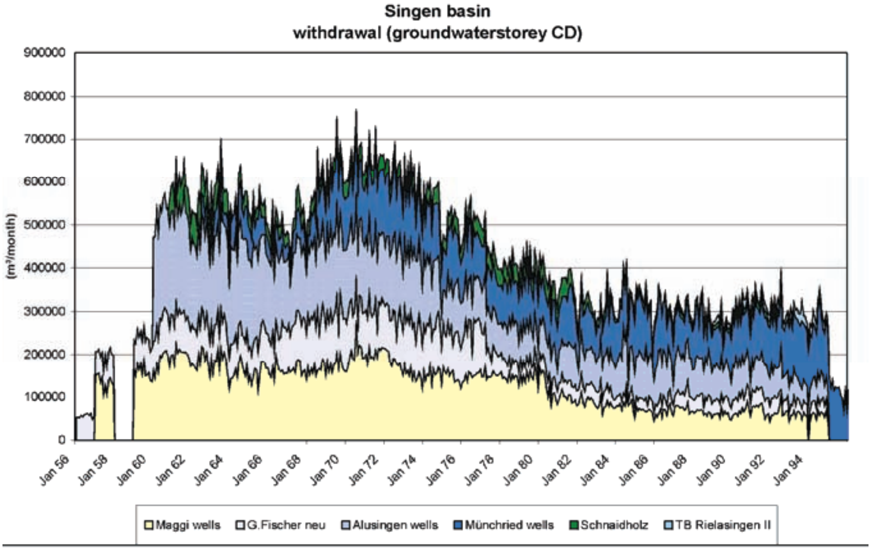

FIG. 4. Groundwater abstraction between 1956 and 1998 in groundwater storey CD.

is water influx from the underlying Upper Jurassic karst into aquifer C. Negative balance terms are groundwater withdrawal and outflow into adjacent gravel channels. Figure 3 gives a conceptual overview of gaining and loosing groundwater components of the aquifer system.

Although the reservoir has been used for drinking and industrial water supply since the early 20th century, the reliable data record of groundwater withdrawal starts in the 1960s (Fig. 4). Two important phases of groundwater exploitation are represented. During the 1960s and early 1970s (period of over-exploitation) the groundwater withdrawal (CD) averaged 150% of the present level with a peak value of 250% in 1971. This over-exploitation caused a drawdown of more than 10 m in the central part of the upper unconfined aquifer E. Since the mid 1970s groundwater discharge was reduced gradually (period of recovery) as a result of reduced industrial water demand and protection measure against negative effects on groundwater quality.

3. HYDROCHEMISTRY AND ISOTOPES

The documentation of groundwater hydrochemistry (major ions in water of production wells) started in 1940. Extensive investigations in the early 1980s and 1990s delivered facts to outline the capacity of the aquifer system. Furthermore, they provided information for the identification and quantification of different groundwater components as well as for understanding the system's dynamics, the contaminant load and the plume movement. Basing on the knowledge gained this chapter summarizes basic relations and briefly describes important events.

Locally recharged groundwater in the basin generally shows an alkaline-bicarbonate type. However, in the major chemical constituents, there are notable admixtures of NaCl-rich groundwater (Fig. 5). Today this groundwater component is found near the waste disposal site (Seewadel) as a result of chloride and ammonium leakage from the site. The site is regarded as the source of major anthropogenic groundwater contamination in the aquifer system. The chloride and ammonium plume resulting from the sites leakage was ascertained in the last 30 years and is detectable until today. Some additional alteration of dissolved solids like Ca-Mg exchange and carbonate solution as well as subdivisions of these water types are detected within the two groundwater storeys. They are connected to upward leaking groundwater influx from the underlying, slow circulating regional Upper Jurassic karst aquifer.

Isotopes in precipitation in South Germany are available from the stations in Stuttgart and Konstanz via the global network for isotopes in precipitation (GNIP) [1]. On the basis of monthly tritium data from GNIP (amount of

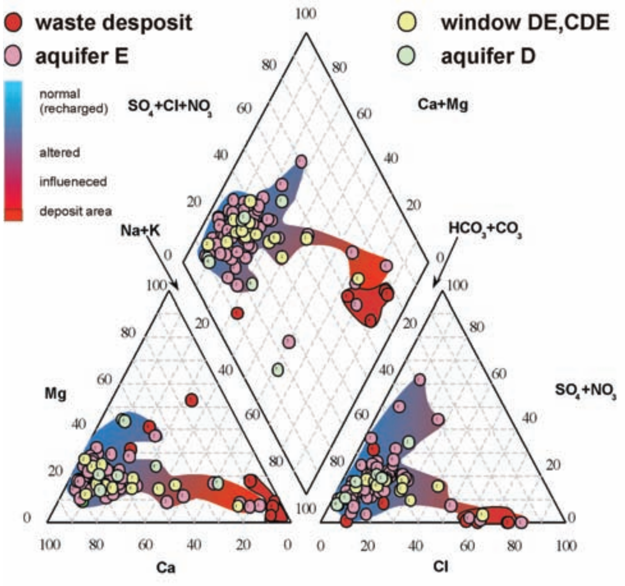

FIG. 5. Piper plot of shallow groundwater (aquifer E, window DE, aquifer D) and relation to seepage waters (1994).

precipitation and tritium value), additional data of a local station (Steißlingen/ Hegau) and correlation calculations to Vienna and Ottawa data sets a tritium input function was derived for local evaluations. The reliability of the derived tritium input function was checked using tritium values of young spring water and lysimeter leachate.

Isotope tracer investigations in groundwater started in 1969-1971 with a sampling of water from selected production wells in aquifers CD for ^{3}H- and ^{13}C/^{14}C-DIC-analyses. During the early 1980s, ^{3}H- and ^{18}O/^{2}H-analyses were performed to create time series and more spatial information about deeper parts of the basin [2]. ^{3}H-analyses of water in major production well waters in aquifers CD and three extensive basin-wide sampling campaigns for ^{3}H-, ^{18}O/^{2}H-analyses were carried out in the early 1990s. Additionally ^{85}Kr-analyses were performed in 1993-1995 to study the deeper parts of the basin. Finally in the context of this study several ^{3}H-analyses were carried out in the wells used as references in 2001 (Table 1).

Mean residence times were calculated using the input-functions, tritium or ^{85}Kr-values and the exponential flow model (EM) and the combined exponential and piston Flow model (EPM; percentage of EM) respectively.

This lumped-parameter model approach [3] was interpreted adjusted to the well position within the flow path in the basin.

Based on isotope tracer data from the extensive sampling campaign in 1994, the derived mean residence times show some increase from the near surface to the deeper parts of the system (2 to 15 years in aquifer E by EM, 8 to 15 years in aquifer D by EPM). Average residence times derived from tritium range between 10 and 20 years for the present situation of exploitation in aquifers C and D respectively. The closer the wells are located to the hydraulic windows, the lower is the mean residence time. Summarizing, in the Singen groundwater, in spite of the effective hydraulic connections between the storeys, a layering effect according to age can be seen. Today, the layering is only slightly disturbed by the fast, downward moving young inflow in the vicinity of hydraulic windows.

Especially groundwater in aquifer C contains an additional influx of old (>45 years), tritium free groundwater from the underlying Upper Jurassic karst aquifer. The influx of a second tritium free groundwater component makes the determination of a mean residence time difficult. The complex mixing relationships of groundwater with strongly varying tritium contents made it necessary to use painstaking, more extensive isotope methods for the evaluation of the total system than just the tritium method. In doing so, the ^{85}Kr-determination method produced important information for the characterization and exact quantification of the recharge from local precipitation and karst component in aquifers C and D.

4. CONTAMINANT SITUATION AND DEVELOPMENT

Beyond the negative effects on groundwater quality due to industrial facilities, urbanization and leakage from waste water sewers, the chloride and ammonium leachate from waste disposal sites (Fig. 1) also led to a detectable impairment in quality. However, heavy metals or organic carbon compounds have only been detected in few areas surrounding the waste deposits. They enter groundwater only subordinately. The presently low discharge of contaminants from the sites is mainly caused by heavy microbiological activity inside the waste deposits. The results from combined hydrochemical and isotope (^{2}H, ^{18}O, ^{3}H, ^{85}Kr, ^{39}Ar, ^{13}C/^{14}C, ^{15}N/^{18}O, ^{34}S/^{18}O) investigations have provided an important data base for deciding these issues. Furthermore, these investigations have shown that contaminants from the waste deposits that enter the near surface aquifer E are strongly diluted or quickly decomposed. For this reason they are no longer detectable in groundwater monitoring wells surrounding the

TABLE 1. RESULTS OF THE ISOTOPE ANALYSES IN SELECTED MAJOR PRODUCTION WELLS.

Well	Date	$\delta^{18}O$ (‰)	$\delta^{2}H$ (‰)	^{3}H (TU)	± (TU)	Well	Date	$\delta^{18}O$ (‰)	$\delta^{2}H$ (‰)	^{3}H (TU)	± (TU)	^{85}Kr (dpm/mLKr)
G. Fischer neu	01.08.69			242.3	6.0	Maggi 1939/69	22.02.93	–9.15		33.7	1.9	
	01.11.71			185.0	5.0		13.09.93			26.6	2.4	29.9±2.1
	13.03.81	–9.71		112.8	27.3		17.05.94	–9.76		27.4	2.0	
	03.04.81	–9.80		86.6	12.3		10.03.01	–9.74	–70.0	18.0	1.2	
	09.05.81	–9.84		86.1	18.8	Münchried IV	01.01.69			2.5	2.5	
	01.06.81	–9.87		97.5	11.7		01.11.71			14.0	4.0	
	09.07.81	–9.88		102.0	11.0		11.03.81	–9.75		81.8	15.2	
	21.10.81	–9.96		99.5	12.2		07.04.81	–9.68		52.2	11.8	
	24.02.82	–9.85		94.5	11.8		29.04.81	–9.84		77.6	16.9	
	18.07.89	–10.30		41.8	3.1		02.06.81	–9.59		67.8	11.0	
	22.02.93	–9.93		35.0	2.6		03.07.81	–9.83		62.6	11.1	
	21.09.93	–9.71		26.4	2.2		14.10.81	–9.67		64.5	10.2	
	08.06.94	–9.68		27.3	2.1		23.02.82	–9.67		71.2	11.3	
	10.03.01	–9.71	–69.0	16.4	1.2		18.07.89	–9.60		32.8	3.1	
Maggi 1957	02.02.82	–9.81		106.0	12.1		19.02.93	–9.76		26.9	1.4	
	22.02.93	–9.59		36.0	2.1		08.06.94	–9.69		22.7	1.5	
	20.09.93	–9.73	–71.0	30.7	2.2		06.02.95	–9.55	–72.0	20.7	1.7	11.1±0.6

	17.05.94	–9.75		30.0	1.7		21.10.97	–9.83	–70.0	18.6	1.0	
	10.03.01	–9.69	–68.0	15.9	1.2		11.03.01	–9.67	–69.0	17.0	1.2	
Maggi 1970	18.03.81	–9.88		97.6	23.0	Münchried VI	11.05.89	–9.91		43.8	2.2	
	03.04.81	–9.83		83.0	13.7		12.05.89	–9.85		41.0	2.0	
	06.05.81	–9.59		88.4	18.1		14.06.89	–9.89		43.7	3.1	
	01.08.81	–9.96		98.1	11.7		18.07.89	–9.88		43.2	2.5	
	14.10.81	–9.93		90.6	12.0		23.02.93	–9.97		40.1	2.1	
	02.02.82	–9.84		97.4	17.4		16.09.93	–9.83	–73.0	32.1	2.5	
	22.02.93	–9.68		31.8	1.5		08.06.94	–9.91		32.8	1.9	
	20.09.93	–9.64	–70.0	26.6	1.7		28.03.95	–9.75		25.8	1.4	
	17.05.94	–9.51		26.6	2.2		28.03.95	–9.83	–72.0	29.6	1.8	
	09.03.01	–9.59	–69.0	15.8	1.2		11.03.01	–9.77	–68.0	16.4	1.4	
Maggi 1939/69	13.03.81	–9.59		97.9	22.0	Münchried VII	01.11.71			16.0	4.0	
	03.04.81	–9.77		85.0	12.3		18.07.89	–9.84		45.2	3.1	
	05.05.81	–9.73		95.6	18.0		23.02.93	–9.88		38.1	2.3	
	01.06.81	–9.69		94.0	11.6		13.09.93			39.5	3.4	7.9±0.6
	14.10.81	–9.76		99.6	13.5		08.06.94	–9.85		34.0	1.8	
	02.02.82	–9.83		95.9	11.9		11.03.01	–9.83	–69.0	16.6	1.2	
	18.07.89	–10.15		55.6	3.9							

dumpsites. Due to the decomposition and dilution processes, only the diluted salt compounds are detected in the groundwater of the area.

However, in deeper aquifers showing higher mean residence times near the waste disposal site Seewadel, massive impairments in the groundwater quality were detected. Detailed investigations using samples taken at different aquifer depths as profiles, showed that contaminated groundwater components are present here, especially with a sudden rise in total dissolved solids at the bottom of aquifer D and C. Using residence times of groundwater and a flow path analysis of groundwater flow the contaminants could be traced back to seepage water discharge from the 1970s and 1980s. By these investigations, the Seewadel waste disposal site could be identified as the source of the major impairment of groundwater quality (Fig. 1).

Due to the connection of the hydraulic window near the Seewadel site in the cone of depression of aquifers CD, dump site leachate flows towards the

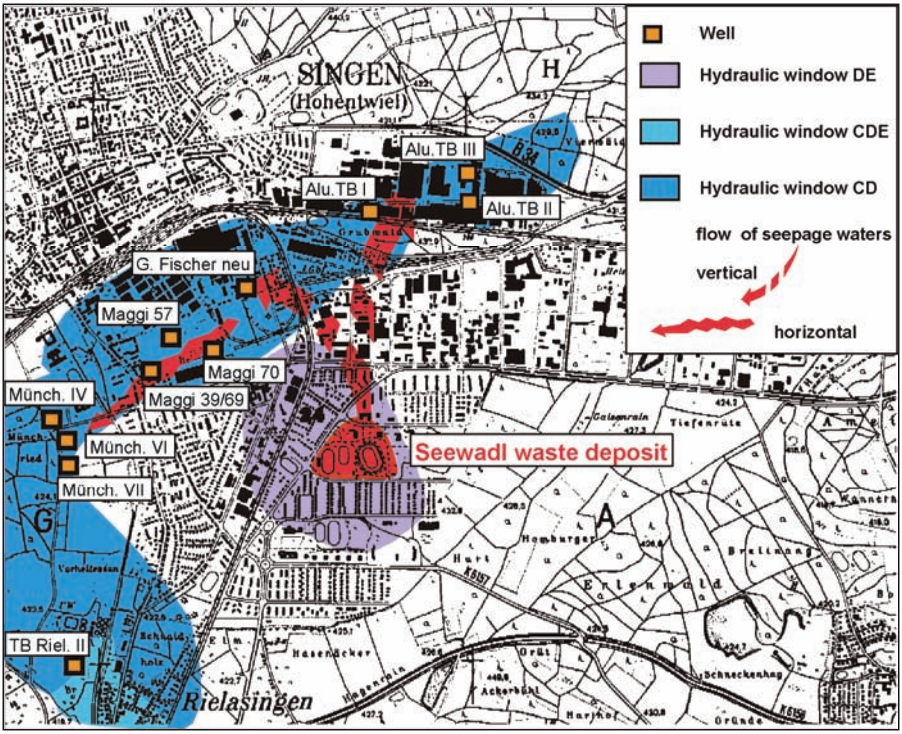

FIG. 6. Flow path of anthropogenic chloride plume.

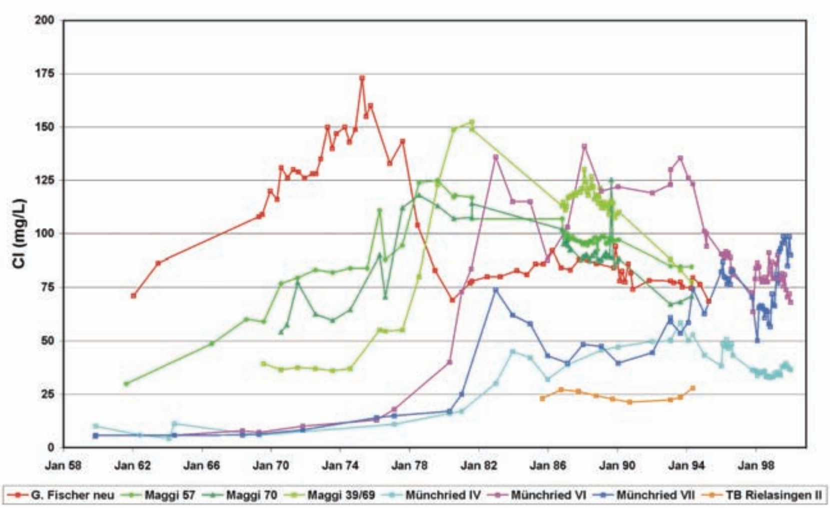

FIG. 7. Chloride concentrations versus time in major production wells.

production wells (Fig. 6) of public drinking water and industrial water supplies. Based on the aquifer geometry and the groundwater flow field, the well G. Fischer has been affected primarily during the period of over-exploitation (Fig. 7). Hereafter the peak of the chloride plume has reached all wells along the flow path into the centre of the cone of depression. Mean flow velocities of 10 to 12.5 m/month can be derived from the long term response over the last decades. Well specific reactions are visible over a long period as chloride concentrations are correlated to well discharge. This indicates that high mineralized groundwater components (undiluted seepage water) were present at the bottom of the aquifer. Throughout the last years most wells showed similar chloride concentrations, which proves that a stable extent of dilution has been established.

Today the contaminant plume still affects the wells of the city's drinking water supply (Münchried wells) seriously. Caused by the position of the wells Münchried VI and VII in the centre of the cone of depression, chloride loads are generally on a raised level here and well specific reactions still exist. Trends of chloride concentrations in individual wells are caused by specific well discharges and the varying dilution with uprising karst water. The karst component mainly affects well Münchried IV [4].

5. DEVELOPMENT IN MEAN RESIDENCE TIMES AND AGE COMPOSITION

The results of tritium analyses reflect the age composition of a groundwater and thus the prevailing flow dynamics in connection with the hydraulic boundary conditions. Former tritium values from production wells still give a valuable insight into the system dynamics in the past.

This fact is important for understanding the long term system reaction, considering the development of the groundwater discharges in the past with peaks between 1969 and 1974 and the following decline (Fig. 4). The set of isotope tracer data, with tritium values covering different periods of exploitation is also helpful for the understanding of contaminant migration into the deeper aquifers. To meet a proper interpretation, an assessment of all available isotope data has been performed. Based on this data sampling sites in the Singen basin with a isotope covering different periods of exploitation were pre-selected.

It has to be stated, that all data form the Singen basin show an increase of mean residence times over the last decades whereas the data do not indicate this for adjacent Quaternary basins. Within this study selected isotope tracer records from production wells in the central and the southern part of the basin have been documented (Table 1). These wells represent major discharge and therefore the historic development of withdrawals as well as the dynamic response of the aquifer system due to exploitation.

To guarantee the comparability of data and results, the calculation of mean residence times during all periods of exploitation was carried out using a lumped parameter approach adjusted to the well position in the Quaternary basin. The calculation of mean residence times was assisted by the computer program MULTIS [5]. Table 2 gives an overview of the results for the selected wells. EM represents exponential model, EPM combined exponential/piston flow model. Numbers express the percentage of the exponential model portion.

In groundwater storey CD near to the central hydraulic window, isotope data of well G. Fischer (Figs. 1, 2 and 6) cover the two periods of exploitation. The tritium values and the calculated mean residence times particularly show a significant difference in the prevailing flow dynamics between 1969 and the current situation (Fig. 8).

During the period of over-exploitation (1960s and early 1970s) very low residence times indicate — stress caused — fast groundwater flow and direct inflow of young groundwater through the hydraulic window into deeper parts of the system. In comparison to present conditions (1993/1994 or 2001), the total and individual well discharges were almost the double. The high discharge rates of over-exploitation affected the total reservoir including groundwater storey

TABLE. 2. MEAN RESIDENCE TIMES DETERMINED BY LUMPED PARAMETER MODELS.

Well	Aquifer	Model	Record	Mean residence time (a)				
				1969–1971	1981–1983	1989–1990	1993–1995	2001
G. Fischer neu	CD	EPM80	1969–2001	1 – 2	3 – 8	8 – 11	9 – 15	12 – 15
Maggi 1957	CD	EPM70	1982–2001	–	7 – 10	–	12 – 15	12 – 15
Maggi 1970	CD	EPM70	1981–2001	–	3 – 8	–	10 – 12	12 – 15
Maggi 1939/69	CD	EPM70	1981–2001	–	3 – 8	12 – 16	10 – 14	15 – 18
Alusingen TB I	CD	EPM80	1981–1994	–	2 – 7	7 – 9	8 – 12	–
Alusingen TB III	CD	EPM80	1992–1994	–	2 – 7	–	8 – 12	–
Alusingen TB II	D	EPM80	1981–1994	–	–	–	6 – 10	–
Münchried IV	CD	EPM60	1969–2001	*	**	**	***60%, 16	? 14 – 16
Münchried VI	CD	EPM60	1989–2001	–	–	? 9 – 12	? 12 – 16	? 14 – 16
Münchried VII	CD	EPM60	1971–2001	*	–	? 9 – 12	***75%, 20	? 14 – 16
Rielasingen II	CD	EPM80	1993–2001	–	–	–	8 – 14	18 – 22
Rielasingen I	E	EM	1981–1994	–	1 – 4	–	8 – 12	–

*– mixing system:	^{3}H-values indicate low portions of young groundwater
**– mixing system:	^{3}H-values indicate relevant portions of young groundwater
***– mixing system:	^{85}Kr-values indicate (portion of young groundwater, mean residence time)
? – mixing system:	^{3}H-values show inadequate low mean residence times (result of lumped parameter model for 100% of young groundwater)

E seriously and caused a lowering of hydraulic heads as well as an acceleration of groundwater flow velocities.

The significant increase in chloride and ammonium concentrations in the 1970s can be attributed to the strongly reduced dilution processes with young groundwater and the direct inflow from the over-exploited groundwater storey E (Fig. 7). The tritium values of well G. Fischer analyzed in the recovery-phase (early 1980s to 1995) show a positive trend in mean residence time. This trend is well correlated to the lowering of total discharge in groundwater storey CD. Wells Alusingen I–III, located near the central hydraulic window within a separate small scale draw down cone, show a similar effect corresponding to the general and well specific decline of withdrawals. Within the central cone of depression, the Maggi wells are situated halfway in the flow-path between well G. Fischer and the drinking water supply of Münchried wells. Due to their greater distance to the central hydraulic window they tend to higher groundwater mean residence times. In this case the recovery of the reservoir is indicated by an increase of mean residence times, too, although there are some overlying effects associated to well specific exploitation rates. The Münchried wells are located in the center of the cone of depression. In this area there is additional high influx of the Upper Jurassic karst water (^{3}H ≈ 0 TU; ^{14}C-DIC ≈ 50–60 pMC) via tectonically stressed zones.

Due to the complex mixing-system (karst influx and locally recharged groundwater) at each well and time-related variations, tritium values can not

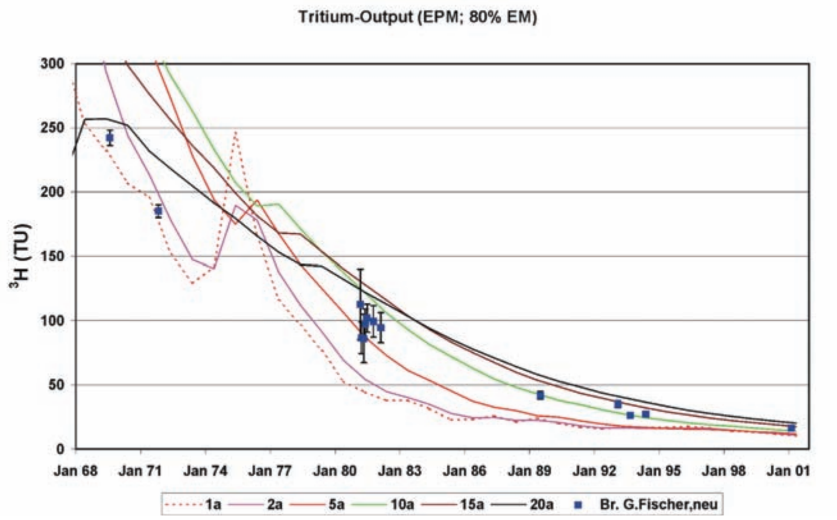

FIG. 8. Calculated ^{3}H-output-curves and analysed ^{3}H-values for well G. Fischer.

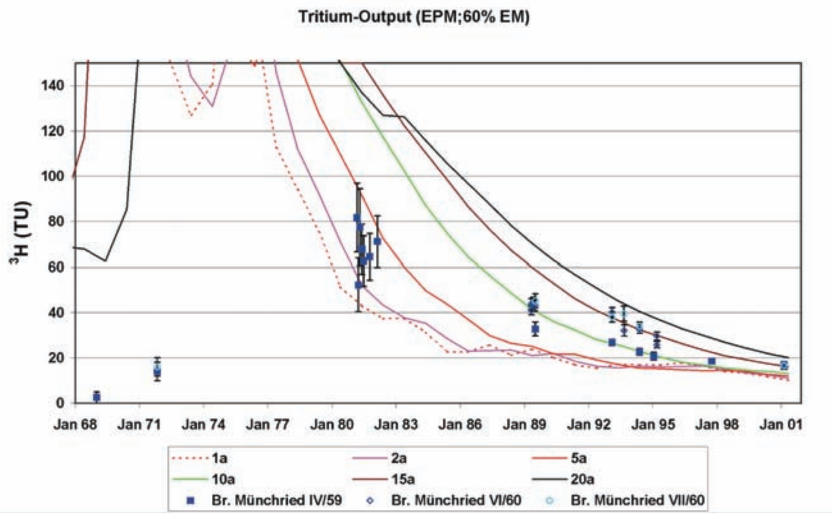

FIG. 9. Calculated ^3H-output-curves and analysed ^3H-values for Münchried wells.

be interpreted by using a simple lumped parameter approach here. Only the combination of ^3H- and ^{85}Kr-values analyzed in 1994-1995 and the definition of the groundwater components involved allows the interpretation of mean residence times in detail. Based on the total withdrawal and the results of the combined isotope methods, the local karst water influx was quantified as 30% of the total present water budget or 40–50 L/s [4].

Hydro-chemical data (Fig. 7) and tritium data (Fig. 8 and 9) show that during the late 1960s and early 1970s in spite of high exploitation rates, portions of karst water were dominant. In contrast to this, the tritium values analyzed in 1981–1982 (period of rising chloride concentrations), indicated as an early warning signal the progressive shift of the mixing system caused by increased portions of locally recharged groundwater. This shift influenced the three wells differently throughout the following years. While the influx of uprising karst water supplied well Münchried IV to a higher extent, the wells Münchried VI and VII have been affected more by the young groundwater component and the anthropogenic chloride plume. Especially Münchried VI was connected tightly to the central hydraulic window whereas the catchment area of Münchried VII was dominated by the slower circulating groundwater of southern part of the central cone of depression (Rielasingen II). Today the modern well management succeeded in stabilizing the hydro-chemical situation of the Münchried wells. Differences in karst water portions do not become apparent when using only the tritium values sampled in 2001. If differences still existed, their detection and quantification would need the combination of the ^{85}Kr- and tritium analyses. It was decided to put this question on the agenda of a planned INTERREG III research program dealing with the regional flow and discharge rates of the regional Upper Jurassic karst aquifer system (border area Switzerland-Germany).

6. NUMERICAL SIMULATION

A 3-dimensional, transient numerical groundwater flow model was established for the Quaternary porous media sediments of the Singen basin using the graphic-interactive simulation system FEFLOW [6]. The finite element mesh is built up of triangular prisms. For the horizontal triangular interconnexion, model relevant geometric features were taken into account in order to provide the best fit for watercourses, for setting the boundaries of areas with different hydraulic conductivity and to best determine the position of the discharge wells. The vertical discretion was oriented on the hydrogeological five-layer-model. Aquifers and confining layers are represented by at least one element layer. Figure 3 shows a review of the hydrogeological concept model and the layering. The finite element mesh has 6750 nodes and 11444 elements, set up in 9 node slices and 8 element layers. Hydraulic conductivity was based on a vertical anisotropy of 10. Water exchange through the hydraulic windows was not controlled by boundary conditions, but rather calculated from the calibrated hydraulic gradients and assigned hydraulic conductivity.

The flow model was calibrated for two steady-states (August 1993 and April 1994) and transient for the period of February 1992 to December 1993. Calculated hydraulic heads fit observed water levels very well. The numerical values for the individual groundwater balance terms are also in good agreement with field measurements. These were, as already mentioned, verified through painstaking hydraulic, hydro-chemical and isotope studies.

The short term transient model was extended to a long term transient flow model that covers a period of almost 50 years (1953–2001). The transient flow model can also be constrained by the long term record of hydrochemical and isotope data. Flow simulations are able to reproduce and to quantify the change in flow dynamics during the period of over-exploitation which are provided from isotope data. The model can simulate the lowering of hydraulic heads and therefore calculate the increase in groundwater flow velocity during the period of over-exploitation. Isotope data help to constrain the models' uncertainties. Travel times of groundwater between the Seewadel waste disposal site and the major production wells aquifers CD are calculated by means of a dispersion-free pathline algorithm. For the period of over-exploitation calculated mean travel times between the site and the wells are in the order of less than 5 years. For the period of recovery calculated mean travel times are approx. 20 years. These values match very well the isotope based mean residence times for various snapshots during the exploitation history of the system (Table 2).

Due to the enormous consumption of computing time and a lack of working resources during the year 2001 the planned numerical transport simulation of tritium movement through the aquifer system (period from 1953 to 2001) was cancelled.

The existing model enables experts to simulate the effect of hypothetic groundwater abstractions to groundwater budget and the movement of contaminants in the system. It is the basis for all future management strategies. The goal of water authorities is to use the system in a sustainable way with respect to groundwater budget and to protect wells of public drinking water supply against pollutants which already entered the deeper layers of the system.

7. CONCLUSION

The groundwater of the Singen basin is primarily recharged by the infiltration of the local precipitation and is subject to the manifold impacts from urban, commercial, and industrial settlements. However, the contribution from the ascending Upper Jurassic karst water is very important for the water balance and quality.

Tritium values of the major production wells show that a definite decline in the groundwater dynamics of the groundwater storey CD occurred since the early 1970s. This is visible in the increasing mean residence times of the groundwater and linked with a gradual decline of the total discharge out of the groundwater storey CD. Summarizing the comparisons, it can be stated that, under the present boundary conditions of the groundwater resources, groundwater flow conditions and discharge rates, a stable groundwater circulation system and a reduced affection by the anthropogenic chloride plume has been achieved.

The main reasons for the clear isotope and hydrochemical response due to exploitation in the Singen aquifer systems are:

- small, shallow flow systems with flow velocities in the range of meter per day;
- the small reservoir is sensitive to groundwater discharge in the order of 0.010–0.100 m^3/s;

- the two major groundwater components (locally recharged and deep karst water) represent perfect end members of a mixing line with respect to tritium and chloride at the Münchried wells.

The groundwater balance calculations and model calculations completed show that an essential increase in groundwater withdrawal is not possible. This would develop a flow situation similar to the one developed during the years of over-exploitation, with the corresponding consequences for pollution transport. Large scale urbanization would cause a decrease in recharge from precipitation and also leads to the same result as an increase in discharge. This must be considered in future city planning and development. Much lower withdrawals are also not recommended, since they would lead to a rise in the groundwater level and could cause imbibation in different regions of the area modelled.

The management concepts for the total withdrawals from the basin have resulted today in a much better balanced groundwater reservoir. Withdrawal rates that are too high have been avoided, as well as rates that are too low. The underground flow system can and must be adjusted to anthropogenic withdrawals, so that the existing pollutant plume affections are stable. The groundwater model as a prognosis instrument can only deliver cues for corresponding well operation. The effects in nature must be monitored on the long-term by a suitable monitoring program and if necessary corrected.

The results from isotope investigations carried out over more than 30 years proved the ability of the method as a monitoring tool reflecting the age composition of a groundwater and thus the prevailing flow dynamics in connection with the hydraulic boundary conditions. If the interpretation of the data is adjusted to an even complex groundwater circulation system, isotope results can be used as a very effective early warning system.

Using these experiences from a small, shallow and fast responding aquifer system, groundwater managers and experts working on strongly exploited aquifers can be encouraged to detect and quantify groundwater components, to start monitoring the components, to work on the understanding of possible movements of components and the change of mixing, to start predicting the future development using simulation models and finally to improve model based predictions by monitoring results.

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ISOTOPE HYDROLOGY EVOLUTION IN HAITI

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Abstract

Water resources in Haiti need a more rational management. In fact, the availability of water in Haiti can be described as follows: the country receives as annual precipitation about 40 billion m^3 of water. However, 70 % of this water is lost by evapotranspiration and of the remaining fraction, considered as a renewable resource, about 20 % drains through rivers and discharges into the sea. The remaining 10 % infiltrates into local aquifers. In Haiti water is not always available in the place where it is needed, depending on the precipitation regime, geography, geology, vegetation, etc. In fact, most difficulties lie in the regulation, protection and mobilization of the available resources. Since each economic sector in Haiti has specific needs, water resources management becomes a very important issue to provide access to water of sufficient quality and quantity to the population. This point is also relevant for adequate preservation of natural ecosystems and other uses.

In Haiti there are many areas which contain aquifers: Plaine de l'Arbre, Cayes, Leôgane, Gonaives and Plaine du Cul-de-Sac. The last one is heavily exploited due to its geographical location. In fact, since 1980, many studies, using isotope hydrology tools, have been carried out on this aquifer. Almost all studies conducted in the Plaine du Cul-de-Sac showed the same conclusion: the aquifer system is overexploited. Some recommendations have been made, but the anarchical exploitation of this aquifer still continues. Many years after these studies were conducted, the situation has not changed. In 2001, a project dealing with the integrated management of Plaine du Cul-de-Sac aquifer was initiated with the cooperation of the IAEA. Despite the difficulties, it is considered that this is the best way to solve this water resources problem.

1. INTRODUCTION

1.1. General aspects

Water is more important than what many see as the simple H_2O molecule. It is a unique molecule with unique properties. Water has been called the universal solvent. For keeping life on Earth we need water, always present where life exists. In addition to that, it is even necessary in any stage of our life. A human being, as well as a plant will die in a few days without water. It is needed for many human activities and therefore is a precious resource. However, when we do not pay attention about the way this resource is used, the consequences can be disastrous. This is why a rational management of this resource is very important above all, in a country like Haiti, where some people always thinks that water is inexhaustible. In fact, water management is impossible without a proper knowledge of the quantity and quality of water resources. It is important to know how water evolves in nature, and the factors affecting its presence and movement, as well as how water resources can be protected. In order to manage them, different approaches can be followed. Among them, Isotope Hydrology provides one of the best methods to obtain this information. These tools have been used in Haiti in the case of aquifers in different areas. Thanks to these methodologies, it is possible to have a better control of aquifers in Haiti. Actually, we still continue the implementation of some projects with the IAEA, despite some difficulties.

1.2. Location and climate

Haiti is part of an island, which borders with the People's Republic of Dominican in the east and the Caribbean Sea in the north, south and west. Haiti has a population of about 8 million inhabitants, and its area is 27,750 km^2. Maximum altitude in Haiti is 2,680 m (Pic La Selle).

The climate of Haiti is characterized by two major seasons namely: May–July corresponds to the dry summer season and August–October corresponds to the autumn rainy season. Temperature varies between 25° and 38°C, with an average annual precipitation of 1500 mm.

2. WATER RESOURCES MANAGEMENT AND PROTECTION IN HAITI

2.1. Institutional framework

The legislation should be constituted as the base were public powers must lean before intervening in this sector. In fact, responsibilities on the water sector in Haiti are dispersed into five Ministries:

(a) Ministry of Agriculture, with many organizations dealing with irrigation issues and the management of irrigation systems through out the country. It is responsible of data collection and processing as well as water resource management through the Service National des Resources en Eau (SNRE).

(b) Ministry of Public Works, Transport and Communications (TPTC). This Ministry has big responsibilities since it is involved in the field of water supply, (CAMEP), sanitation, hydroelectricity (EDH), etc.
(c) Ministry of Public Health and Population. It is responsible of public health, vaccination, control of water and food quality.
(d) Ministry of External Cooperation of Planning. This Ministry is responsible of the national policy on water resources.
(e) Ministry of the Environment, which has the responsibility of managing all natural resources of the country.

Practically the SNRE is the only institute with a centralized water resources inventory in the country. It provides information about meteorology, climatology and water resources for the whole country. However, the institute faces weakness. The institute conducted studies on water resources management and has reported on the pressure on the available water resources and on the negative influence of human activities in water quality. For these reasons, many initiatives have been taken in order to protect and manage water resources in Haiti.

Among these, these are some of approaches taken on the integrated management of water resources:

(a) Separation of management and planning functions;
(b) Presence of a water management authority;
(c) Participation of users in all decisions;
(d) Processing of water as an economical product;
(e) Carry out a water resources inventory;
(f) Access of water information to the users.

2.2. Water avaibility

The availability of water in Haiti can be presented as follows: The country receives about 41.6 billion m^3 of water through precipitation. About 70% of that amount is lost by evapotranspiration, and of the remaining part, which represents the renewable fraction, about 20 % drains through rivers to the sea. The remaining 10% infiltrates into the aquifers.

These values represent only the highest estimates, because water is not always available on the place where it is needed. This availability varies from one area to another, depending of some factors such as: precipitation regime, geography, geology, vegetation cover, etc. The difficulties are in the regulation, protection and mobilization of this resource.

We consider that only 10% of the potential resources are used. The satisfaction level of the population is very low, despite of many investments which have been made during the last years in the sector of drinking water. In the sector of irrigation about 150,000 ha of land are irrigable, but only 39,000 ha are in operation.

2.3. Aquifers in Haiti

In Haiti two major types of aquifer have been defined:

Continuous aquifers

They are constituted by alluvial plain, generally in coastal areas. Water resources in these aquifers are particularly important and represent more than 45 % of groundwater resources. Among the most important aquifer in this category we can list:

- Leôgane and Cayes plains, which contain the biggest unexploited aquifer in the country.
- The valley Artibonite and the plain of North.
- Cul-de-Sac and Gonaives plains are the most used and exploited, and where saline intrusion has been observed. Because they are located in the coastal area, these aquifers are vulnerable to marine intrusion.

Discontinuous aquifers

They are located in the relief areas and their characteristics as aquifers are controlled by some features such as karst development and intense fracture development. The most important aquifers in this category are:

- Karstic aquifers. They cover about 20% of the total area of Haiti. These aquifers show a very particular type of flow, constituted by a drainage network which is made into a hierarchy from top to the bottom. They produce springs with considerable but variable flow. Because of the flow type which exists through these formations, these aquifers are difficult to be exploited by drilling. In the littoral area, they are very often affected by marine intrusion, and for this reason, the exploitation becomes very difficult.
- Carbonatic aquifers. With variable yield, these aquifers extend over 24% of the total area and contain about 5 % of the accessible water resources. Their productivity is function of the degree of development of the fracture systems. In this category we include marlstone carbonatic aquifers (3%), with very low yield.

- Coralline limestones. Very porous and permeable aquifers, which may constitute important water reserve in specific zones. However, they are very often contaminated in littoral areas.
- Crystalline formations. These aquifers are located on intrusive volcanic or metamorphic rocks. These formations are of low permeability and constitute reserves in fracture zones, as well as in areas with superficial alteration.
- Sedimentary formations. These very low permeability formations are made by sandstones mainly of Miocene or Pliocene ages. They hardly can be considered as aquifers due to their low yield and water is always saline.

2.4. Sources and causes of pollution

The water problems in Haiti can be presented as follows:

Because of the demographic expansion, economic growth, and the improved standards of living, water quality decreases in many areas. At present, almost a third of the population lives in areas where water access is insufficient.

Water is therefore a limited resource and irregularly distributed. For this reason it should be shared between many users. Since each user has different needs and contradictory interests, water use is often a source of conflicts. The anarchical exploitation of water influences its quality and quantity, which very often brings the lack of balance between ecological and economical or social considerations.

Water resources management becomes a need so as to be able to distribute water in sufficient quality and quantity for actual needs and for future generations as well as for the preservation of natural ecosystems.

2.5. Previous studies

Haiti is a very mountainous country, and as a result, most streams have a torrential profile (slopes >30%). As a consequence, there is no natural regulation of flow and the variation of these flows reflects the precipitation regime.

In fact, Haiti had a meteorology network of 96 rain stations, 38 of them managed by TPTC, 25 by St Martial Petit Séminaire College, and 32 by a sugar company. Between 1930 and 1960 the total number of stations was reduced from 75 to 27. Since the 1970s, we only have climatological stations.

The first measurements of hydrological gauges were conducted in 1919 and between 1922 and 1943, Haiti had a hydrological network of 36 limnimetric stations and 1148 flow measurements were made on 29 streams. A second series of measurements was made between 1961 and 1966 (with FAO support) in Gonaives Plains and the North-west department. In 1988 there was decrease in the control, but the national hydrologic network was constituted and functioned until 1991. At present, there are no hydrological stations in the country [1].

Many field studies on ground water have been conducted in many areas of country, where a piezometric network existed from 1980 to 1990. Measurements were conducted on piezometers in the aquifers of Gonaives Plains, L'Artibonite Plains, Leogane Plains, Cayes Plains and Cul-de-Sac Plains. Among them we can cite Cul-de- Sac Plains, for example, one of the most exploited aquifers of the country, where CAMEP exploits almost 40% of the water distributed. Since 1980, SNRE has been conducting a study of this aquifer.

Two mathematical models have been developed; firstly a model by Pallas in 1986 for SNRE and then a second by BRGM–GERSAR, established in 1989. The study focussed on the water resources of the metropolitan region, for CAMEP.

In spite of their different approaches, these models have been arrived to almost the same result, showing that the exploitation limit of this aquifer was affected and recommended the prohibition of new pumping stations. But unfortunately, the anarchical exploitation still continues, and since 1990 there is no regular control in the Plains, nor protection measures adopted.

3. IAEA – 2004 PROJECT

The IAEA provided support through a TC project in 2001 to the Ministry of Agriculture, in collaboration with MTPTC, and particularly CAMEP. The project dealt with the integrated management of the Cul-de-Sac aquifer. The basic idea was to collect information on existing water resources in order to develop a mathematic model of this aquifer.

Because of the political circumstances and insecurity in the country, the project went through a number of difficult periods. SNRE has the technical responsibility of the project, which is to coordinate and supervise all the technical activities of the project and CAMEP has the administrative responsibility and provides partial financial support to the project.

The activities already conducted are:

(a) Examination of drilling phase in October 2005
(b) About 170 water points were identified from 125 boreholes and 45 piezometers. Some piezometers of the network are only accessible up to a depth of 20 m. Part of the network can not be used.

(c) In other cases, well heads are rusted, and for that reason it is not possible to carry out the measurements. All manual pumps provide water to the population for drinking purposes. Most of the wells are drilled by ONGs such as: Plan Parrainage and evangelical missions, usually to a depth of 60 to 100 m.

(d) Some of the manual pumps worked very well, while others very bad. We also found some irrigation wells with a test tube, and those wells are actually incorporated into the network. On these water points we had analysed the following parameters: pH, electrical conductivity, temperature, geographical coordinates, and piezometric level.

(e) This initial part of work allowed us to obtain the necessary information for the rehabilitation of the piezometric network. We selected some wells with manual pumps for the network. In other cases, we eliminated some piezometers because of the high density of points.

4. SUGGESTED FUTURE WORK ON ISOTOPE HYDROLOGY

Due to the importance of water resources in the country, the efficient and rational management of water resources is required. At the end of the project we expect to have obtained the full collaboration of all concerned parts.

The isotope and chemical study of water is the one of the best methods available to make a rational management of aquifers. By using isotope hydrology methods it is possible to obtain valuable hydrological information, since isotopes are good tracers of groundwater origin. Tritium is the only radioactive isotope of hydrogen, which has the same behaviour as other water molecules. Its presence in the aquifer allows a quantitative estimation of recharge. In Haiti, we have already conducted work in the field of isotope hydrology, though the project HAI/8/003 [2]. The project allowed the study of some aquifer systems.

As mentioned before a number of important aquifers have to be investigated:

(a) Leôgane and Cayes plains, which constitutes the biggest untapped water resource of the country;

(b) The valley Artibonite and the plain of North;

(c) Cul-de-Sac and Gonaives plains and Plaine de l'Arbre.

The Plaine de l'Arbre has been sampled (about 20 samples) for hydrochemistry and isotope contents. Eight samples represent karstic streamflows, 5 are boreholes, 4 are well waters and a sample representing surface water.

Except three points (AR2, AR-11 and AR-15) all other points cluster along the GMWL. The points which represent karstic water streamflow, form a homogeneous group, with isotope values ranging between –4 and –3.25 ‰ in $\delta^{18}O$ and between –21 and –15 ‰ in δD.

The chemical and isotope study of Plaine de l'Arbre waters allowed us to conclude the following: recharge of karstic stream flow is assured by rain falling on relieves surrounding the plain. The transit time of water in the karst is, in the majority of cases, larger than forty years. Basins located at high elevation also represent recharge areas. The only deep drilling existing in the plain does not cross any important aquifer, but brings by artesianism connate waters. These waters are of a different origin.

5. CONCLUSION

Water is desirable but not available because it's very often mixed with others substances which make it useless or dangerous for human health. As a renewable resource and because of the high demand, water should be protected and controlled. On the other hand; resolute measures must be taken including the introduction of legislation to tighten control over water use.

6. RECOMMENDATIONS

Rational water management is more and more pressing. Many scientists should think about the serious problem of groundwater pollution in order to find some efficient ways to protect aquifers against different pollution sources (chemical, physical or biological) and bring to the end its anarchical exploitation.

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STABLE ISOTOPE RESEARCH AS A BASIS FOR LONG-TERM EXPLOITATION PLANS ON THE SORSKO POLJE AQUIFER, SLOVENIA

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Abstract

From the hydrogeological point of view, the Sorsko polje area is a sink, filled with porous conglomerate and gravel, where large quantities of groundwater are accumulated. The Sorsko polje aquifer is one of the richest regions of groundwater and represents an important water source reserve for the central part of Slovenia. The determination of the ^{18}O isotope composition in water ($\delta^{18}O$) represents an independent completion of previous hydrogeological investigations of Sorsko polje. Research results give more reliable information about water origin, as well as about the influence of local precipitation and the Sava River water on the dynamics of groundwater restoration in the aquifer.

1. INTRODUCTION

The Sorsko polje alluvial aquifer is a small part of large water body that extends over the northern part of the Sava River flow, the longest Slovenian river. The aquifer is recharged by infiltration of local precipitation, by small tributaries from the western hilly part of the area and from the Sava river that flows through its eastern edge. Geological, hydrological and hydrogeological characteristics of the aquifer had been investigated in the 60s and 70s of the previous century [1, 2], just before the hydropower plant objects, including a dam, were built. The changes in the aquifer, connected with the water-storage reservoir, were expected and controlled. In the last decades the research activities were less intensive. In the meantime the interest for the public water supply usage has diminished due to high concentrations of various contaminants in the groundwater.

The main information source about groundwater quality in the Sorsko polje aquifer is a database of the national groundwater quality monitoring [3]. The main purpose of the present research activities was to complete the knowledge of the area's hydrogeological characteristics with up-to-date hydrochemical and isotopic data. These data form a basis for the determination of the river water portion in various parts of the aquifer and its changes in relation to groundwater flow and the distance from the river bed. At the same time the influence of different hydrological circumstances can be examined.

2. DATA COLLECTION

The successive measurements of hydrochemical and ^{18}O isotopic composition ($\delta^{18}O$) of groundwater took place from February 2005 until January 2006 at the sampling sites shown in Table 1.

Sampling sites for the research were the same as the sampling sites for the national groundwater quality monitoring and are equally distributed over the research area.

The samples were taken at approximately monthly intervals. Hydrochemical analyses were performed in the JP Vodovod-Kanalizacija laboratory, whereas isotopic analyses were made in the Jozef Stefan Institute laboratory.

TABLE 1. GROUNDWATER SAMPLING SITES AT THE SORSKO POLJE AQUIFER.

Sampling site	Type of sampling site
Sava	river water
Iskra	industrial well
Zabnica	private well
Meja	private well
Sv. Duh	private well
Podreca	private well on the farm
Goricane	industrial well

3. RESULTS AND DISCUSSION

In the groundwater of the Sorsko polje aquifer two main recharging components can be found. Their ^{18}O isotopic composition differs noticeably. The local precipitation is the first recharging component. Due to the low hinterland area altitude, the precipitation is relatively enriched in the heavier oxygen isotope, ^{18}O. The second recharging component is the Sava River, which recharges the aquifer from the north-east. The hinterland of the Sava River covers the highest parts of the Slovenian Alps and consequently the river water shows a lower content of the heavier oxygen isotope, ^{18}O. The ^{18}O isotope composition in the Sava River reaches more negative values. In the aquifer the mixing processes of both recharging components can be observed.

According to the average ^{18}O isotope composition, the groundwater samples can be classified into three groups (Fig. 1.) The first group represents the Sava River and groundwater on the Iskra sampling site. Their average ^{18}O isotopic composition is around –9.4 ‰. According to the composition at the Iskra sampling site, which is similar to the composition of the Sava river, it can be concluded that river water is a predominating component on that location.

In comparison to the other sampling sites the Zabnica samples are the most enriched with the heavier oxygen isotope. Their average isotopic composition reaches –8.3 ‰. The result leads to the conclusion that locally infiltrated precipitation can be found on this location and that the influence of river water is almost negligible.

The sampling sites named Meja, Podreca and Goricane belong to the largest group, where a similarity between the results can be observed. The ^{18}O average values range from –8.8 ‰ to –9.0 ‰. In this case the most reliable interpretation of ^{18}O isotopic composition leads to the conclusion that groundwater is a mixture of equivalent parts of the local precipitation and the Sava River water. A similar average isotopic composition is observed at the Sv. Duh sampling site. However, when its isotopic composition is observed on the time scale, the results are not interpretable on the basis of general characteristics of the mixing processes in the aquifer. The differences are described below.

Fig. 2 shows seasonal changes in isotope composition in the Sorsko polje aquifer. Isotope composition of the Sava River shows a regular sinuous dependence with time: the highest enrichment of heavier oxygen isotope is registered in the late summer, the lower enrichment at the end of winter or in the beginning of spring.

The ^{18}O isotope composition at the Iskra sampling site corresponds to that of the Sava River, which confirms the predominating share of river water on that location. However, a delay in the maximum of the isotopic signal was

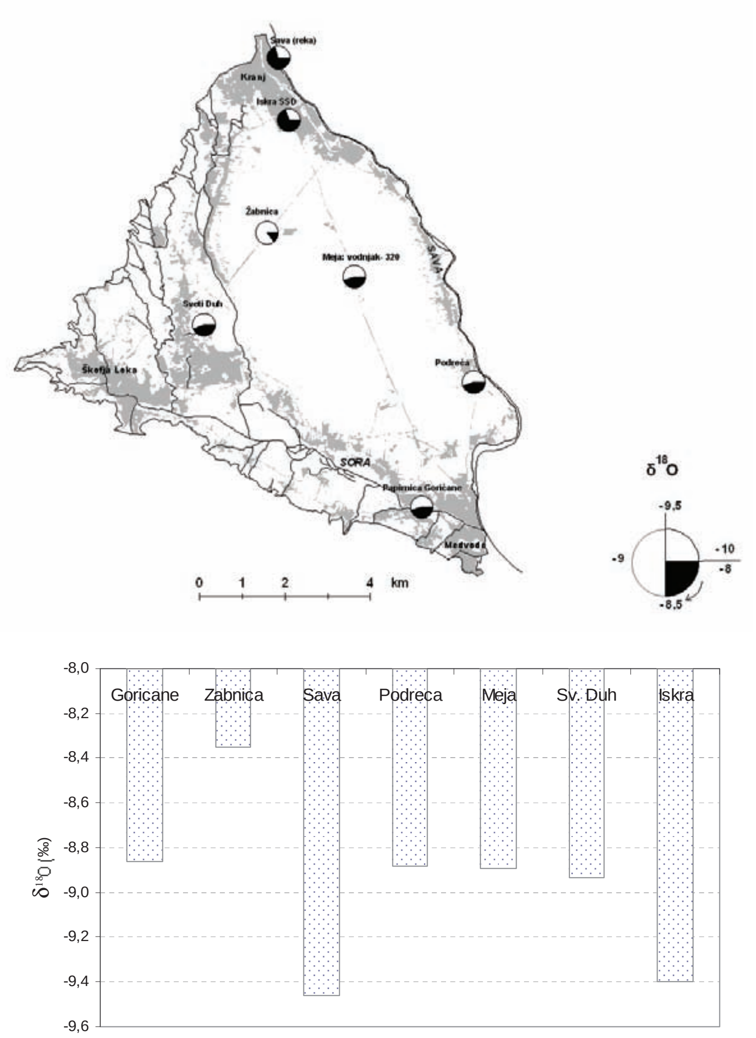

FIG. 1. Location of the sampling sites and the average ^{18}O isotopic composition ($\delta^{18}O$) in the groundwater of Sorsko polje.

observed, which is related to the retardation time of groundwater on its way from the river and through the aquifer.

The sampling sites Meja, Podreca and Goricane show similar changes of ^{18}O isotope composition during the hydrological year. The phenomenon confirms the uniform and homogeneous groundwater flow in the central part of the Sorsko polje.

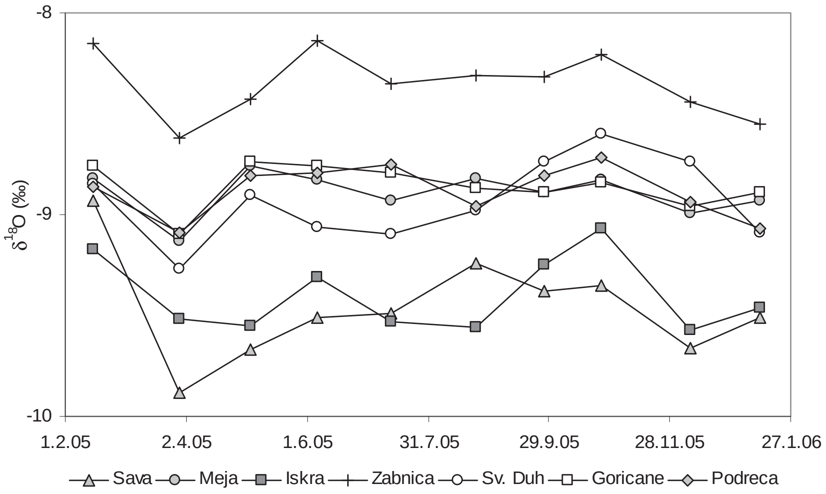

FIG. 2. Seasonal changes in ^{18}O isotope composition ($\delta^{18}O$) at the sampling sites of the Sorsko polje aquifer.

The abstraction well Goricane is situated near the low-permeable rocks which direct and control the groundwater flow. The result shows a predominant groundwater flow from the central part of the Sorsko polje aquifer and a negligible influence of the local component despite the closeness of the Sava river.

In spite of similar average isotope composition of ^{18}O, the groundwater at the Sv. Duh sampling site shows quite different isotopic characteristics. The amplitude of the isotope signal is higher and shows the influence of local precipitation or small streams that sink in the aquifer from the west.

An interrelation between ^{18}O isotope composition and water mineralization was observed. The increasing concentration of calcium (Fig. 3) is related to the increasing portion of the heavier oxygen isotope. The rate of precipitation mineralization on the Sorsko polje plane is higher than in the Sava River because of higher values of partial pressure of CO_2. At the same time the local precipitation is more enriched with ^{18}O due to lower altitude of the area where it appears. The correlation line between both parameters can be treated as a mixing line for recharging components: river water and precipitation, infiltrated locally.

The Sv. Duh sampling site deviates from the mixing line, as its calcium concentration is almost doubled at the isotope composition which is typical of the central part of the aquifer.

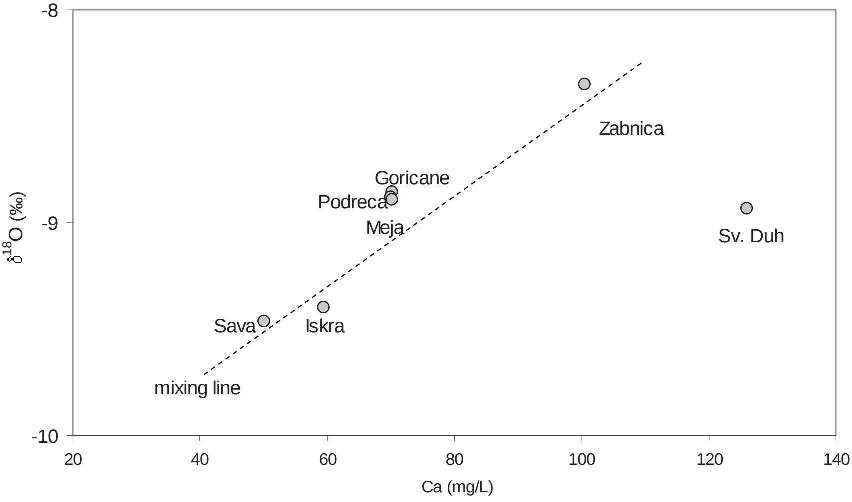

FIG. 3. Relation between ^{18}O isotope composition ($\delta^{18}O$) and calcium concentration in the Sorsko polje groundwater.

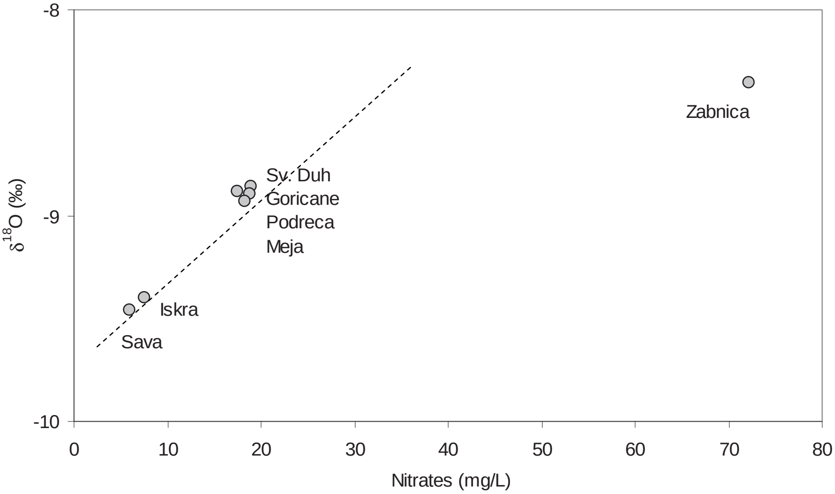

FIG. 4. Relation between ^{18}O isotope composition ($\delta^{18}O$) and nitrate concentration in the Sorsko polje groundwater.

Nitrates can be considered the main contaminant of the Sorsko polje groundwater, as their values locally reach more than 70 mg/L. The research results show (Fig. 4) that higher nitrate concentrations are related to higher content of the heavier oxygen isotope. The rate of nitrate leakage into groundwater increases with the share of local precipitation.

4. CONCLUSIONS

On the basis of isotope and hydrochemical research of the Sorsko polje aquifer new data of the groundwater dynamics and mixing of its recharging component have been acquired. On the larger area of the aquifer the river water is an important recharging component. The mixing processes cause a reduced concentration of various contaminants, especially from agriculture. The most distinctive among them are the nitrates, the concentration of which locally exceeds the maximum permissible level of 50 mg/L.

ACKNOWLEDGEMENTS

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A DEEP, HIGHLY PRODUCTIVE AQUIFER IS IDENTIFIED USING ISOTOPE, HYDROCHEMICAL, AND GEOPHYSICAL TECHNIQUES

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Abstract

An environmental isotope and hydrochemical study was undertaken to assess a conceptual model developed earlier on which a major, regional rural groundwater supply from a basalt aquifer was to be based. Mean residence time and porosity figures indicated that recharge, and therefore sustainable extraction, could be as low as 10% of the model estimates. Variable chemical and isotope data also questioned model predictions of balancing drainage along a major fault line. These results, suggesting upwelling groundwater, prompted a major re-investigation of the area, involving further exploratory drilling and geophysics. A deeper sandstone aquifer, previously thought to be unproductive, was found to produce high yields of excellent quality groundwater and constituting a potentially major regional resource. Further work is aimed at its development and management through conjunctive exploitation.

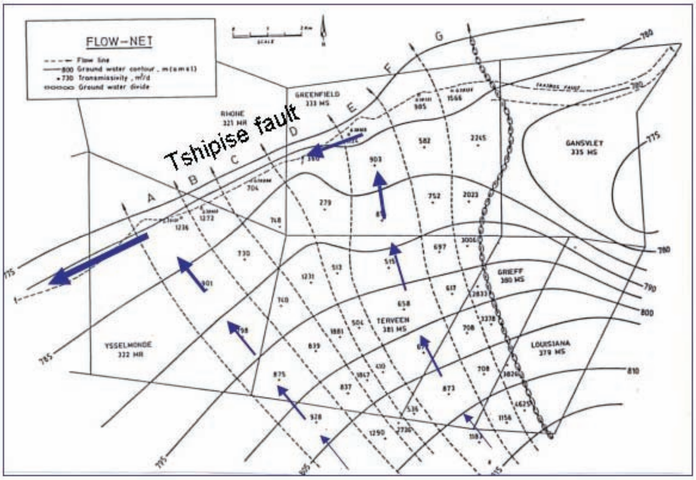

FIG. 1. The original groundwater flow model, showing iso-piezometric contours (after[1]), interpreted N–W flow in the basalt and balancing drainage along fault zone (see Fig. 3).

1. INTRODUCTION

An investigation was conducted in the 1980s into the feasibility of a ground water supply to 26 villages in Limpopo Province, South Africa. This resulted in a hydrological model [1] proposing that groundwater, recharged to a plain of some 600 km^2 in extent drains northwards, away from the mountain watershed in the south, mainly through a superficial basalt aquifer (Fig. 1). The Tshipise fault zone in the north would act as a sink as well as a drain of ground water westwards towards an ephemeral surface drainage.

The underlying Karoo sandstone (Fig. 7), historically encountered mainly in test drilling of upthrown blocks along the fault zone, was found usually to be poorly yielding and not regarded as a worthwhile target for further exploration. The regional supply was designed to be drawn mainly from the fault zone, the abstraction potential estimated at some 1×10^6 m^3 per km fault strike per annum.

2. HYDROGEOLOGY

The area is characterized by a plain underlain by tertiary to cretaceous Karoo sediments, downfaulted against older Soutpansberg sediments of the Blouberg mountains in the south and in the north against basement

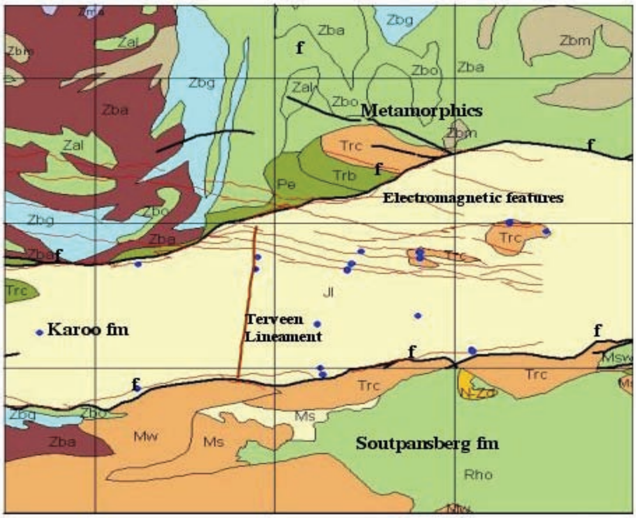

FIG. 2. Geological map [2] of the area showing the Karoo graben between older sediments in the south and metamorphics in the north. Electromagnetic features observed during the project were identified as dykes compartmentalizing the Karoo.

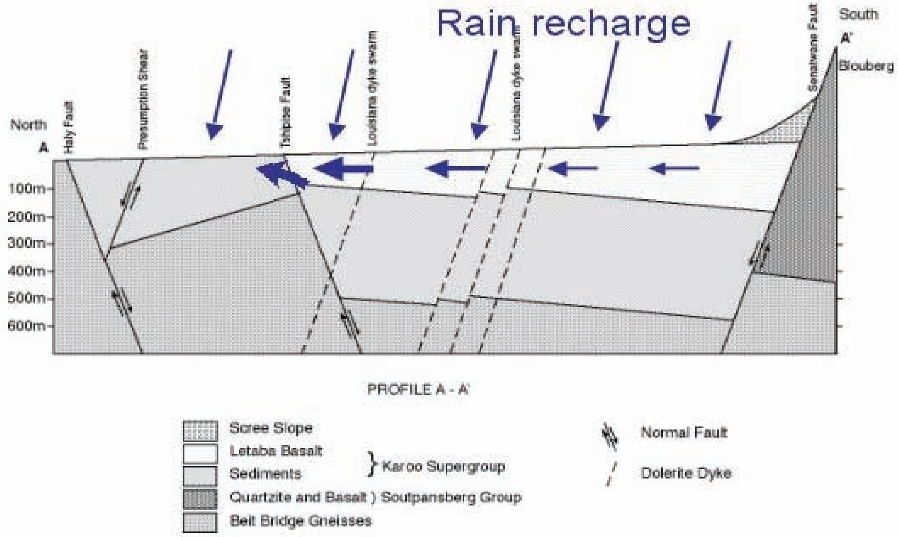

FIG. 3. Schematic geological section (after [2]) showing downthrown Karoo block and original groundwater flow model of the shallow basalt aquifer (see Fig. 1).

metamorphics by the regional Tshipise fault (Fig. 2). The Karoo sequence consists of sandstone capped by superficial basalt up to more than 200 m in thickness (Fig. 3). Groundwater exploitation, mainly for localized village supply and some irrigation farming, was traditionally restricted to the basalt.

3. ISOTOPE AND HYDROCHEMICAL STUDY

The isotope and hydrochemical investigation focused initially on the Tshipise fault zone. Equipped boreholes of small production well fields were first sampled; later a mobile pump was used to sample unequipped exploratory boreholes. Stimulated partly by the isotope investigation, contract drilling both on the west and east side of the fault began to reveal greater complexity of the fault structure than initially believed.

Numerous samples taken from along the fault zone itself and elsewhere showed a pattern of high radiocarbon values, generally in the range of 80–100 pMC, with accompanying tritium mostly in the range 0–1 TU (Fig. 4). Exponential model plots [3, 4] of atmospheric ^{14}C [5] and rainfall ^{3}H [6] data revealed three categories: (1) a substantial number generally conforming to the model, in spite of the heterogeneity of the basalt aquifer; (2) a category,

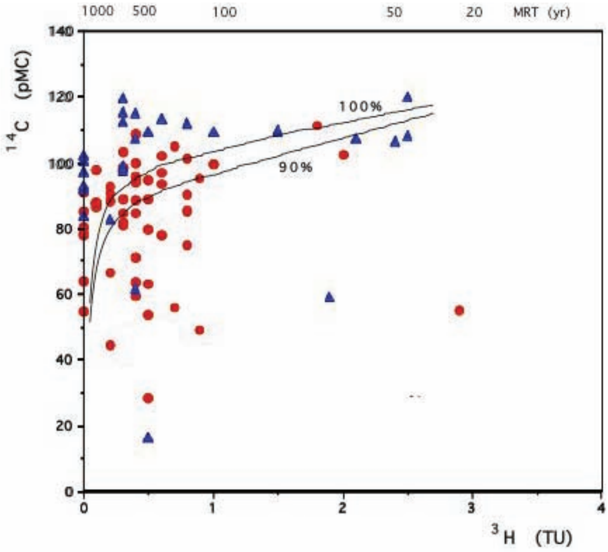

FIG. 4. Scattergram of radiocarbon against tritium values for two sampling episodes (red circles and blue triangles) with exponential model plots for different initial ^{14}C values in % atmospheric.

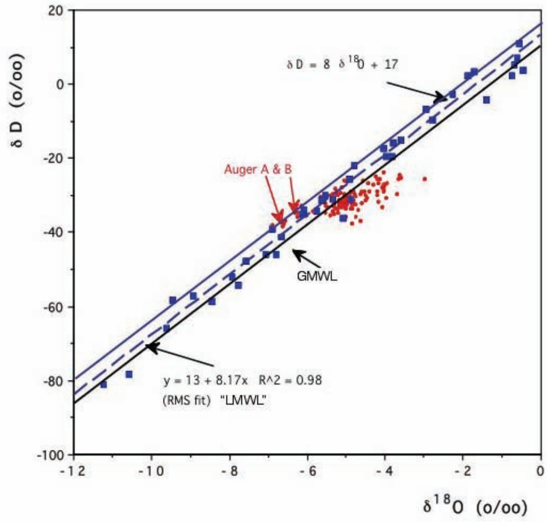

FIG. 5. δ^2H–$\delta^{18}O$ diagram. Notice the close clustering of groundwater values (red dots) with evaporative trend as against the much wider spread of rainfall values(blue squares) over a period of three years

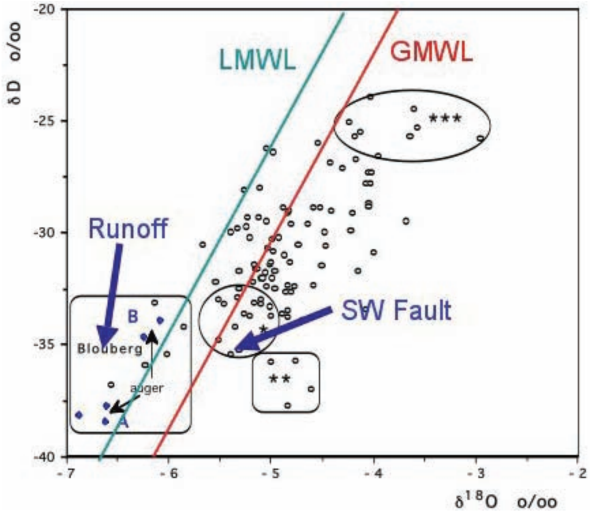

FIG. 6. δ^2H–$\delta^{18}O$ diagram (detail of Fig. 5) showing groundwater values with various geographical categories ringed. Note values including the SW fault zone (cf. Fig. 7) and from samples augered from a wetland at the foot of the Blouberg, taken to represent mountain runoff

at low ^{3}H values that lies above the model curves, ascribed to phreatophyte root activity and (3) ^{14}C values <80 pMC accompanied by ^{3}H values >0.5 TU, ascribed to mixtures with older water.

Groundwater stable isotope values cluster in a fairly narrow range of δ^{18}O ~ –4 to –6 ‰, with a regression slope of ~5.5 ‰. Monthly composite and single major event rain water samples collected from the three collection stations over three years show a spread of δ^{18}O from –12‰ to –2‰ with a regression of $\delta^{2}H = 8.1 \times \delta^{18}O + 14$ (Fig. 5). These facts are taken to indicate that recharge conditions to the basalt are fairly uniform, with a degree of surface ponding, often observed after heavy rains on the plain, producing an evaporation imprint on the data.

Although groundwater values in the region do not show a major spread, variations along the fault, e.g. in ^{14}C and δ^{18}O (Fig. 7), accompanied by variable hydrochemistry, suggest that the concept of consistent, regional drainage along the fault, such as postulated in the initial model, could not be sustained.

In assessing recharge, it was realized that scant hydrological information was available on the highly anisotropic basalt aquifer. The important parameter of porosity had to be based on inspired guesses. However, it became obvious that even optimistic recharge figures based on isotope-derived MRT values (Fig. 4) amounted to at most 10% of those arrived at during the original investigation. Furthermore, the variability of isotopic and hydrochemical parameters in numerous samples taken along the strike of the fault began to cast doubt on the concept of a continuous regional drainage zone. Down-the-hole video observations demonstrated the highly anisotropic nature of the void space in the basalt.

4. INVESTIGATIONS PROMPTED BY THE ISOTOPE STUDY

An airborne geophysical survey and its structural interpretation revealed much greater complexity, such as the W–E dyke swarm (Fig. 2) and N-S structures that may have far-reaching hydrogeological implications [2]. In the NE the Karoo aquifers are compartmentalized, whilst the Tshipise fault was shown to be bisected at various points, as already suggested by the isotopic and hydrochemical data.

Chemical and isotopic data (Fig. 7) furthermore revealed that along a section to the SW of the fault line, borehole samples gave lower radiocarbon values than seen in the rest of the area, associated with more negative stable isotope values, resembling those seen closer to the mountains in the south. Even more negative were the stable isotope values observed in shallow soil samples augered from a wetland at the foot of the Blouberg mountains (Fig. 6). This

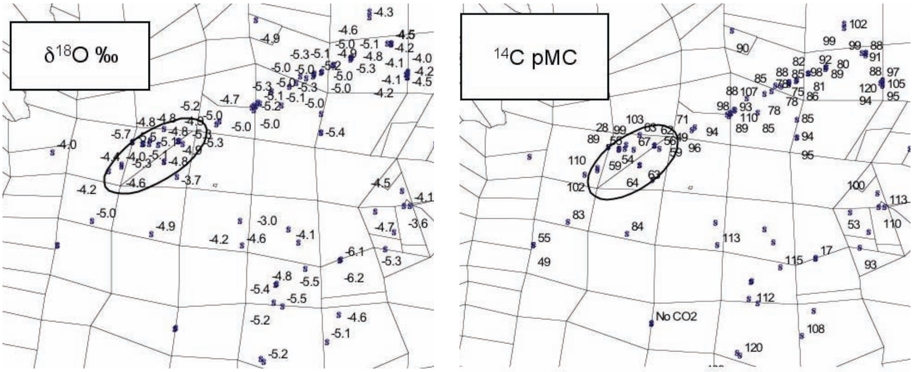

FIG. 7. Geographic spread of $\delta^{18}O$ and ^{14}C values. The linear cluster of sampling points follows the Tshipise fault line. The area containing the exceptionally low values of both parameters in the SW of the fault zone is ringed.

suggested local upwelling of deeper, older groundwater along the fault, with characteristics of groundwater possibly recharged along the scree slopes and fault zone along the mountain to the south. Flow observations on the standing water column in a borehole along the Tshipise fault showed conclusively that there is indeed upwards movement of ground water into the basalt. This may explain some apparently anomalous values ascribed to mixing seen on the ^{14}C–^{3}H diagram in Fig. 4.

This wealth of information from various observations led to the modification of the original conceptual model. The revised model (Fig. 8) postulates major N-W flow through the underlying sandstone, regulating the regional piezometry observed mainly in the basalt aquifer, with local upwelling along faults and fractures into the overlying basalt.

5. THE TSHIPISE SANDSTONE.

Wherever the sandstone is exposed at surface induration of the matrix significantly reduces its hydraulic conductivity. This fact discouraged any systematic development of this formation and the basalt was traditionally targeted for ground water supply. Deeper drilling, down to 340 m, showed that where the sandstone is covered by basalt, its primary porosity and permeability is preserved. Water was always struck just below the basalt/sandstone contact, and yields increased with increasing depth. The sandstone ground water usually

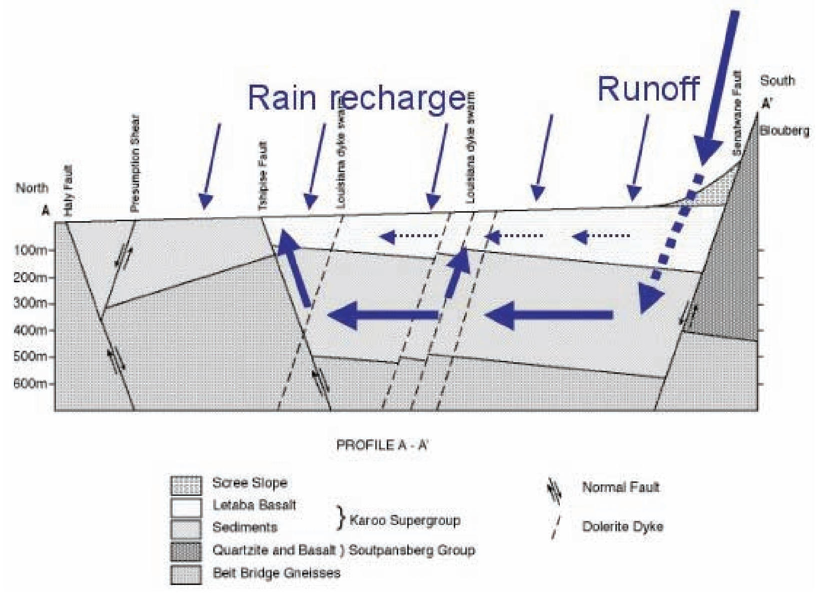

FIG. 8. Updated conceptual groundwater flow model, based on isotopic, chemical and geophysical data. Major recharge to sandstone is from mountain run-off infiltrating along scree slopes and the graben southern bounding fault zone.

has much lower overall mineralization than the basalt, in particular low nitrate contents, in contrast to often problematic high values in the basalt.

^{14}C values range from 55 pMC to 24 pMC with vanishing tritium. These confirm, along with the chemistry, the effective separation of the two main aquifers. Although residence times are higher than for the basalt, coupled to the high storage significant turnover rates are indicated. The chemistry further suggests that the sandstone is recharged mainly through preferential pathways, along faults and fracture zones, rather than diffuse recharge which could only occur through the basalt. Of note too are the very high yields (up to 40 L/s) showing that the sandstone, in addition to its general reliability as an aquifer, can locally support high extraction rates.

A further study phase has been initiated specifically targeting the Tshipise sandstone. It is aimed at developing an aquifer management model of a regional groundwater supply based on the sandstone aquifer. Already, two high-yielding wells have been earmarked as emergency water supply to a nearby town.

The management model will, i.a. have to deal with maintaining the exceptional quality of the sandstone groundwater, that could be compromised by uncontrolled exploitation. An effective recharge rate will have to be arrived at. In some areas, the basalt and sandstone will have to be developed in parallel to allow conjunctive exploitation and blending of water to reasonable potable standards. In all these developments, environmental isotope data will undoubtedly play a crucial role.

ACKNOWLEDGEMENTS

This study was initiated as part of an IAEA regional study RAF8029 entitled Sustainable Water Resources. The authors wish to thank the South African Department of Water Affairs and Forestry for substantial financial support and hydrochemical analyses. The geophysical work was conducted by the South African Council for Geoscience. For the numerous isotope analyses, thanks are due to the staff of the Environmental Isotope Laboratory of the former Schonland Research Institute of the University of the Witwatersrand, Johannesburg.

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ISOTOPE STUDIES OF WATER RESOURCES (TABAS AREA CASE STUDY)

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Abstract

Tabas Town with a surface area of 55,000 km^2 is located in north-east of Yazd City in the east of Iran. It is situated in western slopes of eastern heights of the country, on sediments of fourth era, on the edge of Kavir-e-Namak Desert. The study area falls between 56º to 57º 45’ eastern longitudes and 32º 15’ to 34º 15’ northern latitude. The project aims at providing water for washing carbons, cooling systems and potable water purposes in Tabas carbon power plant. Investigating the origin, age and nature of different water resources and relationships between these resources are the main objective of conducting isotope studies in Tabas area. This will help in providing required water in the area. Determining water resources, taking samples and isotope and chemical analysis of samples form methodology of present research. ^{18}O and ^{2}H stable environmental isotopes and ^{3}H and ^{14}C radioisotopes as well as results of chemical analysis of samples have been used in studies. First stage of studies consists of sample-taking from 34 springs, 13 wells and 8 Qanats both wet and dry seasons. Isotope and chemical analyses have been also made on taken samples.

1. INTRODUCTION

Tabas carbon mines contain most carbon resources in Iran. Exploited carbon provides required fuel for power generation which should be first washed out for being ready for power generation. Establishing such a system do need a considerable amount of water, so that an amount of 1200 m^3/h is predicted to be necessary for washing out carbons, cooling systems and drinking purpose. Regarding hot climate of the region, groundwater resources are considered as the sole source of water provision in the area.

Aiming this and also in order to investigate recharge mechanism, flow patterns in the carbonated and non-carbonated formations, determining different types of water from age, origin and relationship viewpoint and in general in order to have a general concept of nature of waters in the area and

FIG. 1. Map of the study area.

developing groundwater exploitation in Tabas area — central and north-eastern parts of Iran, the area has been studied using ^{18}O, ^{2}H and ^{3}H environmental isotopes during 2003–2004.

2. STUDY AREA

Study area with a surface area of 55,000 km^2 is located in north-east of Yazd Province on eastern slopes of Iran and on fourth era sediments around Kavir-e Namak Desert. It is located between 56º to 57º 45’ eastern longitude and 32º 15’ to 34º 15’ northern latitude. Tabas Town is the center of the area and the area has an arid climate with an average annual precipitation rate of 50 mm which is bounded to Pirhajat and Naybandan from its north and southern parts and to Kalmard Fault from its eastern part.

3. METHODOLOGY

Recognizing groundwater course and relationship between separate aquifers within an area is one of the main essentials in hydrology. Different methods of groundwater tracing are now considered as most precise tools to provide solutions to problems in this regard. Environmental isotopes as well as investigating chemical composition of water have been used in present studies to investigate existing status in the basin.

Isotope tracing method focuses on correct sampling from water resources within the study area. Samples are taken from 55 water resources for isotope and chemical studies in two seasons (June 2002 and November 2003). Water resources in the area consist of 34 springs, 8 Qanats and 13 deep wells. Measurements have been made on EC, T, pH and TDS in these water when taking samples.

Stable isotopes (^{18}O and ^{2}H and radio isotopes (^{3}H and ^{14}C) are used for isotope studies in the study area (Table 1). Full chemical analysis of water samples includes measuring EC, Total dissolved solid, total hardness, determining concentration of CO_3^{-2}, HCO_3^-, Cl^-, SO_4^{-2}, Ca^{2+}, Mg^{2+}, Na^+ and K^+ anions and cations. Meteoric water line, i.e. ^{2}H – ^{18}O diagram shows a similar typical relationship to that of Mediterranean rains. Results of isotope analysis of precipitation in the area show that: first, the samples have been evaporated before infiltration. Second: the rate of direct recharge of precipitation into aquifers is very low (Fig. 2).

Some water resources in Tabas area contain deepest and oldest waters based on the results of isotope tests on samples taken from these resources shown by solid circles. Some other waters have been evaporated before infiltration. These waters are among shallow water resources in the area. Since most water resources of this type are springs, it could be concluded that they are formed as a consequence of joining a number of shallow resources. The other water samples are a mixture of shallow and deep waters which are shown by empty circles.

Moreover, results of isotope analysis on Tritium content of water show that all waters in the study area are of some type which are mainly recharged by some sources beyond the study area. So, water resources in this area are classified as modern – submodern type. ^{14}C and ^{3}H results also indicate a longer residence time in aquifers in the area.

Results of chemical analysis show that waters in the area are mostly of Cl–Na and SO_4–Na type which indicate that water samples in this area are completely far from recharge centers and close to discharge and evaporation regions.

^{18}O and Cl ion relationship graph has been presented to investigate the effect of evaporation on chlorine ions in water resources in the study area. As it is shown. the rate of increase in chlorine and sulfate ions generally depends on salt dissolving in evaporative rocks and desert rocks on the course of groundwater flows.

TABLE 1. ISOTOPE RESULTS ON ^{18}O. D. T AND ^{14}C.

Sample ID	^{18}O	^{2}H (‰ SMOW)	^{3}H (TU)	^{14}C (pMC)	Sample Name
1	–8.00	–50.00	1.60	70.57 ± 1.2	Nastang–Spring
2	–8.60	–56.00	1.50	68.35 ± 1.6	Kashaneh–Spring
3	–7.00	–46.00	3.70	–	Shirgesht–Qanat
4	–9.00	–59.00	2.50	58.36 ± 1.2	Pirhajat–Spring
5	–8.80	–59.00	0.15	–	Peyestan–Qanat
6	–8.70	–56.00	0.00	60.67 ± 1.5	Halvan–Qanat
7	–8.20	–50.00	2.40	80.28 ± 1.5	Dehe Mohammad–Qanat
8	–7.80	–48.00	2.40	76.31 ± 1.6	Azmighan–Spring
9	–8.40	–51.00	1.90	89.68 ± 1.7	Dareh bid–Spring
10	–7.10	–47.00	1.60	85.17 ± 1.2	Nakhlak–spring
11	–8.20	–55.00	0.65	51.21 ± 1.1	Dehe Bisheh–Qanat
12	–8.30	57.00	0.66	–	Dareh Gholshan (warm spring)
13	–7.00	–41.00	3.70	54.76 ± 1.5	Dareh Gholshan (cold spring)
14	–7.60	–48.00	1.20	57.24 ± 1.5	Well coal mine
15	–7.50	–47.00	3.32	71.09 ± 1.5	Well–Hossein Abad Park
16	–7.60	–55.00	0.60	77.43 ± 1.6	Darya–Spring
17	–8.10	–54.00	1.47	94.19 ± 2.2	Mohamadiyeh–Qanat
18	–7.90	–56.00	1.05	63.63 ± 1.3	Robat Kalmard–Spring
19	–6.40	–44.00	1.62	52.21 ± 1.2	Mardan–Spring
20	–7.40	–45.00	2.90	65.48 ± 1.4	Korit–Well
21	–8.20	–49.00	1.28	29.44 ± 1	Korit–Spring
22	–8.50	–54.00	1.47	57.33 ± 1.3	Cheyrook–Qanat
23	–7.80	–48.00	2.27	62.10 ± 1	Kosar–Well
24	–8.20	–52.00	1.15	56.50 ± 1.6	Abasabad–Well
25	–8.00	–48.00	0.23	60.39 ± 1.8	Esfahak–Agriculture water–Well
26	–7.90	–46.00	2.67	33.65 ± 1.3	Esfahak–Drinking water–Well
27	–7.40	–47.00	1.59	51.11 ± 1.1	Well No. 103
28	–8.00	–48.00	3.30	–	Well No. 109
29	–9.20	–62.00	1.85	48.36 ± 1.2	Hasoom–Spring
30	–6.80	–51.00	0.73	78.70 ± 1.6	Mazino–Spring
31	–5.50	–42.00	2.60	48.11 ± 1	Talzard–Spring

32	–6.60	–40.00	2.60	42.51 ± 1.4	Howz–Spring
33	–7.60	–44.00	2.70	54.7 ± 2	Kalateh–Baghamza–Spring
34	–7.20	–43.00	6.80	50.49 ± 0.9	Gazo–Qanat
35	–8.30	–51.00	0.31	40.48 ± 0.9	Baghamza Village Spring
36	–8.10	–50.00	0.25	–	Well No. 4 Neyetan–Well
37	–8.40	–52.00	0.72	59.00 ± 1.7	Neyestan–Spring
38	–5.30	–39.00	2.80	32.47 ± 1.2	Magoo–Spring
39	–8.50	–53.00	1.50	35.97 ± 1.4	Peykoh–Spring
40	–8.50	–52.00	1.61	27.34 ± 1.3	Warm Water Spring
41	–8.30	–53.00	0.72	35.04 ± 1.3	Cold water Spring
42	–8.30	–57.17	6.00		Hajiabad– Spring
43	–6.88	–51.00	5.30	78.50 ± 1.1	Mazino–spring No. 1
44	–7.58	–52.19	–		–
45	–8.21	–50.35	–		–
46	–7.66	–47.10	–		–
47	–8.27	–54.46	2.80	–	Deg–e–Rostam–Warm Spring
48	–6.73	–41.68	6.90	–	Aliabad–Spring
49	–8.61	–60.02	4.10	43.12 ± 1.3	Well No. 116
50	–9.02	–61.60	2.60	34.96 ± 1.3	Well No. 114
51	–9.22	–60.08	2.80	41.76 ± 1.3	Well No. 115
52	–9.16	–61.46	0.30	49.86 ± 1.0	Hasoom–Spring
53	–6.68	–51.40	5.10	84.90 ± 1.2	Mazino–Spring No.3
54	–7.03	–46.82	0.50	–	Sepidabeh–Spring No. 1
55	–5.9	–37.33	1.00	–	Sepidabeh–Spring No. 1

4. CONCLUSION

Following results have been achieved using geologic, hydrologic, isotope and geochemical surveys and also considering main objectives of studies and problems:

- Recharge centers of water resources are found in some parts beyond the study area.

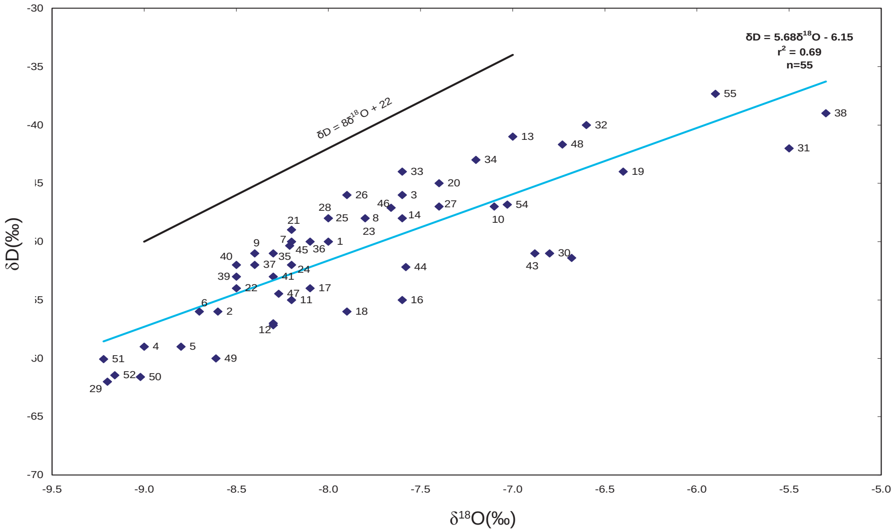

FIG. 2. *Location of water resources in Tabas area comparing to meteoric water line.*

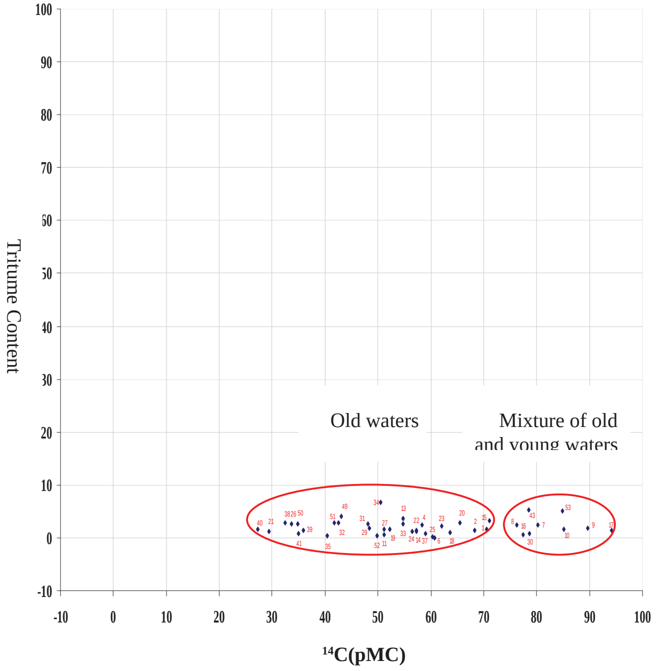

FIG. 3. Age classification of groundwaters in Tabas area based on the tritium and ^{14}C contents, according to Mook table.

- Regarding stable environmental isotopes tests results, recharge centers of water resources within the study area are mainly located in heights over 2,700 m.
- Isotope and chemical results indicate a slight effect of evaporation on increasing salts contents of water resources in the area, whereas the increasing rate mainly depend on the rate of dissolving salts in evaporative and desert rocks on the course of groundwater flows.

5. RECOMMENDATION

Estimating the amount of water resources in Tabas area and determining their durability could not be feasible within performing isotope studies, if more exploitation is performed on existing water resources. The reason is that isotope techniques could only be used to determine the age and nature of waters and aquifers extension and groundwater flow velocity could not be investigated in this way. Hence, more comprehensive hydrology studies are required aiming at having more precise knowledge on aquifers extension and their storage.

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IDENTIFYING AND DATING THE ORIGIN OF GROUNDWATER RESOURCES IN RECLAMATION AREAS OF EGYPT

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Abstract

So-called reclamation areas southwest of the Nile Delta, Egypt, depend almost exclusively on groundwater for irrigation of new agricultural land. We applied stable isotopes and noble gases to study the origin of the groundwater, and several environmental tracer methods (SF_6, ^3H–^3He, ^{14}C) to determine its age. The stable isotopes clearly identify the Nile river as the main source of the water, and due to the change of the river's isotopic composition in response to the construction of the Aswan High Dam, they also provide time information. The environmental tracers show that water recharged during the past 40 years is present only in wells close to surface water features.

Further away from the surface water, ^{14}C data indicate ages up to a few thousand years. We conclude from the isotope data that the regional aquifers are recharged from the surface water, but the recharge and flow velocities are rather low.

1. INTRODUCTION

The high and rapidly growing population density and the constant rate of inflow of Nile river water in Egypt is a great challenge to the Egyptians. To solve this problem, Egypt adopted aggressive policies to develop new agricultural communities outside the overpopulated Nile Delta and Nile Valley. Such so-called reclamation areas depend almost exclusively on groundwater as water resource. For the long-term sustainability of these developments, it is of central importance to understand the processes and rates of recharge of the groundwater resources.

The main goal of this work is to determine the main recharge resources and the recharge rates for reclamation areas located near the south western Nile Delta. The SF_6 and ^3H–^3He methods are used to date the shallow groundwater, whereas noble gases and stable isotopes are applied to obtain information on

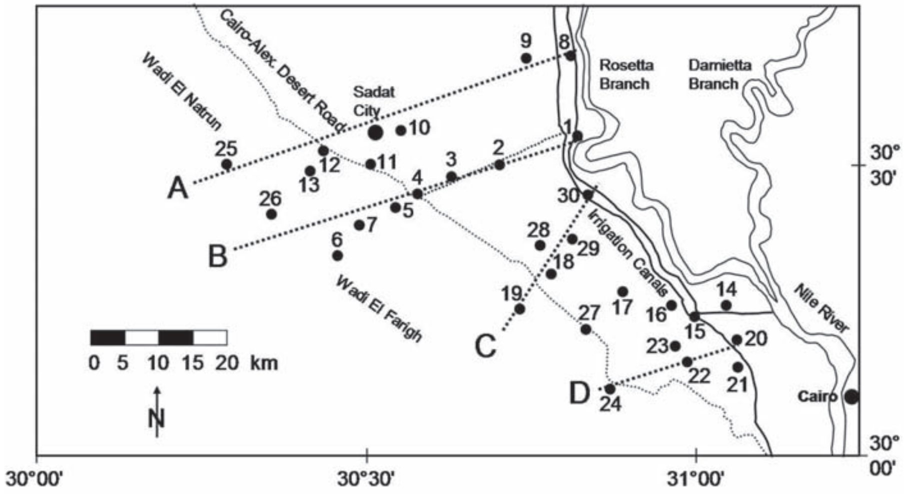

FIG. 1. Map of the investigation area southwest of the Nile Delta and northwest of Cairo. The sampled wells are indicated by dots and well numbers. The area extends from the border of the Nile Delta close to the Rosetta branch of the Nile River and parallel canals to the southwest out into the desert, where reclamation areas are developing, in particular along the Cairo – Alexandria Desert Road. The four sampled transects A – D are indicated by broken lines.

the conditions during recharge and to study groundwater mixing. Radiocarbon is further used to obtain age information for the deeper groundwater in the area.

The investigation area is located southwest of the Nile delta and within about 100 km west-northwest of Cairo (Fig. 1). Its climate is characterized by long hot summers and short warm winters. Monthly mean temperatures in Cairo vary between about 14°C in January/February and 28°C in July/August. With a mean annual rainfall of about 30 mm and a high evaporation rate, the area can be classified as extremely arid, where no or very little groundwater recharge through precipitation can be expected.

The study area is characterized by a low relief and a mild topography with pronounced depressions, e.g. Wadi El Natrun (–23 m) and Wadi El Farigh (–4 m). These depressions act as prominent discharge areas for groundwater movement in the whole area. The surface water canals running along the Rosetta Branch of the Nile River (El Rayah El-Behary and El Rayah El-Nasiry) have levels of the order of 13–15 m above sea level and likely act as the main sources of groundwater recharge.

The water-bearing formations in the investigation area are classified into five aquifers: The Recent, Pleistocene, Pliocene, Miocene and Oligocene aquifers. These sandy to clayey aquifers are hydraulically connected and considered as one hydrological unit. In this work, samples were collected along four different transects (Fig. 1) in the direction of flow, which is generally from northeast to southwest.

2. METHODS

A total of 30 groundwater wells from the area south west of the Nile Delta were sampled in August 2003 for stable isotopes, SF_6, tritium, noble gases, and ^{14}C. Stable isotope samples were collected in 50 ml glass bottles and analyzed on a Finnigan MAT 252 mass spectrometer. SF_6 samples were collected in 1 L special glass bottles and measured on a gas chromatographic system (Shimadzu GC-8AIE) equipped with with an ECD (see [1] for further details). Tritium samples were taken in 1 L glass bottles and were analyzed radiometrically using low-level gas proportional counters with a precision and detection limit of about 1.5 TU. The water samples for noble gas analysis were collected in copper tubes containing about 40 g of water with stainless steel pinch-off clamps at each end, and the measurements were performed on a mass spectrometric system at ETH Zurich (see [2] for further details). Samples for ^{14}C-analysis were taken in 1 L glass bottles, poisoned in the field, and DIC was extracted by acidification in Heidelberg. Radiocarbon measurements were performed at the AMS facility jointly operated by PSI and ETH Zurich.

The basis of the interpretation of the SF_6 and He isotope data is provided by the noble gas concentrations, which were interpreted in terms of recharge temperature and excess air using an inverse modeling technique [3] and the closed-system equilibration (CE) model for excess air formation in groundwater [4]. Based on the results of this procedure, in principle the atmospheric (equilibrium and excess air) components of He and SF_6 can be calculated, and the non-atmospheric (radiogenic and tritiogenic) components of ^4He and ^3He can be determined from the difference of the measured total and modeled atmospheric concentrations.

In practice, however, a more traditional approach to calculate the excess air contributions to He and SF_6 based on the Ne concentrations was used. For SF_6, the ratio of the excess air to equilbrium components was derived from the respective ratio for Ne, assuming that the CE-model holds and taking the different solubilities of the two gases into account. The excess air component of He was calculated from the respective Ne component, but instead of using the atmospheric He/Ne ratio, a slightly lower ratio representing fractionated excess air derived from the fitting procedure was used. The two approaches yield very similar results for the tritiogenic ^3He, but the errors are slightly smaller and easier to interpret if only Ne rather than all noble gases is used. Moreover, if no radiogenic He component is present in a given sample, the calculation of the ^3He components can be entirely based on the He data, instead of using Ne to estimate the atmospheric components. This simplified excess air correction leads to smaller errors because the $^3He/^4He$ ratio is measured with a better precision than the $^3He/Ne$ ratio. This approach was used for samples where the parameters obtained from the heavy noble gases yielded insignificant radiogenic He. If radiogenic He was present, a radiogenic $^3He/^4He$ ratio of 2×10^{-8} was assumed.

Residence times of the young groundwater were determined from the excess-air corrected SF_6 [5] and the ratio of the calculated tritiogenic ^3He to the measured ^3H concentrations [6]. The so derived SF_6 and ^3H–^3He tracer ages are to be interpreted as apparent water ages, since the influence of mixing is not considered. The apparent ages correspond to piston-flow model ages, and do not necessarily reflect the true mean water ages of mixed water parcels [7].

3. RESULTS AND DISCUSSION

The δD and $\delta^{18}O$ values systematically decrease with distance from the surface water. In the stable isotope diagram, linear mixing trends are observed (Fig. 2). Two mixing lines can be distinguished, the first between paleowater ($\delta D = -84‰$, $\delta^{18}O = -10‰$, [8]) and Nile water before the completion of the

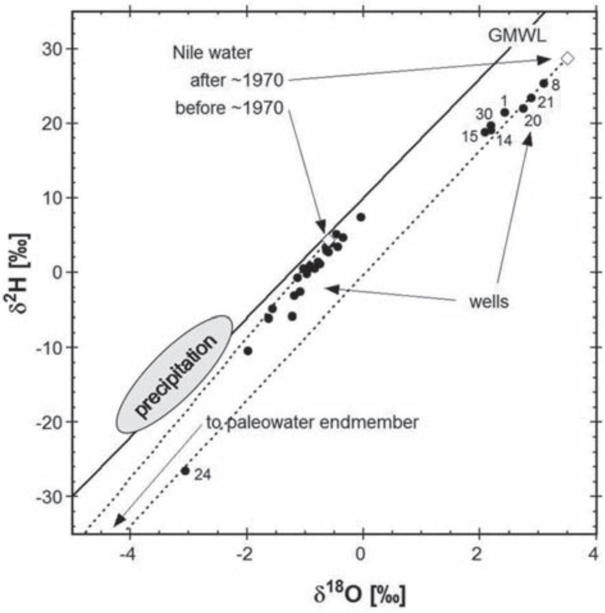

FIG. 2. Stable isotope diagram showing the alignment of the samples along two mixing lines (dashed) between endmembers as defined by Dahab et al.[8], namely paleogroundwater (lower left, outside of the plot range) and Nile water from before and after the construction of the Aswan High Dam in 1970 (diamonds). The range of modern precipitation from Alexandria and Sedi Barany (shaded ellipse) and the global meteoric water line (solid) are also indicated.

Aswan High Dam (δD = 4.3‰, $\delta^{18}O$ = –0.60‰), the second line between paleowater and the Nile water after the completion of the Aswan High Dam (δD = 28.7‰, $\delta^{18}O$ = 3.5‰). The change in isotopic content of Nile water is due to the accumulation of Nile water behind the Aswan High Dam, where a high evaporation rate causes an isotopic enrichment in the present day Nile water compared to the one which was present before the completion of the dam [8].

Most of the values obtained from the wells of this study lie on the mixing line with the old Nile water endmember, indicating that most of the water infiltrated before the completion of the dam in 1970. Only groundwater within the Nile Delta and close to surface water features clearly reflects the recent change in isotopic content of Nile water. The close agreement of the isotopic composition of the groundwater and the two Nile water compositions indicates that the groundwater originates from the surface water, either the Nile River itself or the irrigation canals fed by the Nile. In contrast, the δD and $\delta^{18}O$ values of precipitation in Alexandria and Sedi Barany [9], located to the northwest

TABLE 1. ^{3}H/^{3}HE AND SF$_6$ AGES FOR SAMPLES THAT HAVE SIGNIFICANT ^{3}H AND SF$_6$ CONCENTRATIONS, ALL LOCATED CLOSE TO THE IRRIGATION CANALS AND HAVING ISOTOPIC SIGNATURES SIMILAR TO MODERN NILE WATER. THE SF$_6$ SAMPLES FROM WELL 21 WERE LOST. WELL 20 WAS NOT SAMPLED FOR TRANSIENT TRACERS.

Well. no.	Well Name	^{3}H (TU)	^{3}H/^{3}He age (yr)	SF$_6$ (fmol/L)	SF$_6$ age (yr)
1	El-Khatatba Station	8.4 ± 1.4	1.75 ± 0.51	1.61 ± 0.10	2.0 ± 1.1
8	Kfr Dawod West	10.3 ± 1.4	9.63 ± 1.03	1.26 ± 0.10	4.8 ± 1.3
14	Nekla station	4.6 ± 1.6	24.7 ± 4.7	0.21 ± 0.10	27.0 ± 3.8
15	Roshedy	4.8 ± 1.1	20.2 ± 2.8	1.05 ± 0.10	10.2 ± 1.3
21	Giza	11.4 ± 1.3	4.93 ± 0.66		
30	Said	3.1 ± 1.1	18.9 ± 4.3	0.17 ± 0.10	26.0 ± 5.0

of the study area, are significantly lighter than those of the Nile waters. Thus, significant recharge from precipitation can be ruled out.

The measured atmospheric noble gas concentrations can be adequately described by the CE-model for excess air [4]. The derived recharge temperatures scatter around 23.7 ± 1.4°C, slightly higher than the mean annual air temperature of 21.7°C at Cairo, but likely representing soil temperatures. The good model fits to the noble gas data enable a reliable interpretation of the transient gas tracers SF$_6$ and ^{3}He.

Only six wells located very close to the surface water (within 1.6 km of the irrigation canals) have clearly significant ^{3}H concentrations between 3.1 and 11.4 TU, allowing reliable ^{3}H–^{3}He dating with ages ranging from 2 to 25 years (Table 1). These wells also have high SF$_6$ concentrations and consequently young SF$_6$ ages ranging from 2 to 27 years (Table 1). In the stable isotope diagram (FIG. 2), these samples all lie close to the modern Nile endmember, indicating infiltration after the completion of the Aswan High Dam, in agreement with the tracer ages. The young ages and the isotopic composition proof that the wells nearest to the surface water are recharged by water derived from the river (i.e., directly from river branches or via canals or irrigation).

Among these young wells, the ^{3}H–^{3}He and SF$_6$ ages for wells No. 1, 14, and 30 are in a good agreement (Table 1), while there is disagreement between them for wells No. 8 and 15. The SF$_6$ ages for these two wells are less than the ^{3}H-^{3}He ages, which might be explained by a small air contamination of the SF_6 samples, which would lead to an underestimation of SF_6 ages. SF_6 is very sensitive to air contamination, and the sampling procedure that was applied using glass bottles that were pre-filled with N_2 and partly evacuated in the field may be more prone to contamination both during sampling and transport than the copper tube method used for He. Duplicate samples were taken from most wells, and several samples could clearly be identified as leaky and were excluded from the interpretation. The remaining samples still exhibited a slight overpressure in the N_2-headspace before analysis, indicating that no air contamination should have taken place during storage and transport. However, a slight air contamination during sampling cannot be entirely excluded.

Most of the wells that are located further away from the irrigation area around the artificial canals have insignificant tritium and very low, although detectable, SF_6 concentrations. These SF_6 concentrations near to but usually significantly above the analytical detection limit of about 0.02 fmol/L translate to atmospheric mixing ratios at solubility equilibrium on the order of 0.2 ppt, somewhat above the expected natural background of 0.054 ppt [5]. They may thus either indicate a high local natural component or a slight general air contamination. In view of this general SF_6 background, the uncertainty of the SF_6 results was estimated to be 0.1 fmol/L, about five times higher than the analytical error. Only one well at large distance (No. 7) has a clearly higher SF_6 concentration. This well also appears to contain some tritium (1.7 ± 1.3 TU) and may be influenced by local recharge or admixing of a young component. The apparent SF_6 age at this well of about 5 yr is nevertheless at odds with the low tritium content, and therefore most likely due to SF_6 contamination.

The ^{14}C-activity of the DIC in the groundwater generally decreases with distance from the surface water, in agreement with the expected flow direction. However, most of the measured activities lie in a range of 60 to 90 pMC, where the calculation of a ^{14}C age is difficult because the common correction models for the effect of carbonate dissolution (e.g. [10]) indicate similar initial ^{14}C activities. Only the two most distant wells in the Wadi El-Natrun area (Nos 25, 26) and one well from the southern end of the study area have significantly lower ^{14}C activities, allowing more reliable age estimates ranging between 4 and 10 kyr. An old age of the water in wells 22 and 25 is also supported by high radiogenic ^{4}He concentrations in these wells, but not as clearly for well 26. High radiogenic ^{4}He is also present in well 24, where, as in the neighbouring well 22, it occurs together with a high salinity, which is typical for the Oligocene aquifer and may indicate admixing of old fluids from deep or low-permeable layers. A large fraction of paleowater in well 24 is also indicated by its isotopic composition (Fig. 2).

4. CONCLUSIONS

The new reclamation areas south west of the Nile delta seem to be recharged mainly from Nile water. Most of the recharge took place before the completion of the Aswan High Dam in 1970, as indicated by stable isotope data and corroborated by the absence of the transient tracers tritium and SF_6 in most wells. The few samples that lie on the stable isotope mixing line between paleo-groundwater and recent river water, indicating recharge by Nile water after the completion of the Aswan High Dam, are from wells located very close to the surface water. These samples are also characterized by significant ^3H and SF_6 concentrations, yielding young ages of less than 27 years.

While the isotopic signature of the groundwater in the reclaimed areas indicates that it originates from the Nile River and therefore is a renewable resource, the absence of recent recharge shows that the groundwater renewal is a slow process. The exact timescale of water flow from the surface water to the reclamation areas in the southwest of the delta is difficult to be determined, as the ages of these waters exceed the dating range of the transient-tracer based methods discussed above but are too low for reliable dating by ^{14}C. It would therefore be of great interest to use ^{39}Ar, the only dating tool available in the age range of more than 50 but less than a few thousand years, to date this groundwater. Knowing the age of the groundwater along our transects should be useful to determine the flow velocities in the area and to estimate the total groundwater renewal rate.

Our results show that at present recharge is slow and therefore only a limited amount of groundwater is available for pumping in a sustainable resource management regime. Numerical groundwater modeling, preferably making use of the age information from tracer studies, will be needed to make quantitative predictions on the groundwater flow regime in the future for different pumping scenarios.

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MULTI ISOTOPIC AND GEOCHEMICAL CONSTRAINTS ON INTERCONNECTION AND HETEROGENEITIES OF WATER BODIES IN THE ADOUR–GARONNE DISTRICT (SW FRANCE) — THE CARISMEAU RESEARCH PROJECT

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Abstract

The main objective of the Water Framework Directive (2000/60/EC) is to prevent further deterioration and protect and enhance the status of aquatic ecosystems in Europe. The success of the WFD will be mainly measured by the status of water bodies. Aims of the research project *Carismeau* are to provide further characterization of the groundwater bodies which have been identified as being of primary importance and/or at risk in the Adour-Garonne district (1/5 of the French territory). For that purpose, combined geochemical analysis (major and trace elements), and isotopes ($\delta^{18}O$ and $\delta^{2}H$, $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$, strontium, boron, lithium, uranium and lead isotopes) are applied on one demonstrative water body named the Eocene sands aquifer. Preliminary results point out the extreme heterogeneity of water signatures between the selected water bodies but also within a single aquifer. The ongoing research will set out to demonstrate the role of lateral variation of facies and the interconnections between aquifers.

1. INTRODUCTION

The purpose of the Water Framework Directive (WFD, 2000/60/EC) is to establish a framework for the protection of inland surface waters, transitional waters, coastal waters and groundwater aiming at prevents further deterioration and protects aquatic ecosystems. WFD promotes sustainable water use based on a long-term protection of available water resources, ensures the progressive reduction of pollution of groundwater and prevents its further pollution in Europe. The WFD came into force in December 2000 and defined the water body as common frame. The WFDs overall environmental objective is the achievement of "good status" for all of Europe's surface- and groundwater bodies by 2015, using the river basins as the basic unit for all water planning and management actions. In October 2006, an agreement has been reached for a new directive to protect groundwater from pollution (2006/118/CE).

Within the framework of the WFD, the research project Carismeau for "multi isotopic and geochemical characterisation of water bodies" in the Adour-Garonne district (SW France) was initiated jointly between the French Water Agency Adour-Garonne and BRGM. Aims of Carismeau are to provide further characterization of those groundwater bodies or groups of bodies which have been identified as being of primary importance and/or at risk in the district. This approach is based on the WFD/Annex II which stated, among others, that this characterization shall include (1) information on the stratification characteristics of the groundwater within the groundwater body, (2) on the estimates of the directions and rates of exchange of water between the groundwater body and associated surface systems, (3) provide further characterization of the chemical composition of the groundwater, including specification of the contributions from human activity.

For that purpose, combined geochemical analysis (major and trace elements), common isotopic methods with $\delta^{18}O$ and $\delta^{2}H$ of the water molecule and $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$, innovative isotopic method with strontium and uranium isotopes and potential isotopic methods with boron, lithium and lead isotopes will be applied on one demonstrative water body named the Eocene sands aquifer in the research project Carismeau.

Aim of this paper is to present the results of the $\delta^{18}O$ and $\delta^{2}H$ of the water samples and strontium isotopes in order to constraint the origin of the water and the water-rock interactions.

2. GENERAL SETTINGS OF THE ADOUR GARONNE DISTRICT (S.W. FRANCE) AND THE CARISMEAU PROJECT

The Adour-Garonne district covers 116 000 km² and represents 1/5 of the French territory. It is limited by the Massif Central and Montagne Noire to the east, by the Armorican Massif to the north, by the Pyrénées to the south and by the Atlantic Ocean to the west (Fig. 1). It represents 6900 councils for a total of around 6.7 millions inhabitants.

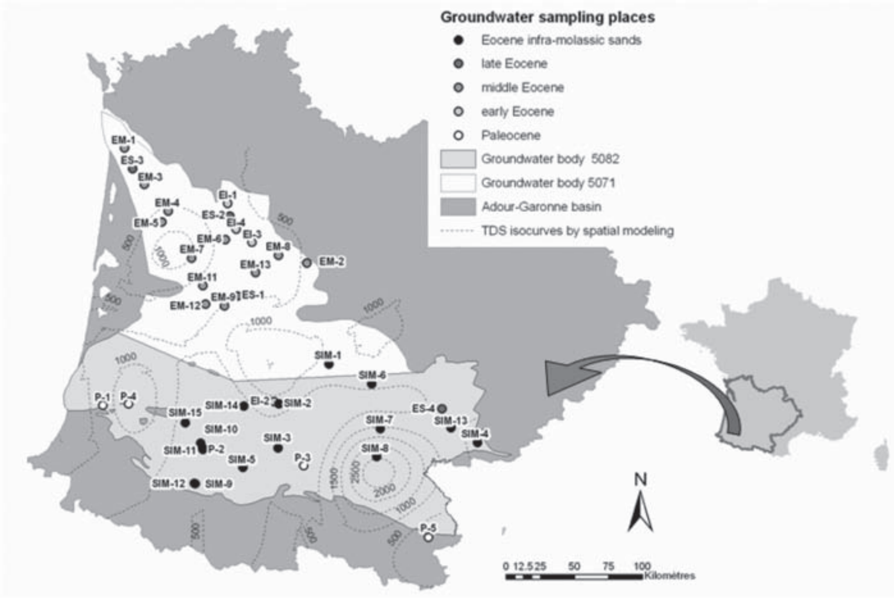

FIG. 1. General setting of the Adour Garonne district (SW France) and isocurve map of the Total Dissolved Solids (TDS, mg/l) in the targeted aquifers

The Eocene sands water body constitutes a series of major aquifers used for drinking water, agriculture, irrigation and thermo-mineral water resource [1]. This system extends over the Adour-Garonne district, being an artesian system to the west of the district and confined with piezometric levels around 250 m to the east of the district. The Eocene sands aquifer composed by sandy Tertiary sediments alternating with carbonate deposits, is a multi-layer system. The Eocene aquifer system, presents a high permeability and a thickness of several tenths of metres to a hundred metres. It is covered by molassic sediments, which form an aquiclude with a thickness up to some hundred meters. The Eocene aquifer system is constituted by at least five aquifers: Paleocene, Eocene infra-molassic sands (IMS), early Eocene, middle Eocene, late Eocene. The deposit sequences characterising the Eocene aquifer system are progradational westward, from detrital deposits to carbonates with evaporites domes [1]. Groundwater recharge may occur to the east by the edge of the Massif Central, to the south by the edge of the Pyrenees and by inflow from the Paleocene aquifer.

Sand deposits mineralogy is very poor, containing mainly quartz augmented with calcite and at places dolomite and K-feldspars [1]. Detrital sediments were eroded from the Massif Central, the Montagne Noire, and the emerging Pyrenees mountains.

3. ISOTOPE TOOLS

Waters were sampled in May 2006 in different types of boreholes used for drinking water supply, irrigation, geothermal activities or groundwater quantity and quality survey in the frame of the WFD. Samples for stable isotope determination were stored in polyethylene bottles. After collection, the water samples were filtered through pre-cleaned 0.22 μm acetate filters, 100 and 250 mL were acidified with double-distilled nitric acid and stored in pre-cleaned polyethylene bottles for major-cation and elemental Sr analysis and strontium isotope ratio and 100 mL were stored unacidified in polyethylene bottles for anion analysis. The stable isotopes (δ^2H and δ^{18}O) were measured using a Finnigan MAT 252 mass spectrometer with a precision of 0.1‰ *vs.* SMOW for δ^{18}O and 0.8‰ for δ^2H. Isotopic compositions are reported in the usual δ-scale in ‰ with reference to VSMOW according to δ_{sample} (‰) = $\{(R_{sample} / R_{standard}) - 1\} \times 1000$, where R is the ^{2}H/^{1}H and ^{18}O/^{16}O atomic ratios. Chemical separation of Sr was performed using an ion-exchange column (Sr-Spec), with total blank <0.3 ng for the entire chemical procedure. After chemical separation, around 150 ng of Sr was loaded onto a tungsten filament and analysed with a Finnigan MAT 262 multiple collector mass spectrometer. The measured ^{87}Sr/^{86}Sr ratios were normalised to an ^{86}Sr/^{88}Sr of 0.1194 and then adjusted to the NBS-987 standard value of 0.710240. An average internal precision of $\pm 10 \times 10^{-6}$ (2σ) was obtained during this study; reproducibility of the ^{87}Sr/^{86}Sr ratio measurements was tested through duplicate analyses of the NBS 987 standard and the mean value was $0.710235 \pm 20 \times 10^{-6}$ (2σ; n = 19).

4. RESULTS

4.1. Chemical overview

The Total Dissolved Solids (TDS) represents the total mineralization of water with respect to the inorganic content by summing cations and anions. TDS values varied between 74 mg/L (P3) and 2513 mg/L (SIM8). Large variations are also observed in the aquifers, from 74 up to 1253 mg/L in the Paleocene aquifer; from 255 up to 1033 mg/L in the middle Eocene aquifer and 230 up to 2513 mg/L in the Eocene infra-molassic sand (IMS), for example. The highest mineralization is generally encountered in water draining forces evaporite formations (gypsum and/or halite) as evidenced in a previous study in the southern part of the Eocene sand aquifer [1] (Fig.1). The source of the high dissolved species content cannot be related to anthropogenic activities such as agricultural practises that may have occurred as the NO_3 content is always lower than 0.5 mg/L.

Waters from the Eocene aquifers mostly show a calcium bicarbonate facies but sodium bicarbonate, sodium chlorine and sodium sulphate waters can be observed in several locations [1]. For example, in the Eocene infra-molassic sand, the calcium bicarbonate facies is predominantly observed, changing eastward to sodium chlorine and then to sodium bicarbonate. These facies reflect well the geology of the basin, from silicates (sands with quartz, calcite, feldspars, kaolinite, mixture of iron oxides/hydroxides, pyrite in some parts; argillaceous or argillaceous-sandstones interbeds) to carbonates and evaporites deposits (to the west and north of the basin). However, most of the groundwaters show low TDS values when compared to the geologic environment (carbonate, evaporite) and the estimated age of the ground waters (close to 16–35 ky using ^{14}C [1]). The spatial distribution of the TDS values indicates several places with high salinities in the water (values > 1000 mg/L); the highest being observed in the southeast part of the basin (Fig. 1).

4.2. Variations of isotopic signature of the water molecule ($\delta^{18}O$ and δ^2H)

A wide range in isotope composition was observed in the collected groundwaters with isotope composition that varies between –5.6‰ and –10.4‰ for $\delta^{18}O$ and –35.0‰ and –72.3‰ for δ^2H.

The δ^2H and $\delta^{18}O$ values of the groundwater are plotted in the Fig. 2 with the global meteroric water line (GMWL) and the local meteoric line (Massif Central, BRGM unpublish data). The present day weighted mean signatures of Atlantic coastal rain (Dax) and Massif Central are also reported. All the data from the collected groundwaters plot along the global meteoric water line ($\delta^2H = 8 \times \delta^{18}O + 10$), the most enriched samples plot close to the present weigted mean signature of Atlantic coastal rain.

4.3. Variations of Sr content and isotopic signature ($^{87}Sr/^{86}Sr$)

Strontium-isotope ratios vary in nature because one of the strontium isotopes (^{87}Sr) is formed by the radioactive decay of the naturally occurring element rubidium (^{87}Rb). The $^{87}Sr/^{86}Sr$ ratios are mainly used as tracers of water-rock interaction [2–4]. The primary sources of Sr in groundwater are atmospheric input, dissolution of Sr-bearing minerals, and anthopogenic input [2, 3].

Sr^{2+} shows large content variations in the ground waters, from 156 μg/L (ES3) to 3419 μg/L (EI2), however not proportionally to TDS (R^2~0.32). This reflects that part of the main source of salinity does not necessarily provide Sr^{2+} to groundwaters and vice versa. Large variation are observed in the $^{87}Sr/^{86}Sr$ ratios, from 0.707597 (EI2) to 0.711847 (SIM4), thus leading to large ΔSr variations from –1571 to 2679, respectively; ΔSr being the presentation of the $^{87}Sr/^{86}Sr$ ratios with reference to modern sea water ($0.709168 \pm 1x10^{-6}$), according to $\Delta Sr = (^{87}Sr/^{86}Sr\ sample - {}^{87}Sr/^{86}Sr\ seawater) \times 10^6$. Variations by ± 2 ΔSr between two samples is significative regarding the analytical reproducibility of the Sr isotope ratios measurement and the uncertainties on the seawater value. The lowest $^{87}Sr/^{86}Sr$ values agree with the weathering of carbonates and evaporites as they have recorded the seawater signal at time of deposition and their weathering release the same signal in the water [2, 5]. Contrary to that, highest $^{87}Sr/^{86}Sr$ values refer to the weathering of silicate such as granite that deliver to water $^{87}Sr/^{86}Sr$ ratios higher than 0.710 [3, 4]. The spatial variation reveals two areas of high ΔSr (> 1000), one located south near the central zone of the Pyrenees, and the other one eastward near the Massif Central, certainly reflecting the weathering of granites. On the other hand, low values are observed along a transect northwest-southeast (ΔSr < –500).

5. DISCUSSION

5.1. Groundwater origin through stable isotopes of the water molecule

The groundwater data present a wide range of stable isotopic composition (δ^2H, $\delta^{18}O$) both between the different aquifers and inside a single aquifer (Fig. 2). The most enriched samples (EM1, EM2, ES3) originate from the north of the area, in the vicinity of the Gironde estuary and present a signature quite similar to that of present day coastal precipitations. At the opposite, the most depleted sample (P3) originates from the Paleocene aquifer (860 m depth), and may reflect an old recharge as its signature is clearly lowest than that of present-day precipitations from the Massif Central or Pyrenees. The IMS aquifer presents a wide range of variation along the global meteoric water line which excludes significant evaporation of infiltrating waters and any continental effect on the stable isotope composition. These variations cannot be easily correlated with the data spatial location, and are probably mostly due to the period and location of the recharge of the aquifer. The most depleted sample of IMS (SIM4) is located in the eastern border of the study basin and originates from 177 m depth, it may represent an old recharge (as the estimated age of some ground waters are close to 16–35 ky using ^{14}C [1]). Indeed, similar shift was revealed by several studies

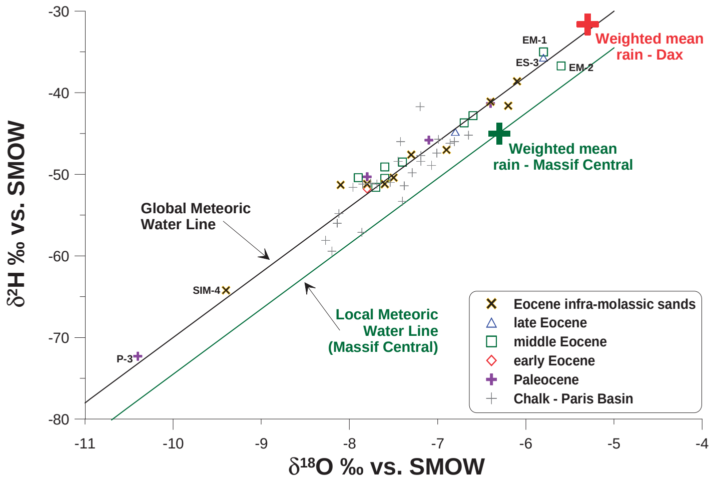

FIG. 2. $\delta^{18}O$ – $\delta^{2}H$ plot for the groundwater samples collected in the aquifers. GMWL corresponds to the global meteoric water line ($\delta^{2}H = 8 \times {}^{18}O + 10$). Chalk – Paris Basin data from [6].

of paleo-waters in European aquifers and such significant isotopic depletion of ground waters may be due to a lower recharge temperature at the time of infiltration [6].

5.2. Sr isotopes as mixing tracers

Sr isotopic ratios coupled with Sr^{2+} concentrations can be used to investigate mixing of different groundwater bodies or connections between surface and groundwater. When plotted against the $^{87}Sr/^{86}Sr$ ratio, the Sr contents (or 1/Sr) enable clear identification of geochemical end-members (Fig. 3). Most of the signatures of the groundwater samples in this diagram can be explained by mixtures in various proportions of at least three identified geochemical end-members (1 to 3). Theoretical mixing lines between different geochemical end-members can be calculated by considering two-component mixtures. End-members are characterized as to encompass all the considered samples. The first mixing curve rely end-member 1 and 2 which characteristics are ($^{87}Sr/^{86}Sr = 0.70725$; $Sr^{2+} = 60$ µmol/L and $^{87}Sr/^{86}Sr = 0.70900$; $Sr^{2+} = 1.4$ µmol/L respectively). The second mixing curve rely end-member 1 and 3, the characteristics for the latter are ($^{87}Sr/^{86}Sr = 0.71500$; $Sr^{2+} = 6$ µmol/L). The third mixing curve rely end-member 2 and 3.

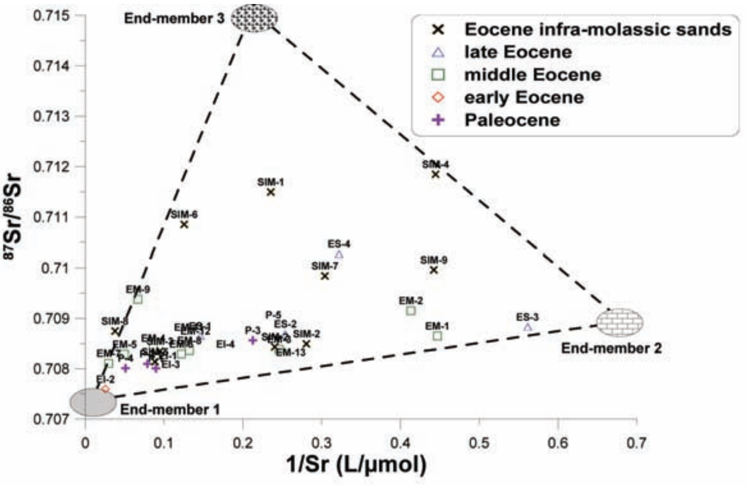

FIG. 3. Plot of $^{87}Sr/^{86}Sr$ vs. 1/Sr (1/µmol/L) for the groundwaters collected in the aquifers.

The end-member 1 may represent the weathering of evaporite formations. Water that experienced interaction with evaporites generally display high Sr^{2+} contents (up to 350 µmol/L [2]) that is reflected in the Sr^{2+} content of end-member 1. As the Sr isotope ratios in seawater are constant at any point in time and evaporite (as well as carbonate) are Rb-free [2] [5], the $^{87}Sr/^{86}Sr$ ratio of theses rocks reflect that of the seawater at time of deposition. The $^{87}Sr/^{86}Sr$ ratio of end-member 1, representing the evaporite, fully agrees with the value of marine evaporites from the Eocene sulphate minerals from Cenozoic evaporites located in Anatolia (Turkey) with a mean $^{87}Sr/^{86}Sr$ ratio of 0.707271 (standard deviation = 0.000604, n = 16 [7]). It is worth noting that this ratio also agrees with the seawater value given for the Eocene [8].

The end-member 2 may correspond to the weathering of carbonate as suggested by the increase in the Ca/Sr ratio from around 30-100 for end-member 1 up to 500-1300 for end-member 2. However, the Sr^{2+} content for this end-member is the lowest observed in the three end-members and its $^{87}Sr/^{86}Sr$ (0.70900) is clearly higher than that of Eocene carbonate that may display a $^{87}Sr/^{86}Sr$ ratio of around 0.7072 [8]. Thus this end-member may not represent the Eocene carbonate as there is no evidence of carbonate with such high $^{87}Sr/^{86}Sr$ ratio in the considered aquifers. Two samples located north of the area in the vicinity of the Gironde estuary characterize this end-member (EM1 and ES3) and an impact of seawater intrusion may be considered. However, the Ca/Sr ratio of these samples refers to carbonate weathering (700 and 1000 respectively [2]) and do not plead in favour of a relict of seawater or to direct seawater intrusion yielding to a $^{87}Sr/^{86}Sr$ ratio close to that observed for the past 8 Ma (0.7089–0.7092 [8]. Otherwise this end-member may represent the leakage effect due to the overexploitation of the aquifer in this northern part of the basin and the origin of the dissolved Sr should be the weathering of the Miocene carbonate deposits with $^{87}Sr/^{86}Sr$ ratio around 0.7089–0.7091.

The end-member 3 with a radiogenic value clearly refers to the weathering of silicate. The highest $^{87}Sr/^{86}Sr$ ratios are observed in the southern part of the basin, near the Pyrenees and in the eastern part, on the edge of the Massif Central where the silicate rocks are present. Part of the Sr mass-balance in a crystalline environment should be controlled by Sr supplied by chemical weathering of Sr-bearing phases from the host rock. Minerals from granites that most commonly influence the Sr isotopic budget in waters are apatite, plagioclase, K-feldspar and biotite and muscovite and the $^{87}Sr/^{86}Sr$ ratio of water draining crystalline environment generally fall in the interval 0.712–0.718 [3, 4].

The mixing proportion can be calculated for each sample on the mixing trend as well as for those lying within the triangle. Along the mixing line between the end-members 1 and 2, the proportions of end-member 2 is around 70% in sample ES3, 60% in sample EM1 and 35% in sample EM13. Along the mixing line between the end-members 2 and 3, the proportions of end-member 2 is around 80% in sample SIM4. Along the mixing line between the end-members 1 and 3, the proportions of end-member 1 is around 94% in sample EI2, 50% in sample EM7 and reach 20% in sample EM9.

6. SUMMARY

This study presents the first investigation of stable and Sr isotopes in an aquifer system in the south of France. Large variations are observed in $\delta^{18}O$ and $\delta^{2}H$ due to different steps of recharge. The Sr isotope of groundwaters suggests variable origin in which mixing processes and water-rock interaction have both contributed to the observed values. These results point out the extreme heterogeneity of water signatures between the selected water bodies but also within a same aquifer and will be used to define specific strategies for groundwater monitoring.

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GROUNDWATER QUALITY AND URBAN HYDROLOGY

ASSESSING THE IMPACTS OF ANTHROPOGENIC ACTIVITIES ON GROUNDWATER QUALITY USING NITROGEN ISOTOPES — AVEIRO QUATERNARY AQUIFER (PORTUGAL)

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Abstract

The Aveiro region, situated on the northwest coast of Portugal is one of the most industrialized areas of Portugal, with a high demographic density and an intensive agriculture. The shallow Quaternary aquifer system, which consists mainly of detrital sediments of Pleistocene and Holocene ages, is still today an important water resource for this region despite growing evidence of diffuse pollution problems. Isotope techniques have been used to evaluate the aquifer vulnerability to nitrate contamination. Groundwater samples were collected from 30 wells and springs for isotopic analysis ($\delta^{18}O$ and $\delta^{15}N$ from NO_3 and δ^2H and $\delta^{18}O$ from H_2O). Nitrogen isotopes were used to identify nitrogen sources and assess agriculture, cattle-breeding, urban and industrial contribution to nitrogen cycle in Aveiro ecosystem, based on the fact that the main sources of nitrate in the area have isotopic distinct $\delta^{15}N$ and $\delta^{18}O$ signatures. This methodology contributed to the identification of the main nitrate sources in the region (agriculture and industrial).

1. INTRODUCTION

Large-scale diffuse pollution is of great concern in most European countries where nitrate concentrations in public water supplies have risen above acceptable levels largely as a result of overuse of fertilizers in agriculture practices, as well as contamination by factories, and human and animal wastes. Related to these possible anthropogenic inputs leading to the water resources degradation, this study focused on origin/sources of nitrate in water resources (surface and groundwater bodies) using nitrogen isotopes. The studied area, the Aveiro region, is located in the NW of Portugal, presenting important industrial and agriculture activities, which have an impact on the water quality of the shallow Quaternary aquifer and the Vouga River.

The water supply in the Aveiro region is guaranteed using both surface and groundwater resources. Industry and agriculture use, mainly groundwater resources, from both the shallow Quaternary aquifer and the deep confined Cretaceous aquifer. Drinking water supply is guaranteed by integrated management of surface water resources from the Vouga river and groundwater from the Cretaceous aquifer. In some parts of the region, surface water resources are used also to irrigate the crops in the river, stream and lagoon banks.

2. HYDROGEOLOGICAL SETTING

Two main groundwater bodies have been identified in the Lower Vouga Sedimentary Basin: the shallow Quaternary system and the Cretaceous multilayer system (Fig. 1). The shallow aquifer system consists mainly of detrital sediments of Pleistocene and Holocene age (dunes, fluvial terraces and ancient

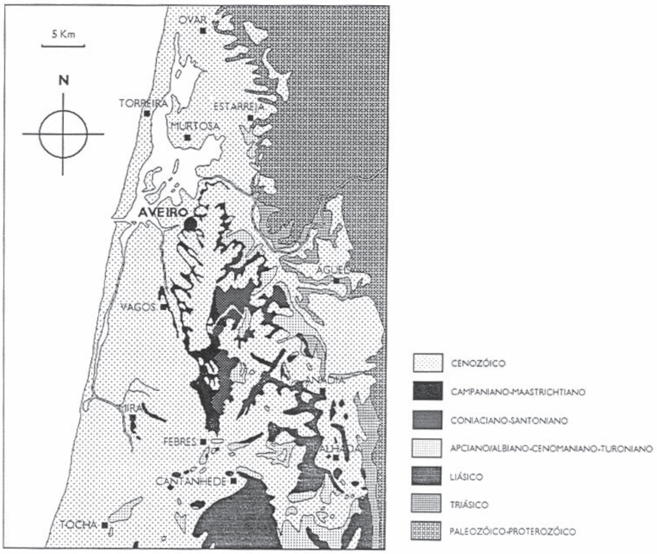

FIG. 1. Geological map of the Aveiro area [3].

beaches) related to different marine regression events. The shallow aquifer units are very permeable and have a high rate of recharge from direct infiltration of rainfall or irrigation [2]. Owing to easy exploitation and high productivity, these water bearing units represented, until the late sixties, the main groundwater resource in the region.

The second groundwater system consists of a confined multilayer sequence of Cretaceous age with an overall thickness of around 100 m, mainly made up of sandstones and clays, where the carbonate layers make up only 1 to 8% of total thickness. This multilayer system is made up of stratified layers of quartz sandstones and clay sediments overlying the schist-graywacke complex [2].

3. METHODOLOGY

In this study 16 samples of groundwater were collected from the superficial Quaternary aquifer, all of them presenting nitrates contamination with concentrations higher than 25 mg/L. Ph, temperature and electrical condutivity in all the samples were analysed in situ. It was determined for the collected samples δ^2H and δ^{18}O from H_2O and δ^{18}O and δ^{15}N from NO_3.

The Nuclear and Technological Institute (ITN) in Portugal carried out the determinations of δ^{18}O and δ^2H values by mass spectrometry. Common isotope methods [8, 9] were used for the determination of δ^2H and δ^{18}O. Water samples were measured by the Sira 10 da VG ISOGAS mass spectrometer with an analytical precision of ±0.1‰ for δ^{18}O and ±1‰ for δ^2H. The standard δ notation per mil is used throughout the paper and is relative to values found in references V-SMOW (Vienna standard mean ocean water) for δ^2H and δ^{18}O [4].

The determination of δ^{18}O and δ^{15}N from NO_3 requires the collection of nitrate from groundwater. This collection was made followig the method described in [5]. Nitrate is collected by passing the water sample through cation and anion exchanging columns, subsequently this nitrate is extracted from the anion column, converted to $AgNO_3$ and analysed for its isotope composition. Nitrate is eluted from the anion exchange column with HCl, this nitrate-bearing acid is neutralized with Ag_2O, then freeze-dried to obtain solid $AgNO_3$ for δ^{15}N. For δ^{18}O analysis, aliquots of the neutralized eluant are processed further to remove non-nitrate oxygen-bearing anions. Barium chloride is added to precipitate sulfate and phosphate; the solution is then filtered, passed through a cation exchange column to remove excess Ba^{2+}, re-neutralized with Ag_2NO_3, and freeze-dried. The resulting $AgNO_3$ is then analysed through spectrometry with the use of EUROVECTOR elemental analyser.

4. ISOTOPIC CHARACTERIZATION

From previous studies it is known that this Quaternary aquifer represents a shallow aquifer unit, and collection of groundwater samples from wells and springs (with medium depths of 20 m). It is admited that this water group represents the isotpic composition of Baixo Vouga recent precipitation. The isotopic composition ranges between –29 to –25‰ and –5.0 to –4.4‰, respectivelly for δ^2H and $\delta^{18}O$, in samplings made in dry and wet seasons. Based on the δ values were calculated the correlation coeficients between δ^2H and $\delta^{18}O$ and the equivalente regression line, respectively , r= 0,83 and $\delta^2H = (8.29 \pm 1.07)\ \delta^{18}O + 12.06$ (n = 19) (Fig. 2) [6].

The samples analysed in this study present values of δ^2H and $\delta^{18}O$ slightly enriched relative to the values mentioned above (Table 1), however it is important to mention that these samples were mainly collected in wells, and so it is possible to affirm that these groundwater samples had suffered evaporation.

4.1. Identification of nitrate antropogenic contamination sources

Stable nitrogen isotopes can offer a direct mean of source identification, because the major sources of nitrate have isotopically distinct $\delta^{15}N$ values. The relative contribution of the different sources to groundwater or surface water can be estimated by mass balance. However in some situations, such as soil-derived nitrate and fertilizer, nitrate has overlapping $\delta^{15}N$ values, preventing their separation using $\delta^{15}N$ alone, but the analysis of $\delta^{18}O$ of nitrate in conjunction with $\delta^{15}N$ is fundamental to improve the ability to trace

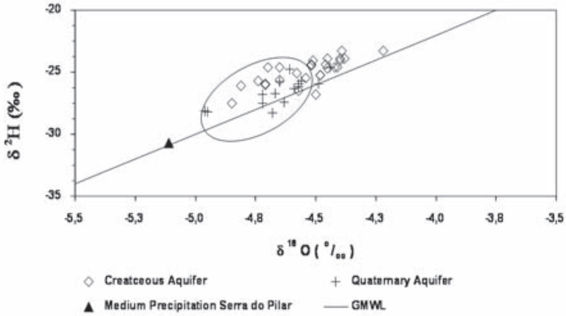

FIG. 2. δ^2H versus $\delta^{18}O$ represented by samples from de Cretaceous multiaquifer system and from the Quaternary aquifer. In the diagram it is plotted the mean isotopic composition from the meteorological station of Serra do Pilar. The ellipse delimits the Quarternary aquifer mean isotopic composition [6].

TABLE 1. ISOTOPIC COMPOSITION OF SAMPLES COLLECTED IN AVEIRO QUATERNARY AQUIFER. T STANDS FOR TEMPERATURE (ºC) , THE δ RESULTS ARE IN ‰.

Sample	pH	EC (μS/cm)	T	$\delta^{18}O$	$\delta^{2}H$
1	6.13	837	13	–3.76	–21.2
2	6.11	668	16	–4.02	–18.8
3	6.40	923	12	–4.17	–27.8
4	6.21	844	16	–3.89	–24.6
7	6.15	429	12	–3.85	–24.3
9	6.94	913	10	–4.08	–25.9
10	6.66	482	16	–3.94	–24.5
11	7.48	588	7	–3.85	–25.6
12	6.04	350	15	–4.16	–27.5
13	7.03	460	18	–3.89	–24.7
14	6.97	535	9	–4.18	–26.0
15	6.89	570	12	–3.93	–24.7
16	6.77	360	10	–3.90	–24.1
18	6.59	620	12	–2.57	–18.7
25	6.84	785	12	–4.00	–25.9
26				–4.07	–21.9

nitrate sources. With the expansion in Instituto Tecnológico e Nuclear of the field of isotope hydrology in $\delta^{15}N$ and $\delta^{18}O$ of nitrates made possible, by the development and increased availability of preparation and analysis systems for mass spectrometers, the identification of the isotopic composition of various sources of waters and solutes, including nitrate [7].

Fig. 3A shows the normal range of $\delta^{15}N$ and $\delta^{18}O$ values for dominant sources of nitrate. Nitrate derive from ammonium fertlilizer, soil organic matter, and animal manure have overlapping $\delta^{18}O$ values; for these sources $\delta^{15}N$ is a better discriminator. In contrast, nitrate derived from nitrate fertilizer or atmospheric sources are readily distinct from microbial nitrate using $\delta^{18}O$, even though the $\delta^{15}N$ values are overlapping. The dual isotope study of groundwater nitrate that was collected proved to be useful in source identification (Fig. 3B) allowing to establish the manure and septic waste as the main nitrate source

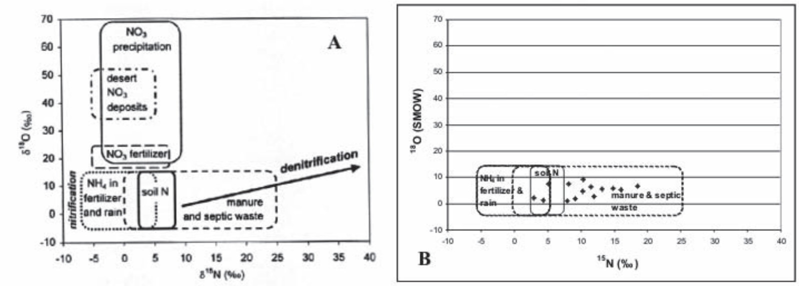

FIG. 3. A — Schematic of typical ranges of $\delta^{15}N$ and $\delta^{18}O$ values of nitrate from various sources [7]; B — $\delta^{18}N$ versus $\delta^{18}O$ values of nitrate of Aveiro Quaternary aquifer samples.

in the analysed waters. Three samples were also identified where the nitrates derive from NH_4 in fertilizer and rain, samples that correspond to agricultural locations or industrial sources.

It is likely that the O_2 (and perhaps H_2O) available to nitrifiers in the small soil pores has been significantly affected by microbial processes, and is commonly enriched in ^{18}O relative to “bulk” compositions. When ^{18}O enriched sources of O are utilized by microorganism, the resulting nitrate is also enriched in ^{18}O. If microbial nitrate is “labelled” by the $\delta^{18}O$ value of ambient water, the seasonal change in the $\delta^{18}O$ of water might cause a seasonal change in soil nitrate $\delta^{18}O$. Alternatively, if fields are irrigated with evaporated water at the same time that ammonium fertilizer is applied, the nitrate formed might reflect the evaporated signature of the water $\delta^{18}O$ [7].

In order to evaluate if $\delta^{18}O$ value of nitrate was affected by changes in the $\delta^{18}O$ values of water and O_2 the obtained results were plotted in graphic from

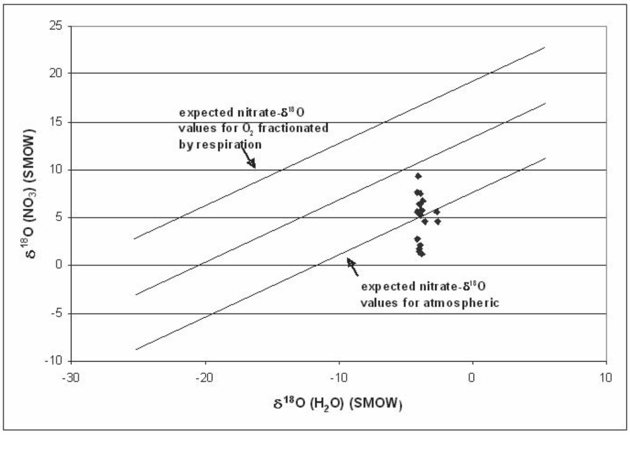

FIG. 4. $\delta\ ^{18}O$ (H_2O) versus $\delta\ ^{18}O$ (NO_3) adapted from Ref. [7].

Fig. 4. It is possible to notice that the obtained values do not seem to present neither nitrate $\delta^{18}O$ values for microbial nitrification with ambient H_2O $\delta^{18}O$ or O_2 $\delta^{18}O$ values from atmosphere.

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INPUT OF ISOTOPIC (^{18}O, ^{2}H AND ^{3}H) AND GEOCHEMICAL STUDIES IN THE ASSESSMENT OF GROUNDWATER RESOURCES IN PORTO URBAN AREA (NW PORTUGAL)

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Abstract

The paper attempts to assess surface water–groundwater interaction in Porto urban area. The region is mainly characterized by Variscan granitic rocks. Several underground galleries were excavated throughout the centuries to conduct spring waters. Paranhos spring collection chambers constitute one of the galleries studied. Preliminary isotopic signatures of groundwaters indicate that: (i) those collected along gutters present a homogeneous composition; (ii) an isotopic depletion of about 1‰ in ^{18}O and 7.5‰ in ^{2}H was found in groundwater samples colleted from the granitic fractures. These groundwaters display ^{3}H concentrations higher than those in gutter groundwater. Coupled isotopic and geochemical signatures indicates that: (i) groundwaters collected along the gutter sampling points could be ascribed to meteoric waters infiltrated along the residual granitic soil, all over the years; (ii) groundwater samples collected from the granitic fractures could be ascribed to random precipitation events, resulting into a direct infiltration along the fissured granitic rocks. In the first case, sea water and agricultural fertilizers should be regarded as sole sources of the Cl and NO_3, while in the second case, wastewaters should be considered as typical sources of both Cl and NO_3 concentrations.

1. INTRODUCTION

This paper is strongly connected with one of the most crucial water-related research issues of the UNESCO International Hydrological Programme [1] at the turn of the millennium: “Water and Society” and “Land habitat hydrology in urban areas”. Urbanization can have a great effect on the hydrological cycle. The urban subsurface is a network of conduits, pipes, and other structures that provide pathways for the movement of urban contaminants into the underlying aquifers. As a result of such problems, urban groundwater resources are frequently subjected to degradation ascribed to indiscriminate effluent and waste disposal practices [2, 3]. Facing (i) the increasing worldwide pressure on water resources demand and, (ii) contamination and climatic change problems, it is becoming evident that integrated multidisciplinary approaches should be adopted to address the scientific issues related to surface and ground water resources in urban areas. In order to assess the role of the regional geological, morphotectonical and hydrogeological features of Porto metropolitan area (NW Portugal) in the local groundwater resources, the R&D Project “GROUNDURBAN — Urban groundwater and environmental management in the Northwest Portugal” was lanched. Three main thematic areas of research include the (i) identification of the processes of groundwater contamination, (ii) the surface water/groundwater interaction, (iii) impact of groundwater exploitation on the hydrologic system and finally (iv) assessment of potential artificial recharge in and in the surroundings of urban areas.

The overall objective of this paper is to assess the usefulness of coupled isotopic and geochemical techniques to address the management and development issues relevant to urban aquifers. Isotopic and geochemical analyses of waters collected from springs, dug-wells and boreholes can provide important information concerning the evaluation of mixing processes between surface waters and groundwaters, where the intense urbanization and agricultural practices control the conditions occurring at shallow levels. This multidisciplinary work presents the preliminary results of coupled geochemical and isotopic studies employed to assess the nature and suitability for the use of groundwater from the Paranhos’ spring horizontal galleries catchworks.

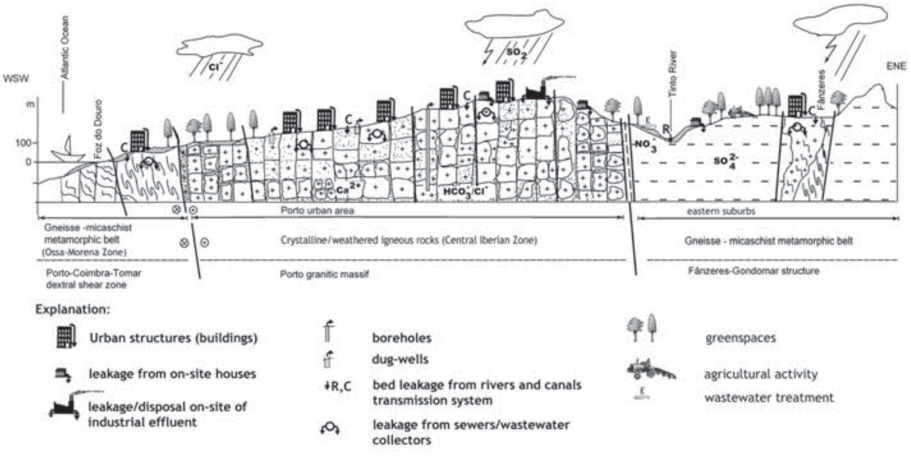

FIG. 1. Schematic cross-section of the study area (no scale).

2. SITE DESCRIPTION

Porto City is the second most important city of the Portuguese mainland and supports about 1 million inhabitants. It is one of the oldest cities in Europe and dates back to the days of the Suevi prior to the 6th century, when it was known as *Portucale* (*Harbour of Cale*). Much of the original Porto City was built in the 12th century and the architectural and historical attributes of its old neighborhoods led Porto to be recognized by UNESCO as a World Heritage Site in 1996. The study area is located in a complex geotectonic domain of the Iberian Massif, near the so-called Porto–Coimbra–Tomar shear zone [4, 5].

The crystalline bedrock of Porto urban area consists of granites in the eastern part and a gneisses-micaschists complex in the western part. This major fault zone — Porto-Coimbra-Tomar shear zone — trending NNW-SSE, defines the boundary between these two major geological units. Variscan granitic rocks, representing the Porto granite *facies* and Ermesinde porphyritic *facies*, underlay the Porto site (s.str.). A schematic cross-section illustrating these relationships is presented in Fig. 1. The Porto granite consists of two-micas, coarse grained, and grayish in color, changing to yellowish when weathered. The geomorphologic framework of the region corresponds to a wide flat area dipping gently to the south and west [6].

3. HYDROGEOLOGICAL OVERVIEW

In the study area the hydrogeological data are still scarce, so the proposed regional hydrogeological classifications correspond mainly to the main geological features [7]: (i) sedimentary cover (post-Miocene), including alluvium and fluvial deposits; (ii) metasedimentary rocks (upper Proterozoic-Palaeozoic), which include schists, greywackes, quartz-phyllites and quartzites; and (iii) granitic rocks (Variscan and/or pre-Variscan), including gneisses, migmatites and gneissic granites. The granite is generally weathered to different grades, from fresh-rock to residual soil, showing highly variable conditions, resulting in arenization and kaolinization, which may reach depths of more than 100 m [8, 9]. The chemical palaeoweathering took place during the Cenozoic times under tropical/subtropical climate conditions. Almost all aquifers in this region are ascribed to fissured hard rocks and usually comprise a weathering zone that plays an important role on the extent to which recharge reaches underlying aquifers.

4. METHODOLOGY

Initially, in 1995–1996, a geochemical monitoring network was established with a special emphasis placed on sampling sites within the focus area. About 35 sampling sites: 28 boreholes (mean depth of 103 m), 4 dug-wells and 3 spring-collection chambers were tested on a non-regular basis [10]. However, the research continued and recently, under the scope of the GROUNDURBAN R&D Project new sampling sites were continually added. The new 21 sampling sites are located along the so-called Paranhos spring collection chambers, an underground area (ca. 3 km extension and a 25 m depth b.g.l.), constituted mainly by granitic rocks (Fig. 2). For more than five centuries, the water supply of Porto city was provided by fountains feeded by numerous springs (e.g., Ref. [11]). Several underground galleries were excavated throughout the centuries to conduct the water of these springs from one place to another. Paranhos spring collection chambers were one of those main galleries. These tunnels constitute a unique opportunity to predict the probable negative effects of surface water–groundwater interaction in Porto city area.

Hydrogeological fieldwork campaigns were therefore carried out and *in situ* determinations included: temperature (ºC), pH and electrical conductivity (μS/cm). The sampling sites were selected based on the surface antropic activities located along the course of the spring galleries catchworks, and 21 water samples were collected for isotopic and chemical analyses.

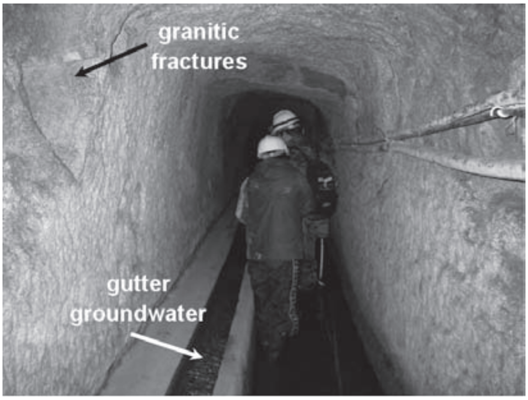

FIG. 2. Paranhos spring collection chambers, Porto urban area.

The chemical analysis (Na, K, Ca, Mg, HCO_3, Cl, NO_3, SO_4 and SiO_2) were performed at Centro de Estudos de Águas/ SEP/Porto, Portugal, using conventional techniques. The environmental isotopes (^{18}O, ^{2}H and ^{3}H) were measured at Instituto Tecnológico e Nuclear/ITN–Sacavém/Portugal. The δ^{18}O and δ^{2}H determinations were carried out using a mass spectrometer SIRA 10 VG-ISOGAS, applying the analytical methods described in Refs [12, 13], respectively. The results are reported with respect to the Vienna — Standard Mean Ocean Water (V-SMOW). The accuracy of the measurements was ±1‰ for δ^{2}H and ±0.1‰ for δ^{18}O. The determinations of tritium (^{3}H) concentrations were carried out by electrolytic enrichment followed by liquid scintillation counting method (PACKARD TRI-CARB 2000 CA/LL). The detection limit of this equipment (liquid scintillation counter) is 0.5 TU. The associated error to the measurements is ±0.6 TU, depending on the ^{3}H content of the water samples. The analytical method is described in [14].

5. RESULTS AND DISCUSSION

Preliminary results driven from 1995–1996 field work campaigns indicated that groundwaters circulating in the deeper granitic aquifers exhibit a wide range of chemical signatures, difficult to explain only on the basis of water-rock interaction processes. Most of the sampled groundwaters presented near-neutral pH values and electrical conductivity values around 430 μS/cm. Concerning the geochemical signatures, cations were dominated by Ca^{2+} followed by Na^{+}, while anions were dominated by SO_4^{2-} and Cl^-. Through the projection of the groundwater composition in a Piper diagram [10], it was possible to conclude that most of the groundwaters were “*mixed*” $SO_4^{2-}/Cl^- – Ca^{2+}/Na^+$ waters.

Recently, the results obtained on the geochemical signatures of the groundwaters collected along the Paranhos spring collection chambers seem to show the same trend of those sampled in boreholes and dug-wells (during 1995–1996). However, groundwater samples collected from the granitic fractures present a clearer HCO_3–Ca *facies*. Bearing in mind that the Porto urban area is mainly located in a granitic environment, it should be taken into due consideration that the higher Ca concentrations found in groundwaters from the granitic fractures could be partially attributed to a ion exchange process, where the Ca is being released from the clay minerals by the infiltrated sodium-rich groundwaters.

Isotope techniques (δ^2H and $\delta^{18}O$) have been employed in combination with major hydrogeochemical indicators. The vulnerability of groundwater protection areas is also being assessed using environmental ^3H. The application of stable and radioactive isotope techniques, in co-ordination with major element hydrogeochemistry has been extremely useful in delineating the downward infiltration and horizontal spread of urban recharge, which, in most cases, is a key question in aquifer management.

Concerning the isotopic approach, in the diagram $\delta^{18}O$ *vs* δ^2H in Fig. 3, two main groundwater groups can be observed. One of the groups (**A**) stands for groundwaters collected along the gutter (“*caleira*”) sampling points, in the Paranhos spring collection chambers, presenting a homogeneous isotopic composition, with average values of –5.33‰ and –33.5‰ for $\delta^{18}O$ and δ^2H, respectively. The other group (**B**) corresponds to depleted groundwater samples (by about 1‰ in oxygen-18 and 7.5‰ in deuterium) colleted from the granitic

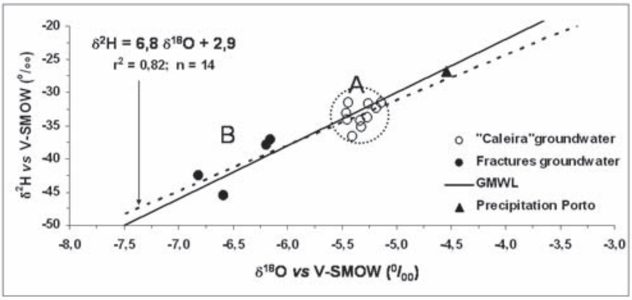

FIG. 3. $\delta^{18}O$ vs δ^2H signatures of groundwater samples from Paranhos spring collection chambers. The Global Meteoric Water Line (GMWL: $\delta^2H = 8\ \delta^{18}O + 10$ in [15]), and the Local Meteoric Water Line (LMWL: $\delta^2H = 6.8\ \delta^{18}O + 2.9$; $r^2 = 0.82$) were plotted as Ref. [16].

fractures, presenting a heterogeneous isotopic composition.

The observed isotopic depletion in groundwaters from group (B) could be related with:

(i) Groundwaters from group (A) could be ascribed to meteoric waters infiltrated along the granitic weathering zone. This weathering zone has an important influence on the extent to which recharge reaches underlying aquifers, presenting a homogeneous isotopic composition due to a continuous recharge all over the time. In fact, these group of groundwaters presents an isotopic composition that approaches the long-term mean isotopic composition of precipitation at Porto meteorological station ($\delta^2H = -26.9$ ‰; $\delta^{18}O = -4.54$ ‰, [16]).

(ii) Groundwaters from group (B) could be ascribed to random precipitation events, resulting into a directly infiltration of meteoric waters along the fractured granitic rocks. In fact, these groundwaters present higher ^{3}H concentrations (≈3.8 TU) than the groundwaters collected along the gutters ("c*aleira*"), with a mean ^{3}H concentration of 2.4 TU. Besides, the current arithmetic mean at Porto meteorological station presents a weight annual mean of 4.5 TU [17].

In the diagram presented in Fig. 4 the NO_3 *vs* Cl scatter plot reveals two trends: (i) trend line (1) corresponds to groundwaters from group (**A**, ○) for which the Cl and NO_3 sources appear to be different; (ii) trend line (2) corresponds to groundwaters from group (**B**, ●) where Cl and NO_3 are likely derived from the same source. In the first case, sea water and agricultural fertilizers should be regarded as sole sources of the Cl and NO_3, respectively. In fact, agricultural activity is relatively common in the NW and NE sectors of the city. In the second case, wastewaters should be faced as typical sources of both Cl and NO_3.

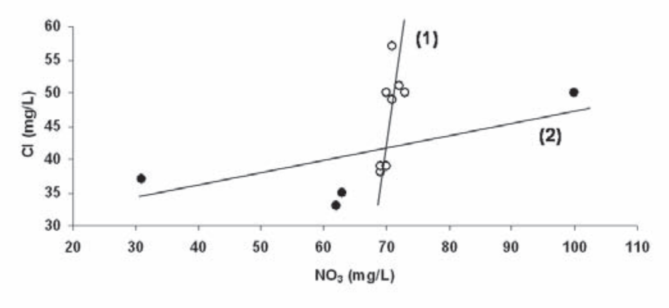

FIG. 4. Cl vs SO_4 scatter diagram for groundwater samples collected (○) along the gutter sampling points and (●) from the granitic fractures, in the Paranhos spring collection chambers.

6. CONCLUDING REMARKS AND OUTLOOOK

This paper seeks to demonstrate that urbanization can have a profound effect on groundwater resources of big cities. In fact, urban groundwater resources are frequently exposed to uncontrolled exploitation and to degradation resulting from indiscriminate effluent, waste disposal and even agricultural practices. In Porto City urban areas, groundwater is increasingly polluted due to rural practices as well as domestic and industrial wastewater releases. Future $\delta^{15}N$ determinations on groundwater samples from Paranhos spring collection chambers will provide important information on the contribution of nitrate from different sources such as precipitation, microbial nitrification, septic tank leakages or agriculture practices. Since the cost of remediation a polluted aquifer is very high, an “attack” to problems related to groundwater pollution will be need to understand the complex processes involved. Thus, in urban areas, hydrogeological data acquisition namely geological, morphotectonical, isotopic and geochemical should be integrated as the most appropriate muldisciplinary approach to predict the possible negative impacts of surface water–groundwater interactions.

ACKNOWLEDGEMENTS

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ASSESSMENT OF GROUNDWATER SALINIZATION MECHANISMS IN SANTIAGO ISLAND — CABO VERDE: AN ENVIRONMENTAL ISOTOPIC APPROACH

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Abstract

Two sampling campaigns were carried out at Santiago Island - Cabo Verde under the scope of an isotopic and geochemical research study. An evaluation of the groundwater systems was carried out through the application of environmental isotopes and geochemical data in order to answer questions such as: origin and mechanisms of groundwater recharge; relation between the hydrochemical evolution of the groundwater systems with the geological matrix (minerals dissolution) or mixture with seawater and aerosol marine influence; identification of seawater intrusion mechanisms and, determination of the apparent groundwater "age". The results obtained so far are not conclusive on the identification of the process responsible for the increase of salinity. In general, all the data obtained seems to indicate that the waters have the same isotopic history but different geochemical evolution, which depends on the weathering and permeability of the rocks.

1. INTRODUCTION

Water is a vital resource for the development of any society. Problems related to water scarcity and quality are dramatic in several countries, mostly in those located in semi-arid and arid regions. A research study was initiated in 2005 at Santiago Island — Cabo Verde. From the hydrological point of view Santiago Island is characterized by scarce water resources as a result of the low and irregular precipitation (321 mm/year in the highest mountains — Pico da Antónia and Serra Malagueta, and round 170 mm/year at low altitudes). This situation is responsible for the lack of water and sometimes for a catastrophic drought. Fresh water management is in a delicate balance with the seawater, expressed by the movement of fresh-seawater interface. Associated with these features, water administration difficulties increased in the island. Besides, concerning land water exploitation near the coast, and in the valleys, a careful monitoring of the fresh-salt water interface is being carried out in order to avoid saltwater intrusion.

The importance of such knowledge is enhanced by the fact that most part of the population at Santiago Island lives by the shoreline and the main activity is agriculture. In those areas, flash floods immediately after the rainfall events and subsequent erosion of the landscape is the general rule. Surface waters are either seasonal or non-existent, and groundwater becomes the perennial source of water supply.

Under the scope of the R&D Project “Hydroarid — Evaluation of hydrogeological potential and sea water intrusion monitoring in semi-arid zones using a multitechnique approach: application to the Santiago and Maio Islands (Cabo Verde)”, groundwater sampling campaigns were carried out at Santiago island for isotopic and chemical analyses. The main goal of this study was to evaluate the application of coupled environmental isotopes (^{2}H, ^{18}O and ^{3}H) and geochemistry to answering some hydrogeological questions such as: (i) the origin and mechanisms of groundwater recharge; (ii) the relation between shallow and deep aquifer systems; (iii) investigate the existence of salt water intrusion problems and (iv) determine the apparent groundwater “age”. Simultaneously to the isotopic and geochemical surveys a geoelectromagnetic research was carried out at Santiago Island.

2. GEOLOGICAL AND HYDROGEOLOGICAL SETTING

Santiago Island is part of Cabo Verde archipelago situated in the Sahelian zone of the West African coast. It is located between latitudes 14º18'N and 17º11'N and longitudes 22º44'W and 25º22'W (Fig. 1). From the geological point of view the Santiago Island is constituted by a vulcano-stratigraphic sequence, established by Ref. [1] and later improved by Ref. [2], and has been used as the basic support for hydrogeological and hydrological research. The main geological units with hydrogeological interest are the following: (1) the eruptive complex of Pico da Antonia (***PA***), (2) The Monte das Vacas formation (***MV***) and (3) the recent sedimentary Quaternary formations (***a***). The most important reservoir of fresh water is the PA formation presenting a terrestrial and submarine *facies* (pillow-lavas). This geological unit covers an impermeable formation known as Basic Unit composed by Ancient Internal Eruptive Complex (***AIEC***). The Flamengo formation and the Conglomeratic-Breccia formation, two components of the ***AIEC*** are characterized by an alteration level practically generalized, high rate of compactness and low permeability, [3].

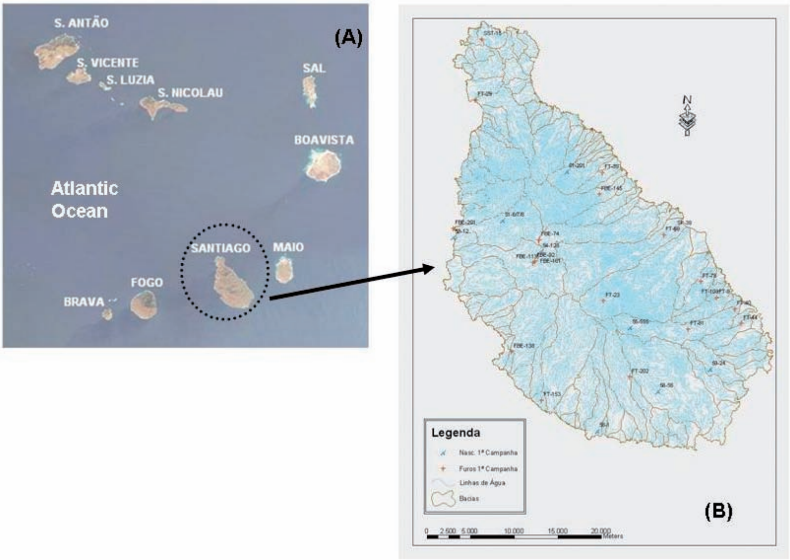

*FIG. 1. (**A**) Cabo Verde archipelago. (**B**) Santiago Island; location of the sampling sites.*

3. SAMPLING AND METHODS

Two sampling campaigns were carried out at Santiago Island (November 2005 and February 2006). Groundwater samples were collected from boreholes and springs (exploiting mostly the PA formation) for isotope (δ^2H, δ^{18}O and ^{3}H) and chemical analysis. The ^{2}H and ^{18}O results are reported in δ notation and were measured with the accuracy of ±1‰ for δ^2H and ±0.1‰ for δ^{18}O. The δ^2H and δ^{18}O were determined three times for each sample in order to increase the precision analysis. The measurements were carried out using a mass spectrometer SIRA 10 VG-ISOGAS using the methods proposed by Ref. [4] and Ref. [5] respectively for ^{2}H and ^{18}O. The tritium content was determined using the electrolytic enrichment and liquid scintillation counting method (PACKARD TRI-CARB 2000 CA/LL). The error associated to the ^{3}H measurements (usually is around 0.7 TU) varies with the ^{3}H concentration in the sample. Chemical analyses (major species) were performed in these groundwater samples; electrical conductivity (μS/cm), pH and temperature (ºC) were obtained during the sampling.

4. RESULTS AND DISCUSSION

Although the study has not yet been concluded, results obtained so far permit the description of basic features of some parts of Santiago Island, based on combined information provided by hydrochemistry, stable isotopes and tritium content, in groundwater.

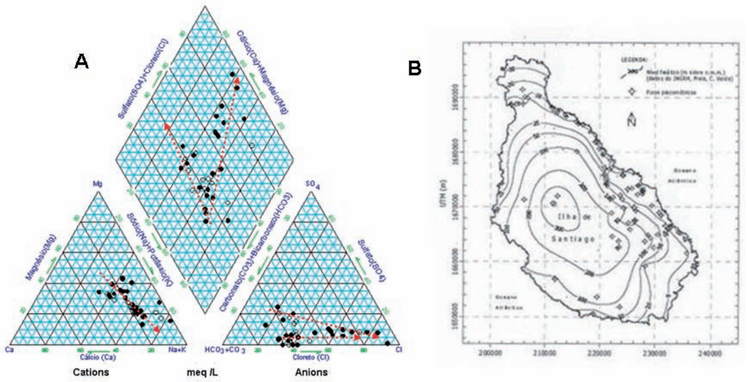

*FIG. 2. (**A**) Representation of the chemical composition of groundwater samples in Piper diagram. The symbol (●) stands for boreholes and (○) for springs. (**B**) Piezometric map of Santiago Island [6].*

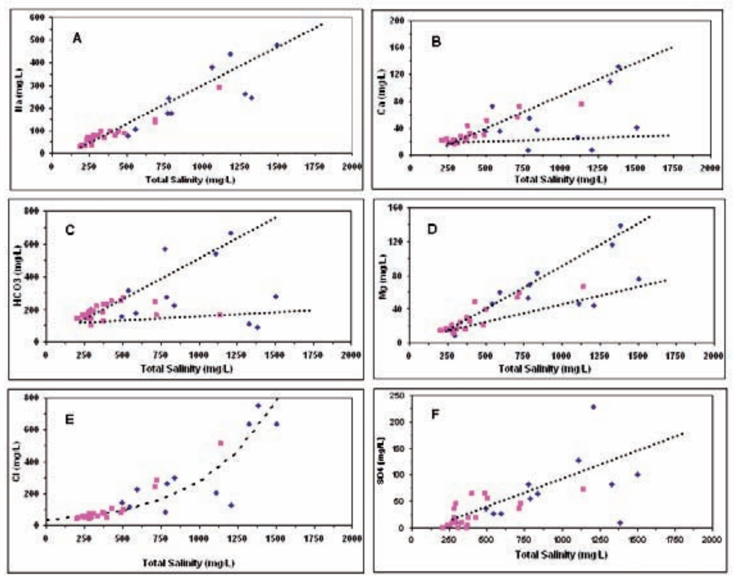

FIG. 3. Major ions evolution in the groundwater samples from Santiago Islands as a function of the total salinity (mg/L). The different symbols stand for (■) base formation and (♦) for intermediate formation.

4.1 HYDROCHEMICAL EVOLUTION

The hydrochemical composition of groundwater samples collected in Santiago Island was represented by the Piper diagram (Fig. 2). Two evolution trend lines can be distinguished associated with two major processes: (i) the groundwater evolution/mineralization controlled by the seawater spraying and by mixing with underlying seawater in the Quaternary formations, particularly in the valley zones; (ii) water-rock interaction processes, representing the major mechanism in the geochemical aquifer systems evolution at Santiago island.

The water samples collected in the central part of Santiago Island belong to the Na-HCO_3 type, revealing the influence of the geological matrix (volcanic terrains). However the influence of marine aerosol in the infiltrated groundwaters can not be excluded. A geochemical approach to the groundwater chemical signatures permit to say that groundwater samples collected at high mountain areas located in the central part of Santiago Island, such as Pico da Antónia or Serra Malagueta, belong to the Na-HCO_3 type, while the highest salt content, sometimes inducing electrical conductivity values up to 9400 µS/cm, are located in the valleys, areas of intense agriculture practices (sugar cane, banana and papaya fields).

Spatial variations of the chemical data were plotted *versus* the total salinity of the water samples. The selected points were divided through the geological formations but no correlation was found between the chemical evolution and the specific geological layer (Fig. 3). In the diagrams representing the Na, Cl, and SO_4 only one evolution trend line is recognized, pointing out to moisture with seawater or marine aerosol influence. However, in the diagrams Ca, HCO_3 and Mg *versus* total salinity two evolution lines were identified after the waters reach a TDS of 500 mg/L, reflecting: (i) water-rock interaction processes and (ii) with a lower slope value, the influence of the seawater composition (mixing and/or aerosol).

The landward extent of seawater intrusion or the influence of marine aerosol appears to be moving forward, as indicated by the recent increase in electrical conductivity data. The high salt content within the groundwater systems appears to be restricted to agricultural zones in the valleys by the seaside surroundings. This salt increase is interconnected with intense exploitation of the hydrological resources and the scarcity of precipitation. The deterioration of the water quality limits its use for human supply and for irrigation purposes (agriculture). The salt increase leads to a potential outlet for soil salinization and alkalinisation, with the inherent soil deterioration and loss of productivity. Besides, the amount of water supplied for irrigation usually exceeds the drainage capacity of the soil. So, brackish groundwater for agriculture and human supply (for instance at Praia Baixo, Montenegro, Charco) is provided to many parts of the island as the only type of available water.

4.2 ENVIRONMENTAL ISOTOPES

Close to 60 samples for comprehensive environmental isotopic (^3H, ^2H and ^{18}O) analysis were taken from boreholes and springs during two field campaigns. The geographic distribution of all parameters shows very few clear trends, as in the case of geochemical data. The isotopic data is therefore treated also semi-statistically. Since no correlation was found between the geological formations and the groundwater's chemical features, the isotopic approach will be based on the separation between boreholes and springs.

The tritium determinations were carried out in all water samples, and the results range between 0±0.7 and 3±0.7 TU. No correlation was found linking tritium concentration either with the altitude of the sampling sites or with the electrical conductivity. Unfortunately, no long series of ^3H content in rainfall area are available on the Cabo Verde archipelago. In fact, due to the absence of ^3H and the lower content found in remaining points it is difficult to point the turnover rates of the groundwater. Nevertheless, according to the work

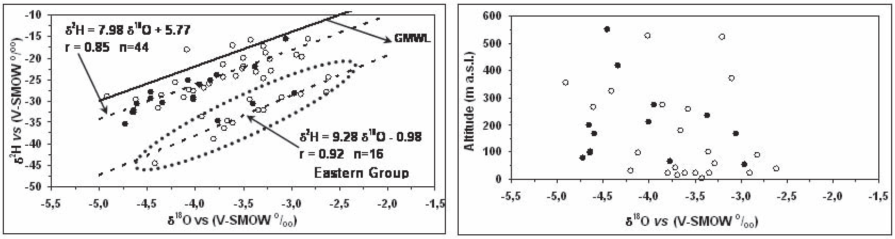

*FIG. 4. (**A**) $\delta^{18}O$ vs. δ^2H for the sampled groundwaters. (**B**) $\delta^{18}O$ vs. altitude in the sampling sites.*

performed by Akiti in 1985, [6] in the N part of the island (Tarrafal) a mean residence time of 30 years was attributed. Moreover, according to Ref. [7] in the eastern part of Santiago Island, in Achada Baleia, it seems that the shallow boreholes were receiving contemporaneous recharge while the deep boreholes were receiving water slowly from joints and fractures.

The isotopic composition of groundwater samples collected at Santiago Island range from –4.72 to –2.61‰ in $\delta^{18}O$ and from –44.6 to –15.8‰ in δ^2H, with a mean isotope content of –3.80 ± 0.53‰ in $\delta^{18}O$ and –26.6 ± 5.8‰ in δ^2H *vs.* V-SMOW. The isotopic contents obtained are close to the average isotopic composition over the Island as discussed in Ref. [7], suggesting that the infiltrated meteoric waters were not subjected to previous evaporation. With these data we tried to use them in the identification and characterization of the recharge areas (Fig. 4). No strong correlation was found between the altitude of the sampling sites and the isotopic composition of the groundwater. However, in the diagram $\delta^{18}O$ *vs.* δ^2H two groups of groundwater samples are identified: one group composed by the samples collected in the eastern part of Santiago Island, in most cases located near to the coast line. The other group is ascribed to high-altitude sampling sites.

Using electrical conductivity, total salinity and Cl^-, SO_4^{2-} and Na^+ contents of groundwater samples and plotting them in a diagram as a function of the oxygen-18 content, we tried to identify the main mechanisms responsible for groundwater salinization at Santiago Island (Fig. 5). In these diagrams, two evolution lines can be observed: one showing the influence/mixture with seawater with a progressive enrichment in oxygen-18 and in the mineralization, where the influence of marine aerosol can not be excluded. On the other hand, another trend line can be defined based only on the isotopic composition. A shift in the $\delta^{18}O$ values can be observed varying between approximately –5 to –2.75‰. This progressive enrichment is not visualized when the $\delta^{18}O$ is plotted as a function of altitude of the sampling site (Fig. 4B) or as a function

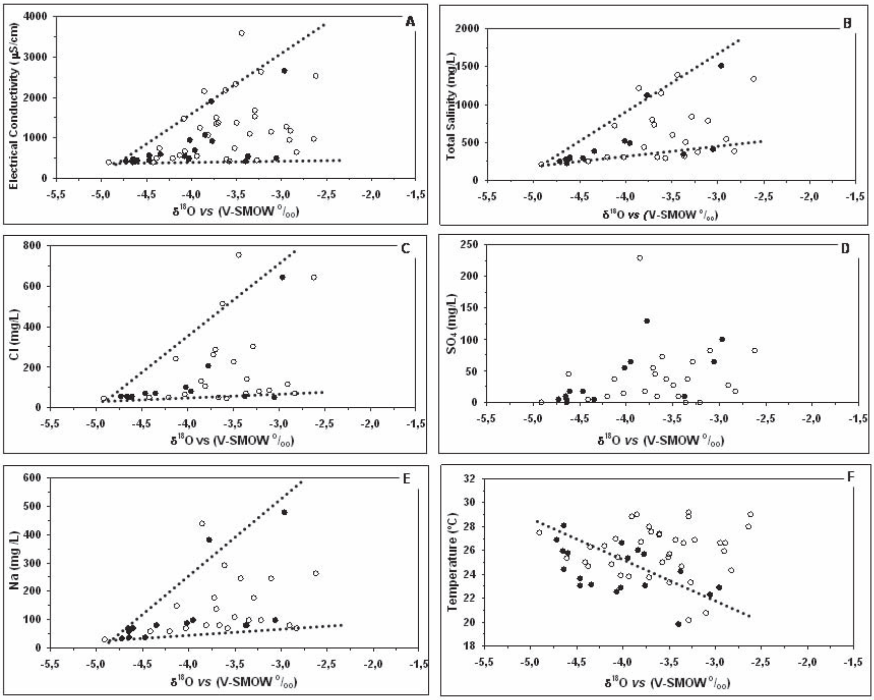

FIG. 5. $\delta^{18}O$ vs. electrical conductivity, the total salinity, Cl^-, SO_4^{2-} and Na^+ content and temperature of the groundwater samples

of groundwater temperature. This type of pattern was mention also in Ref. [7]. According to this reference waters have the same isotopic history but different geochemical signatures which are contrlled by the degree of weathering and permeability of the rocks.

ACKNOWLEDGEMENTS

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APPLICATION OF COMPOUND-SPECIFIC CARBON AND CHLORINE STABLE ISOTOPE FOR FINGERPRINTING SOURCES OF CHLORINATED COMPOUNDS IN GROUNDWATER

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Abstract

A combined use of carbon and chlorine stable isotopes was applied to evaluate the origin of TCE (trichloroethene) in a contaminated groundwater plume. The TCE at the site can be associated to a primary source of TCE and a separate (off-site) source associated to biodegradation of PCE. The TCE concentration pattern showed that the two sources of TCE formed a comingled plume in the downgradient part of the study site. The ^{13}C and ^{37}Cl data on TCE showed a very significant difference in the isotopic fingerprint of the primary TCE source compared to the TCE originated by biodegradation of PCE. This difference is clearly observed in the comingled plume, which permit to demonstrate that the TCE is this part of the plume is indeed associated to the two TCE sources. This study showed the potential of the combined use of ^{13}C and ^{37}Cl for fingerprinting chlorinated compounds in groundwater even in situations where biodegradation of these compounds is taking place in the groundwater.

1. INTRODUCTION

Chlorinated compound plumes can originate from more than one source or during different episodes of release from one source. Published isotope (^{13}C and ^{37}Cl) data have shown that chlorinated solvents from different manufacturers may have the same isotopic signature if only one isotope is measured but can be differentiated if both ^{13}C and ^{37}Cl are considered [1, 2]. Therefore, a combined measurement of ^{13}C and ^{37}Cl will significantly increase the chances of differentiating between multiple contaminant sources. The recent development of an analytical protocol for compound specific Cl isotopes established at the University of Waterloo [3] raises new possibilities for the application of Cl isotopes in the field of source evaluation, for assessing fate and remediation technologies for chlorinated compounds in groundwater. Since the new UW method is fast and has a low detection limit, it is well suited for field studies where contaminant mass is often limited as well as for detailed investigation of contaminant plumes composed of several chlorinated compounds.

This work present the first fingerprinting study applying stable isotopes (^{13}C and ^{37}Cl) to evaluate the origin of trichloroethene (TCE) in a contaminated groundwater plume. The TCE at the site can be associated to a primary source of TCE near the southwest corner of the site (a former mag wheel manufacturer), and a separate (off-site) source of tetrachloroethene (PCE) located west of Vincent Road (Fig. 1). A hot spot of TCE was also found near well MW-14A and it is postulated that it may be due to releases from an off-site sewer line at that location, and may be unrelated to the Hookston TCE source near the southwest property corner. The working theory for the site is that some of the TCE mass located within the down-gradient residential area is due to the breakdown of PCE from the off-site source area.

2. METODOLOGY

2.1. Study Site and Sampling Approach

The Hookston Station site is in Pleasant Hill, California. There appears to be a primary source of TCE near the southwest corner of the site (a former mag wheel manufacturer), and a separate (off-site) source of PCE located west of Vincent Road (Fig. 1). The contamination is present in two aquifer zones. The A-Zone represents relatively thin unconfined to semiconfined sand stringers within a fairly tight silty clay matrix, and is generally found from the water table surface (20–25 ft bgs) to a depth of approximately 30 feet bgs. The B-Zone is a confined aquifer, consisting of a fairly continuous sand bed

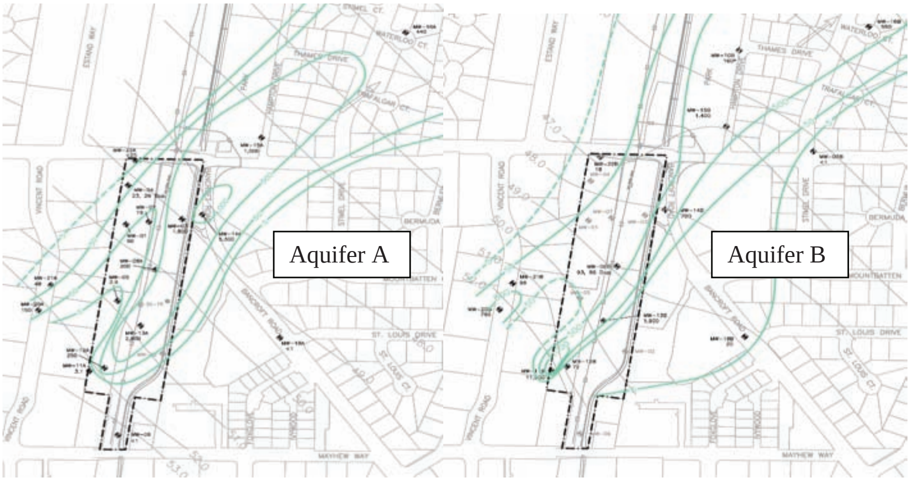

FIG. 1. Distribution of TCE in aquifers A and B.

found between approximately 30 to 70 feet bgs. The sampling approach for the isotope fingerprinting application focused on the isotope characterization of the primary TCE source, the TCE originated by biodegradation of PCE and the TCE at the hot spot (MW-14A). The approach also included collection of samples along the flow system in the plume associated to the primary TCE source, the off-site source and samples that seem to be in a commingled plume. Samples were also collected down gradient of the hot spot.

2.2. Analytical Aspects

The chlorine isotopes analyses of chlorinated ethenes were performed at the Environmental Isotope Laboratory University of Waterloo using a CF-IRMS (IsoPrime, Micromass) designed to be used in both continuous flow (CF) and dual-inlet (DI) modes, with nine collectors, four of which are designed for the analysis of PCE, TCE, cis-DCE and VC. An Agilent 6890 Gas Chromatograph (GC) equipped with a CTC Analytics CombiPAL SPME autosampler is attached to the IRMS. A detailed information about this novel analytical method can be found in Refs [1–3]. Carbon isotope ratios of chlorinated ethenes were performed at the University of Neuchatel laboratory using a gas chromatograph coupled to an isotope-ratio mass spectrometer with a combustion interface (Thermo Finnigan, Germany). The system is equipped with a purge-and-trap concentrator (Velocity XPT, USA) connected via a

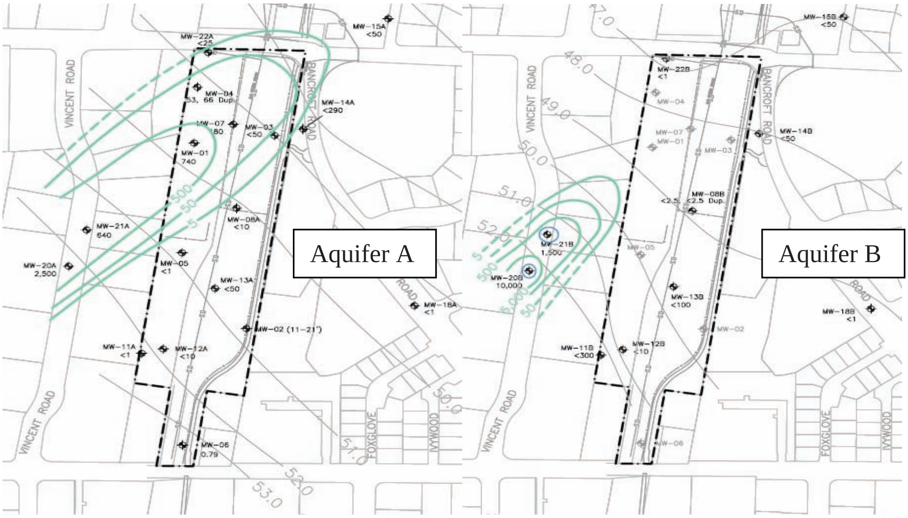

FIG. 2. Distribution of PCE in aquifers A and B.

cryogenic trap. All isotope ratios are reported in δ‰ relative to VPDB for carbon isotopes and SMOC for chlorine isotopes with an analytical uncertainty of 0.14‰ for ^{13}C and 0.1‰ for ^{37}Cl.

3. RESULTS AND DISCUSSION

3.1. Concentration Data

The concentration data showed an off-site PCE plume in aquifer A ranging in concentration from 2,400 μg/L (well MW 20A) representing the source to 740 μg/L (well MW-01) down gradient within the property. The PCE in the aquifer B showed values between 10,000 μg/L at the source and 1,500 μg/L in the downgradient wells but it does not reach the property (Fig. 2). The TCE data at aquifer A within the property showed values that vary between 2,800 μg/L representing the source to values that varies between 1,800 μg/L and 19 μg/L in the downgradient areas. In case of Aquifer B, the TCE concentration range between 11,000 to 1,900 μg/L in the downgradient areas (Fig. 1). The TCE plume associated with the PCE plume show concentration values of 150 and 48 μg/L in aquifer A and 790 and 98 μg/L in aquifer B (Fig. 1). The hot spot off-site of the property showed TCE ranging between 5,300 μg/L (MW-14A, aquifer A) and 780 µg/L (MW-14B, aquifer B) to values of 440 and 550 ug/L in downgradient areas of aquifer A and B, respectively (Fig. 1).

3.2. Isotope Data

The isotope data showed δ values ranging between –24.4‰ and –22.7‰ and –0.70‰ and –0.31‰ for ^{13}C and ^{37}Cl, respectively, at and near the TCE source in both aquifers (Fig. 3). A very different isotopic composition is observed in the TCE in the off-site TCE plume that is characterized by δ values between –33.3‰ and –31.5‰ for ^{13}C and 0.30‰ and 1.78‰ for ^{37}Cl (Fig. 3). Two set of δ values are observed in the proposed commingled plumes with one group showing δ values similar to the TCE source, –23.9‰ for ^{13}C and –0.49‰ for ^{37}Cl and another group with δ values of –31.8‰ and –32.6‰ for ^{13}C and 1.08‰ and 2.03‰ for ^{37}Cl, representing the off-site TCE plume (Fig. 3). The plume associated to the hot spot (well MW 14-A) is characterized by δ values between –24.2‰ and –25.7‰ for ^{13}C and 0.3‰ and –0.07‰ for ^{37}Cl (Fig. 3). These data are very different than the isotope composition of the TCE source inside the property.

The isotope data on cis-DCE also showed that the cis-DCE produced by biodegradation of the in-situ TCE source is isotopically different (δ^{13}C = –23.7‰; ^{37}Cl = 0.14‰) than the cis-DCE associated to the off-site TCE plume (δ^{13}C = –28.5‰; ^{37}Cl = 4.3‰).

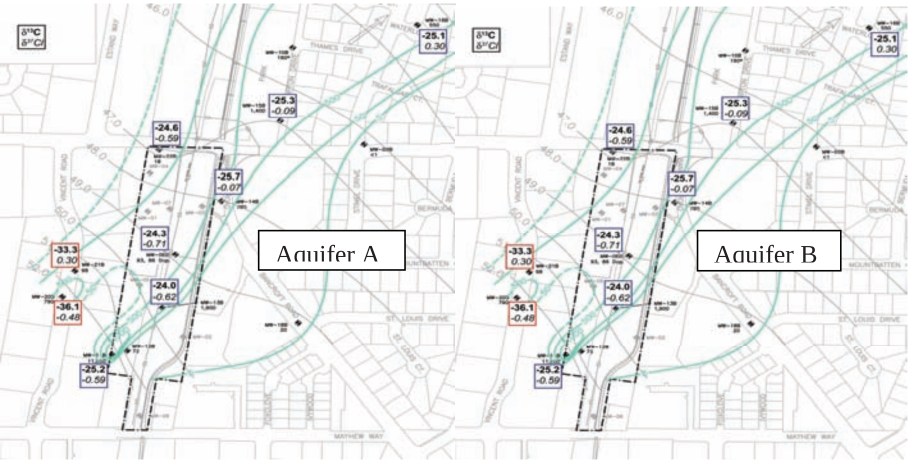

FIG. 3. Isotopic Composition of TCE in aquifers A and B.

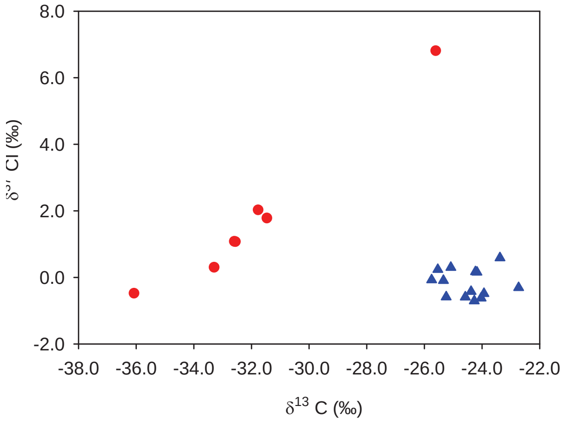

FIG. 4. Summary of isotope data.

4. CONCLUSIONS

Summarizing, the carbon and chlorine isotope data show very significant isotopic differences between the TCE associated to the Hookston TCE source located near the southwest property corner and the off-site TCE source linked to biodegradation of PCE. This is further highlighted on Fig. 4 that summarized the isotope data. The different isotopic signature makes it possible to evaluate the origin of TCE in the commingled area of the plume. It is clear than the TCE present in well MW-07 and MW-01 is associated to the off-site plume and the TCE present in wells MW-08A and MW-03 is related to the on-site TCE source. The isotope data also showed the TCE at the hotspot represented by wells MW- 14A and MW-14B is not related to the primary TCE source at the site.

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ISOTOPE AND CHEMICAL TECHNIQUES IN ASSESSING GROUNDWATER CONTAMINATION FROM METRO MANILA LANDFILL

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Abstract

Investigations were conducted to establish benchmark isotopic characteristics of water sources and baseline concentrations of trace elements related to contamination from the Montalban landfill. Water samples were collected from the production wells and surface water in Rodriguez and in San Mateo, both in the province of Rizal. These municipalities are nearest to the Montalban landfill. Stable isotope characterization of the deep groundwater and rivers shows isotopic values clustering along the LMWL with $\delta^{18}O$ ranging from –7.5‰ to –6.5‰ and $\delta^{2}H$ ranging from –53.59‰ to –42.91. Shallow groundwater is isotopically enriched, trending towards the evaporation line, with mean $\delta^{18}O$ and δD values of –6.46‰ and –44.14‰, respectively, The mean isotopic signatures of surface water, with mean $\delta^{18}O$ of –7.19 ‰, and deep groundwater, with mean $\delta^{18}O$ of –6.67 ‰, in Rodriguez are significantly distinct. San Mateo groundwater appear to be more isotopically enriched, indicating recharge different from that of Rodriguez groundwater. Leachate from the landfill exhibits a distinct isotopic composition from the freshwaters, with most enriched δD values of +5.84‰ for the leachate run-off and + 16.55‰ in the leachate pond. The significant differences in the isotopic signatures of the different water sources in the study area facilitates detection of contamination from leachate run-off to surface water, and eventually, to groundwater. Trace metals in the water samples collected, generally, were below the regulatory limits for drinking water and surface water.

1. INTRODUCTION

The issue of the disposal of solid waste is of paramount importance to the country especially in Metro Manila where daily waste generation of 10.5 million inhabitants was, in 2001, an estimated 6000 tons per day [1]. Most of these wastes are disposed in open dumpsites but which are now being phased out with the implementation of RA 9003, "Ecological Solid Waste Management Act of 2000." This Act provides for the prohibition against the use of open dumps and setting of guidelines/criteria for the establishment of controlled dumpsites and sanitary landfills.

In January 2002, the "controlled landfill" in Montalban (now Rodriguez), Rizal commenced operation as the site for Metro Manila's solid waste disposal. Some issues and concerns arise from the selection of the site. This includes its being situated on a mountain ridge, around 250 m elevation. Its geology that is volcanic sequence and heavily fractured [2, 3], lies close to the Marikina fault, a landslide prone area. Surface water affected by the landfill comprises one of the headwaters of Marikina River system which drains the whole Pasig and Marikina river watershed. Any contamination brought about by the landfill on the stream bounding the landfill site follows a pathway defined by the river networks, covering most of the watershed area.

The degree of potential impacts of the landfill to groundwater, spring, and surface water, would mainly depend on its operation. Indication of springs in the site is evidence that the fracture systems allow permeability and porosity [1]. Without leachate management (collection and treatment) leachate may possibly infiltrate the shallow, and consequently by the deep groundwater resources. Contamination of nearby Lukutan River by mixing with leachate and the storm water, as well as siltation via runoff is a potential source of surface water contamination. The results of this study will be useful in assessing the effectiveness of leachate management and mitigation plans or whether these have been put in place, which will be use as a basis for mitigation and control.

2. THE STUDY AREA

Figure 1 shows a satellite image of the study area. It is within longitudes 14°46'50" N to 14° 40'11" N and latitudes 121°06'30" E to 121°10'12" E. The Montalban landfill is hosted by the municipality of Rodriguez (formerly Montalban). It is officially referred as the "Montalban Sanitary Landfill", but at its present form, it most closely approximates the description of a "controlled dumpsite".

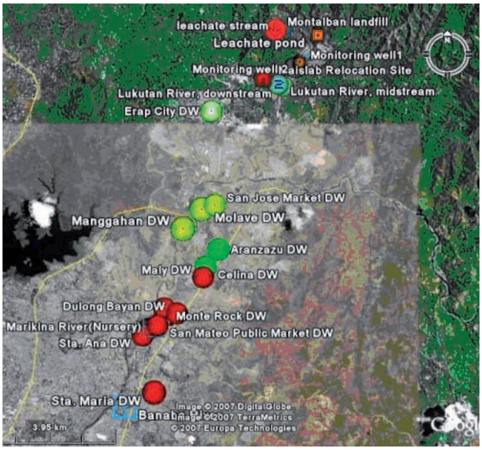

FIG. 1. The study area with sampling locations: Red buttons: San Mateo deep wells; blue buttons: Rodriguez deep wells; blue squares and circles : rivers, brown buttons: monitoring wells. (Satellite image from Google Earth).

Elevation in the dumpsite ranges from 50 m to 260 masl. The site is part of the Marikina Graben. The Montalban landfill is within the catchment of the Marikina River. Drainage in the site is part of the northern tributary of the Marikina River, the Lukutan Munti River. This river flows southward until it crosses the western flowing Montalban River which meanders at the western side of the Marikina valley before finally discharging into the Manila Bay. The head water of the Lukutan Munti River is located in the immediate vicinity of the landfill.

3. METHODOLOGY

3.1. Sampling

Field investigations commenced in June 2003, in the early part of the rainy season and went on until March 2006. Two sampling regimes were generally conducted within the year, one each before and after the rainy season.

Water samples were collected for chemical characterization (major ions and trace components) and isotopic analysis (deuterium, O-18, and tritium) from production wells, shallow wells near the dumpsite which served as monitoring wells, and from the Lukutan River and the Marikina River. Sediment samples along the river bank were collected for trace metal analysis.

3.2. Analysis

Isotopic analysis for ^2H and ^{18}O were performed by the Pakistan Institute of Nuclear Science and Technology (PINSTECH), Islamabad, Pakistan.

All samples for chemical analysis were filtered through a 0.45 µm Millipore filter in the field. Samples for action analysis were acidified to pH 2. Parameters such as pH, EC, temperature, chloride, nitrate, TDS, and DO were determined in the field. Groundwater samples were collected in pails and were allowed to continuously flow while measurements were taken. Surface water measurements were done directly by submerging the probes into the water.

The MWC Central Laboratory performed analysis for Ca, Mg, and Cl. Ca and hardness were determined by the by titration, obtaining Mg concentration by difference. Cl was determined by argentometry. The PNRI performed the other analyses. K, and Na were determined by Perkin Elmer Model 2380 Atomic Absorption Spcctrophotometer (AAS); SO_4 by turbidimetry; and HCO_3 by titrimetry. Trace metal analysis was done using Total Reflectance X-ray Fluorescence (TXRF). Pub and Cod were determined by differential pulse anodic stripping voltammetry (DPASV) using Metrohm 626 Polarecord with a rotating glassy carbon electrode against an Ag/AgCl reference electrode.

4. RESULTS AND DISCUSSION

4.1. Water Chemistry — Major ions

The chemical composition of the waters from Rodriguez and San Mateo sampled at the end of wet season in 2003 are plotted on a Piper diagram (Fig. 2) to classify the waters. Based on these plots, groundwaters are generally classified as $Ca+Na\text{-}HCO_3$. Enrichment in Na is attributed to the underlying volcanic rock composed mostly of basalt and sodium rich andesite. Three groups of water, are however recognized: the first, including most of the San Mateo groundwater, contain higher percentage of Na (50%), the second, including the Rodriguez groundwater and the river, have higher %Ca (80%), and , the third, is more of the $Ca+Mg+Na\text{-}HCO_3$ type, includes some Rodriguez groundwater and the river. In September 2003, the decreasing Cl concentration in the Lukutan river from upstream to downstream indicates contamination from the leachate mixing with streamflow which is attenuated as it travels downstream.

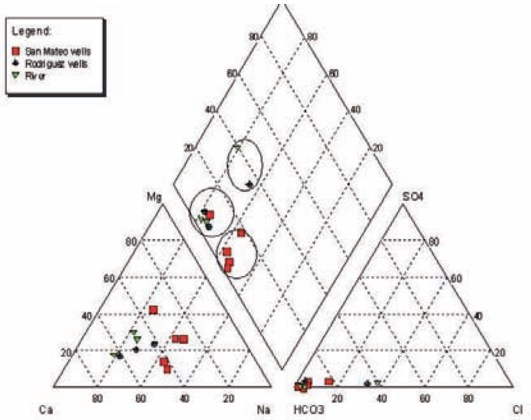

FIG. 2. Piper diagram of different waters in Rodriguez and San Mateo taken after the rainy season in September 2003.

4.2. Minor and Trace Elements

The minor and trace dissolved elements in the deep groundwater of Rodriguez and San Mateo, which is the source of drinking water in these municipalities, were determined in 2003 and 2005 by TRXRF. The elements Cr, Fe, Cu, Zn, Mn, Br, Sr, Cd, and Pb were determined. Except for chromium (Cr), the concentrations of the elements detected did not exceed the maximum level set by the Philippine National Standards for drinking water. Cr concentrations in most wells exceeded the 0.05 mg/L standard for drinking water [4]. In 2005, sample of groundwater tapped by the residents in the Maislab rehabilitation area, downstream of the landfill and the Lukutan River, contained 0.05 mg/L [5] which exceeds 0.01 mg/L maximum limit for Pb in drinking water. The concentrations of elements detected in the water collected from the shallow monitoring wells did not exceed the allowable limits for drinking water.

Except for the presence of chromium above the maximum limit of 0.05 mg/L, samples collected from the Lukutan River, leachate run-off and leachate holding pond comply with the water quality criteria for toxic and other deleterious substances for fresh surface waters [6].

4.3. Stable Isotopes in groundwater and surface water

Most of the deep groundwater wells exhibited seasonal variation in the isotopic composition greater than 0.1‰. Isotopic values clustered along the LMWL with $\delta^{18}O$ ranging from –7.5‰ to –6.5‰ and $\delta^{2}H$ ranging from –53.59‰ to –42.91. Fig. 3 shows the relationship of the isotopic composition

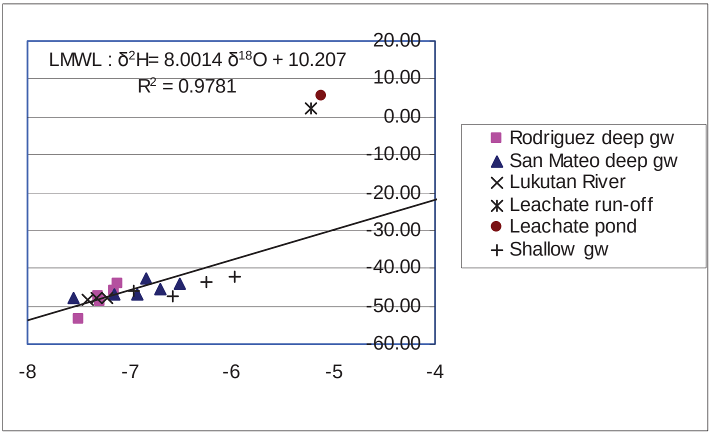

FIG. 3. The isotopic composition of deep and shallow groundwater, surface water, and leachate, after the rainy season with respect to the LMWL.

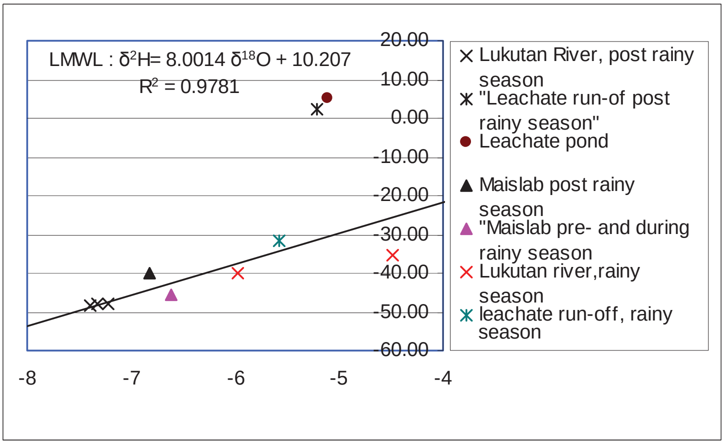

FIG. 4. Contamination of the Lukutan River and eventually, the Maislab well from leachate run-off is shown by their enrichment in δD.

of deep and shallow groundwater, surface water, and leachate after the rainy season with respect to the LMWL. San Mateo groundwater appear to be more isotopic ally enriched than the Rodriguez groundwater and the Lukutan River, indicating different sources of recharge. Shallow groundwaters are isotopically more enriched, trending towards the evaporation line, with mean $\delta^{18}O$ and δD values of –6.46‰ and –44.14‰, respectively. Leachate from the landfill exhibits a distinct isotopic composition from the freshwaters, with most enriched δD values of +2.36‰ for the leachate run-off and +5.31‰ in the leachate pond. In the later part of the dry season, In March 2006, more enriched δD values were obtained at 5.84‰ for leachate run-off, and 16.55‰ for the leachate pond.

The significant differences in the isotopic signatures of the different water sources in the study area would facilitate detection of contamination from leachate run-off to the surface water, and eventually, to the groundwater. In Fig. 4, the effect of leachate run-off on the nearby Lukutan River is evident from the observed enrichment in δD of the river during the rainy season. Evidence of contamination of the shallow groundwater downstream is later seen after the rainy season as demonstrated by the enrichment in δD of water taken from the Maislab rehabilitation community well.

This initial study has demonstrated the potential of applying environmental isotopes in tracing and assessing contamination from the landfill to nearby surface water sources and eventually to the groundwater.

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TRACING NITRIFICATION AND DENITRIFICATION PROCESSES IN A PERIODICALLY FLOODED SHALLOW SANDY AQUIFER

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Abstract

The study defines the transfer mechanisms of nutrients and heavy metals from soil to groundwater operating in periodically water saturated soils. The study site is located in Lomellina (Po plain, Northern Italy), which is intensively cultivated with rice. Soils are dominantly constituted by sands, with acidic pH and low organic carbon content. The region generally displays low nitrate contamination in shallow groundwater, despite the intensive land use, while Fe and Mn often exceed drinking water limits. Monitoring performed through a yearly cycle closely followed the water table fluctuations in response to periodical flooding and drying of cultivated fields. pH, conductivity and Eh were measured in the field. Water samples were analysed for major ions, trace elements, nutrients and stable isotopes of dissolved inorganic nitrate (DIN). Results evidence the seasonal migration of nutrients, the redox and associated metal cycling, and allow defining nitrification and denitrification processes.

1. INTRODUCTION

The Po plain, located in Northern Italy, supports most of the agricultural and industrial activities of Northern Italy, which are associated with groundwater exploitation and pollution mainly in the shallower aquifers. The Lomellina region represents a limited portion of the Po plain, of approximately 900 km^2 (Fig. 1). The investigated aquifer is constituted by sediments belonging to the continental depositional system of Plio-Pleistocenic age [1, 2] and is made of gravels and sands with interbedded clay layers. This formation, reaching a depth of 150–200 m, creates a multilayer aquifer system with a water table a few meters deep; it is an aquifer of great importance for the lateral extension and for high transmissivity, of about 10^{-2} m^{2}s^{-1}. Two units can be locally recognised due to the presence of a discontinuous, impervious, silt and clay layer to a depth of 60–80 m. Groundwater flow direction is roughly oriented N to S, but, in the phreatic aquifer, is strongly controlled by draining action of the Po, Sesia and Ticino rivers (Fig. 1).

The Lomellina region is characterised by an elevated potential infiltration [3] and is intensively cultivated with, mainly, rice and corn fields. The recharge areas for the multilayer aquifer are located in the Alpine piedmont, but severe recharge takes place from seepages of channel network and from rice ponds.

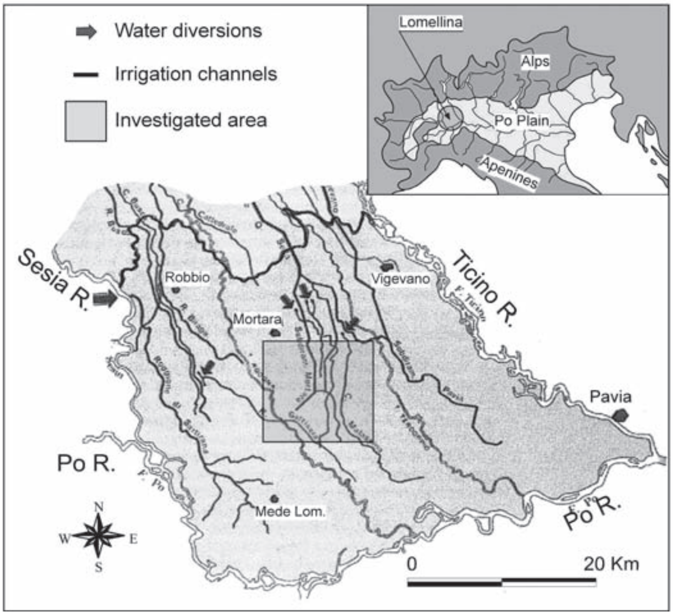

FIG. 1. *Location of the investigated area.*

Soils are arenosols and luvisols, with acidic pH, mainly constituted by quartz and feldspars. A strong depletion of Mn and Fe in the topsoil is often observed in rice paddies, together with the formation, at a depth greater than 80 cm, of Fe and Mn oxi-hydroxides [4]. Soil Fe-Mn precipitates and nodules are formed within the soil pore network as a result of seasonal changes in the soil redox potential and pH. Under reducing conditions, Fe and Mn oxides release Fe(II) and Mn(II) ions to the soil solution. When the soil dries out, Fe(II) and Mn(II) oxidise and precipitate, forming new metal oxides [5]. Manganese is more mobile than Fe and requires a higher oxidation potential compared with Fe(II), leading to the formation of alternate layers of Fe-rich and Mn-rich material [6].

2. METHODS OF INVESTIGATION

Eleven very shallow wells (<20 m depth) were selected in a limited area (50 km^2) for water level, hydrochemical and isotopic monitoring. The water table depth was measured daily at the centre of the investigated area. Groundwater sampling closely followed the agronomical practices and was performed approximately once per month, from March 2006 to January 2007. Analyses included: pH, Eh, temperature, conductivity, major ions, trace metals, and, stable isotopes of dissolved nitrates. The pH, redox potential, temperature and conductivity were measured in situ. Chemical analyses were performed at the Dipartimento di Scienze della Terra, University of Pavia. Anions and cations were determined by ion chromatography and trace metals by ICP-AES. All reported values have ionic balance within 5%. Samples for $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$ analysis were collected and prepared according to standard procedures [7, 8]. All gases were analysed on a Finningan™ MAT 250 Mass Spectrometer at ISO4 s.s., Turin, Italy. The analytical errors are ±0.2 and ±1‰ respectively.

3. RESULTS

In the Lomellina region, the phreatic aquifer displays waters of poor quality: high salinity, high nitrate, sulphate and chloride contents and, locally, detectable amounts of heavy metals (Fe, Mn, As) and pesticides [9]. The seasonal fluctuation of the water table (Fig. 2) shows a steep rise of the water table of 1.6 m, related to field waterlogging, rising the piezometric surface to about 1.5 m below the surface. Data collected from local irrigation agencies allowed calculating for the entire season a recharge of about 38,000 m^3/ha, highly exceeding natural recharge from precipitation. The seasonal variation

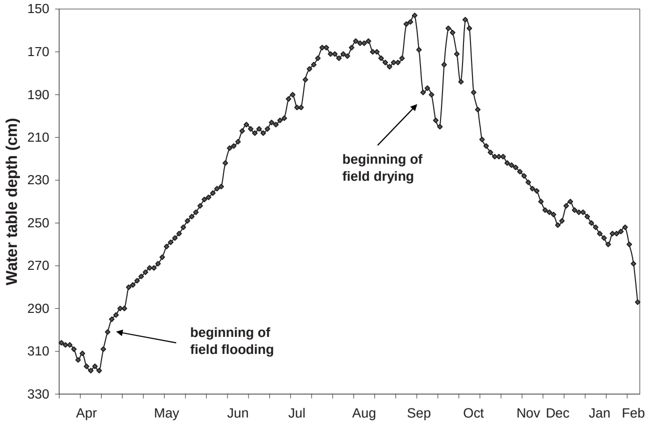

FIG. 2. Water table level fluctuation in response to soil flooding.

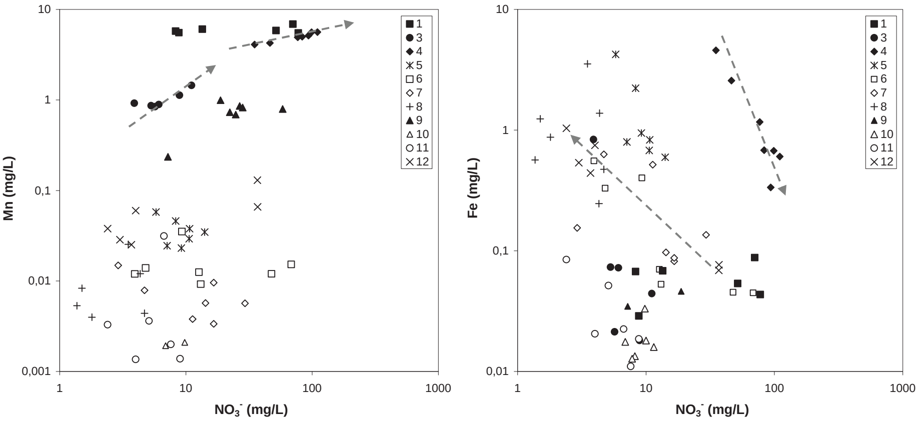

FIG. 3. Seasonal evolution of DIN and heavy metals. Grey arrows indicate the seasonal trends observed in different wells. Group 1 = empty symbols, group 2 = full symbols.

of groundwater quality includes a rise in temperature and conductivity, and a decrease in pH, a typical evolution for shallow groundwater. On the other hand, Eh is highly variable from well to well, ranging from 450 to 210 mV and indicating the presence of localised oxido-reduction phenomena. Based on hydrochemical characteristics and seasonal evolution two groups of waters may be distinguished:

- Group 1 (wells 5, 6, 7, 8, 10, 11 and 12, empty symbols in all figures). After soil flooding, this group of wells shows a progressive decrease in Eh and

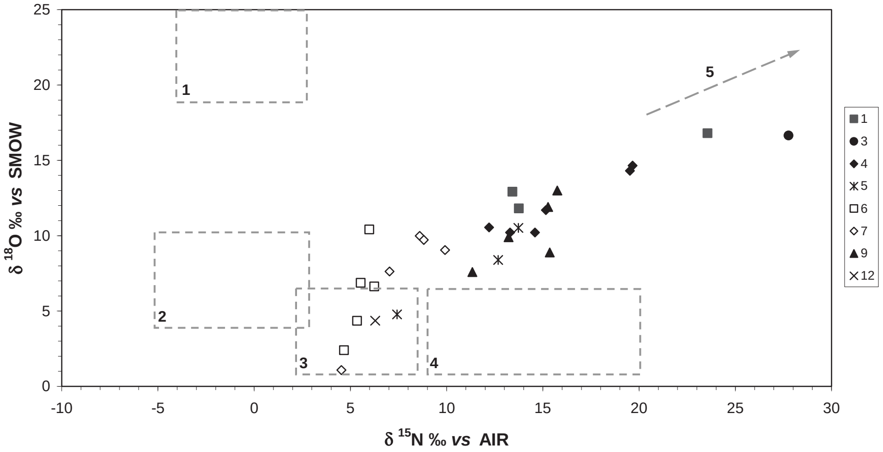

FIG. 4. Isotopic composition of DIN. 1= synthetic fertilisers; 2 = mineralised synthetic fertilisers; 3 = soil organic matter; 4 = manure and septic tank effluents; 5 = slope of the denitrification trend.

dissolved nitrates (DIN), increase in alkalinity and Fe content. Mn is always low and Zn content may rise up to 2.6 mg/L.

- Group 2 (wells 1, 4, 9 and 3, full symbols in all figures). These wells show an inverse seasonal evolution, i.e. an increase in Eh, dissolved nitrate and Mn contents, decrease in Fe and low Zn content. These wells also show very high K contents (up to 60 mg/L).

The behaviour of heavy metals is closely connected to that of DIN (Fig. 3), although the two groups display an opposite seasonal trend. Most wells show an inverse correlation between Fe and DIN. In addition, samples of group 2 containing high Mn show a direct correlation between Mn and DIN. Zn contents up to 2 mg/L are observed in wells of group 1; group 2 displays lower Zn contents, showing a positive correlation with Fe (and negative correlation with DIN).

The isotopic composition of dissolved nitrates also clearly differentiates the two groundwater types (Fig. 4). Group 1 shows δ^{15}N ranging from +4 to +13‰, and several samples fall in the compositional field of soil organic matter; group 2 shows more enriched values for both stable isotopes and aligns along the slope of the denitrification trend.

4. INTERPRETATION

Fig. 5 shows the seasonal trends observed in DIN content and isotopic composition for the two groups of samples. After soil flooding, group 1 shows a marked decrease in nitrate contents associated to enrichment in the nitrogen isotopic composition. This trend is easily interpreted as a denitrification, operated *via* the oxidation of the dissolved inorganic matter and producing an increase in alkalinity. Samples with the highest nitrate concentrations show $\delta^{15}N$ composition typical of the soil organic matter and a $\delta^{18}O$ composition in equilibrium with the water isotopic composition ($\delta^{18}O \approx -9‰$) [10]. On the other hand, the observed increase in $\delta^{18}O$ of DIN cannot be justified by a contribution from enriched nitrates or by the reopening of the system to atmospheric O_2. It is therefore suggested that the Fe oxi-hydroxides may play a role in modifying this isotopic signal. During denitrification, the increase in Fe content is probably due to the destabilization of Fe oxi-hydroxides, as it is not coupled to a parallel increase in sulphates: therefore a denitrification operated *via* pyrite oxidation can be excluded.

Previous studies have highlighted the important role of Fe and Mn dynamics in trace metal mobilisation in soils. A marked increase in the soil solution concentrations of metals like Cu, Zn or Cd, related to Mn and Fe reduction and mobilization as effect of lowered Eh in flooded soils is reported [11]. This mechanism could explain the direct relationship observed between Fe and Zn in several wells.

Following waterlogging, group 2 shows a seasonal evolution of progressive increase in DIN and depletion in $\delta^{15}N$ and $\delta^{18}O$; this evolution is also accompanied by an increase in dissolved Mn and a decrease in dissolved Fe and alkalinity. This evolution follows the slope of the denitrification trend, but in the opposite direction, and could therefore be interpreted as a mixing process between a residual and a "fresh" nitrate source. Nevertheless, samples with the highest nitrate concentrations have an isotopic composition of about +12.5‰ in $\delta^{15}N$ and +10.5‰ in $\delta^{18}O$,which cannot be readily attributed to any precise source.

Flooded rice paddies are microbiologically very active systems where, within few cm depths, rapid changes in the redox conditions are observed [12]. In late spring, fields are waterlogged and a reducing environment is established; two or three periods of drying up are performed to allow for pesticide and herbicide treatments, followed by re-flooding. Finally, at the end of the growing season, the field is desaturated and water is allowed to evaporate; as a consequence an oxic environment is established during winter. Rice cultivation requires the use of reduced ammonium-based fertilizers, generally urea. This compound can be oxidized to nitrate, if oxygen is present. After flooding,

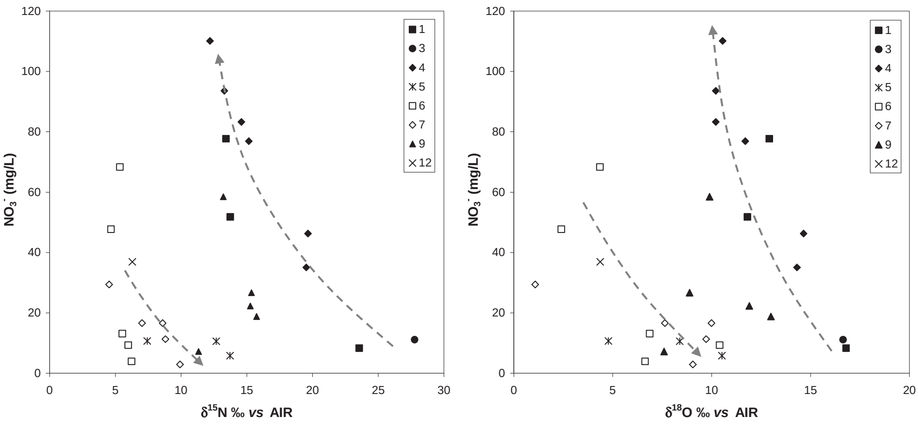

FIG. 5. Seasonal evolution of DIN content and isotopic composition.

dissolved oxygen is rapidly consumed and nitrate is the first molecule reduced after oxygen depletion, followed by Mn(IV), Fe(III) and sulphates, according to the redox potential of the electron acceptor. Along oxic-anoxic interfaces, directly beneath the waterlogged soil, alternative electron acceptors will be regenerated because of the re-oxidation of reduced compounds [12]. The oxygen isotopic composition of biogenic manganese oxides indicate that they derive 50% of their oxygen from water and 50% from dissolved oxygen [13]. Therefore their isotopic composition is enriched in δ^{18}O with respect to water, despite the absence of fractionation during precipitation. In our case study their isotopic composition, in equilibrium with local groundwater ($\delta^{18}O \approx -9‰$) should be approximately of +6–7‰.

An enriched δ^{15}N in DIN from agricultural environments is generally attributed to manure spreading [14–15]. Nevertheless ammonification, volatilization and plant uptake may enrich the isotopic signal of synthetic fertilizers of several deltas [14]. Given the close relationship observed between dissolved nitrate and Mn content in samples from group 2, it is suggested that their enriched isotopic composition could be obtained by nitrification of residual ammonium using MnO_2 as an oxygen source. A simple calculation estimates this contribution to the nitrate-oxygen to less than 1/3. On the other hand, this does not agree with the amount of dissolved Mn. Therefore, to explain the enriched oxygen isotope composition of DIN, we need to consider that the oxidation likely occurs during the drying up of the paddies, when the water isotopic composition can be enriched due to evaporation.

The difference in hydrochemical and isotopic evolution between group 1 and 2 cannot be readily justified on the basis of location, land use, permeability or redox conditions. Nevertheless, it should be noted that the conspicuous recharge from the surface likely induces a chemical stratification within the first meters of the aquifer. In addition, at the same location, the redox conditions may quickly vary with depth and time in response to soil flooding and drying episodes.

5. CONCLUSION

Flooded rice paddies provide a unique environment where, in ideal conditions, nitrification and denitrification processes can be traced and rates calculated. This was not possible at the end of this monitoring year, because the cycle was not completely closed by a return to the initial conditions. This is attributed to the exceptionally warm winter experienced this year, allowing the biological activity in soils to persist.

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A REGIONAL SURVEY ON NITRATE CONTAMINATION OF THE PO VALLEY ALLUVIAL AQUIFER (NORTHERN ITALY)

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Abstract

The origin, distribution and abatement of nitrate contamination in surface and groundwater are traced by hydrochemical and stable isotope analyses. The studied sector of the Po Valley is approximately 3 600 km^2 wide, extending from the Alps to the Apennine along a N–S transect. The phreatic aquifer is fed by local infiltration and by streams and irrigation channels, while the Po river represents the major discharge axis. The main diffuse source of nitrates is from synthetic fertilisers, exceedingly used for crop raising. Peak concentrations are instead associated to local leakage from the sewage network. The distribution of groundwater contamination is closely related to the hydraulic characteristics of the unsaturated zone, to agricultural input and irrigation practices. Denitrification is observed along major draining rivers and below rice fields. Results are interpreted in terms of aquifer vulnerability, groundwater circulation and land use.

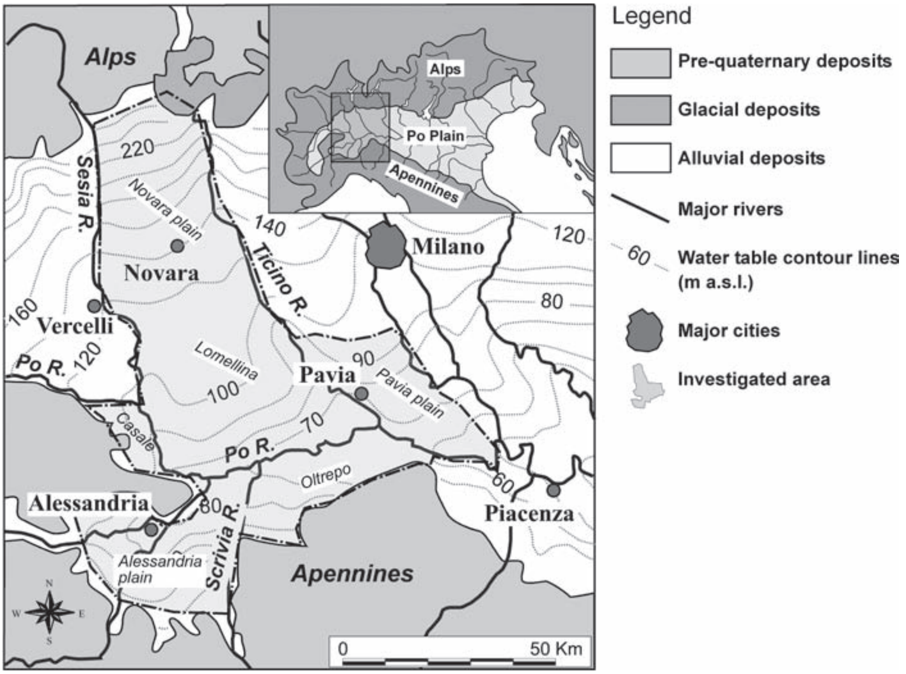

FIG. 1. Location of the investigated area.

1. INTRODUCTION

Nitrate concentration in surface and groundwater is an environmental concern. Nitrate pollution may be attributed to point sources, such as landfills, septic tanks or factory farming. Agricultural regions commonly suffer diffuse water pollution, which, in contrast, cannot be attributed to a precise source. Rather, it is the cumulative effect of day to day activities over large areas, including application of synthetic fertilisers, manure spreading and sewage sludge disposal.

Distinction between different sources of nitrates in groundwater can be made using hydrochemistry [1, 2] or/and by determining the isotopic signature of oxygen and nitrogen in the nitrate molecule [3]. While the first approach may be useful in simple cases such as point source pollution, the combination of $\delta^{15}N$ and $\delta^{18}O$ data in nitrate allows to evidence cumulative effects in regional contamination problems and, in addition, to recognise nitrification and denitrification processes [4, 5].

The Po plain hosts a multilayer alluvial aquifer, of Quaternary age, which is constituted by gravels and sands with interbedded clay layers. The thickness of the sedimentary sequence is strongly conditioned by the presence of buried structures of the marine substratum, which are dislocated and affected by Alpine and Apennine thrusts. The area covered by this study is of approximately 3,600 km^2, crossing the Po plain from N to S in correspondence to the Piedmont-Lombardy administrative boundary (Fig. 1). Agricultural land use includes corn, wheat and rice fields (Fig. 3).

A preliminary selection of samples for hydrochemical and isotopic characterisation was carried out based on available data on groundwater quality monitoring programmes. About 100 monitored wells and natural outflows were selected, considering also rivers and irrigation channels, all with nitrate concentration exceeding 10 mg/L. Groundwater flow direction in the phreatic aquifer is oriented N to S in the pre-alpine sector and S to N in the Apennine one (Fig. 1).

2. THE TERRITORIAL DISTRIBUTION

2.1. The Novara province

The Novara province is characterised by the presence of a phreatic aquifer of great permeability and thickness. The water table is located few tens of meters below surface, close to the Alps, and becomes shallower moving south, locally originating natural outflows. This is also evidenced by differences in land use: the northern part is intensively cultivated with corn and wheat, while the southern area is covered by rice fields.

Nitrate concentration in groundwater rarely exceeds the drinking water limits, and water quality is generally good. The isotopic composition of dissolved nitrates matches that of mineralised synthetic fertilisers with little denitrification (Fig. 2). Denitrification is also evidenced by a decrease in the NO_3/SO_4 and NO_3/Cl ratios. this process is observed in wells tapping deeper portions of the aquifer or experiencing high withdrawal rates (e.g. the Novara municipal wells).

2.2. The Lomellina region and the Pavia plain

The Lomellina region and the Pavia plain are characterised by an elevated potential infiltration and are intensively cultivated with, mainly, rice and corn fields. The water table is only few meters deep. Severe recharge takes place from seepages of the channel network and from rice ponds. The phreatic aquifer displays waters of poor quality, with higher nitrate, sulphate and chloride contents and, locally, detectable amounts of pesticides. Indeed, rice cultivation uses ammonium sulphate, urea and potassium chloride as fertilisers.

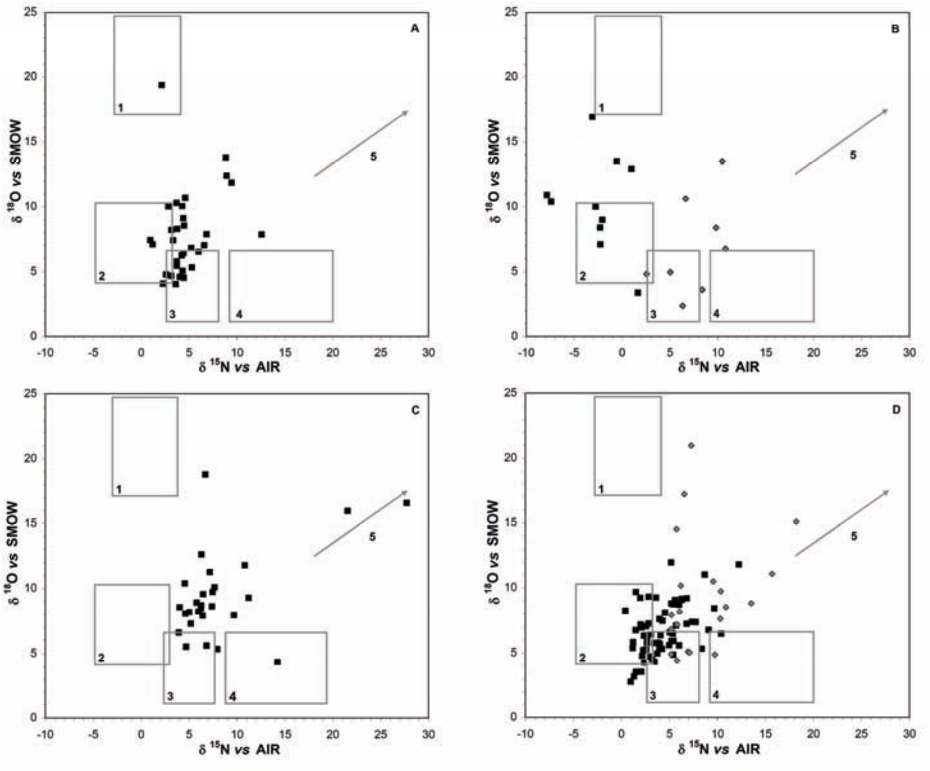

FIG. 2. Isotopic composition of dissolved nitrates. A: Novara province; B: Lomellina region (black squares= fall sampling; grey diamonds = summer sampling); C: Oltrepo region; D: Alessandria province (black squares = Alessandria plain; grey diamonds = Casale area). 1= synthetic fertilisers; 2 = mineralised synthetic fertilisers; 3 = soil organic matter; 4 = manure and septic tank effluents; 5 = slope of the denitrification trend.

The isotopic composition of dissolved nitrates confirms the agricultural origin of contaminants due to the nitrification of synthetic fertilisers (Fig. 2) [6]. A seasonal effect, related to soil flooding, can be observed, as the same samples show, with a few months gap, evidence of a strong denitrification occurring. A correlation of isotopic composition with nitrate concentrations (and consequently with depth) is also observed [6]. A detailed investigation on the seasonal variation of nitrate content and isotopic composition in the Lomellina region is reported in a companion paper [7].

2.3. The Oltrepo region

In the Oltrepo region, the phreatic aquifer is of limited thickness because of the presence at shallow depth of the dislocated marine substratum. In addition, a clay layer of few meters thickness covering the aquifer formation is present, locally imparting a confined or semi-confined character. Groundwater is high in sulphate (100–250 mg/L) and chloride (locally up to 1600 mg/L) content, while nitrate concentration is generally low. Intensive agricultural activity is hindered by the absence of good quality groundwater and by soil salinisation problems [8].

The isotopic composition of dissolved nitrates confirms the presence, at shallow depth, of an anoxic boundary. Low nitrate concentration would then reflect both a lower agricultural input and denitrification, which is favoured by the hydrogeologic setting and by mixing with anoxic brines. An enriched contribution is alsoobserved (Fig. 3). Due to the elevated contents (>90 mg/L) and its position, this contribution is attributed to a leakage from the sewage network.

2.4. The Alessandria province

The Alessandria province may be divided into two regions of very different hydrogeologic characteristics, both experiencing very high nitrate contamination. In the Casale area, the hydrogeologic setting closely resembles that of the Oltrepo: the marine substratum is found at shallow depth, and is also evidenced by the presence of highly saline groundwater. The dominant land-use type is rice cultivation, enhancing recharge and favouring nitrate input to groundwater. The area East of Alessandria also experiences high nitrate contamination: the aquifer is constituted by a great thickness of gravels and sands, originated by the migration eastward of the Scrivia river during the Quaternary in response to tectonic deformation. The area is intensively cultivated with corn and wheat.

Surface waters and phreatic groundwater display evidence of regional contamination from agricultural activities. This is indicated by high levels of nitrates (10–160 mg/L), sulphate and chloride contents, and, locally, detectable levels of pesticides. In the Alessandria province, high nitrate contents are positively correlated with Ca^{2+} concentration. This seems to indicate that the acidity associated with nitrate pollution is buffered by the presence of carbonates in the aquifer matrix; this phenomenon leads to an increase of water hardness and TDS [2].

The isotopic composition allows identifying the different sources of nitrates: both mineralised synthetic fertilisers and manure contribute to the contamination

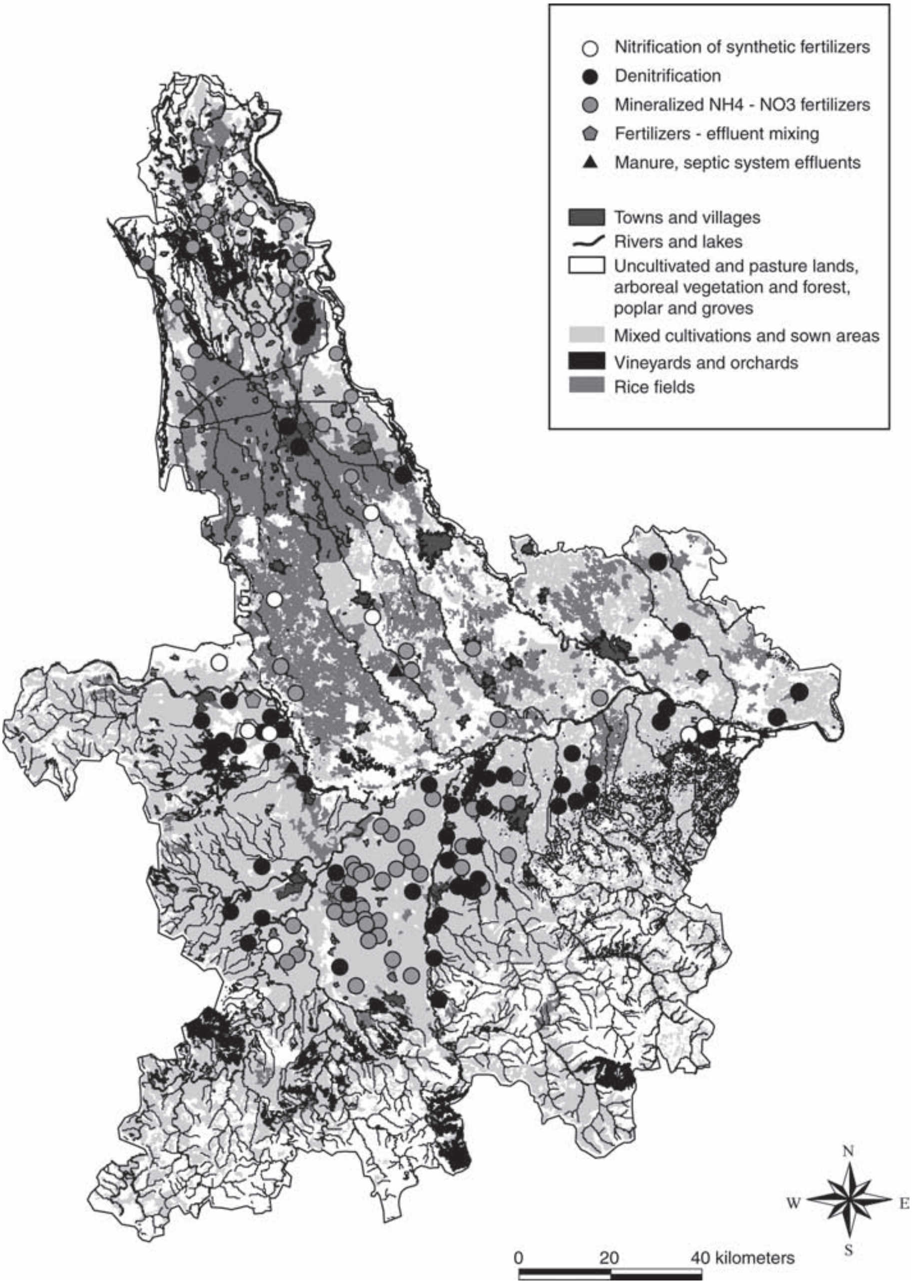

FIG. 3. Origin of and processes affecting dissolved nitrates, derived from their isotopic composition, as a function of location and land use.

(Fig. 2). Denitrification phenomena dominantly occur in the Casale area and East of the Scrivia River, because of favourable hydrogeologic settings, while near Alessandria, the high aquifer permeability and thickness do not allow the establishment of anaerobic conditions, favouring the build up of nitrates.

3. DISCUSSION AND CONCLUSION

This study dramatically evidences the impact of intense agriculture activities over groundwater resources. Contamination from synthetic fertilisers is widespread and nitrate accumulation is a threat to large groundwater supplies. Peak concentrations are instead associated to point source pollution and can be attributed to leakage of the sewage network. Nitrate concentrations being higher than 10 mg/L, the isotopic compositions in the compositional field of soil organic matter likely correspond to a mixed contribution from both synthetic fertilisers and manure spreading (Fig. 3).

The distribution of groundwater contamination is closely related to:

(1) The hydraulic characteristics of the unsaturated zone: clay rich soils reduce infiltration and favour denitrification through the establishment of anoxic conditions;

(2) the agricultural input: corn and wheat cultivation seems to be mostly responsible for nitrate contribution to groundwater;

(3) irrigation practices: the artificial recharge associated with rice cultivation also represents a preferential pathway for input of exotic substances to groundwater, but in this case, the input of nitrogen compounds is partially reduced by denitrification, as it is observed in the Casale and Lomellina areas.

The isotopic composition of nitrates confirms the hydrogeologic model of the phreatic aquifer. In the Po plain, the depth of the denitrification zone is strongly conditioned by the presence of buried structures and associated saline waters: it may be as shallow as 15 m below surface, like in the Oltrepo region, or deeper than 100 m, like in the Alessandria plain. Therefore stable isotopes of the nitrate molecule may also represent a useful tool to evidence aquifer overexploitation associated with high withdrawal rates.

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ISOTOPE HYDROGEOCHEMICAL INVESTIGATION ON THE OCCURRENCE OF FLUORIDE IN GROUNDWATERS OF ALAPPUZHA DISTRICT, KERALA, INDIA

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Abstract

Environmental isotopes (^{2}H, ^{18}O, ^{3}H, ^{13}C and ^{14}C) along with hydrochemical and hydrogeological information were used to understand the source and mechanism of fluoride release into the groundwaters of a heavily exploited multilayered regional aquifer system in Alappuzha district, Kerala, India. The results of the study show that the shallow Quaternary aquifers are uncontaminated whereas the deep Tertiary aquifers are contaminated with fluoride (up to 2.6 mg/L). The observed positive correlation of F^- with pH, alkalinity, Na^+ and ^{13}C and negative correlation with Ca^{2+} along the flow path point out that the leaching of fluoride bearing aquifer material is responsible for the release of fluoride into the groundwater. F^- versus ^{18}O plot also confirms the leaching process. The rate of fluoride release is different in various flow paths and it depends upon the residence time of groundwater and length of the flow path. ^{2}H, ^{18}O, ^{3}H and ^{14}C data indicate that the contaminated groundwater is very old with ^{14}C ages varying from 15 to 30 ka B.P. in the down gradient and probably recharged during an arid climate in the past.

1. INTRODUCTION

Fluoride and arsenic are the two major geogenic contaminants observed in groundwater world wide. In India, more than 62 million people are affected by fluorosis because of the consumption of fluoride contaminated water [1]. Permissible limit of flouride in drinking water is 1.0 mg/L [2]. Deficiency of fluoride (less than 0.5 mg/L) causes health problems like lack of formation of dental enamel and mineralization of bones, especially among children. While higher concentration of fluoride (more than 1 mg/L) affect the metabolic processes of both the young and the old, resulting in skeletal fluorosis, dental fluorosis, fluorosis in soft tissues such as muscles and ligaments or their combinations.

Fluoride generally occurs in groundwater because of weathering processes. High concentrations are generally observed in hardrock areas which are rich in fluoride bearing minerals. Edmunds and Smedley [3] reviewed the global research on fluoride contamination in groundwater and focus on the influence of hydrogeology on the occurrence of fluoride. Even though several studies are reported on flouride contamination, issues such as source and mechanism of flouride release and its transport in groundwater are still need to be addressed.

Prevalence of dental fluorosis among children below 15 years are reported in Alappuzha district, Kerala, India [4]. Here, the deep groundwater is the only source of potable water supply to the Alapuzha town and the nearby rural areas because of the inherent water quality problems in surface waters. In many places, the shallow groundwater is saline or contaminated due to its proximity to the backwaters and the wetlands. Water consumption being the main pathway of flouride to human beings, an attempt has been made in the present study to

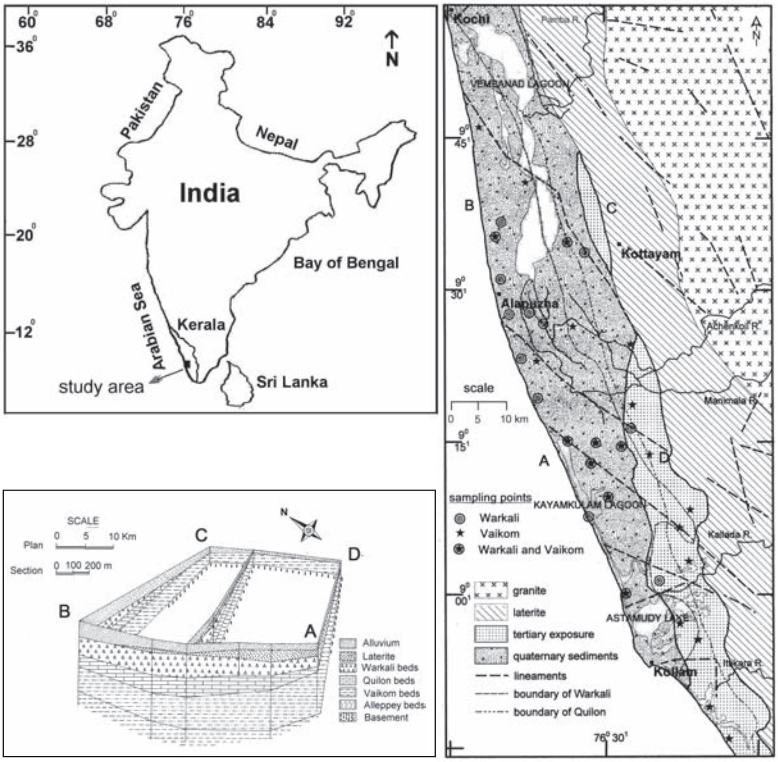

FIG. 1. Location map showing the hydrogeology of the study area and sampling points for isotope analysis.

understand the source and mechanism of fluoride release into groundwaters of Alappuzha district using isotope hydrogeochemical techniques.

2. THE STUDY AREA

The investigated multilayered aquifer system is a major regional aquifer in Kerala, India located in the southern part of the state (Fig. 1). The study area has a curvilinear shape with a maximum width of 45 km in Alapuzha and having an area of about 3000 km^2 between 8°45' to 10°00' N and 76° 17' to 76°40' E, occupying the entire Kollam and Alapuzha districts and parts of and Kottayam and Pathanamthitta districts. The Arabian Sea borders the study area in the west and Vembanad Lagoon, the largest backwater lake in the state is situated in the northern part. The eastern border is marked by the foot hills of Western Ghats. Topographically, the area is classified as coastal plain comprising of three major river basins, mainly drained by Ittikara River, Kallada River, Pamba River and its tributaries viz, Achenkovil and Manimala rivers. The area receives an average annual rainfall of 2880 mm.

3. HYDROGEOLOGICAL SETUP

It is a sedimentary basin consisting of formations of Eocene to Recent age. Unconsolidated Quaternary alluvium and laterite is underlain by unconsolidated to semi-consolidated Tertiary sediments (Fig. 1). Archaean crystalline rock comprising of Charnockites and Khondalite forms the basement and is exposed at the eastern periphery of the area. Quaternary alluvium and laterite form the top phreatic aquifer and is underlain by Tertiary sediments in which groundwater exist under confined condition.

There are four distinct groups of formations in the Tertiary sediments namely, Warkali bed, Quilon bed, Vaikom bed, Alleppey bed. Warkali bed is the uppermost and most extensively developed aquifers among the Tertiary formations. It consists of alternate layers of fine to medium sand with clay and thin bands of lignite. Underlying the Warkali bed is the marine Quilon bed comprising of hard compact gray limestone, calcareous clay and marl with fine to medium sand. It is not a potential aquifer. Vaikom is the most potential aquifer among the Tertiary formation. It is less developed near Alappuzha because the water is not potable due to salinity. It is composed of gravel, coarse to medium sand and pebble beds interbedded with ash gray clay and thin bands of lignite [5]. The potentiometric map of Warkali aquifer in 1987 depicting the various flow paths is given in Fig. 2 (modified from [6]).

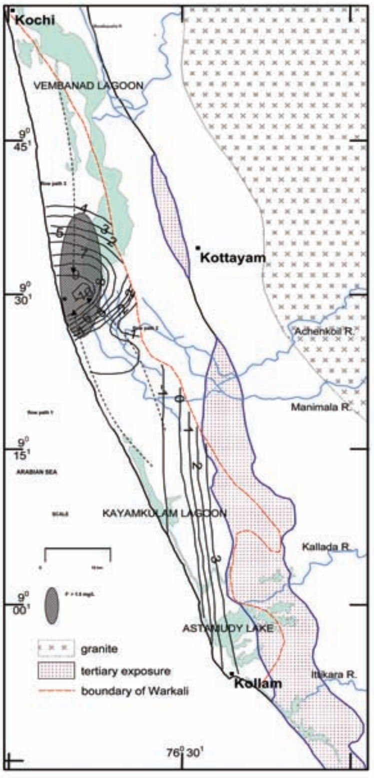

FIG. 2. Potentiometric map of Warkali aquifer in 1987 showing the various flow paths (modified from [6]).

4. SAMPLING AND ANALYTICAL METHODS

More than 35 groundwater samples were collected from Tertiary aquifers such as Warkali, Quilon and Vaikom aquifers for the analysis of ^{2}H, ^{18}O, ^{13}C, ^{3}H, ^{14}C and hydrochemistry. A few water samples were also collected from the alluvial aquifers for the measurement of above isotopes. Stable isotopes such as ^{2}H and ^{18}O were measured by Isotope Ratio Mass Spectrometer (IRMS) using the equilibration method. For ^{13}C analysis, about one litre of each sample was taken in a polythene bottle, adjusted the pH above 9 by adding 10 N NaOH and $BaCO_3$ was precipitated by adding saturated $BaCl_2$ solution. In the lab, the precipitate was treated with conc. H_3PO_4 under vacuum and the evolved CO_2 gas was directly measured using an IRMS. Stable isotopes such as δ^{2}H and δ^{18}O are reported as permil (‰) deviation (δ) with respect to VSMOW where as δ^{13}C is expressed with respect to V-PDB standard as:

$$\delta_{sample}\,(‰) = \left[\frac{R_{sample} - R_{std}}{R_{std}}\right] \times 1000 \qquad (1)$$

where, R_{sample} and R_{std} are the isotope ratios ($\frac{^{2}H}{^{1}H}$, $\frac{^{18}O}{^{16}O}$ or $\frac{^{13}C}{^{12}C}$) of the sample and the standard respectively.

Tritium contents (^{3}H) of groundwater samples were measured using a Liquid Scintillation Counter (LSC) after electrolytic enrichment. Tritium contents are expressed in terms of Tritium Units (TU). For ^{14}C assays, carbonate is precipitated in the form of $BaCO_3$ and were measured by CO_2 absorption technique using liquid scintillation counter following the standard procedures. ^{14}C values are expressed as percentage Modern Carbon (pMC). Hydrochemical analyses including the measurement of fluoride were carried out using ion chromatographic techniques.

5. RESULTS AND DISCUSSION

Hydrochemical analysis of groundwater samples show that shallow aquifers are free from fluoride contamination whereas the deep Tertiary aquifers (especially Warkali aquifer) near Alappuzha region are contaminated with fluoride up to 2.6 mg/L (Fig. 2). Stable isotope content of groundwaters from the alluvial aquifer varies between –3.5‰ to –2.5‰ for $\delta^{18}O$ and between –17.7‰ to –9.5‰ for $\delta^{2}H$, where as corresponding values for Tertiary aquifer is –2.9‰ to –0.4‰ and –13.4‰ to +5.1‰ respectively. The $\delta^{2}H$ – $\delta^{18}O$ relationship of the samples are shown in Fig. 3 along with Global Meteoric Water Line (GMWL). Most of the groundwater samples from alluvial and Tertiary aquifers fall on or close to the GMWL in different clusters indicating that these waters are of meteoric origin and are not affected by secondary isotope effects such as evaporation. The tritium content of groundwater from the alluvial aquifer varies from 3–4 TU, which is similar to the present day precipitation values indicating modern recharge. The Tertiary aquifers contain negligible tritium except at the southeastern parts of the study area where they are exposed. Their ^{14}C values in the central part are in the range of <1 to 20 pMC. The corrected groundwater ages for these groundwaters are in the range of 15 to 30 ka B.P. The enriched stable isotopic composition compared to the present day recharge indicate that these are paleowaters which are recharged during an arid phase in the late Pleistocene period.

Since the groundwater from the Warkali aquifer is heavily exploited for the municipal supply, the hydrogeochemical evolution of flouride is studied in detail along the various flow paths (Fig. 4). Based on the hydrochemistry of groundwater and the mineralogy of the aquifer sediments, it can be deduced that

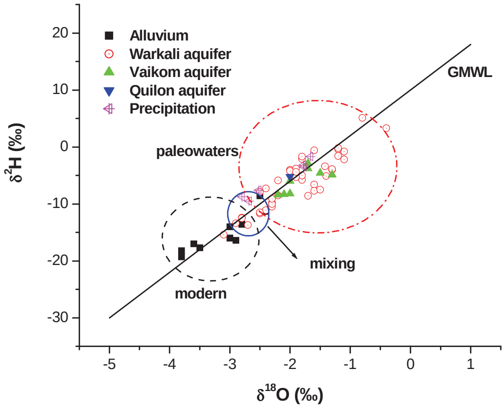

FIG. 3. ^2H–$\delta^{18}O$ relationships in groundwaters of the study area.

dissolution of aquifer material (derived from the granitic terrain of the western Ghats) containing pyroxene, pegmatite, fluorite and fluoroapatite may be the source for fluoride contamination in groundwater. Since these are paleowaters, the leaching of flouride from the formation is a function of residence time. pH of these groundwaters range from 8.0 to 8.8 indicating that they are alkaline. The fluoride contaminated groundwaters are in general Na–HCO_3 type.

Leachability of fluoride from the minerals is mainly controlled by adsorption equilibria and fluoride solubility. The concentration of fluoride in groundwater increases until the saturation level of fluorite is attained [7]:

$$Ca^{2+} + 2F^- \Leftrightarrow CaF_2 \qquad (2)$$

Hence, the presence of elevated amount of Ca^{2+} lowers the amount of F^- in groundwater and vice versa. If the pH of the groundwaters remains reasonably constant, any increase/decrease in the bicarbonate concentration will be accompanied by increase/decrease in the concentration of fluoride, indicating positive correlation between these two variables [7].

The measured F^- concentrations in groundwaters are plotted against pH, Ca^{2+}, Na^+, Mg^{2+}, HCO_3^- and $\delta^{18}O$ and given in Fig. 4. It is seen that F^- is positively correlated with pH, Na^+ and HCO_3^- and negatively correlated with Ca^{2+} and Mg^{2+} along different flow paths. As $CaCO_3$ is progressively dissolved along the flow path, the Ca^{2+} in groundwater will be exchanged with Na^+ in the clay material (ion exchange) and hence Ca^{2+} will decrease and Na^+ will increase as flow advances. Now, the high HCO_3^- and low Ca^{2+} waters promote fluorite dissolution and precipitation of calcite. Hence the observed high fluoride in groundwater is because of the leaching of fluorite from the formation.

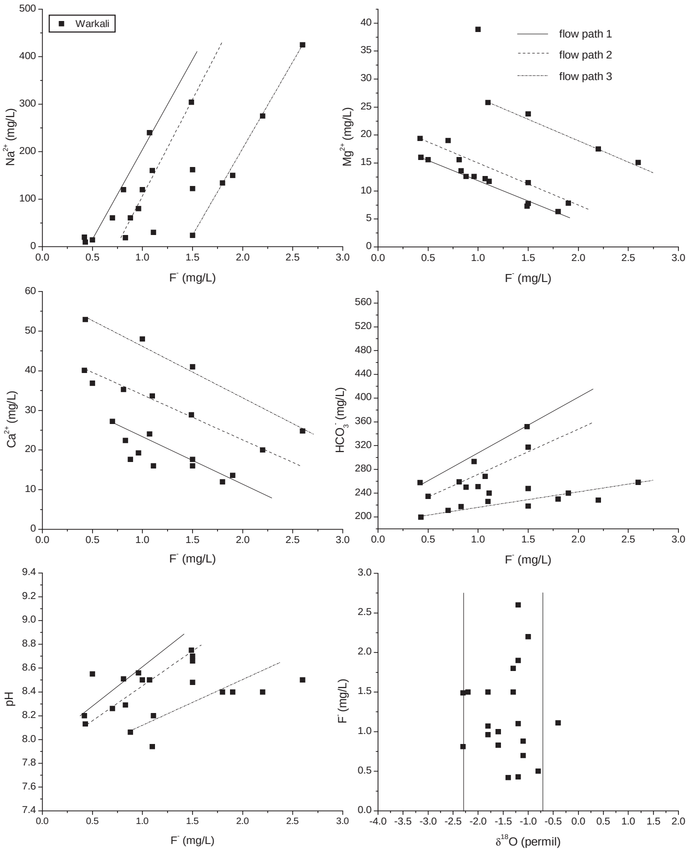

FIG. 4. Plot of F against Na^+, Mg^{2+}, Ca^{2+}, HCO_3^-, pH and $\delta^{18}O$ along various flow paths in Warkali aquifer.

In order to verify the feasibility of fluorite dissolution, saturation indices for water samples (SI) for fluorite, calcite and dolomite were calculated using WATEQF computer program [8]. It is seen that most of the groundwater from the Tertiary aquifers are undersaturated with fluorite and supersaturated with calcite and dolomite. This shows that dissolution of fluorite as a crucial process affecting fluoride concentration in these groundwaters. Supersaturation of calcite and dolomite indicates that precipitation is taking place.

Fig. 4 also shows a plot of F^- versus $\delta^{18}O$ of groundwaters from theWarkali aquifer. It is seen that the $\delta^{18}O$ falls in a narrow range of –2.5 to –1.2 ‰, and it is not correlated with F^- concentrations. This also confirms the leaching process. The rate of fluoride release is different in various flow paths and it depends upon the residence time of groundwater and length of the flow path.

6. CONCLUSION

From the isotope hydrogeochemical study, it can be concluded that the observed high flouride concentration in Warkali aquifer in the Alappuzha district is due to the leaching of fluoride bearing minerals from the aquifer because of the long rock water interaction. ^{2}H, ^{18}O, ^{3}H and ^{14}C data indicate that the contaminated groundwater is very old with ^{14}C ages varying from 15 to 30 ka B.P. in the down gradient and probably recharged during an arid climate in the past. The rate of fluoride release is different in various flow paths and it depends upon the residence time of groundwater and length of the flow path. Thus the study illustrates the usefulness of isotope techniques in conjunction with hydrogeological and geochemical methods for understanding the geogenic (fluoride) contamination in groundwater.

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APPLICATION OF ^{15}N ISOTOPES TO MANAGEMENT OF GROUNDWATER QUALITY, JABAL HASOUNA WELLFIELDS, GREAT MAN-MADE RIVER PROJECT, LIBYAN ARAB JAMAHIRIYA

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Abstract

The Jabal Hasouna wellfields are located some 700 kilometres south of Tripoli, the capital of Libya, and are part of the Great Man-Made River Project for water supply to coastal areas. The wellfields include 484 deep wells with a total design production rate of 2.5 million cubic metres per day from the Cambro-Ordovician sandstone aquifer. The aquifer is unconfined in the southwestern portion of the wellfields and the remainder is confined, but most of the wells are located in the unconfined part. Water quality is good, but concentrations of nitrate up to 133 mg/L occur in the wellfields, with slightly higher concentrations in the unconfined aquifer. Previous ^{14}C dating of the groundwater gave ages of 10.4 ka ± 0.4 ka to 17.2 ka ± 0.1 ka BP and stable isotope data indicate a meteoric origin from recharge during a humid climate phase of the Sahara. Analysis of δ^{15}N and δ^{18}O from groundwater nitrate showed a range of 7.11 to 12.64‰ for the δ^{15}N and 12.51 to 22.35‰ for the δ^{18}O. At Jabal Hasouna these ranges suggest that soil nitrate may be the source. There appears to be a low rate of denitrification so high nitrate levels will be a long-term concern for water quality.

1. BACKGROUND AND INTRODUCTION

The Libyan Arab Jamahiriya is a country in North Africa stretching from approximately 25°04’ E at its eastern border with Egypt to about 9°50’ E at the mid point of its western border with Algeria. It is bounded by Sudan on the southeast, and by Chad and Niger on the south. It shares a border with Tunisia in the northwest and has an extensive Mediterranean coastline to the north.

The vast majority of the six million Libyan citizens live along the narrow Mediterranean coastal strip where the rainfall is adequate for winter agriculture and small-scale summer irrigation schemes. In the absence of reliable sources of surface water for supply to the capital, Tripoli and the eastern urban centre of Benghazi, groundwater in the coastal aquifers was developed for domestic, municipal and irrigation applications. These sources are relatively limited in quantity and are subject to contamination by seawater intrusion, pesticides and fertilisers. During the course of exploration for hydrocarbons in the major sedimentary basins beneath the Sahara desert in the central and southern parts

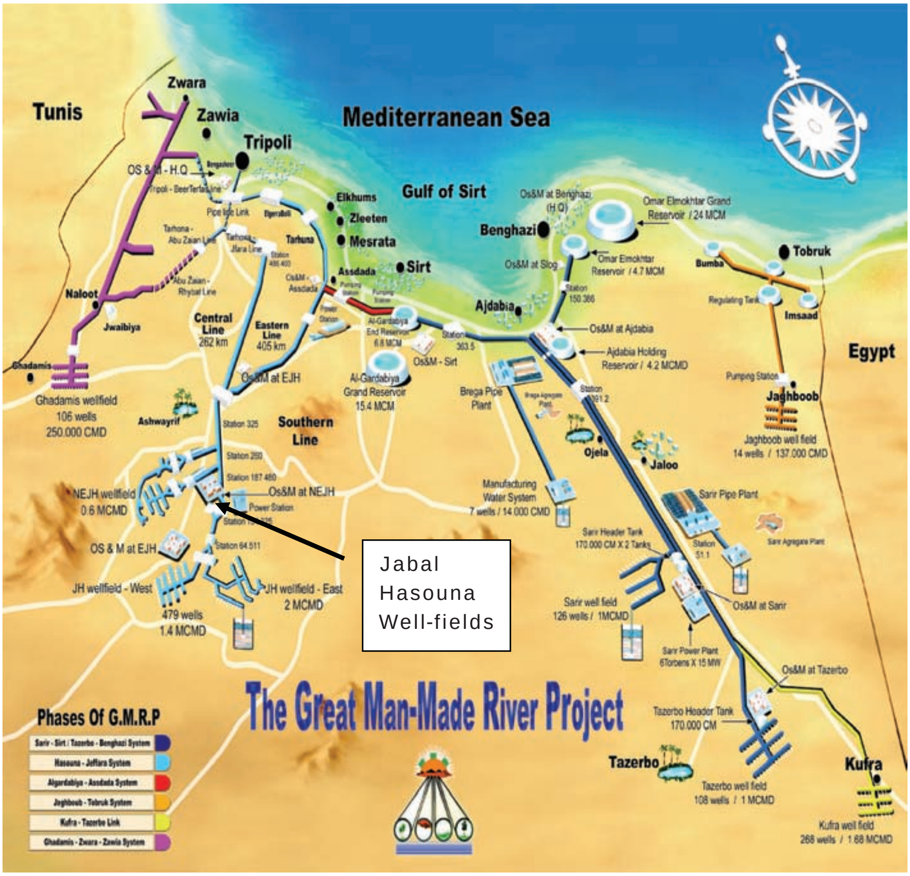

FIG. 1. Configuration of well-fields and pipelines of the GMRP, showing the Jabal Hasouna Well-fields [1].

of Libya, extensive reserves of good quality groundwater were discovered. These reserves are found in major, regional aquifer systems situated both in Libya and in neighbouring countries. The Libyan Great Man-Made River Project (GMRP) was initiated in 1983 to produce groundwater from desert well-fields and transport an estimated 6.5 million cubic metres of water daily to the coastal strip. Figure 1 shows the configuration of the component systems of the GMRP and the location of the Jabal Hasouna well-fields which are the subject of this paper.

The Jabal Hasouna Well-fields are the largest production facility in the GRMP, comprising 484 wells. They are divided into four groups. The northern well-fields are termed North East Jabal Hasouna North (NEJH(N)), containing 78 wells, and North East Jabal Hasouna South (NEJH(S)) with 90 wells, respectively. The southern well-fields are grouped into the East Jabal Hasouna East (EJH(E)), comprising 156 wells, and the East Jabal Hasouna West (EJH(W)) which includes 160 wells. The entire well-field system is designed to produce 2.5 million cubic metres of water per day for transport 700 kilometres northwards mainly to the Tripoli region on the coast.

1.1. Hydrogeology and groundwater quality

The groundwater is produced from the Cambro-Ordovician (CO) aquifer formed by fractured sandstones of the Hasouna Formation. This aquifer is unconfined within the southwestern part of the well-field area, but is confined elsewhere by the overlying Zimam Formation of Upper Cretaceous age. The Zimam Formation consists of limestone and sandy limestone with interbedded marl and clay layers [2, 3]. Geologically, the region is divided into the Murzuq Basin in southwestern Libya and the Hammada Al Hamra Basin in the north and northwest. These synclinal basins are separated by the Gargaf uplift, an east-trending, anticlinal structure, but the Hasouna Formation is continuous across it. The CO aquifer occurs in both basins but the Zimam Formation, which is a minor, perched aquifer in the Jabal Hasouna area is found in the Hammada Al Hamra Basin. The Jabal Hasouna well-fields are located just north of the Gargaf uplift within the Hammada Al Hamra Basin. The natural gradient of regional groundwater flow is towards the north and northeast.

Although the groundwater quality is good, some areas of moderate to high salinity appear to be related to the presence of saline Zimam aquifer [4]. Saline water leaks downward through vertical faults originating in the tectonics associated with the Gargaf uplift. The range of composition of water from the Jabal Hasouna well-fields is shown in Table 1.

The constituent of concern for potable water is the dissolved nitrate and a prime objective for the management of groundwater quality is to maintain the

TABLE 1. GROUNDWATER QUALITY AND CHEMISTRY VARIATION, JABAL HASOUNA WELL-FIELDS.

Constituent (mg/L)	Maximum	Minimum	Mean	Median	Standard deviation	Coefficient of Variation (%)
pH*	7.96	6.32	7.17	7.20	2.28	3.32
Dissolved O_2	8.55	0.10	4.92	5.20	1.53	31.18
ORP	360	20	154.93	143.00	64.01	41.31
TDS	1973	563	1039.42	1005.78	226.00	21.74
NH_4^+	0.11	0.01	0.05			
Ca^{2+}	195.59	49.00	114.57	116.00	20.25	17.68
Mg^+	68.81	7.30	28.33	26.32	9.60	33.87
K^+	56.00	0.00	8.44	6.65	5.44	64.41
Na^+	429.89	78.16	188.27	189.43	48.68	25.86
Cl^-	600.14	97.00	297.35	291.52	92.16	30.99
SO_4^{2-}	589.82	72.53	210.19	201.00	69.28	32.96
NO_3^-	133.00	0.00	53.59	55.42	17.30	32.27
HCO_3^-	301.34	98.94	169.7	170.84	22.67	13.40

*pH units; ORP = oxidation-reduction potential, millivolts; TDS = total dissolved solids; number of samples, n = 484.

nitrate concentration below the World Health Organisation (WHO) guideline of 50 mg/L. Currently this is achieved by manipulating well pumping rates of high and low nitrate water for an acceptable blend. The isotopes $\delta^{15}N$ and $\delta^{18}O$ from NO_3^- were determined as part of the investigation into the occurrence and origin of dissolved nitrate across the well-fields. The analyses were guided by the results of earlier sampling of the groundwater for the stable isotopes $\delta^{18}O$ and δ^2H, and age dating by the ^{14}C method.

1.2. Previous isotopic studies in the well-fields

The British Geological Survey (BGS) analysed eight samples of groundwater from wells in the NEJH(S) and NEJH(N) well-fields for ^{14}C, $\delta^{13}C$, $\delta^{18}O$ and δ^2H [5]. The most probable radiocarbon ages ranged between 10.4 ± 0.4 ka and 17.2 ± 0.1 ka. A single age of 6.4 ± 0.1 ka was interpreted as a mixture with younger water. The $\delta^{18}O$ values ranged from −9.99‰ to −9.50‰ on the Vienna Standard Mean Ocean Water (VSMOW) standard. Those for δ^2H ranged between −72.9‰ and −68.9‰ VSMOW. The mean values were −9.73‰ and −70.52‰ for $\delta^{18}O$ and δ^2H respectively.

The stable isotope data plotted along the global meteoric water line (GMWL) on the δ^2H versus $\delta^{18}O$ graph, but are strongly depleted compared to modern long-term weighted mean rainfall values of −3.29‰ for $\delta^{18}O$ and −20.02‰ for δ^2H from Sfax in Tunisia. Corresponding values from Sidi Barrani on the Mediterranean coast of northwest Egypt are −3.39‰ for $\delta^{18}O$ and −14.93‰ for δ^2H. Measurements at N'Djamena in Chad yielded −1.54‰ for $\delta^{18}O$ and −6.11‰ for δ^2H. These stations in the Global Network for Isotopes in Precipitation (GNIP) database are the closest to the Jabal Hasouna well-fields.

The radioisotope and stable isotope data indicate that the groundwater in the Jabal Hasouna well-fields is palaeowater which was recharged under past pluvial conditions. The $\delta^{18}O$ and δ^2H values reflect the influence of the prevailing atmospheric circulation patterns in northwestern Africa during the late Pleistocene or very early Holocene periods [5, 6]. These climatic conditions may have influenced the origin and continuing occurrence of nitrate in the groundwater of the Jabal Hasouna well-fields.

2. MANAGEMENT OF GROUNDWATER QUALITY IN THE JABAL HASOUNA WELL-FIELDS

2.1. Nitrate in the Jabal Hasouna well-fields

Sampling every well in the Jabal Hasouna well-fields for the concentration of NO_3 showed that there is a relatively uniform distribution across all four well-fields but there is a slight decrease towards the northeast in the direction of groundwater flow. The range in concentration is from 133 mg/L to 0 mg/L, as shown in Table 1. The spatial distribution of nitrate is similar to that of dissolved oxygen but there is less correspondence with the distribution of the related parameter, oxidation — reduction potential (ORP). The very low concentrations of NH_4^+, mostly below the level of detection (0.01 mg/L), suggest that nitrification has occurred in the groundwater and is maintained by the oxidising conditions. Regional groundwater in the neighbouring Wadi Ash Shati, some 100 km to the south, and the more distant Wadi Aril and Fazzan areas, contains less than 2 mg/L of nitrate. The occurrence of high concentrations of nitrate in the groundwater in the Jabal Hasouna well-fields is anomalous and its origin has not been identified unequivocally.

Several wells were cored through the Zimam and Hasouna Formations and examined for lithology of the crystalline phases. The concentrations of nitrogen and carbon were also measured on the cores. All of these analyses showed negative results. The Jabal Hasouna area is stony desert with an annual rainfall of about 20–30 mm and sparse vegetation mostly in sandy wadi beds. Negligible recharge can be expected under these conditions and it is hypothesised that the nitrate entered the groundwater during earlier recharge episodes and has undergone very slow denitrification. In this situation high concentration of nitrate is likely to be present throughout the design life of the well-fields. It was decided to examine the hypothesis by the use of the ^{15}N isotope and $\delta^{18}O$ from NO_3^-.

2.1.1. ^{15}N isotope and $\delta^{18}O$ from NO_3^- in the Jabal Hasouna groundwater

The Jabal Hasouna well-fields were divided into six areas, representing high, medium and low concentrations of nitrate, respectively. Five samples were taken from each of five wells and an extra sample was added for a total of 31 samples. The samples were sent to Iso-Analytical Ltd in England for determination of $\delta^{15}N$ by elemental analyser isotope ratio mass spectrometry (EA-IRMS). After review of these results, six wells were sampled for analysis of $\delta^{18}O$ from NO_3^- by the same laboratory. The method of Silva et al. [7] was used for the oxygen isotope analyses.

The results of the EA-IRMS analyses are expressed as the ratio of $^{15}N/^{14}N$ per mil (‰) compared to N_2 in the atmosphere, so that

$$\delta^{15}N‰ = \{[(^{15}N/^{14}N)_S / (^{15}N/^{14}N)_{AIR}] - 1] \times 1000$$

where S = sample and AIR = international reference standard atmospheric nitrogen, [8]. The primary reference material used by Iso-Analytical Ltd was the IAEA-N-1 (ammonium sulphate) with an accepted $\delta^{15}N$ value of 0.40‰ compared to air. The $\delta^{15}N$ values for the Jabal Hasouna wells range from 7.11‰ to 12.64‰ with a mean of 9.25‰. According to published tabulations of $\delta^{15}N$ values relative to atmospheric N_2 this range is typical of soil and subsurface nitrate, ammonium, gaseous and organic nitrogen, and effluent or manure [9, 10]. Effluent and manure can be eliminated on grounds of practicality but the remaining sources of nitrogen are still feasible. Although the spatial distributions of NO_3^- and $\delta^{15}N$ are inversely related, consistent with the isotopic enrichment accompanying the decrease in nitrate concentration due to denitrification [11], [12], the diagnostic plots of $\delta^{15}N$ against ln NO_3-N and against 1/ NO_3-N are not linear [12]. The first plot can distinguish between a Rayleigh fractionation model of denitrification and the second can indicate mixing or dilution of nitrogen from different sources by the linearity of the

TABLE 2. RESULTS OF $\delta^{15}N$ AND $\delta^{18}O$ (NO_3^-) ANALYSES.

Wellfield	Well Number	NO_3^- (mg/L)	$\delta^{15}N$‰	$\delta^{18}O$ (NO_3^-)‰
NEJH(S)	27	60.6	nd	19.83
NEJH(S)	25	54.6	10.26	nd
NEJH(N)	100	30.1	9.32	12.51
NEJH(N)	145	85.0	9.17	21.06
EJH(E)	270	45.7	10.38	16.12
EJH(E)	290	53.0	9.75	18.37
EJH(E)	310	48.1	9.57	22.35

nd = not determined

plots. More insight into the origin of the NO_3^- in the Jabal Hasouna well-fields is found from including the $\delta^{18}O$ concentration in the investigation.

Data from wells which were sampled for both $\delta^{15}N$ and $\delta^{18}O$ (NO_3^-) analysis are provided in Table 2.

The $\delta^{18}O$ (NO_3^-) samples were measured using the IAEA-NO-3 standard (KNO_3, $\delta^{18}O$ = 25.6‰ vs V-SMOW) as a reference. Comparison of the $\delta^{18}O(NO_3^-)$‰ and $\delta^{15}N$‰ with published ranges [13] show that the nitrate in the Jabal Hasouna groundwater may have its origins in precipitation and soil water without significant denitrification.

3. CONCLUSIONS

The studies of groundwater chemistry and isotopes in the Jabal Hasouna well-fields have shown tentatively that future concentrations of NO_3^- are unlikely to decrease as the well-fields approach their design capacity. Nevertheless this finding should be tested by more detailed investigations including multi-isotope studies and groundwater modelling.

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ORIGIN AND FATE OF NITROGEN POLLUTION IN GROUNDWATER TRACED BY $\delta^{15}N_{-NO3}$ AND $\delta^{18}O_{-NO3}$: THE CASE OF SUBURBAN AREA OF DAKAR (SENEGAL)

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Abstract

In recent years, the rapid increase of the population in the region of Dakar, especially in suburban settlements, together with the lack of policies for urban waste management, has become a source of concern for water supply, needs, and quality control. Approximately 80% of water resources in the region come from groundwater reservoirs. In order to identify the origin of groundwater pollution a survey of 26 piezometers and wells was conducted in march 2006. In this study, both major and trace elements were measured as well as the stable isotopic signature of water molecules and dissolved compounds. Nitrates often exceed drinking water limits and are associated with microbiological pollutants, while sea water intrusion represents the major threat to rapidly declining groundwater quality. Stable isotopes of dissolved nitrates allow for the identification of urban sewage and fertilizers as a major source of contamination, and the ability to define the distribution of their impacts. The occurrence of denitrification processes, although limited, suggest the potential for auto-purification of the contaminated water, if the source of the pollution were to cease.

1. INTRODUCTION

The social change that exerts the most pressure on water resources in the region of Dakar is represented by the rapid urban growth of recent years. The region of Dakar occupies only 0.3% of the surface area but accounts for 23% of the total population of Senegal. This is the most densely populated region of the country with 4,387 inhabitants per km^2 as compared to the mean density of 54 inhabitants per km^2. In addition, immigrants exert pressure on the available spaces and, as more favourable areas are occupied, they settle into marginal land lacking both control and sanitary measures.

The current social situation, as well as the presence of 90% of Senegal's industries (including agribusiness, textile and fertilizer production) have been widely recognized to be the main drivers of the severe groundwater pollution by nitrate in the region [1]. In fact, the decrease in groundwater quality can be primarily explained by the proximity of confirmed sources of pollution to the wells [2].

In order to discriminate between different sources of contamination, the main objective of the present study was to examine patterns of NO_3^- concentrations and $\delta^{15}N$ in 26 wells (13 drilled wells and 13 dug wells) spread across the aquifer which is characterized by Quaternary sand formations.

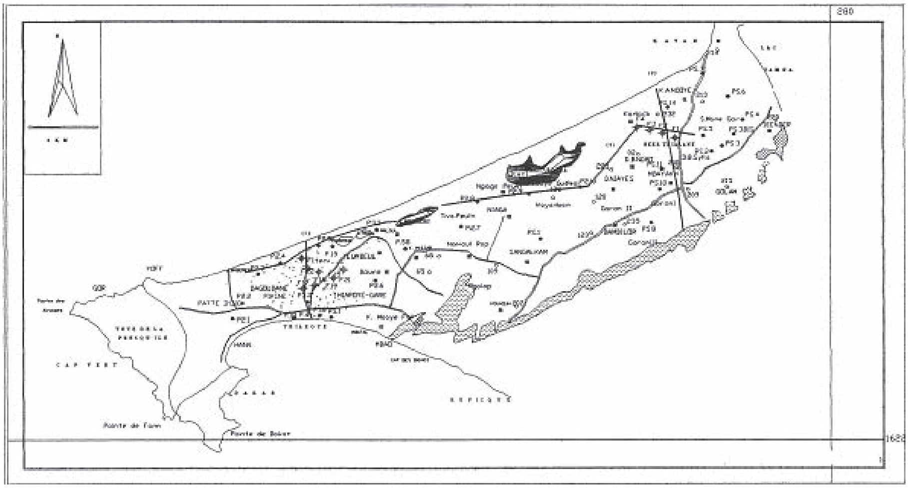

FIG. 1. Location of the study area and wells positions [4].

2. SITE DESCRIPTION

The region of Dakar is located in the mid-western section of Senegal and it extends as a peninsula 50 km in the W–E direction. In the N–S direction, the area has a maximum width of 15 km, decreasing at the Cambérène isthmus to a narrow strip of 4.5 km [3]. The peninsula of Cap-Vert is constituted by a rocky headland linked to the continent by the isthmus of Thiaroye and it extends up to the cliff of Thiès, which represents its eastern limit (Fig. 1).

The main morphological features of the region are an uplift of the sedimentary deposits related to the Dakar Quaternary volcanism and the eastern depression located in the Thiaroye suburban area. Two aquifers systems are present in the peninsula: the infrabasaltic semi-confined aquifer in the horst of Dakar and the unconfined aquifers of Thiaroye to the East [4] which supplies 7% of Dakar's drinking water.

3. RESULTS AND DISCUSSION

In situ measurements of pH varied between 4 and 9 and the electrical conductivity ranged from 190 to 4,200 $\mu S \cdot cm^{-1}$, in both drilled and dug wells. Concentration values of major-elements found in the groundwater of the Cap-Vert peninsula permitted the classification of waters as sodium-chloride (Fig. 2). Mineralization processes are relevant and concern areas where farming and rural or urban life can affect the groundwater quality. The data indicate high cation content and low alkalinity values, together with an increase in dissolved nitrate and chloride. The abundance of major ions, especially of nitrates, chlorides and sulphates suggest an elevated alteration of physical-chemical properties in fresh water resources, and thus an increased risk for public health.

In particular, the content of nitrate is very high, and, for 50% of wells, the concentrations were exceeding the WHO regulatory limit of 50 mg/L. Several studies [5, 6] have pointed out how an excess of nitrate in drinkable water can lead to occurrence of serious disease, especially concerning children (i.e. methemoglobinemia and gastric cancer).

In order to identify the different sources of nitrate, the isotopic composition for nitrogen and oxygen [7] has been investigated. Figure 3 presents the comparison between the samples' content of NO_3^- and $\delta^{15}N$. It was possible to distinguish two main sources of nitrogen input in groundwater, the first is a point source, derived from septic effluents, and the second is a non-point source, caused by infiltration of effluents spread on soils. These inputs cause the processes of oxidation or nitrification in sandy media, such as is

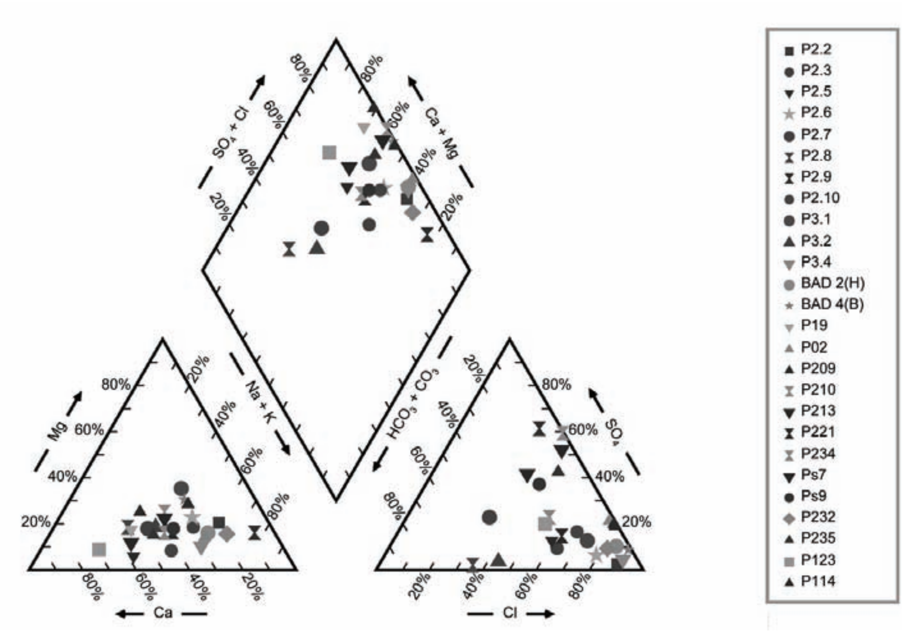

FIG. 2. Piper diagram for groundwater in the region of Dakar.

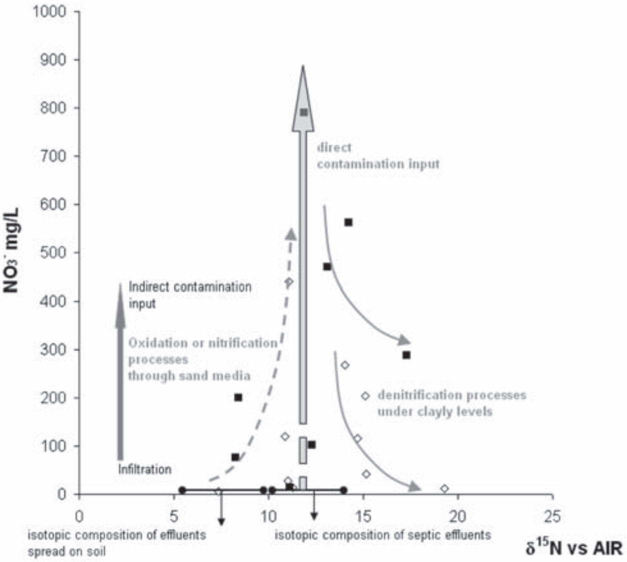

FIG. 3. Simplified isotopic evolution of effluents and groundwater in the region of Dakar. Black squares and empty diamonds represent dug wells and drilled wells respectively.

found in the superficial drilled and dug wells. Meanwhile denitrification is seen to occur in the deepest wells specifically where wells draw water from strata located above clay layers.

Groundwater contains tracers derived from seepage from septic systems or from domestic wells. Results from this study indicate that groundwater under clayey soil or close to septic drain fields are clearly affected by denitrification processes as indicated by the trends observed in $\delta^{18}O$ vs $\delta^{15}N$ (Fig. 4). On the other side groundwater collected in sand-point wells, more vulnerable to septic-waste contamination spread at the surface, indicate significant nitrification processes.

By plotting $\delta^{15}N$ VS $\delta^{13}C$ (Fig. 5) it is possible to distinguish the same trend previously displayed. The carbon isotopic composition for the samples ranged from approximately –7 to –15 ‰ indicating a significant difference in the $\delta^{13}C$ values of dissolved inorganic carbon (DIC). The most negative $\delta^{13}C$ values correspond to water in sand aquifer near the surface and are controlled by the isotopic composition of soil CO_2 and microbial activity on OM at the surface, which is usually quite negative, –15 to –22 ‰ [8].

With depth, the $\delta^{13}C$ shifts to more positive values and then back to more negative values. The shift in $\delta^{13}C$ composition of DIC toward more negative values is indicative of a contribution of an isotopically light carbon into the DIC phase. The isotopically light carbon source may be the oxidation of organic carbon to carbon dioxide in the system and the corresponding reduction of nitrogen. The increased $\delta^{15}N$ and $\delta^{18}O$ of the nitrate indicates that denitrification is occurring as confirmed by the carbon isotopic data.

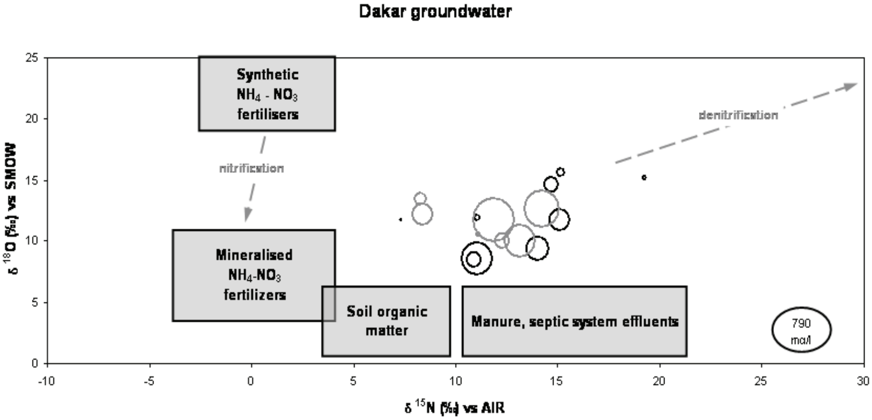

FIG. 4. . Isotopic composition of Nitrates for the Cap Vert peninsula groundwater.

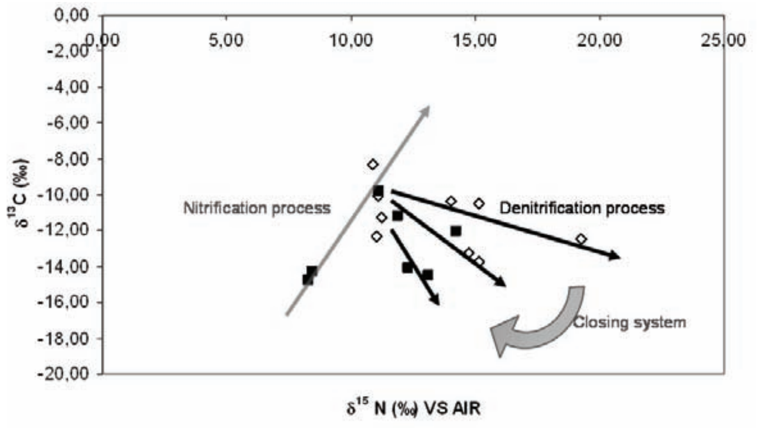

FIG. 5. $\delta^{15}N$ vs $\delta^{13}C$ in groundwater.

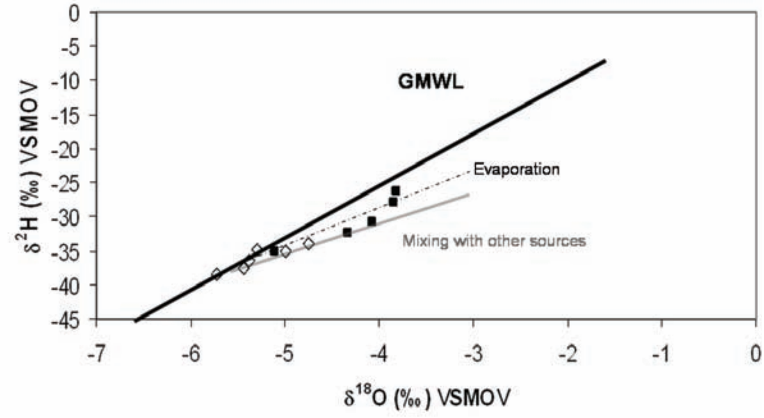

FIG. 6. Deuterium and oxygen-18 variations in the Cap Vert peninsula groundwater

The evidence of denitrification processes inside the aquifers has been mostly correlated to the high usage in the territory of fertilizers and the presence of uncontrolled septic effluents.

By monitoring ^{18}O and ^{2}H it is possible to verify the occurrence of mixing processes in groundwater. Points lying on Global Meteoric Water Line (Fig. 6) have the same isotopic composition of rainwater. This means that they are derived from direct infiltration of meteoric waters in soils, while other trends, with different slope and intercept, are a consequence of mixing process

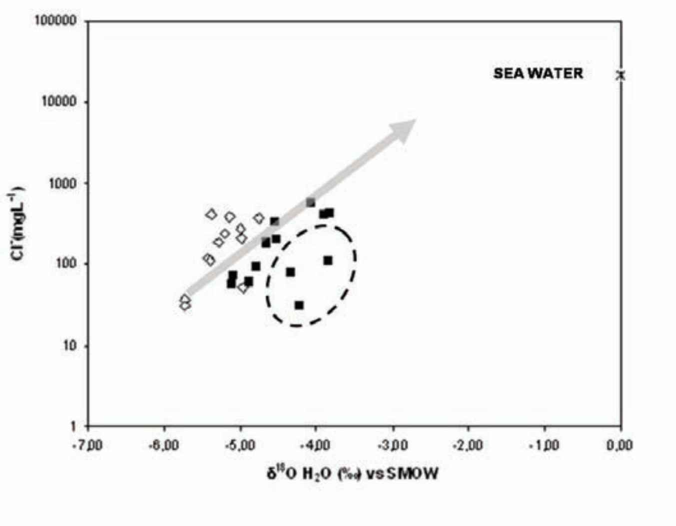

FIG. 7. Variation of $\delta^{18}O$ *vs chloride. The grey line indicates the occurrence of mixing process. Dotted line put on evidence dug wells affected by evaporation process.*

(grey line in Figure 6) or of evaporation processes, in act in superficial wells corresponding to sites with highest nitrification.

In order to identify the origin of the mixing process it can be useful to consider the concentration of $\delta^{18}O$ versus chloride (Fig. 7). This can confirm the dilution of groundwater with waters enriched in chloride, whose origin can be traced to either seawater intrusion or sewage.

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ISOTOPE TECHNIQUES ON GROUNDWATER CONTAMINATION STUDIES IN URBANIZED AND INDUSTRIALIZED AREAS, HAT YAI BASIN

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Abstract

Anthropogenic activities are of a major force in changing the hydrological cycle as well as the climate warming. Assessing the impacts of human activities on hydrological environments is becoming a wide-focused topic.

In this research, the authors attempt to link the urbanization, agricultural development, and the subsequent water resources exploitation with the change of water environments in Hat Yai basin, southern of Thailand. The source of water for domestic use mainly comes from Utapao River which flows through the area. Now this area is facing the shortage of water in dry season and pollution due to domestic and industrial activities. Isotope techniques in conjunction with hydrological and chemical data can play the important role for identifying recharge zone, flow dynamic, recharge mechanism and surface and groundwater interaction. By using the numerical model the information for proper groundwater management can be obtained. As a result, the quality of ground water in Hat Yai basin was show that the quality of iron (Fe) was higher than Notification of the Ministry of Industry permissible level for groundwater quality standards for drinking purposes at many locations. Groundwater in many locations should not use to drinking water. The water types of Hat Yai Aquifer were Na-Cl and Ca-HCO3. The water type of Khu Tao aquifer was Ca-Mg-HCO3 and Kho Hong aquifer was Ca-Mg-HCO3. The Origin of groundwater in hat yai aquifer is local rainfall. The Origin of groundwater in Khu Tao and Kho Hong aquifer come from ancient rainfall. The ground water from Khu Tao and Kho Hong aquifer were old water and low flow rate. The recharge zone was located west and east of Hat Yai Basin. After that the groundwater will flow to middle basin and northward to Songkhla Lake.

1. INTRODUCTION

Study area is located in the Hat Yai district where is the largest commercial and tourism city in the southern part of Thailand. The source of water for domestic use mainly comes from Utapao River which flows through the area. Now this area is facing the shortage of water in dry season and pollution due to domestic and industrial activities. To improve the water quality as WHO standard, complicated water treatment process is needed. The local governor has solved the problem in this area for many years and groundwater is a resource to be developed for providing the clean drinking water.

Isotope techniques in conjunction with hydrological and chemical data can play the important role for identifying recharge zone, flow dynamic, recharge mechanism and surface and groundwater interaction. By using the numerical model the information for proper groundwater management can be obtained.

2. OBJECTIVES

(a) To use isotope techniques to obtain the origin, age, flow dynamic, recharge mechanism surface and groundwater interaction.
(b) To develop a flow and transport model capable of managing of groundwater resource for domestic and agricultural purposes by combination of information obtained from isotope and hydrogeochemical studies.
(c) To identify the sources and types of contamination in Hat Yai Basin.

3. Hydrogeology Settings

The classification of hydrogeological unit of the Hat Yai basin is based on the Structural geology and the hydrogeology of the study area. It follows the nomenclature of the hydrogeological units of Thailand prepared by the Hydrogeological Survey Section, Groundwater Division, Department of Mineral Resources in the year 2000 as shown in the Hydrogeological Map (Fig. 1) as follows:

(a) **Sedimentary Aquifers:**
  (i) **Meta-sedimentary Aquifer (PCms):** It is consisted of shale, sandstone, and mudstone of the Kaeng Krachan Group. It occurs on both the western and eastern edges of the basin and yields water at the rate of 5 to 8 m^3/hr
  (ii) **Middle Khorat Aquifer (Jmk):** It is consisted of shale, sandstone and mudstone of the Lam Thab Formation and is found only on the western edge of the basin. It has a yield of 5 m^3/hr.
(b) **Granitic Aquifer (Gr):** It is consisted of coarse-grained granite which was intruded at the eastern edge of the basin. Its yield is 3 to 5 m^3/hr from fracture in the granite.

(c) **Unconsolidated Aquifers:** It comprises gravels and sands intercalated in the clay bed at various depths and can be divided into 4 hydrogeological units as follows.

  (i) **High Terrace Aquifers (Qht):** It consisted of gravels, sands, and clays which were deposited by the ancient river system. The high terrace aquifer in represented by undulating plain and high land of 15 to 20 meter in elevation above mean level both sides of the basin. The wider western part extends from Tambon Tha Chang, Amphoe Bang Klam down to Tambon Khok Muang, Amphoe Hoi Khong. The depth of the aquifer ranges from 40–60 m to 100 m from the edge to the center of the basin respectively. This aquifer has the yield of 10 to 15 m^3/hr.

  (ii) **Colluvium Aquifer (Qcl):** It is consisted of sediments derived from in situ weathering of bedrock and colluvium deposits along hillside or steep valley. The deposits are poorly sorted, and consist of angular rock fragments. The aquifers are 20 to 30 m deep and have the yield rate of 3 to 5 m^3/hr.

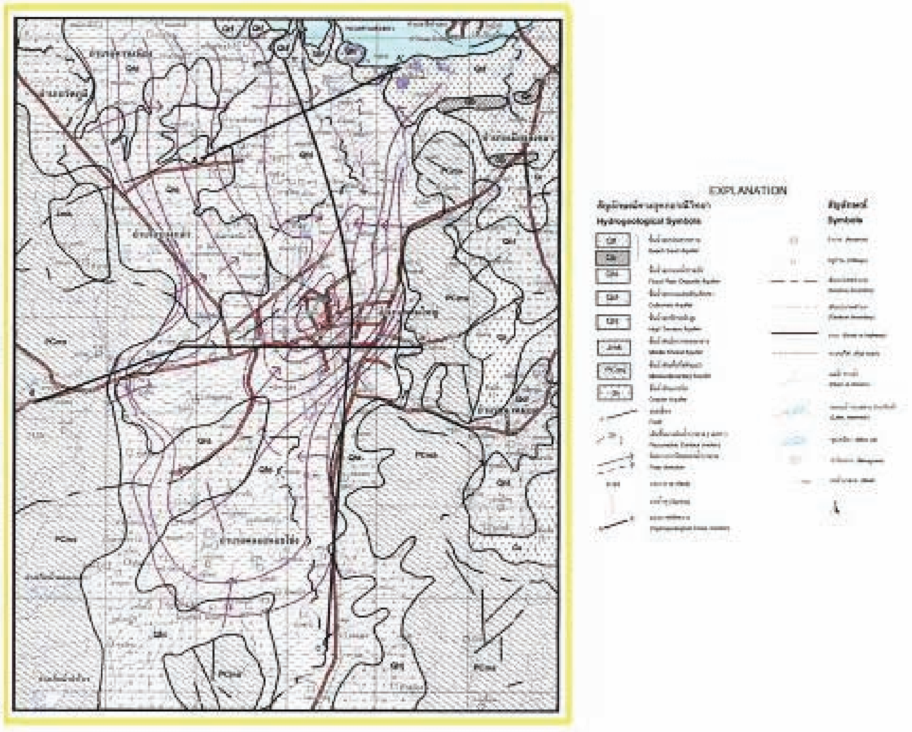

FIG.1. Hydrogeological Map of Hat Yai Basin.

(iii) **Flood Plain Aquifer (Qfd):** It is consisted of sands, gravels, silt, and clays which deposited in flood plain of Khlong U-topao and its tributaries and cover the area from Tambon Pha Tong and Ban Phru, Amphoe Hat Yai northwards up to the Songkhla Lake. The aquifer comprises of 2 intervals, the Hat Yai and the Khu Tao Aquifers, which are at the depth of 30 to 50 m and 70 to 100 m, respectively. The yield from western and southern edges of the basin is moderate at the rate of 10 to 15 m^3/hr. But the yield from the center of basin as Hat Yai City to periphery of Songkhla Lake is relatively high at the rate of 50 m^3/hr. This aquifer is the main. supply for domestic use of Hat Yai and its periphery.It has a high water quality except the northern part in which the water is salty.

(iv) **Beach Sand Aquifer (Qbs):** Two kinds of beach sands aquifer can be distinguished in the study area:

- **Barrier beach deposits** are formed by long shore current and coastal wave. They are represented by alternation of sand rides and furrows parallel to coast line.
- **Tidal flat deposits** are formed by alternation of high and low tides on the tidal flat and Khlong U-tapao delta. They are represented by alternation of clay and silt with plant remains and bivalve shells fragments which indicate the mangrove and swamp environments.

This aquifer contains alternation of fresh and brackish water at 30 to 40 m deep. The yield is moderate but salt water can be infiltrated into the well if the yield is over 10 m^3/hr.

The study area is located on the Hat Yai basin cover the area of about 300 sq. km. and consists of unconsolidated formation of alluvial deposit. The unconsolidated formation can be divided into 3 major aquifers.

- 1st Hat Yai Aquifer: Depth to aquifer range from 20 to 40 m. below ground surface with average thickness of about 15 m. Yield range from 30 to 100 m^3/hr. The groundwater has a moderately high concentration of iron. The aquifer is mostly developed for domestic water supply.
- 2nd Khu Tao Aquifer: Depth to aquifer range from 45 to 80 m. below ground surface with average thickness of about 15 m. Yield range from 20 to 50 m^3/hr. The groundwater has high concentration of iron.
- 3rd Kho Hong Aquifer: Depth to aquifer range from 100 to 120 m. below ground surface with average thickness of about 15 m. Yield range from 30 to 100 m^3/hr.

4. METHODOLOGY

Locations of the sampling points in Hat Yai Basin are shown in Figure 3. Water samples were collected firstly in March 2004 (dry season). There are total of 27 samples in which 24 samples are from production and monitoring wells, another 3 samples are from springs, and surface water in the region (Fig. 4). The second set, 37 samples, was collected in rainy season of July 2004. The third set was collected in January 2005 just after the rainy season. The Physico-chemical parameters like EC, pH, TDS and temperature were measured in the field. The samples were analyzed for D, H-3, O-18, C-14 and major chemical ions. The last set of 25 samples were collected in January 2006. These are mainly analyzed for

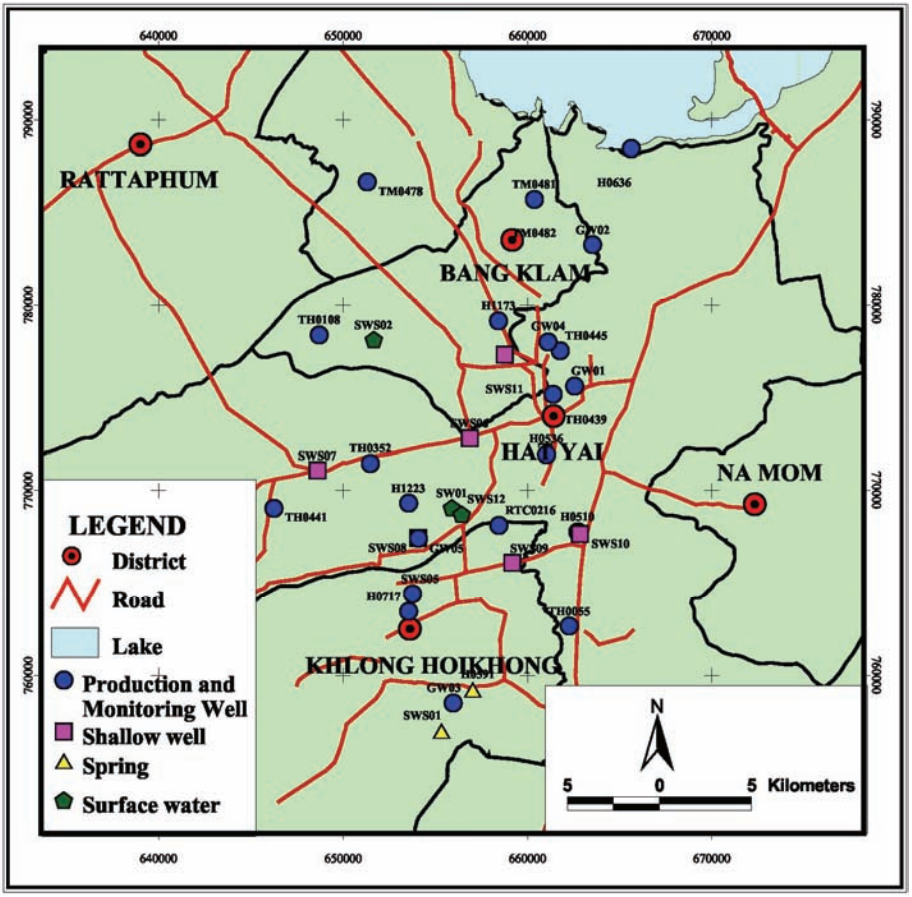

FIG. 2. Location map of water sampling wells in the study area.

missing data of C-13 data in groundwater as well as chemical parameter and stable isotopes of surface water, rainwater and shallow groundwater next to dump site.

Groundwater sample and surface water were sent to PINSTECH, Pakistan for D and O-18 and C-13 analysis. Chemical analysis of water samples were carried out at the Department of Groundwater Resources Laboratory. Tritium concentrations were measured by liquid scintillation counting (Quantulus 1220) after electrolytic enrichment. Carbon-14 were analyzed by liquid scintillation counting (Quantulus 1220) after direct absorption method.

5. RESULTS AND DISCUSSION

5.1. Hydrochemical Characteristics

The data indicate that EC values of groundwater samples range from 23 to 2940 μS/cm. Concentration of sodium, potassium, calcium and magnesium vary from 1 to 840, 0.1 to 16, 0 to 92 and 0 to 45 mg/L, respectively. The concentration (mg/L) of chloride, and bicarbonate ions vary from <1.5 to 200, 4 to 2470, respectively.

5.1.1. Chemical Quality

Quality of groundwater was evaluated for drinking purpose by comparing with Notification of the Ministry of Industry permissible level for groundwater quality standards for drinking purposes. Thus it can be concluded that several samples should not be used as drinking water.

Data of river and rainwater and groundwater near dump site.

5.1.2. Hydrogeochemical Facies

The piper diagram to determine the geochemical facies of groundwater of each aquifers shown that there are two types of groundwater in Hat Yai Aquifer, i.e., Na-Cl and Ca-HCO_3 types. While both groundwater in Khu Tao Aquifer and Kho Hong Aquifer consists of only Ca-Mg-HCO_3 type.

5.2. Isotope Studies

Few surface water samples and spring water were analyzed for D and ^{18}O content. The δD and $\delta^{18}O$ values in surface water vary from –17.99‰ to

4.31‰ and –1.72‰ to 0.55‰ respectively. These samples show the effect of evaporation on the δD and δ^{18}O plot. The δD and δ^{18}O values in spring water vary –7.46‰ to –7.32‰ and –46.98‰ to –45.96‰ respectively. Isotopic data of ground water in Hat Yai Basin from the three periods of collections are given that the δ^{18}O and δD of groundwater samples in Hat Yai aquifer range from -6.2 to –7.39‰ and –35.25 to –46.02‰ respectively while Khu Tao Aquifer range from –6.82 to –7.65‰ and –43.48 to –52.68‰ respectively. Kho Hong aquifer data range from –6.9 to –8.31‰ and –42.18 to –55.31‰ respectively. The local meteoric water line has to be established from samples of individual rain events, or monthly means of precipitation. The meteoric water line is a convenient reference line for the understanding and tracing of local groundwater origin and movements. The local meteoric water line in Thailand is obtained from the equation $\delta D = 7.67\ \delta^{18}O+6.88$. In the plot of δ^{18}O and δD of the first and second samplings , the value of δ^{18}O and δD scatter along the LMWL. Isotopic of deep groundwater (Khu Tao and Khohong Aquifers) are lighter (more negative) than shallow groundwater (Hat Yai Aquifer). This indicated that the deep groundwater were older and originated from rains of a climatic regime. Hat Yai aquifer is modern recharge come from local rain. Most of samples fall in the classes –6.5 to –7.5‰.

The results form δ^{18}O and δD confirmed that the groundwater of Khu Tao Aquifer can be identified into 2 groups. The first group is groundwater of Hat Yai aquifer. The second group is groundwater of Kho Hong Aquifer. Thus, it may be concluded that groundwater in Khu Tao Aquifer is a mixture of Hat Yai Aquifer and Kho Hong Aquifer.

5.3. Carbon-14 and Tritium

Carbon-14 values of Hat Yai, Khu Tao and Kho Hong aquifers collected in March 2004 are found in the range 70–134 pMC, 7–136 pMC and 6–56 pMC, respectively. Tritium value of Hat Yai, Khu Tao and Kho Hong Aquifers are found in the range 0.6–1.4 TU, 0.0–2.7 TU and 0.0–4.9 TU, respectively. The same type of calculation for those samples collected in July 2004 and January 2005, respectively. However, there are some missing tritium data since the analysis is still in progress. Theoretically, C-14 value higher than 100 pMC indicates the presence of modern water (post bomb test) while those less than 100 pMC indicates old groundwater (pre bomb test). The plot between C-14 and H-3 values of groundwater in the three different aquifers indicate that the groundwater in Khu Tao and Kho Hong Aquifer are mostly old water (pre bomb test) while those in Hat Yai Aquifer reflect modern water. However, some groundwater samples in the first two aquifers which has carbon-14 lower than 100 pMC but with high tritium value indicates the interaction of groundwater with carbonate rock. Positive relation between C-14 and H-3 indicates little or no interaction between groundwater and carbonate rocks.

The results of isotopic data can also indicate that the recharge zone is located west and east of Hat Yai Basin. Then the groundwater will flow towards the center of the basin and move northward towards Songkhla Lake.

6. CONCLUSIONS

(a) The chemical data of groundwater in Hat Yai basin shows that most of the ionic level are higher than the Notification of the Ministry of Industry permissible level for groundwater quality standards for drinking purposes (ref). Groundwater in many locations should not be used as drinking water.
(b) The water types of Hat Yai Aquifer were Na-Cl and Ca-HCO_3. The water type of Khu Tao aquifer and Kho Hong aquifer was Ca-Mg-HCO_3.
(c) The Origin of groundwater in Hat Yai aquifer is local rainfall. The Origin of groundwater in Khu Tao and Kho Hong aquifers are from ancient rainfall. The groundwater from Khu Tao and Kho Hong aquifer were old water with low flow rate.
(d) The recharge zone was located on the west and east of Hat Yai Basin. After that the groundwater will flow toward the center of the basin then northward into Songkhla Lake.
(e) No serious contamination from household or dump site is observed from the present study. However, most groundwater in the area are not good for drinking.

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THE STABLE ISOTOPE OF HYDROGEN AS AN INDICATOR OF MEDIOUNA LANDFILL LEACHATE POLLUTION
(Casablanca, Morocco)

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Abstract

Since 1986 the municipal solid wastes produced by the city of Casablanca are stockpiled in Mediouna landfill installed on old quarries without liner or leachate collection system. A previous study had showed an advance of the pollution plume from landfill, according to the faults affecting the fractured aquifer matrix. The aim of our study is to use the unique isotopic characteristics observed in landfill leachate as an indicator for confirming whether contamination is from landfill or some other local sources. Oxygen-18 and deuterium investigation was undertaken on samples collected, from wells upstream and downstream the landfill. Compared to hydrogen and oxygen isotopes of local precipitation samples of some wells show an enrichment of hydrogen isotope values. This data is used to delimit pollution plume extension.The deuterium is useful as an environmental indicator for municipal landfill pollution.

1. INTRODUCTION

Sanitary landfilling in Morocco is still the preferred management option for the disposal of solid urban wastes, for its financial advantages. However, leachates produced during landfill operation present a real danger for groundwater quality, especially for the landfill sites operating without bottom liner or an effective collection system. This problem is made worst by the fact that the urban waste contains 70% of moisture and produces consequently a great quantity of leachate. The Landfill of Casablanca city known to be largest in the country does not derogate from this rule.

In absence of groundwater monitoring program, few studies undertaken in Morocco [1–3], based on the standard pollution parameters have shown the impact of this landfill leachate on the aquifer, but encountered problems of interpretation due to interference with local climatic and hydrogeological conditions, and also to the anthropogenic activity.

To overcome this kind of problems, oxygen-18 and deuterium investigation was undertaken. This work is an application of the results obtained by researchers who noted that the leachates present deuterium enrichment, and recommend to use it as reliable index of landfill pollution.

2. SANITARY LANDFILLS

A landfill is like a reactor fed with solid waste, rainwater, leachate and biogas. A complex sequence of physically, chemically and biologically mediated events occurs within a landfill.

As consequences of theses processes, waste is degraded or transformed. Landfill investigation studies have suggested that the stabilization of waste proceeds in five sequential and distinct phases [4]. The rate and quality of leachate and biogas generated from a landfill change from one phase to another and reflect the microbially mediated processes taking place inside the landfill.

Anaerobic decomposition of organic waste produces isotopically light methane, leaving the water enriched in the heavier hydrogen isotope. The methanogenesis process does not affect the oxygen isotopic composition: the ratio of stable hydrogen isotopes in water from background wells differed from those of ground water collected downgradient of the landfill and the ratios of stable oxygen isotopes in water from background wells were similar to those in ground water downgradient of the landfill [5], which indicate an enrichment of deuterium. The enrichment can reach 30 to 60‰ [6].

The isotopic composition of landfill leachate collected over multiple years from the municipal landfill of Dyer Boulevard (Florida) shows that hydrogen isotope enrichment is strongest (20‰) during early landfill history, when rates of microbial respiration and methane generation are the greatest, and lessens with age of waste [3].

3. PHYSICAL SETTING

3.1. Climate

The climate is semi-arid at hot winter, with one dry season spreading out in June and in August, and a wet season characterized by two of precipitation maximums: the main during December, the secondary during March. The annual average rainfall is about 450 mm. The minimum average temperature varies between 7 and 9°C from December to February, while the maximum average temperature oscillates between 26 and 28°C in August and September. During the period 1990—2001 the area knew two period of dryness: the first from 1992 to 1995 with a pluviometric deficit of 40% and the second from 1998 to 2001 with a pluviometric deficit of 29%.

3.2. Hydrogeological setting

The primary formations are Cambrian and Ordovician marine sediments affected by the Hercynian orogeny [7]. They were compressed and their transformation gave green schists surmounted by quartzites, between psammitic series [8]. They were folded, faulted and immersed. Their reliefs were eroded and peneplained. This unit is covered directly by plio-quaternary rocks since the secondary deposits are missed completely in the sector.

As the calcarenites mask the aquiferous formation, the research of the fracturing indices was carried out from the aerial photographs at 1/20,000 scale. The results show the predominance of two families of discontinuities, one ranging between N20–N40 and the other ranging between N120 and N140.

In a local context the examination of the geological logs of drillings, showed under the plio- quaternary cover, a lithological variation of facies: the primary formations quartzitic become schistous right downstream of the landfill.

The hydrogeologic study shows that water circulation is carried out in the primary formations, due to fracturation. The calcarenites, though permeable, are dry. The depth of water in the wells varies between 4 and 21 m.

The succession of the periods of dryness and overexploitation were at the origin of an important decline in groundwater level, materialized by the drying up of a local spring.

3.3. Monitoring

The first indication of the aquifer pollution by the landfill leachate was detected in 1990 [1], three years after the beginning of its exploitation. Another study undertaken in 2001 had shown that pollution progressed. It distinguished three groups of wells (Fig. 1): first group characterized by an organic and mineral pollution proving in a univocal way its pollution by leachate, second group characterized by an increase in electric conductivity without organic matter indication, and third group whose chemistry remained quasi unchanged compared to situation in 1990 confirming absence of any pollution. The increase in mineralization of the second group cannot be charged in a formal way to the landfill. Indeed, other factors can interfere like the change of lithologic facies already identified or the effect of the dryness on groundwater quality. To determine the origin of this mineralization increase, isotopic analyses were carried out. The measured parameters are the stable isotopes of the water (deuterium and oxygen-18).

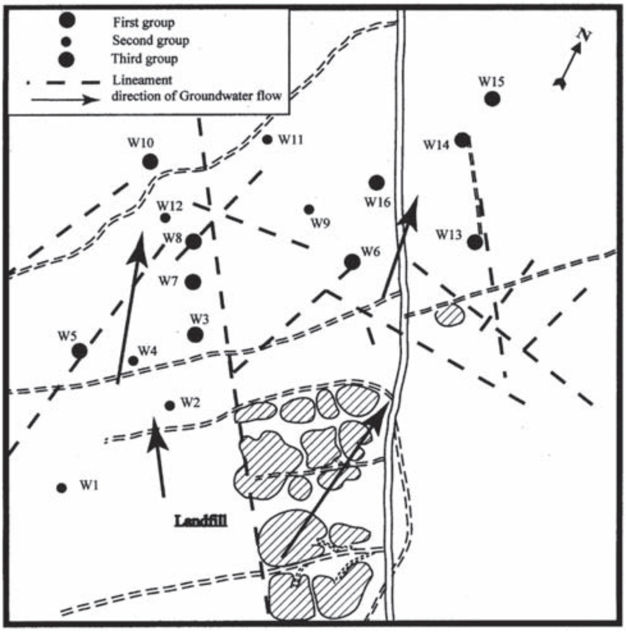

FIG. 1. Location of different groups of wells.

TABLE 1. ISOTOPIC VALUES OF GROUNDWATER (IN ‰).

Wells	$\delta^{18}O$	$\delta^{2}H$
Upa	–4.91	–28.72
Upb	–4.17	–21.4
w1	–4.4	–18.07
W2	–3.96	–22.95
w3	–3.77	–20.86
w4	–4.16	–21.75
w5	–4.46	–24
w6	–4.12	–17.31
w7	–3.87	–19.66
w8	–4.26	–20.04
w9	–4.05	–23.29
w10	–4.68	–25.83
w11	–4.22	–24.1
w12	–4.14	–21.73
w13	–4.44	–25.53
w14	–3.88	–20.34
w15	–4.03	–20.63
w16	–4.43	–20.78

4. RESULTS AND DISCUSSION

Sampling was carried out at the beginning of July 2005. It related to wells upstream and downstream. The measured isotopes are deuterium and oxygen-18. The analyses are carried out by the National Center of the Energy and Nuclear Sciences (CNESTEN). The results obtained are presented in Table 1.

The results are expressed in ‰ compared to the V-SMOW with ± 0.15‰ for ^{18}O and with ±2‰ for deuterium.

The first step was to establish the local meteoric line which binds the ^{18}O deuterium contents in precipitations. In the absence of isotopic data of precipitations at Casablanca, the equation for Rabat city located at 80 km in north, was used for its proximity to study site and comparable with those of the sector of study. The established equation [9] is as follows:

$$\delta^2H = 7.75 \times \delta^{18}O + 10.9$$

For better determining the variations of the values of the isotopes measured in wells, the line $\delta^2H = 8.3 \times \delta^{18}O + 10.4$ (n=12) characterizing groundwater of the area of coastal Chaouia [4] was adopted as reference.

The analysis of the Fig. 2 shows two great sets of well: Unit 1: located between the line of local precipitations and that which corresponds to the isotopic composition of regional groundwater. It also includes the two wells located upstream, and the majority of the wells located downstream. It is a unit whose isotopic composition agrees with the local hydrological and hydrogeological context. Unit 2: it is composed of the wells w6 and w8 (first group), w1 (second group) and the well w16 (third group). These 4 wells are plot above the local precipitation line. This position testifies to a clear enrichment of deuterium, synonymous with the presence of the lixiviats.

We noted also that the two other polluted wells w3 and w7 belonging to the first group were not detected by this tool. This can be explained by their near position to the landfill. Indeed the young leachate produced during the early years of exploitation of the landfill having an isotopic composition rich in deuterium has advanced, leaving the place to an increasingly old lixiviat and consequently less marked by enrichment of deuterium.

A lateral pollution have been detected. It was probably carried out with the profit of a fault undetectable by airal photographs.

The use of this isotope allowed to reach an additional degree of accuracy in the delimitation of the landfill pollution extension. These results will be made profitable to formulate a conceptual hydrogeological model essential to design a local groundwater monitoring network.

5. CONCLUSION

Using deuterium as an index of groundwater pollution by landfill leachate showed through this example that it is a reliable parameter in the detection of the young leachate, however it is without interest in the case of the old one.

This study shows also that this tracer provides indication on the presence of leachate contamination earlier than organic index parameters.

In our country, knowledge on the real width of the damage caused by landfills on aquifers is limited, the use of this parameter would be very useful to work out adequate monitoring programme of groundwater quality.

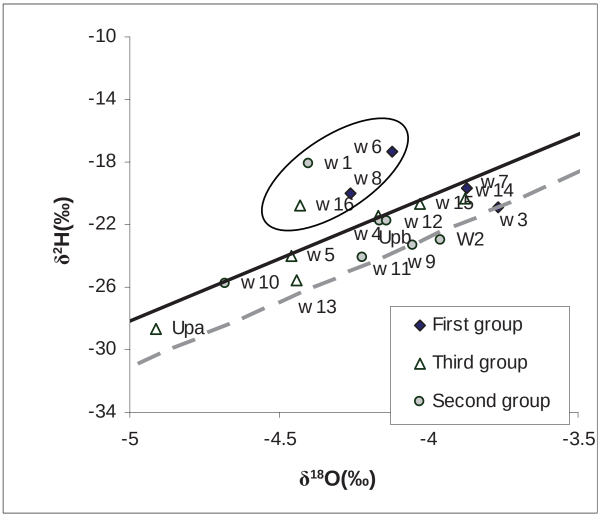

FIG. 2. Relation between deuterium and oxygen 18 from wells near the landfill

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ISOTOPIC APPROACHES FOR MONITORING POTENTIAL CONTAMINATION OF SHALLOW AQUIFERS WITH PRODUCED FLUIDS OR GASES FROM COALBED METHANE OPERATIONS IN ALBERTA, CANADA

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Abstract

Production of coalbed methane (CBM) or natural gas from coal (NGC) from shallow coal seams is a relatively new industry in Alberta (Canada) and constitutes a vital new source of natural gas supply in Western Canada. There are, however, significant environmental concerns, some of them are related to the potential negative impacts on shallow groundwater resources. Since 2004, we have analyzed the chemical and isotopic compositions of fluids and dissolved gases from more than 70 production wells in Alberta. Simultaneously, our research group has begun to generate a database summarizing chemical and isotopic parameters for shallow groundwater and its dissolved gases in the vicinity of coalbed methane operations. Preliminary data indicate that carbon isotope ratios of coalbed-derived methane are often isotopically distinct from dissolved “background” methane in shallow groundwater. Therefore, carbon isotope measurements on dissolved or free methane in shallow aquifers may serve as a suitable tool for monitoring potential contamination of shallow groundwater resources with produced gases. As a consequence, the Alberta government has introduced mandatory baseline testing standards that include carbon isotope measurements for methane for water wells in the vicinity of NGC operations in Alberta.

1. INTRODUCTION

Methane trapped in coal is commonly referred to as Coalbed Methane (CBM) or Natural Gas in Coal (NGC). This unconventional resource is expected to offset depleting conventional gas supplies in the Western Canadian Sedimentary Basin. NGC is a young and rapidly growing industry in Alberta.

At year end in 2003, Alberta had approximately 1000 NGC wells [1]. By December 31 of 2005, there were 7764 NGC wells in Alberta, including both new wells and previously drilled conventional wells re-completed in coal [2]. The National Energy Board forecasts that NGC could constitute up to 65% of the Canadian natural gas supply by 2025 [3].

Currently the primary NGC targets in Alberta are the coal seams of the Upper Cretaceous Horseshoe Canyon Formation that are often exploited together with the coals of the Belly River Group (HSC/BR). In addition, coals of the Lower Cretaceous Mannville Group are increasingly targeted for NGC projects. Coal seams are often aquifers and may contain variable volumes of water. In order to extract methane from water-saturated coal it is necessary to dewater coal seams. Dewatering of seams may induce aquifer drawdown to reduce pressure within the coal matrix, which in turn allows methane to desorb and flow to the well bore.

Concern has been raised over the rapid growth of the NGC industry in Alberta and its potential impact on freshwater resources. Dewatering raises questions regarding the potential hydrogeologic impact drawdown might have on potable shallow groundwater availability. In addition, contamination of aquifers by production water or by gas (e.g. methane) migration via fractures from NGC wells to shallow aquifers is another perceived problem. To address these issues in a scientifically sound manner there is an urgent need for baseline scientific data on fluids and gases associated with the production of natural gas in coal (NGC) in Alberta [4].

The objective of this study was to examine the geochemical and isotopic compositions of production fluids and their dissolved gases from commingled Horseshoe Canyon and Belly River (HSC/BR) wells and from wells targeting the Mannville Group (MG). The goal was to begin to establish a baseline geochemical database for produced NGC fluids that can be compared to data on the geochemical and isotopic composition of shallow groundwater in the vicinity of NGC activities.

2. METHODS

Seventy-three fluid samples were obtained from NGC wells in Alberta. Forty-nine fluid samples from commingled Horseshoe Canyon and Lethbridge coal zone (Belly River Group) wells were collected during swabbing, a procedure in which accumulated borehole water is removed to reinitiate methane flow to the well bore. Mannville fluid samples were collected at the well head when water was being produced, which was the case for 17 of 24 wells sampled. Where waters were not being produced samples were collected from holding tanks. The geochemical and isotopic compositions of the produced fluids and their dissolved gases were determined using standard techniques, and included the following parameters:

- pH value, temperature, alkalinity, electrical conductivity; total dissolved solids;
- major anions (HCO_3^-, F^-, Cl^-, Br^-, SO_4^{2-});
- major cations (Ca^{2+}, Mg^{2+}, Na^+, K^+, Mn^{2+}, Fe^{2+}, Ba^{2+}, Sr^{2+}, Li^+);
- dissolved sulphide and silica;
- trace elements (As, Cd, Cr, Hg, Pb, and U);
- BTEX (benzene, toluene, ethylbenzene, xylene);
- the isotopic composition of water (δ^2H and $\delta^{18}O$ values);
- the isotopic composition of dissolved inorganic carbon ($\delta^{13}C$) and sulphate ($\delta^{34}S$);
- carbon isotope ratios ($\delta^{13}C$) of CH_4, CO_2, C_2H_6, C_3H_8, C_4H_{10} and C_5H_{12} where available.

From 51 shallow groundwater samples, free gas was obtained and analyzed for its chemical and isotopic composition.

The $^{18}O/^{16}O$ ratios of the water samples were determined using the CO_2–H_2O equilibration technique [5] in which millimole quantities of CO_2 were equilibrated, for about 18 hours, with 5 ml water samples at constant temperature. Subsequently, the CO_2 was cryogenically purified and analyzed for its $^{18}O/^{16}O$ ratio using a dual inlet isotope ratio mass spectrometer.

The $^2H/^1H$ ratios of water samples were determined using the Cr reduction technique [6]. 5 uL of a water sample were injected into a quartz reactor filled with chromium metal at 920° C. The $^2H/^1H$ ratio of the generated H_2 gas was then determined on a dual inlet isotope ratio mass spectrometer.

The conventional delta notation is used to express isotope ratios of H, O, C, and S:

$$\delta_{sample}\ (‰) = \{(R_{sample} / R_{standard}) - 1\} \times 1000$$

where R_{sample} and $R_{standard}$ denote the $^2H/^1H$, $^{18}O/^{16}O$, $^{13}C/^{12}C$ or $^{34}S/^{32}S$ ratios of sample and reference materials, respectively. The standard for both hydrogen and oxygen isotope measurements is V-SMOW established and distributed by the International Atomic Agency (IAEA) in Vienna, Austria. Standardization of the δ^2H and $\delta^{18}O$ measurements was achieved using the IAEA reference materials V-SMOW, GISP, and SLAP for calibration, following the guideline of Coplen [7], so that the δ^2H value of SLAP is –428‰ and its $\delta^{18}O$ value is –55.5‰. The uncertainty of δ^2H measurements was better than ±2‰, whereas that of $\delta^{18}O$ measurements was better than ±0.2‰.

Dissolved sulfate was precipitated from the fluids as $BaSO_4$ using an excess of $BaCl_2$ and sulfur isotope ratios of SO_4^{2-} were determined by isotope ratio mass spectrometry using SO_2 generated in an elemental analyzer [8]. Sulfur isotope ratios are reported in the δ-notation in ‰ relative to the internationally accepted standard Canyon Diablo Troilite (V-CDT). Sulfur isotope measurements were normalized using the sulfate reference materials IAEA S05, S06, and NBS 127 with assigned $\delta^{34}S$ values of 0.5 ± 0.2‰, –34.1 ± 0.2‰, 21.1 ± 0.4‰ and the sulfide reference materials IAEA S1, S2, S3, with values of –0.3 ‰, 22.7 ± 0.2‰, –32.6 ± 0.2‰. Uncertainties were better than ±0.5‰.

Carbon isotope ratios of dissolved and free hydrcarbon gases were determined using a GC-C-IRMS system and are reported in the delta (δ) notation in per mil (‰) with respect to V-PDB. The uncertainty of carbon isotope measurements was better than ±0.5‰.

3. RESULTS

Produced fluids from the HSC/BR had on average total dissolved solids (TDS) of 5,427 ± 3,498 mg/L (n = 49). It must, however, be noted that the isotopic composition of several produced waters provided evidence that some evaporation may have occurred in the HSC/BR wells prior to sampling, suggesting that the reported TDS values may be somewhat elevated due to evaporitic enrichment. More than two thirds of the HSC/BR fluids were Na–HCO_3 type waters (average Na concentration 1756 mg/L; average HCO_3 concentration 2597 mg/L). Produced waters from the Mannville Group (MG) had significantly higher average total dissolved solids of 74,491 ± 15,550 mg/L (n = 24) and were of the NaCl type (average Na concentration 26,524 mg/L; average Cl concentration 43,803 mg/L). Ca and Mg concentrations were generally moderate and sulfate concentrations were extremely low in the HSC/BR (average 47.7 mg/L) and the Mannville Group fluids (average 13.7 mg/L). Sulfur isotope data indicated that the low sulfate concentrations are due to bacterial sulfate reduction. Trace metal concentrations in the HSC/BR and MG water samples were generally below 0.2 mg/L, and BTEX concentrations were, with one exception of a Mannville fluid sample, below 1.0 mg/L.

Total dissolved solids in the shallow groundwater ranged from 770 mg/L to circa 2,300 mg/L. The low TDS samples were Na–HCO_3 type waters, while the higher TDS groundwaters were of the Na–HCO_3–SO_4 type. Sulfate concentrations ranged from 84 (low TDS waters) to 784 mg/L (high TDS groundwaters), and were significantly higher than those of the produced waters.

TABLE 1. COMPARISON OF AVERAGE CARBON ISOTOPE RATIOS (EXPRESSED AS $\delta^{13}C$ VALUES IN ‰) OF DISSOLVED METHANE, ETHANE AND PROPANE IN PRODUCED WATERS FROM THE MANNVILLE GROUP, THE HORSESHOE CANYON FORMATION / BELLY RIVER GROUP, AND IN SHALLOW GROUNDWATER. The number of samples with detectable amounts of methane, ethane, and propane is given in brackets.

	$\delta^{13}C$ of methane (‰)	$\delta^{13}C$ of ethane (‰)	$\delta^{13}C$ of propane (‰)
Mannville Group	–49.4 ± 3.6 (n = 24)	–28.8 ± 2.1 (n = 24)	–26.9 ± 1.1 (n = 23)
Horseshoe Canyon Belly River	–54.0 ± 4.1 (n = 45)	–36.5 ± 2.4 (n = 42)	–29.4 ± 1.0 (n = 38)
Shallow Groundwater	–69.9 ± 6.5 (n = 51)	–47.0 ± 3.0 (n = 31)	not detected (n = 0)

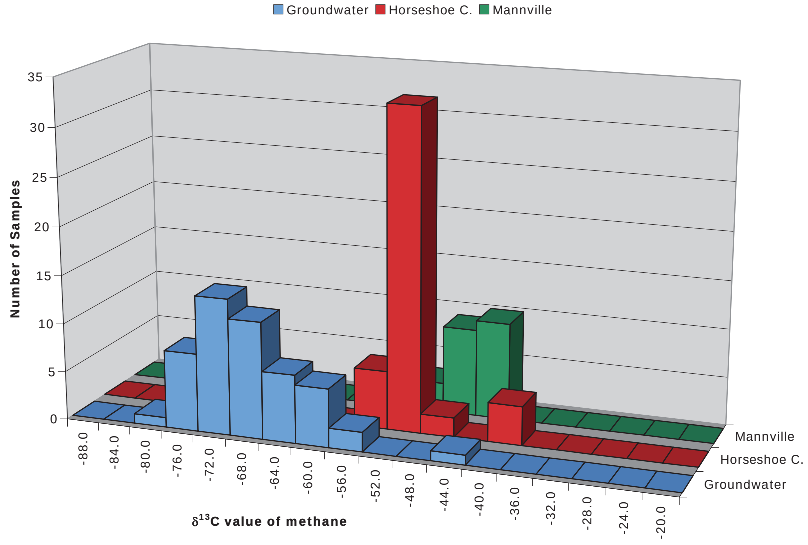

FIG. 1. Histogram displaying $\delta^{13}C$ values of methane (CH_4) in produced waters from the Mannville Group, the Horseshoe Canyon Formation / Belly River Group, and in shallow groundwater.

The carbon isotope ratios of dissolved gases in produced fluids are summarized in Table 1 and Figures 1 and 2. Dissolved hydrocarbon gases in produced fluids from the Mannville Group had the highest average carbon isotope values with –49.4‰ for methane, –28.8‰ for ethane, –26.9‰ for propane, and –25.0‰ (n = 4) for butane. Together with average C1/C2+C3 ratios higher than 5×10^{-2} these data indicate a significant thermogenic gas component. Dissolved hydrocarbon gases from the Horseshoe Canyon Formation / Belly River Group fluids had several per mil more negative carbon isotope ratios with average $\delta^{13}C$ values of –54.0, –36.5, and –29.4‰ respectively, for methane, ethane, and propane. In concert with average C1/C2+C3 ratios around 1×10^{-2}, these data indicate a higher proportion of bacteriogenic gas dissolved in the HSC/BR fluids as compared to dissolved gases from Mannville Group fluids.

By the end of 2006, 51 free gas containing groundwater samples with methane contents of more than 0.15% were analyzed, yielding a mean $\delta^{13}C$ value of –69.9‰. 31 groundwater samples yielded sufficient ethane to conduct carbon isotope measurements yielding a mean $\delta^{13}C$ value of –47.0‰. No propane or butane was detected in free gas of the groundwater samples. The carbon isotope values for methane and ethane in groundwater, that are significantly more negative than those of dissolved methane and ethane in produced fluids from HSC/BR and MG wells, indicate that these gases in groundwater are predominantly of bacteriogenic origin.

4. DISCUSSION

Figures 1 and 2 show histograms summarizing the carbon isotope values of methane and ethane in produced waters from the Mannville Group, the Horseshoe Canyon Formation / Belly River Group, and in shallow groundwater. The carbon isotope values of methane in groundwater and in the produced fluids are rather distinct with 48 of 51 groundwater samples having $\delta^{13}C$ values of less than –60‰, 39 out of 45 HSC/BR samples varying between –52 and –60 ‰, and with 19 out of 24 Mannville samples having $\delta^{13}C$ values of methane between –44 to –52‰ (Fig. 1). There is even less overlap between the carbon isotope values of ethane in groundwater and in the produced HSC/BR and MG fluids. 31 out of 33 groundwater samples with sufficient ethane for analysis had $\delta^{13}C$ values below –44‰. 41 of 42 HSC/BR samples had $\delta^{13}C$ values of dissolved ethane between –32 and –44‰, and all 24 Mannville samples had ethane $\delta^{13}C$ values higher than –32‰ (Fig. 2).

The significant differences in the $\delta^{13}C$ values shown in Figures 1 and 2 in concert with the comparatively low standard deviations of the mean $\delta^{13}C$ values for methane, ethane and propane (Table 1) indicate that carbon isotope values

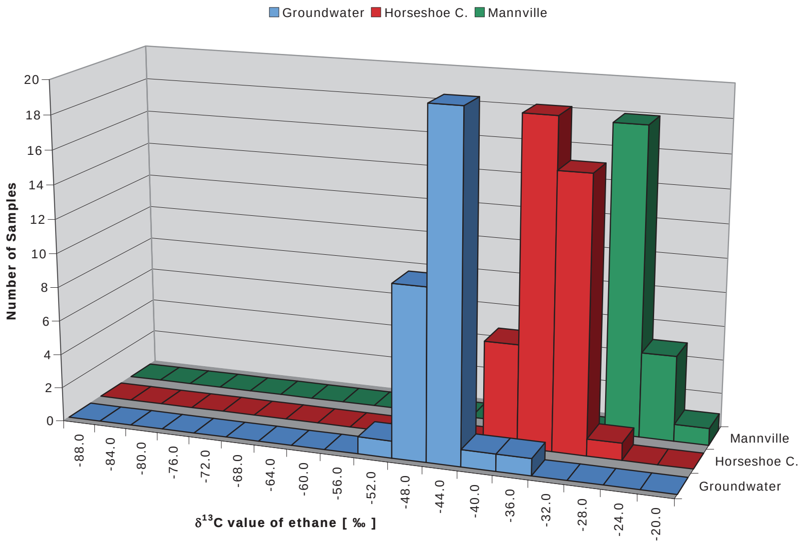

FIG 2. Histogram displaying δ¹³C values of ethane (C_2H_6) in produced waters from the Mannville Group, the Horseshoe Canyon Formation / Belly River Group, and in shallow groundwater.

of dissolved and free gases are in principle suitable for distinguishing between coalbed derived gases and free, predominantly bacteriogenic, gases in shallow groundwater, provided that no transformation processes such as methane or ethane oxidation occur during gas migration.

5. CONCLUSION

Based on the currently available data it appears that carbon isotope ratios of dissolved methane and ethane in produced fluids from the Horseshoe Canyon Formation / Belly River Group and Mannville Group wells are rather distinct from the $\delta^{13}C$ values of methane and ethane in free gas of shallow groundwater. Hence, carbon isotope ratios are in principle a suitable tool for distinguishing between NGC derived gases and bacteriogenic gases in shallow groundwater, provided that no transformation processes such as methane or ethane oxidation occur during gas migration.

Production fluids from the Mannville Group are highly saline NaCl type waters. Produced fluids from the Horseshoe Canyon Formation / Belly River Group and shallow groundwater have markedly lower total dissolved solids and are often of the same Na–HCO_3 water type. Produced fluids are characterized by significantly lower sulfate concentrations compared to shallow groundwater.

The knowledge of the chemical composition of production waters and groundwater will be helpful in assessing whether contamination of shallow groundwater by produced fluids or gases will occur in the future.

ACKNOWLEDGEMENTS

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IMPACT OF TRANSBOUNDARY AIR POLLUTION ON OUR ALPINE WATER RESOURCES: APPLICATION OF MULTI-ISOTOPE (N, S, O, Pb, Sr)

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Abstract

Karst and other sensitive aquifers contribute up to 90% to the total drinking water supply in some European regions. However, they are more vulnerable to contamination than other aquifers due to short transfer times from recharge to source. Therefore, the main objective of this paper is to show possibilities to quantify the impact, even small of long distance air pollution on sensitive water resources (e.g. karst) even in relatively pristine and remote areas as the front-range of the Northern Calcareous Alps in Austria.

The monthly precipitation (May and September 2005) samples show ^{18}O-rich nitrate and sulphate ions, whereas the soil nitrate shows variable contribution of atmospheric nitrogen with depth. Sulphate in the soil profile changes in the direction to lower ^{18}O and higher ^{34}S values with depth. Assuming the values of precipitation and soil for nitrate and precipitation and the dolomite rocks for sulphate and end-members the contribution of atmospheric nitrate and sulphate in the groundwater are estimated in the range of 20-40%. In addition, strontium isotopes support that up to 25% more atmospheric radiogenic Sr is added to the groundwater. Isotope data confirm that considerable amounts of atmospheric pollution is added to sensitive karst-groundwater by preferential flow.

1. INTRODUCTION

The impact of air pollution is a substantial European and global problem which was observed even in the most remote areas of our planet. Theses are unpopulated or nearly unpopulated areas in the Artic and mountaineous areas. Not only surface water, but also groundwater resources are partly endangered by dry and wet deposition from the air. Karst and other sensitive aquifers contribute up to 90% to the total drinking water supply in some European regions. However, they are more vulnerable to contamination than other aquifers due to short transfer times from recharge to source. Therefore, the main objective of this paper is to show possibilities to quantify the impact of air pollution on sensitive water resources (e.g. karst), to develop an innovative surveillance tool based on isotopes and meteorological considerations.

In spite of strong efforts initiated by the European Union and others international organisations in the past 20 years, air pollution from industry, traffic and agriculture is still significant. Transboundary transport processes by atmospheric circulation are responsible for its long distance distribution. There is evidence that even remote mountainous regions in Europe are contaminated by inorganic and organic airborne pollution [1–4]. This is most evident on the surface, but also penetrates into the aquifers, particularly in carbonate areas with strong karstification, characterised by dolines, karst shafts, caves and large springs. Special attention is therefore given in this paper to karst aquifers. They are particularly vulnerable, but very important for many European regions. Indeed, in many areas they are the only natural resources for drinking water supply.

To quantify and manage the problems resulting from the impact of air pollution on sensitive karst groundwater resources nitrogen, sulphur, oxygen and strontium isotopes are used as key-indicators for a wide range of contaminants. Therefore they will seem to be a promising new control system, applied especially for surveillance of sensitive and remote areas.

In order to protect these water resources effectively the amount of the far transported pollutants should be identified and quantified at an early stage. For many transboundary pollution problems the time between recognition and relieve measures are in the range of ten years or more. In the last years, surveillance was focused on surface water. However, airborne pollution of groundwater was rather neglected. To avoid the long term degradation of aquifer systems, new management tools and innovative alarm systems are urgently necessary.

In a pilot study on a number of samples as precipitation, soil, rock and spring waters were collected from the North-front of the Northern Calcareous Alps (Austria) to test the application of isotope analyses to estimate the amount of far transported contaminants and their impact on the spring water quality. The hydrochemistry and the isotopic composition of nitrate-nitrogen, sulphate-sulphur, nitrate and sulphate-oxygen as well as strontium has been analysed in three laboratories, each of them specialized in a certain group of isotopes.

2. DESCRIPTION OF SCENARIO SELECTION PROCEDURES

The Federal Environmental Agency Vienna runs an UN–ECE Integrated Monitoring station (Zöbelboden) within a karstified dolomite with some remnants of limestone on top. The Zöbelboden-site is located south of Linz (Upper Austria) in the front range of the Northern Calcareous Alps (Fig. 1) in form of steep mountain ridges at an altitude of 400–950 m. The monitoring site is divided in plateau and slope areas. The natural mixed mountain forest (beech, fir) is often displaced by production forest dominated by spruce. Transeuropean air masses coming mainly from NW are washed out by relatively high precipitation rates (1650 mm/year). On this Zöbelboden-site in the National Park “Nördliche Kalkalpen” a geology, hydrology and hydrogeology

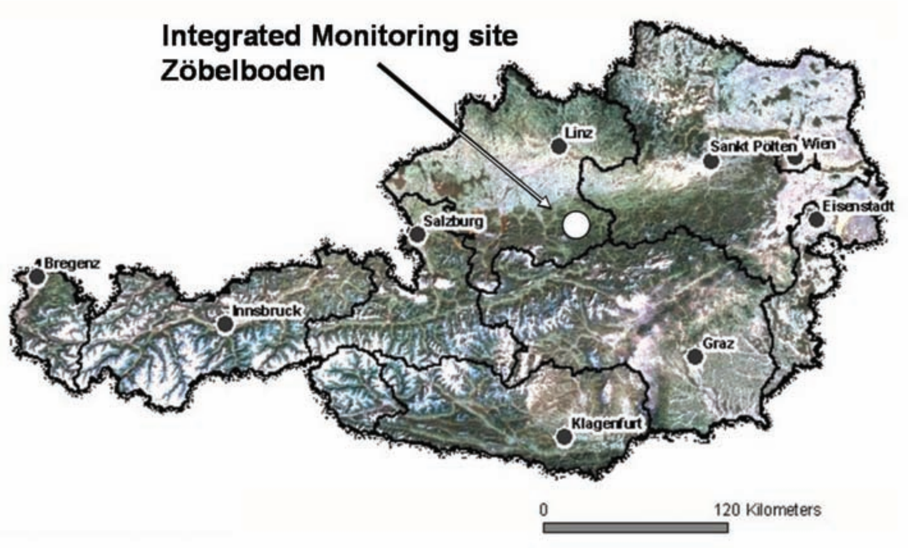

FIG. 1. Location of the IM-site Zöbelboden at the north front of the Eastern Alps in Austria.

research program is running since 1993. Hydrogeological and hydrochemical well studied springs are accessible all year-round. Studies with fluorescence tracers showed passage times of about 20 hrs during storm events [5].

3. MATERIALS AND METHODS

3.1. Sampling

The precipitation was collected as monthly sample either in a wet only sampler (WADOS) installed on top of a research container with immediate cooling (4°C) or with three large containers as open deposition during May and September as well as snow in December 2005.

The spring water samples were all collected during August and October as well as in December 2005 in 0.1 to 10 L containers. The samples for cation analysis were pressure filtered through pre-weight teflon filters and acidified. Two water blanks were transported into the field and treated like the other water samples.

The humus top layers were cut with a 0.3×0.3 m frame. The top soil (0–7 cm) and the mineral soil (7–30 cm) samples were taken with a 7 cm diameter corer. In the core sample the outer rim was peeled off to avoid downward contamination. The carbonate rocks were sampled (1997 and 1998) from outcrops. Many unweathered carbonate chips were collected (total weight of 1–2 kg) over a distance of about 5 m.

3.2. Sample preparation and isotope analyses

Five to 10 L water samples were evaporated on a water bath or in a heating cabin (130°C) down to 0.3–0.5 L. 0.05–0.2 kg soil sample (105°C dried and screened < 2mm; stored deep frozen) was leached with 0.8–1.2 L deionised water with continuous stirring over 1hr. The leachate was concentrated by heating (130°C) to 0.5–0.3 L. The $BaSO_4$ was precipitated after acidification (pH 3–4) with $2N \cdot HCl$ and adding 5–10 mL of $0.2N \cdot BaCl_2 \cdot 2H_2O$ at moderate temperature (40–60°C). The sulphur and oxygen isotopes of sulphate were analysed by the lab of the University of Lublin (Poland) with a dual inlet and triple collector mass spectrometer. The obtained delta values were normalized to $\delta^{34}S$ (VCDT) and $\delta^{18}O$ (VSMOW) of NBS-127. The nitrogen and oxygen isotopes of nitrate were analysed by the lab of the Hydroisotop Ltd. Schweitenkirchen (Germany) with a dual inlet “Delta S” mass spectrometer. The previously purified nitrate was dried down and in vacuum in contact with graphite thermaly converted to N_2 and CO_2 gas. Strontium isotope analyses of water, soil-water and carbonate-HCl-leachates were performed in the Geochronology Lab of the University of Vienna by TIMS. NBS987 (Sr) international standard was used for the external correction of mass discrimination and as a reference material.

4. RESULTS AND DISCUSSION

4.1. Nitrogen and oxygen isotopes of nitrate

Nitrate concentrations in the precipitation samples are 2–4 mg/L and the concentrations in the spring and surface waters are 4–8 mg/L. The concentration is representative for many karst springs from forested areas in the northern front of the Eastern Alps (5–8 mg/L). Concentrations in springs from high altitude areas with thin or not existing soil cover are even lower (<5 mg/L). The concentration of ammonium is mostly below detection limit 0f < 0.025 mg/L [6].

All delta $^{15}N_{nitrate}$ values are in the range of –5 to +2.5‰. However, the spread of $\delta^{18}O_{nitrate}$ is considerable between 17–51‰. Even the nitrate in the soil layers have higher $\delta^{18}O_{nitrate}$ values than those usually found in soil waters

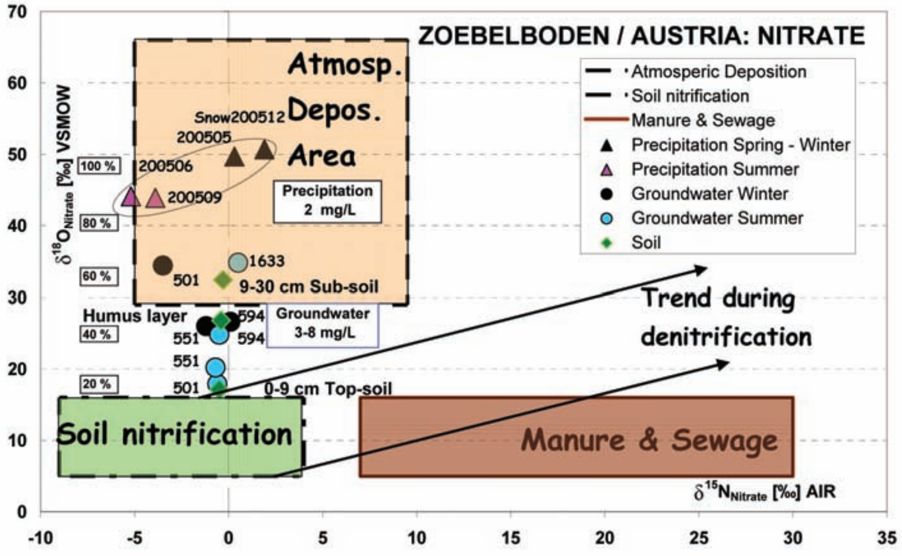

FIG. 2. Nitrogen versus oxygen-isotopes of nitrate in precipitation, soil and groundwater. Area of atmospheric deposition, soil nitrification and manure as well as sewage are reported by [7].

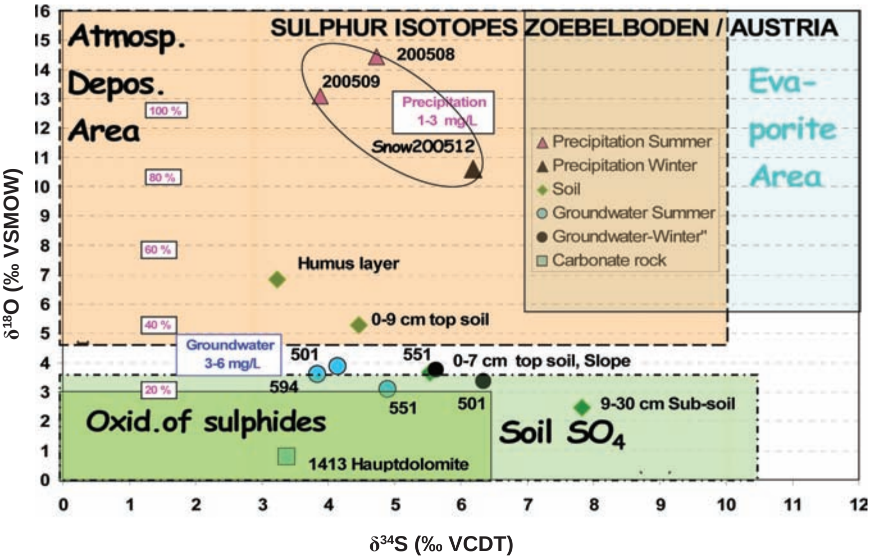

FIG. 3. Sulphur versus oxygen-isotopes of sulphates of precipitation, soil and groundwater as well as of carbonate-leachates. Area of atmospheric deposition, oxidation of sulphides, soil sulphates and evaporates as reported from [7].

(Fig. 2). Assuming the precipitation values ($\delta^{18}O_{nitrate}$ = 45 – 51‰) and soil values ($\delta^{18}O_{nitrate}$= 8 – 12) in the literature as end-members, the spring waters contain 20–60% nitrate from atmospheric nitrogen, which was not involved in the biological cycle. Preferetial flow down to the subsoil (9–30 cm depth) and some springs show even higher portions of atmospheric nitrogen (>60%) (Fig. 2). Therefore nitrate from top soil and in most springs show isotope values indicating 20–40% atmospheric origin, which was not involved in biological fractionation. These results are quite reasonable for karst environments with a considerable fraction of preferential flow.

4.2. Sulphur and oxygen isotopes of sulphates

The sulphate concentration in the precipitation is fairly low (1–2 mg/L) and increases in the spring and surface waters to 2.8–4.2 mg/L only by leaching the soils and carbonate bed rocks. The sulphur content in the carbonate bedrock (0.01%) is fairly low and increases only slightly in the soil samples (0.1–0.2%) [8].

The isotopic composition of precipitation, spring waters, soil and bedrock sulphates were plotted as δ^{34}S‰ VCDT *versus* δ^{18}O‰ VSMOW (Fig. 3). The areas as atmospheric deposition, oxidation of sulphides, soil sulphates and evaporite sulphates were outlined according to [7].

The mean monthly precipitation (May and June 2005) as well as snow samples in December 2005 show ^{18}O-rich sulphate ions, whereas the soil sulphates change to lower ^{18}O- and higher ^{34}S values with depth. The spring waters and the bedrock dolomites show relatively low δ^{34}S values (4–9‰).

The two ^{18}O-rich sulphate ions in the monthly IM-precipitation samples plot in the area of atmospheric deposition [7] and are generally regarded as transported and formed mainly from burning fossil fuel [9]. The soil sulphates show a trend from the field of atmospheric deposition in the humus layer down to the soil-SO_4 in the subsoil (7–30 cm depth) indicating a decreasing influence of atmospheric sulphate.

The isotopic composition of the spring water sulphates are more or less a mixture of theses soil profile sulphates. Assuming the precipitation samples and the dolomite bed rocks as end-members, the contribution of atmospheric sulphate is estimated to be 20–30% in the spring waters and between 10 to 45% in the soil samples.

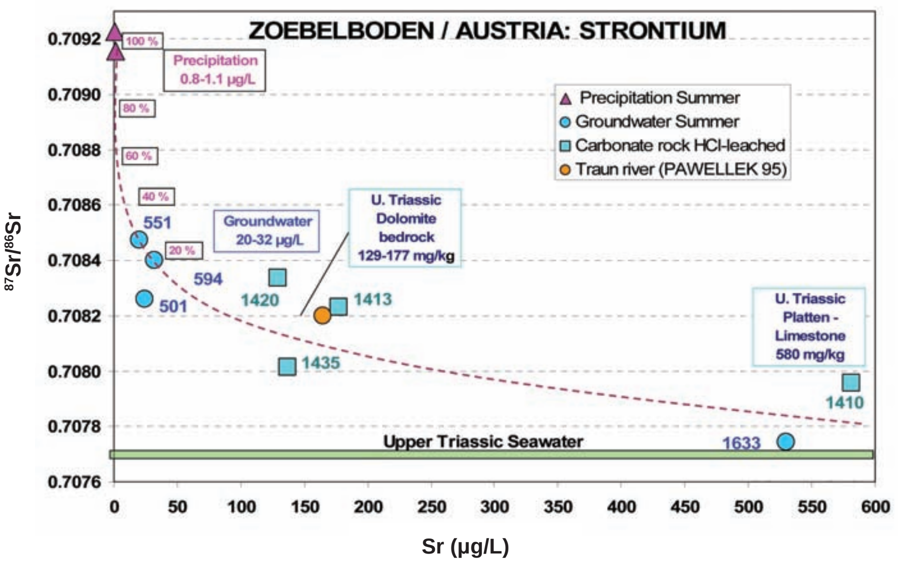

FIG. 4. Content versus isotope-ratios of strontium of precipitation, soil and groundwater as well as carbonate-leachates. Isotopic ratios of U. Triassic seawater and the river Traun are reported by [10] and [11].

4.3. Strontium isotopes

The $^{87}Sr/^{86}Sr$-isotope ratios vary from Sr-rich Platten-Limestone (0.7079), close to U. Triassic seawater [10], and Haupt-Dolomite (0.7080–0.7083) to more radiogenic contributions in the precipitation (0.7092). Spring waters show similar ratios between (0.7083–0.7084). The water of the river Traun dewatering the Northern Calcereous Alps in this region shows a similar isotope ratio [11] (Fig. 4). The significantly higher isotope ratio in the mean wet deposition during May and June 2005 clearly indicate a significant radiogenic contribution through the atmosphere. The most likely explanation is the import of natural atmosperic dust from more Rb-rich crystalline minerals and anthropogenic formed fine dust from industrial incineration. Soot particles and slag particles from industrial high temperature incineration were observed on filters of fine dust collection at this site [12].

Assuming the precipitation values and the dominating Haupt-Dolomite are end-members, a contribution of 0–25% of more radiogenic atmospheric Sr can be calculated. The atmospheric more radiogenic Sr can be of natural dust and /or anthropogenic formed exhaust particles.

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TRACING SOURCES OF NITRATE IN GROUNDWATER BY USING HYDRO-CHEMICAL AND ISOTOPIC METHODS: BEIRUT REGION AND ITS SUBURBS

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Abstract

Analyses of hydrochemical and stable isotopes of ^{2}H and ^{18}O were conducted on groundwater samples collected in Beirut city and its suburbs and tapped in a limestone aquifer. The analyses were done to document the chemical and isotopic characters of the natural groundwater and to determine its origin. Hydrochemical data are classified on the basis of dominant anions. Mineral groundwater quality was found affected by different pollution sources in the southern suburb of Beirut. Isotopic analyses delineate two major groups of groundwater. The first group is directly influenced by direct recharge into the aquifer from precipitation. The second group, showing elevated mineral characteristics, is influenced by a secondary evaporation process reflecting an isotopic enrichment in groundwater. $\delta^{15}N$ investigation of the isotopically enriched samples determines the origin of nitrate pollution from either infiltration of animal waste or septic systems to groundwater.

1. INTRODUCTION

In Lebanon, groundwater is an important source of water supply. It is mainly developed for domestic and industrial uses because of the bad management of surface water. The population and industrial development of Beirut city are increasing. In urban areas, a 205 L/day/capita is considered for Lebanon. At which 70, 20, 10 are for agriculture, domestic use and industrial, respectively. Large-scale groundwater abstraction in Beirut area has resulted in adverse economic and environmental problems, such as declining piezometric levels and deterioration in groundwater quality. These problems will become more serious in the future. Management of the groundwater resources requires an understanding of the main processes controlling the geochemical evolution and origin of exploited groundwater. Therefore, interpretation of the environmental isotope record of both precipitation and groundwater, coupled with hydrochemical characteristics provides a good comprehension of the groundwater system in a basin [1–3]. In fact, the chemical characteristics of groundwater provide information on its geological history and its mode of origin within the hydrogeologic cycle [4–6]. Isotopic characteristics as evaluated from stable isotopic abundance of deuterium and oxygen-18 give clues to the origin and recharge of the groundwater [7, 8]. The application of the environmental isotope method to recharge problems is based on the spatial and temporal variability of the isotopic content of water.

In the present study, combined chemical and isotopic characteristics of water are used to determine the origin of groundwater and the hydrologic relations between precipitation and groundwater in Beirut region and its suburbs. The study was designed to develop a database of the hydrochemical and the isotopic composition (^{2}H and ^{18}O) of precipitation, and groundwater in Beirut; it will also assess the groundwater quality by the presence of nitrate pollution. Uses of $\delta^{15}N$ isotopes in nitrate will determine the source of pollution in the aquifer.

2. MATERIALS AND METHODS

In order to study groundwater quality in Beirut region, 13 samples were taken within the aquifer and analyzed for their chemical and isotopic constituents. The localization of these samples is given in Fig. 1. The depth of these wells varies from 50 to 300 m with an average of about 150 m. The discharge averages 35 L/sec with a range of 20 to 80 L/sec. The geology of the studied area is located in cretaceous and mid-late Miocene strata. The lithology

FIG. 1. Location of sampling sites.

is consisted with thin bedded limestone and conglomerates. This lithology influences the chemistry of groundwater.

Water samples were collected in polyethylene containers. Each sample was divided into three aliquots. The first one is filtered through 0.45 mm Millipore filter for elemental analysis by using ion chromatography. The second aliquot was pre-concentrated and than acidified with concentrated HCl prior to $\delta^{15}N$ isotopic analysis in nitrate. The third aliquot was simply acidified with HCl for deuterium and oxygen-18 analysis in water.

3. RESULTS AND DISCUSSION

3.1. Hydrochemical characteristics of groundwater

Fig. 2 shows TDS and electrical conductivity variation in Beirut groundwater. Typical TDS concentrations in Beirut aquifer are below the recommended level of 500 mg/L. Concentrations in samples 6, 7, 8 and 11 in

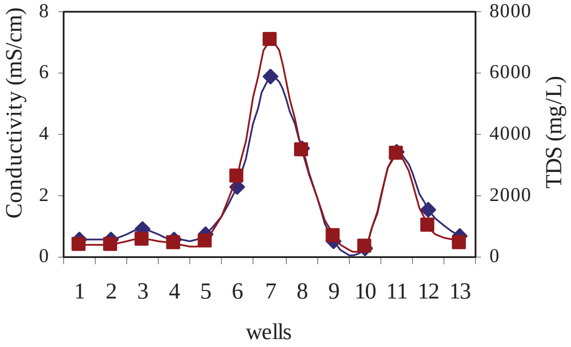

FIG. 2. TDS and specific conductance variations in groundwater.

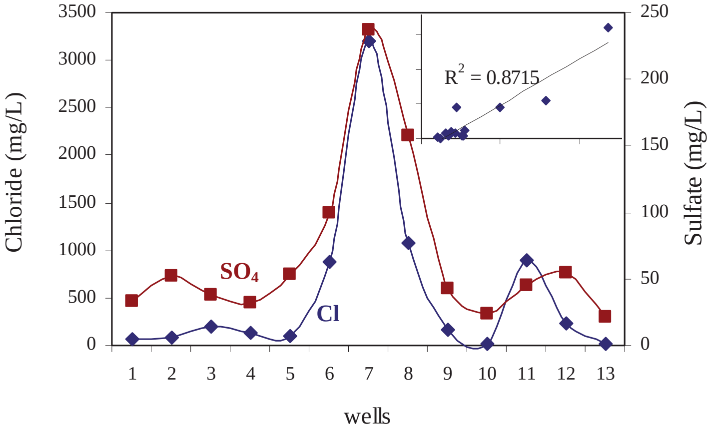

FIG. 3. Chloride and sulfate variations in groundwater.

Beirut southern suburb are higher, with typical concentrations ranging up to 7000 mg/L and thus exceeded the drinking water standard. The specific conductance, which correlates to TDS concentrations, was exceeded in the same wells.

High TDS concentrations and elevated specific conductance may indicate that the concentration of one or more dissolved constituents is high and that more detailed water quality analysis is warranted. The mineral quality of water can be classified based on the predominant cations and anions. Fig. 3 shows additional analysis for chloride and sulfate variation in groundwater. The

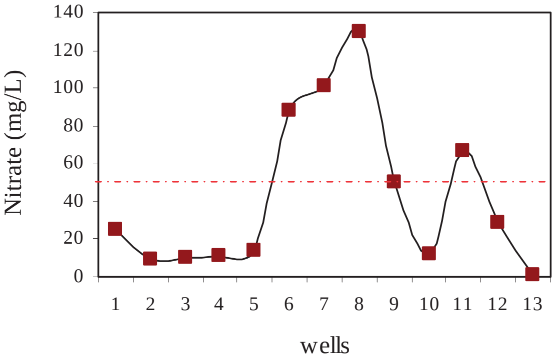

FIG. 4. Nitrate variation in groundwater.

drinking water standard for chloride is 600 mg/L. Chloride concentrations above 600 mg/L were only detected in wells 6, 7, 8 and 11. One of these wells (number 11) is an upper zone well in the Beirut area of known seawater intrusion [9]. The other wells are in the principal aquifer zone in Beirut area. Elevation of sulfate is observed in the same contaminated wells and its source is generally related to direct discharge into groundwater of septic systems and industrial effluents.

Since Beirut suburbs and some principal areas still have septic systems in use, monitoring for nitrate contamination is an essential groundwater management function. Fig. 4 shows that in the principle aquifer zone, wells 6, 7, 8 and 11 contained nitrate concentrations above the drinking water standard. Nitrate in water comes from both natural and anthropogenic sources such as fertilizers, septic systems, and animal waste.

In order to delineate the sources of nitrate in groundwater, additional isotopic analysis is performed for deuterium, oxygen-18 and $\delta^{15}N$ of nitrate ions in water.

3.2. Isotopic characteristics of groundwater

Isotopic compositions of groundwater in Beirut basin are plotted separately in a spatial $\delta^{18}O$ and δD diagrams (Fig. 5).

Fig. 5 shows that samples having high chloride, nitrate and sulfate content are enriched in $\delta^{18}O$ and δD. To understand this feature, isotopic data were plotted as regard to Lebanon's and Mediterranean meteoric water baselines [10].

On the δD–$\delta^{18}O$ diagram (Fig. 6), the isotopic composition of groundwater is close to that of the Lebanese Meteoric Water Line (LMWL). Samples that fall between the Mediterranean Meteoric Water Line (MMWL) and LMWL indicate that groundwater recharge arises from local precipitation and

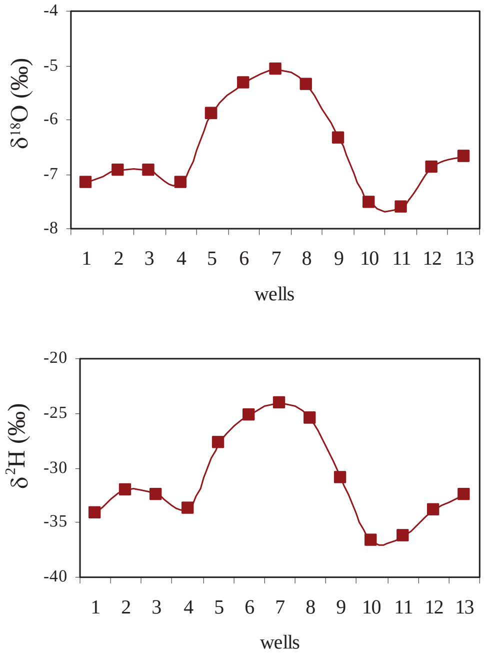

FIG. 5. Spatial variation of isotopic parameters in groundwater.

infiltration. The karstic feature of the aquifer promotes the direct and fast infiltration of precipitation into groundwater. The distribution of groundwater in samples 6, 7 and 8 is found below the local meteoric water baseline (LMWL). This may reflect the evaporation of recharging water as it moves through the unsaturated zone. It is due to differential sorption and evapotranspiration by and from plants growing in the recharge zone. This group of groundwater that lies under the LMWL has thus a different pattern and is influenced by agricultural activity in the sampling area.

In order to stringent the origin of nitrate pollution in samples 6, 7, 8 and 11, isotopes for $\delta^{15}N$ were determined in Georkarst Engineering in Trieste, Italy. Values of $\delta^{15}N$ in wells 6 and 7 are respectively 16.15‰ and 15.5‰; whereas values for wells 8 and 11 are 12.6 and 13.32‰. These results showed that the origin of nitrate in wells 6 and 7 is the infiltration animal waste used as fertilizers in landscape [11, 12]. Source of nitrate in wells 8 and 11 is the infiltration septic systems to groundwater [13, 14].

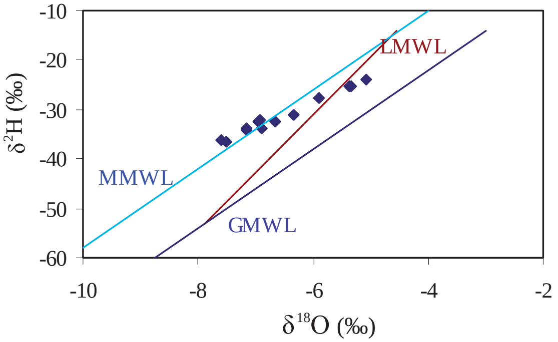

FIG. 6. Plot of δ^2H–$\delta^{18}O$ for Beirut groundwater.

4. CONCLUSIONS

In this study we have reported the hydrochemistry and the stable isotopic content of groundwater in Beirut region and its suburb. The mineral quality of water was found to be different in the southern suburb of Beirut where groundwater is characterized by elevated amounts of anions. Additional sources to the natural recharge of groundwater are thus suggested in the hot polluted samples. In the upper coastal area of Beirut, a seawater intrusion affects groundwater quality.

The stable isotope composition of groundwater was found close to the Lebanese Meteoric Water Line (LMWL). Samples that fall between the Mediterranean Meteoric Water Line (MMWL) and LMWL indicate that groundwater recharge arises from local precipitation and infiltration. Samples showing high chemical parameters were deviated from the LMWL. This may reflect the evaporation of recharging water as it moves through the unsaturated zone. $\delta^{15}N$ values of these samples confirm that high nitrate content originated from either infiltration of animal waste or septic systems to groundwater.

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GEOTHERMAL SYSTEMS

A NEW CONTRIBUTION TO THE ISOTOPIC AND GEOCHEMICAL CHARACTERIZATION OF THE GAS PHASE ASCRIBED TO THE CO_2-RICH MINERAL WATERS (N. PORTUGAL)

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Abstract

In Portuguese mainland the most important sodium bicarbonate CO_2 rich thermomineral waters are found in the Northern part of the country, linked to one major NNE-trending faults, the so-called Verin-Chaves-Régua-Penacova megalineament. Along this tectonic structure different occurrences of CO_2-rich thermomineral waters are found: Chaves hot waters (78ºC) and several cold (17ºC) CO_2-rich waters. The gas phase composition and the isotopic ratios of $^3He/^4He$ and $^{13}C/^{12}C$ point out that 10 to 30% of the gases have mantelic or magmatic source (typical MORB fluids). This primitive chemical signature decreases from S to N, representing an increase of crustal contamination in that direction. Geochemical modeling applied to the hot and cold

waters composition shows that water-rock interaction reactions are mainly controlled by the amount of dissolved CO_2(g) instead of the water temperature.

1. INTRODUCTION

Sodium bicarbonate — CO_2 rich mineral waters have been described and studied from different parts of the world. Several papers are found reporting these type of groundwaters that are fresh to saline, alkaline to acidic, often showing moderate to high chloride content. Examples of these studies are found in the literature, from France [1], Germany [2], Spain [3], United States [4] and Australia [5] for example. Understanding the origin of carbon dioxide and associated CO_2-mineral springs is one of the keys to understand and improve our knowledge on important geological processes. Under this goal, various hydrogeological studies, using coupled isotopic and geochemical methodologies have been performed in the research region [6–9] located in the N of Portuguese mainland, approximately between Vilarelho da Raia and Pedras Salgadas areas (Fig. 1). In the region, some of the warmest thermal springs, are located along one of the major NNE-trending faults, the so-called *Chaves Depression*, within the Galicia-Trás-os-Montes area. Along this lineament lie not only the Chaves hot waters (78ºC) but also numerous emanations of saline cold CO_2-rich waters (e.g. Vilarelho da Raia, Campilho, Vidago, Sabroso and Pedras Salgadas), which are used in local spas.

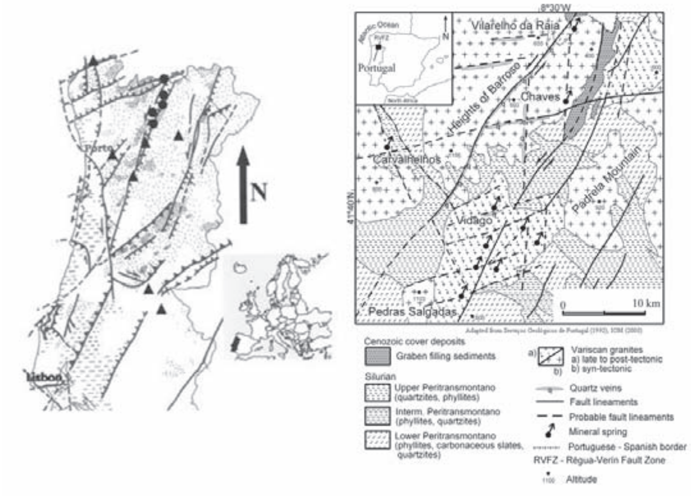

FIG. 1. Geological sketch map of the research region. Location of the main water and gas sampling sites. Maps adapted from [10].

This study presents the interpretation of new data on the chemical and isotopic characteristics of the above mentioned waters and the associated gas phase. With this objective, water and gas samples were colleted in hot (78ºC) and cold (17ºC) hydromineral systems, to characterize the geochemical and isotopic composition of the associated gas phase (CO_2, H_2, CH_4, N_2, CO, O_2, Ar, He, Ne, ^2H, ^3H, ^{13}C, ^{14}C, ^{18}O, $^3H/^3He$, $^3He/^4He$, $^{40}Ar/^{36}Ar$ and ^{15}N), in order to identify the contribution of deep crustal and mantle volatile components ascribed to that main tectonic accident. The research region is located in the Ante-Mesozoic Hesperic Massif, consisting mainly of Hercynian granites and Paleozoic metasediments (Fig. 1). Inserted between the schistoid complex, bands of carbonaceous slates are found, well displayed in Chaves area.

The identification the possible mixing between the geothermal mineral fluids with the local cold dilute groundwater systems, should also be considered as an important environmental issue, which should be addressed either in the exploitation and future development of the these geothermal resources or in the delimitation of well-head protection areas. An important aspect in the low-temperature geothermal systems is the maintenance of the chemical quality of water, since spas are very much dependent on both constant temperature and water quality.

2. METHODOLOGY

Three field campaigns were performed in the N part of Portugal. Groundwater samples were collected in polyethylene bottles for laboratory analyses while temperature (ºC), electrical conductivity (μS/cm) and pH were determined *in situ*. Free gases were collected in two glass containers, and for the determination of the chemical and isotopic composition of the dissolved gases one bottle of 100 ml was used. These measurements were carried out at the Institute Nazionale di Geofísica e Vulcanologia (Palermo, Italy), while the δ^2H, $\delta^{18}O$ and ^3H determinations were carried out at ITN – Sacavém (Portugal). The chemical analyses were performed at IST – Lisbon (Portugal).

3. GEOCHEMICAL AND ISOTOPIC FRAMEWORK

The study area Chaves is the only site where mineral waters present high discharge temperatures (78ºC), while at Vidago, Pedras Salgadas and Vilarelho da Raia present a mean temperature of 17ºC. According to Ref. [6–9] the tectonic and geomorphologic features of the region (Chaves, Vidago and Pedras Salgadas grabens) and the geological environment (dominated by granitic rocks) seem to be responsible for the occurrence of these cold and hot hydromineral systems. The waters present a Na-HCO_3 hydrogeochemical *facies*. Recent hydrogeochemical data confirm the previous thermal and mineral water classification [6, 7], where two groups of waters were identified: i) Chaves spring and borehole waters (78 ºC), with a TDS of 1600–1850 mg/L and a free CO_2 between 350 and 1100 mg/L. pH is close to 7 (Vilarelho da Raia (17ºC) cold spring and borehole waters were included in this group due to the chemical similarity with the Chaves waters) and ii) the second group composed by Vidago and Pedras Salgadas showing a mean temperature around 17ºC, a pH ≈ 6, and higher Ca, Mg, and free CO_2 content, up to 2500 mg/L. Within this group Vidago presents the highest mineralization (TDS ≈ 4300 mg/L).

The degree of mineralization found in these waters seems to be directly related with the dissolved gas content in the aqueous system, namely CO_2, and with the different residence times within the aquifer, ascribed to the strong correlation found between the HCO_3 and Na+K content (Fig. 2A). Although all waters collected belong to the Na-HCO_3 hydrogeochemical *facies,* Vidago, Pedras Salgadas, Campilho and Sabroso waters have the highest content in Ca, Mg (Fig. 2B). Nevertheless, different Ca and Mg content are found within the same water system (i.e. Vidago and Campilho). This variability in the mineralization does not seem to be related with the water temperature, neither with the degree of weathering or the amount of dissolved gases, since low Ca and Mg contents are found either in the hot and cold mineral waters. In this case, the geological matrix of the aquifers seems to have a major role in the water chemistry.

For most of the minerals that constitute the igneous rocks, their dissolution is thermodynamic, dependent having a direct relationship with temperature. This relation is often used in the evaluation of the deep (reservoir) temperatures of the hydrothermal systems. However, in the studied region, comparing the chemical composition of Chaves thermomineral water with the remaining water samples it is possible to observe a complete independence between

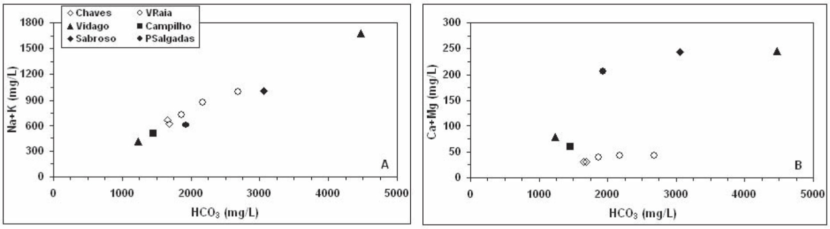

*FIG. 2. Relation between the HCO_3 content of the mineral waters and(**A**) the amount of Na and K, and (**B**) Ca and Mg.*

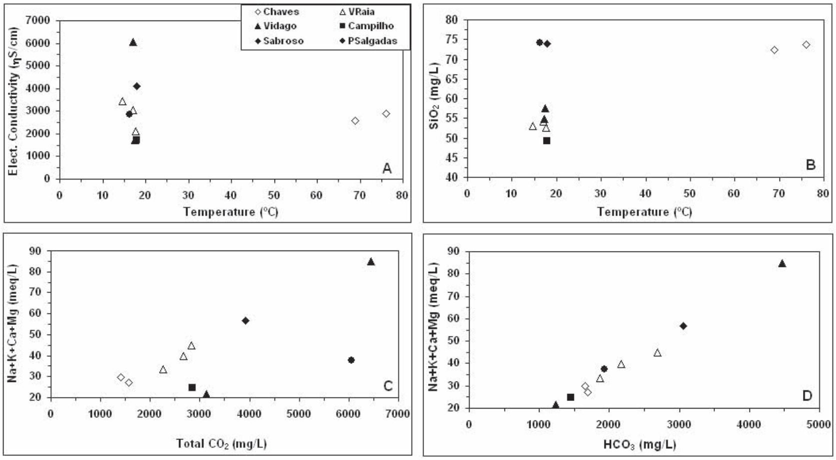

*FIG. 3. (**A**) Relation between sampled temperature and the electrical conductivity of the mineral waters. (**B**) SiO_2 as a function of the issue temperature. (**C**) Relation between the cationic species and the total dissolved CO_2.(**D**) Relation between the cationic species and the amount of bicarbonate in the CO_2-rich mineral waters.*

temperature and the amount of mineralization (Fig. 3A). This independence is also observed when the dissolved SiO_2 of the waters is plotted as a function of temperature; no relation is found (Fig. 3B). Besides, the CO_2 solubility increases with the decrease of temperature; within a CO_2-rich system the mechanisms of water-rock interaction will be favoured by low temperatures. This fact could explain the high mineralization of the hypothermal waters when compared to the hyperthermal waters (Fig. 3C and 3D). These trends (Fig. 3) seem to point out that the water-rock interaction processes are dominated by the presence of CO_2 more than by the existence of high temperatures at depth.

On the other hand, the δ^2H and $\delta^{18}O$ signatures obtained in these two groups of CO_2-rich mineral waters indicate a meteoric origin, and that they have not been subjected to surface evaporation (Fig. 4A). No evidence of water-rock interaction processes at high temperature has been detected in the Chaves thermomineral waters. The isotopic data deviation found within these groundwater systems seems to be related with different recharge altitudes (Fig. 4B). The absence of tritium found in some of the groundwater samples point out to a deeper and/or longer circulation paths/residence times. The circulation paths of the cold CO_2-rich mineral water systems seem to take place at shallow depths in the upper crust, as indicated by the low outflow temperature of these waters.

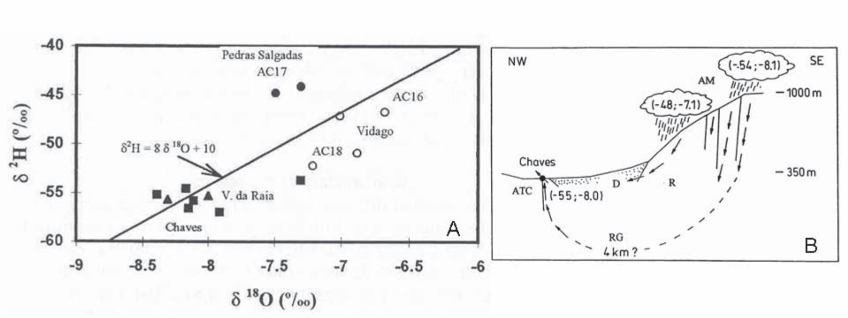

FIG. 4. (A) $\delta^{18}O$ versus $\delta^{2}H$ (‰ versus V-SMOW) for the CO_2-rich mineral waters [6]. Conceptual circulation model; variation in the isotopic composition with the recharge altitude of the sampling site [11].

4. ISOTOPIC AND CHEMICAL FEATURES OF THE GROUNDWATER GAS PHASE

The chemical and isotopic composition of the gas phase determined in the CO_2-rich mineral waters is presented in Table 1. The analysis performed on the free dissolved gases, as well as on the associated isotopic composition (^{13}C, ^{3}He and ^{4}He), enabled the identification of the genesis of the gas phase associated to these mineral water systems. The isotopic ratios of carbon and helium ($\delta^{13}C$, $^{3}He/^{4}He$) and the geochemical composition of the gas phase ascribed to the CO_2-rich mineral waters were used to identify contributions of deep crustal and mantle volatile components associated to the *"Chaves Depression"* tectonic accident.

The $^{3}He/^{4}He$ ratios found in the gas phase of the mineral waters varies between 0.89 and 2.68 times the atmospheric ratio (Ra), at Chaves and AC25 Pedras Salgadas, respectively. These ratios are higher than the expected for a pure crustal origin (≈0.02 Ra), pointing out that 10 to 30% of the gases are originated from the upper mantle. The $\delta^{13}C$ varying between –7.2 and –5.1‰ *vs* PDB, and the $CO_2/^{3}He$ ratios from 1×10^{8} to 1×10^{9} are typical of MORB fluids [12]. The ^{3}He contribution is higher in Pedras Salgadas gas phase than in Chaves, i.e., the gas mantelic signature decreases from S to N, indicating higher ^{4}He crustal contamination to the North (Fig 5). The values obtained are in agreement with the data presented by Ref. [3] concerning the CO_2-rich waters in the N of Spain located along the same tectonic structure.

The gas phase composition in these waters has a CO_2 content higher than 90%, and the N_2 and CH_4 represent the second and third more abundant gases. The values obtained for the $\delta^{13}C$ of the CO_2 gas indicate that the main source of

TABLE 1. GAS PHASE COMPOSITION, $\delta^{13}C$ AND $^3HE/^4HE$ ISOTOPIC RATIOS OF THE STUDIED CO_2-RICH MINERAL WATERS. (B.D.L.) STANDS FOR BELOW DETECTION LIMITS.

Ref.	Gas Phase composition								Isotopic ratios		
	Free Gases								$\delta^{13}C$		$^3He/^4He$
	He (ppm)	O_2(%)	N_2(%)	CO(ppm)	CH_4(ppm)	CO_2(ppm)	Ne(ppm)	Ar(tot.)	CO_2(g)	CITD	R/Ra
P. Salg. AC25	195.9	0.02	1.8	0.6	783	97.45	0.150	330.6	–5.3	–0.88	2.68
P.Salg. AC17	229.6	0.31	2.99	b. dl.	600	95.66	0.126	283.3	–5.2	–0.92	2.50
Vidago AC16	334.0	0.66	5.24	2.2	469	92.31	0.416	711.9	–5.1	–2.32	1.90
Vidago AC18	149.3	b. dl.	0.9	b. dl.	41	97.44	0.243	239.4	–6.2	–0.10	1.34
Vid, Areal 3	1061.0	b. dl.	5.54	b. dl.	1021	94.41	0.417	965.9	–7.2	–2.20	1.26
Chaves AC1	105.1	0.04	1.72	1	500	97.42	0.150	232.0	–5.8	-2.43	0.89
	Dissolved gases (ccSTP/g)										
V. Raia ACP1	1.23E–1	4.42E–2	2.32E+1	2.19E–4	2.10	318.600	1.25E–4	n.m.	n.m.	–4.81	0.5

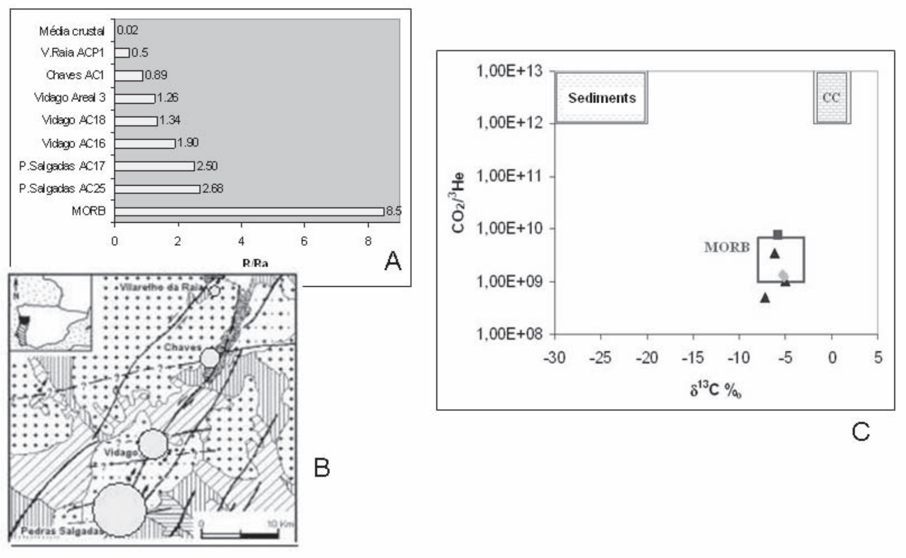

*FIG. 5. (**A**) The $^3He/^4He$ ratio values determined in the gas phase of the CO_2- rich mineral waters. (**B**) Spatial distribution of the $^3He/^4He$ ratios in the gas phase. (**C**) $CO_2/^3He$ ratio vs $\delta^{13}C$ of the gas phase within the typical isotopic ratios field from crustal sediments (sediments), marine limestones (CC) and typical MORB formations, the fields were defined based on the Ref. [12–14]. The $CO_2/^3He$ ratios for crustal and MORB fluids are from Ref. [12, 16]. (■) Chaves, (▲) Vidago and (●) Pedras Salgadas waters.*

this gas have a mantelic origin. This assumption is supported by the $^3He/^4He$ ratio measured in the gas phase, which gives values for a deep (mantelic) source.

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EVALUATION OF ORIGIN OF THE AYAŞ-BEYPAZARI GEOTHERMAL WATERS WITH SULFUR ISOTOPES, CENTRAL ANATOLIA, TURKEY

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Abstract

The aim of this study is to investigate the origin of sulfate in deeply circulating thermal waters around the Ayaş-Beypazarı region in Turkey. The waters of Ayaş resorts and Çoban bath are of Na-Cl-SO_4 hydrochemical facies and waters of Kapullu and Dutlu thermal resorts are represented with Na-SO_4-Cl hydrochemical facies. Kirmir Formation gypsum minerals in Mio-Pliocene age have sulfur-34 isotopes between 17 and 25‰. According to oxygen-18 (SO_4) and sulfur-34 (SO_4) contents, sulfate in waters of Ayaş and Dutlu resorts and Çoban bath is derived from gypsum of Kirmir Formation of primary source. Sulfates of Kapullu bath water and Karakoca mineral water may be originated from atmospheric and terrestrial environments, respectively. Among the cold groundwaters, sulfate of Tahirler fountain is derived from gypsum in the Kirmir Formation (primary source) and sulfate in Kapullu cold water is originated from a secondary origin (atmospheric). Sakarya River water sulfate is probable originated from atmospheric and terrestrial environments.

1. INTRODUCTION

The study area is located among Ayaş, Beypazarı and Mihalıççık settlements and 90 km west of Ankara (Fig. 1). Sakarya River, Ankara creek, Kirmir creek and Ilhan creek run to the Sarıyar Dam Lake. The Beypazarı granitoid is surrounded with Kirmir Creek and Sakarya River in the study area. These granitoid units are almost identical to the granite supersuite of Central Anatolian Crystalline Complex in Central Turkey [1].

Waters of Çoban bath spring (CBS-CBW), Ayaş mineral spring (AMS), Dutlu bath spring (DBS), Kapullu bath spring (KBS) and Karakoca mineral spring (KMS) are the thermal and mineral waters in the area. Karakaya bath and wells waters are thermal. The Ayaş waters have been used for balneologic

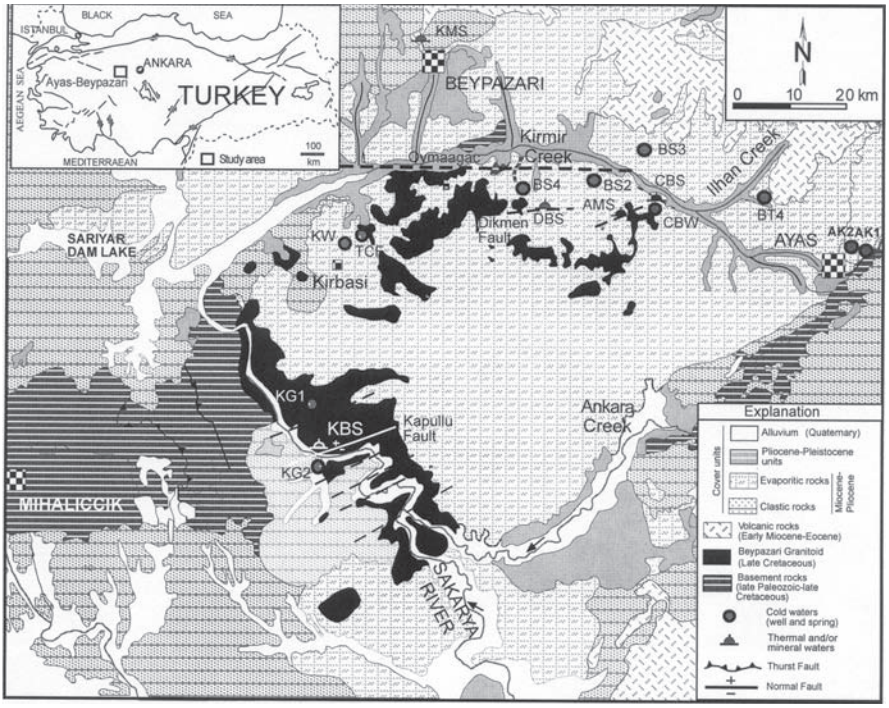

FIG. 1. Geological map of the study area (Modified from [2] and [3]).

purposes since 1982, and the facility is recently operated as a spa as well as physical therapy and rehabilitation center. Similarly, The Dutlu waters are also used as a spa physical therapy and rehabilitation center. The Çoban bath was a spring site in 1970s but all the springs are dry at present. Several exploratory wells (~5) were drilled around the spring site and two of them were artesian wells and others were shut down. The Kapullu bath spring has used as bath. The water of Karakoca mineral spring was sold in the market with the brand of Beypazarı Karakoca mineral water.

The aim of this study is to investigate the hydrochemical characteristics of the Beypazarı Ayaş region geothermal waters and to describe the origin of sulfate in the waters using sulfur isotopes.

2. GEOLOGY AND HYDROGEOLOGY

Basement rocks are formed by metamorphic rocks of Paleozoic age. It is known as Eskişehir metamorphic complex. These rocks are formed by amphibolite, green schist and hornfels facies and outcropped at around Mihalıççık and southern of Ayaş settlement. The rocks are composed of gneiss, granat-schist, biotite-schist, calc-schist, mica-schist, graphite-schist, dolomitic calcareous, crystalline limestone, fillite, amphibolite and metabasite [4, 5] (Fig. 1).

Since magmatic rocks such as granite, granodiorite, monzonite and quartz monzonite exposing at Oymağaç and Kırbaşı in the study area have a same origin and are found in a single intrusive body, they are called as "Beypazarı Granitoid" by [6]. The Beypazarı granitoid was intruded to Eskişehir metamorphic rocks during the Late Cretaceous. The units with Early Miocene-Eocene age composed of proclastic volcanic, proclastic tuff, basalt and agglomerates. It is known as İnözü tuff of proclastics and is located at the bottom. Adaviran basalt is located at upper part of the proclastics [4].

Clastic cover units: The Beypazarı Granitoid is overlain by the middle Eocene Kızılbayır Formation of transgressive character. The formation, consisting of claystone, sandstone and conglomerate, is found at western and eastern parts of the study area (Fig. 1). With its typical red color, the Kızılbayır Formation is easily distinguished from other units. Evaporitic cover units: These cover units are formed by Mio-Pliocene age of Kirmir Formation (Beypazarı Formation). Kirmir Formation is formed three different specifications. Those are consists of conglomerate, sandstone, marl at the bottom; sandstone, marl, clayey limestone, clay, silty and gypsum levels at middle level. At the upper part, it consists of gypsum stratums and clay-marl levels intercalate [7]. These units were precipitated in lacustrine environment. Because of shallowing of the lake level, evaporitic units increase to the top in lacustrine environment. Alluvium units are observed along the Sakarya River, Kirmir Creek and Ankara Creek and its tributaries (Fig. 1).

Basement rocks of Paleozoic age are generally impermeable. Jurassic limestone is observed on the basement units at around Ayaş region. The units are aquifer levels of the Karakaya bath spring. AK1 and AK2 wells have been penetrated in the limestone and cover units. Total flow yields of the wells are 40 L/s [8]. Direction and dips of the joints of the granitoid reveal that the Beypazarı Granitoid was witnessed with NE-SW compressional stress and NW-SE extensional stress in the Kapullu bath spring area [3]. Thermal and mineral springs (CBS, DBS, AMS and KBS) have discharged from fault zones cutting the Beypazarı Granitoid. The Granitoids are generally impermeable, but faulting and cracking upper zones have secondary porosity and permeability.

Conglomerates and sandstones of the cover units are permeable. But intercalated thick marls stratums are impermeable. Therefore, these cover units are impermeable through the vertical direction to the stratum plane. Gypsum strata at the upper part of the cover units constitute limited reservoir for brine cold springs.

The geothermal reservoir is fed by precipitation, river and cold groundwater infiltrating into the generally low permeable cover units and faulting and cracking crystalline rocks. The base of the reservoir system is the very low permeability crystalline (massive) and metamorphic basement which contains negligible groundwater resources. Groundwater flow in this crystalline terrain is slow and estimated to be about 40 years old. Addition, tritium values of the waters (CBW, AMS, DBS and KBS) were zero in 2006.

3 HYDROCHEMICAL AND ISOTOPIC STUDIES

Dutlu and Çoban bath springs have as dominant ions Na^+ and $Cl^- \geq SO_4^{-2}$. Ayaş mineral and Kapullu bath springs have as dominant ions Na^+, SO_4^{-2} and Cl^-. Karakoca mineral spring has as dominant ions Na^+ and HCO_3^-. Dutlu bath spring has a temperature of 46°C and discharge of total 6 L/s [9]. Kapullu bath spring has a temperature of 40.5°C and discharge of 2.49 L/s [3]. Çoban bath and Ayaş mineral springs are not active nowadays. Wells drilled in these thermal areas have obtained water. Çoban and Ayaş wells have groundwater temperatures of 54.5 and 51°C, respectively. Spring water temperatures of the Çoban and Ayaş

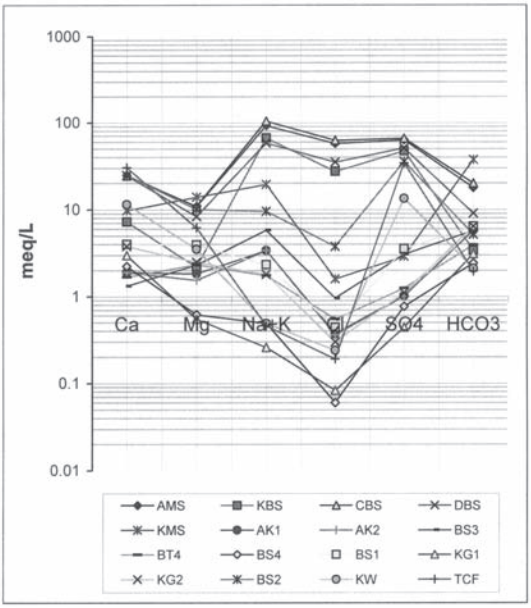

FIG. 2. Schoeller diagram of the waters.

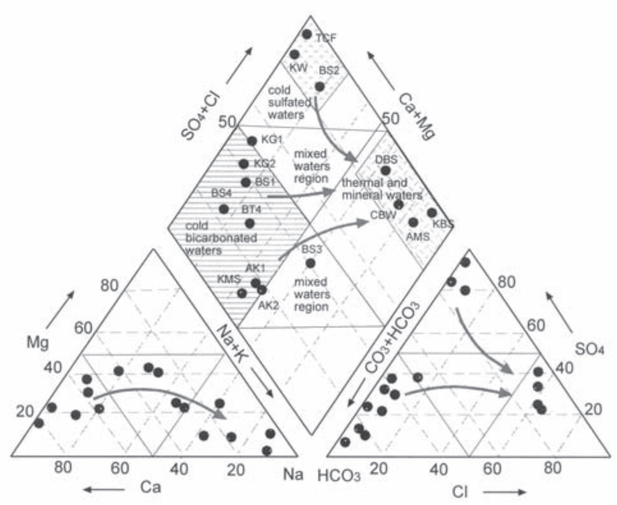

FIG. 3. Piper diagram of the waters.

had been measured as 52 and 51°C, respectively [7]. Temperature of Karakaya bath spring is measured as 30°C [10].

Cold waters present two main types water chemistry. First type has dominant ions of Ca^{2+} and HCO_3^- , second type has dominant ions of Ca^{2+} and SO_4^{-2}. Some cold waters have dominant Mg^{2+} and Na^+ ions (Figs. 2 and 3).

If gypsum ($CaSO_4{\cdot}2H_2O$ is a major source of sulfate, then the Ca/SO_4 ratio (in mg/L) in the corresponding groundwater is approximately 0.4 and the $\delta^{34}S$ of SO_4 should be very close to that of the gypsum [11]. Only TCF satisfies these requirements, thus the dissolution of gypsum in an unlikely source for the elevated sulfate in the gypsiferous Kirmir Formation (Fig. 4). The sources of sulfate in the Upper Floridan aquifer were able to identify gypsum dissolution, based on $\delta^{34}S$ values and chloride/sulfate ratio indicates gypsum dissolution [12]. Chloride/sulfate ratios are low in the TCF (0.004), KW (0.013), BS2 (0.078) and BS4 (0.055). These springs points are manifested from Kirmir Formation. TCF, KW and BS2 waters have Ca and SO_4 water types (Figs. 2 and 3). According to saturation index calculation of all the waters, the waters are saturated in aragonite, calcite and dolomite minerals. But, only TCF spring is saturated to aragonite, calcite, dolomite and gypsum minerals.

Tritium values of samples collected from the Kapullu and Dutlu bath springs, Çoban bath and Ayaş mineral wells, and the tritium values are 0 TU. Considering the hydrochemical and isotopic data, the thermal and/or mineral waters are deeply circulated, old waters and it is derived from waters rising to

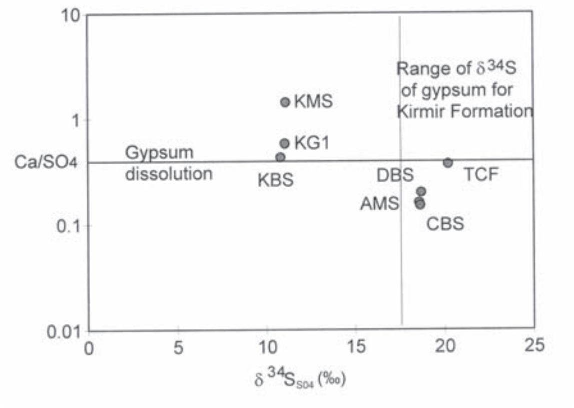

FIG. 4. Ca/SO_4 versus sulfur-34 (in sulfate) diagram.

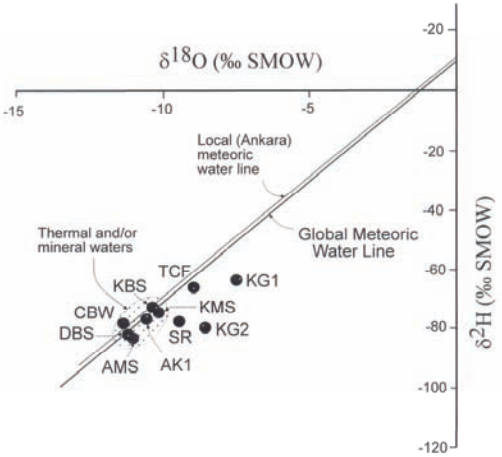

FIG. 5. Oxygen-18 (‰, SMOW) versus deuterium (‰, SMOW) diagram.

the surface through the fault zones cutting the granitoids. Some cold waters (KG1, KG2 and SR) have exposed to evaporation (Figs. 1 and 5).

3.1. Sulfur isotope evaluation

Sulfur isotope analyses are analyzed and applied for the first time to the thermal and mineral waters in the study area. It is thought due to that mixing processes of the waters, SO_4-H_2O geothermometers are applied rather than cation geothermometers. The $\delta^{18}O$ (SO_4-H_2O) geothermometer is based on the oxygen isotope exchange reaction:

$$S^{16}O_4 + H_2{}^{18}O <=> S^{16}O_3{}^{18}O + H_2{}^{16}O$$

Experimental fractionation factors for the sulfate-water system [13] are in reasonable agreement between 100–200°C [14]. It is reported that an equilibrium fractionation between dissolved sulfate and water [13].

$$1000 \ln \alpha_{SO_4-H_2O} = 3.251 \frac{10^6}{T^2} - 5.6$$

but [14] found

$$1000 \ln \alpha_{SO_4-H_2O} = 2.88 \frac{10^6}{T^2} - 4.1$$

where T is in K.

The results of SO_4–H_2O geothermometer reveal that the reservoir temperatures of the study area geothermal waters are between 42 and 73°C in the region.

According to oxygen-18 (SO_4) and sulfur-34 (SO_4) contents, sulfate in waters of Ayaş and Dutlu baths and Çoban bath waters are derived from gypsum of the Kirmir Formation of primary source. But, sulfates of the KMS, KCS (KG1), KBS

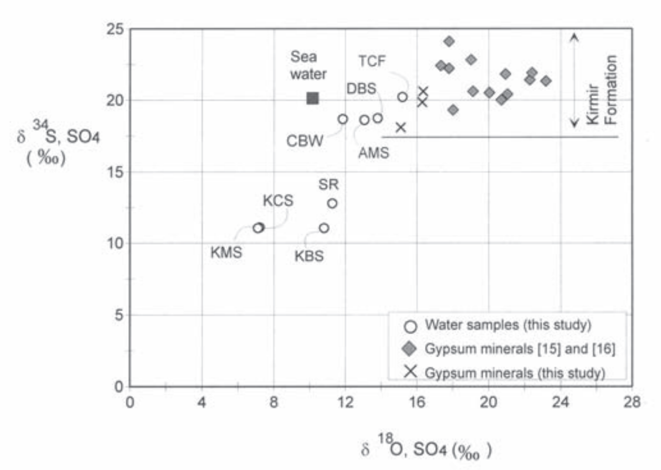

FIG. 6. *Sulfur-34 (SO_4) versus oxygen-18 (SO_4) diagram.*

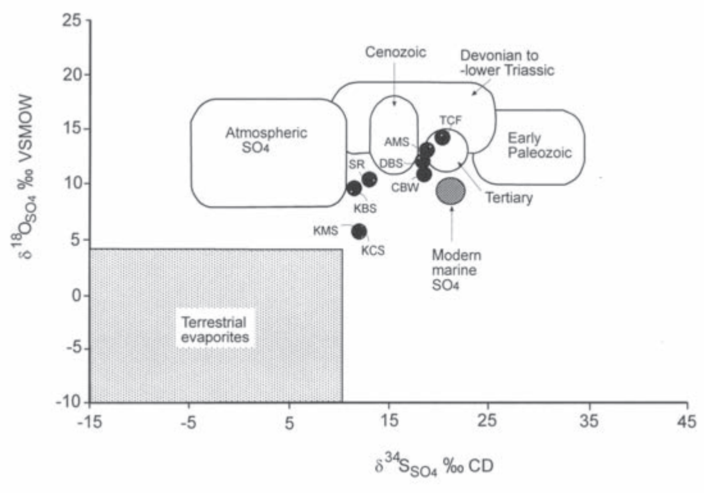

FIG. 7. Oxygen-18 (SO_4) versus sulfur-34 (SO_4) diagram [17].

and SR waters are probably originated by mixing of terrestrial, atmospheric and Tertiary origins (Figs. 6 and 7). It is thought that Kapullu bath spring has probably diluted by Sakarya River waters. But, isotopic and hydrochemical indicator of dilution are not clear on the Kapullu bath spring.

4. RESULTS

Hydrochemical and isotopic characteristics, discharge rates and temperature values of the thermal and/or mineral waters indicate that the waters are deeply circulated and manifested in the fault zones.

Hydrochemical characteristics of the cold springs cluster on two main water types in the region. First type is mainly composed of Ca^{2+} and SO_4^{2-} ions. Second type water is mainly composed of Ca^{2+} and HCO_3^- ions. Thermal and mineral springs have been formed in Na^+, SO_4^{2-} and Cl^- hydrochemical facies. It was thought that thermal characteristics are the result from uplifting of basaltic rocks.

Kirmir Formation gypsum minerals of Mio-Pliocene age have sulfur-34 isotopes between 17 and 25‰. According to oxygen-18 (SO_4) and sulfur-34 (SO_4) contents, sulfate in waters of Ayaş and Dutlu mineral and Çoban bath waters are derived from gypsum of Kirmir Formation of primary source. Sulfates of Kapullu bath water and Karakoca mineral water is located near the atmospheric and terrestrial regions, respectively.

Among the cold groundwaters, sulfate of Tahirler fountain is derived from gypsum in the Kirmir Formation (primary source) and sulfate in Kapullu cold water is originated from a secondary origin (atmospheric). Sakarya River water sulfate is probable originated from atmospheric and terrestrial.

According to SO_4-H_2O geothermometer application, reservoir temperature of the geothermal springs is of up to 73°C.

ACKNOWLEDGEMENT

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ISOTOPIC ASSESSMENT OF TRABZON MINERAL SPRINGS AND AYDER (ÇAMLIHEMŞIN-RIZE)-ILICAKÖY (İKIZDERE-RIZE) HOT SPRINGS

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Abstract

In the study area generally, basalt, andesite and basaltic-andesitic pyroclastic and sandstone, sandy limestone and marl interbedded volcano-sedimentary rocks crop out. Age of these units ranged between Liassic and Quatenary. Volcanic rocks cropped out near the mineral springs are not aquifer because of the low permeability. Mineral springs generally are controlled with fault and contacts. The pH values of the cold mineral springs range from 5.5–6.23, electrical conductivity values range from 506–5070 μS/cm, total dissolved solid values range from 374–5098 mg/L. Bereketli, Selimoğlu and Durali mineral springs are in class of "carbonate and sulphate water", İkisu and Kisarna mineral springs are in class of "salty and sodic water". Ayder hot spring temperature is 57°C; pH value is 9.07; electrical conductivity value is 21 μS/cm; total dissolved solid value is 163 mg/L; the water type is $CaHCO_3$. Ilıcaköy hot spring temperature range from 20–63°C; pH value range from 6.5–6.78; electrical conductivity values ranges from 4300–5500 μS/cm; total dissolved solid values range from 4012–4115 mg/L; the water type is $NaHCO_3$. Environmental isotopes ($\delta^{18}O$, δ^2H and tritium) were analyzed to clarify the relationship between surface and groundwater circulation, and recharge–discharge condition of the aquifers. According to oxygen-18 and deuterium values, mineral springs are close to General Meteoric Water Line. Transit time of the hot spring is longer than the mineral springs. Recharge elevation of the Ayder hot spring is the highest of all springs. Recharge elevation and transit time of the water system of the İkisu mineral spring is the longest considering to oxygen-18 and tritium values. Although Kisarna mineral spring and İkisu mineral spring have the same recharge elevation, Kisarna mineral spring has a shorter transit time of the water system. Mineral springs have shallow circulation based on deuterium and tritium values.

1. INTRODUCTION

Mineral springs in Trabzon and in its vicinities and Ayder and Ilıcaköy hot springs are located in the Eastern Black Sea Region (Fig. 1). Several researchers Ayder hot spring [1] Ilıcaköy hot spring [2] Trabzon mineral springs [3, 4] have studied those areas, but in these studies hot springs are investigated in the perspective of chemical and geothermal energy however cold waters investigated in the perspective of chemical and economical values. In this study it's aimed to determine the depth of circulation and recharge elevation with the help of isotopic values besides hydro chemical features of hot and mineral springs.

2. SAMPLING AND ANALITICAL METHODS

Field and sampling studies concerning the inspection area were started in July 2003 and were finished about the end of 2005. Along this period data which belong the springs locating in the study area, were gathered and geological studies around spring environment were conducted. In situ measurements of pH, electrical conductivity (EC) and Total Dissolved Solids amount (TDS) were done in July 2003 at Selimoğlu and Durali and the gathered samples were

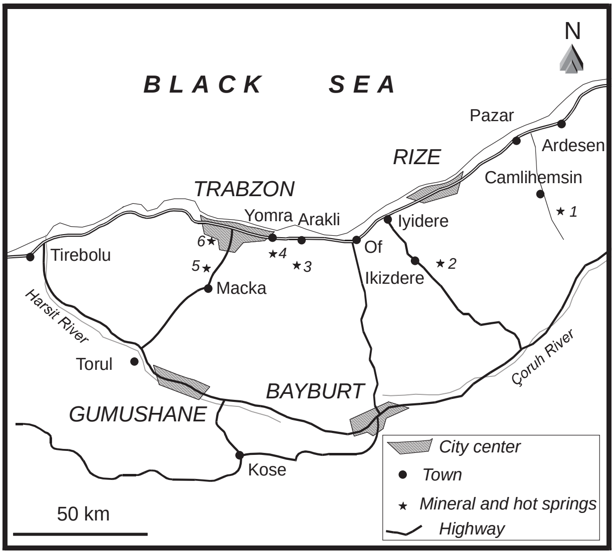

FIG.1. Location map of investigation area 1. Ayder, 2. Ilıcaköy, 3. Bereketli, 4. İkisu, 5. Durali-Selimoğlu, 6. Kisarna.

analyzed in General Directorate of State Hydraulic Works (DSI), Department of Technical Research and Quality Control. However, in 2004 summer and 2005 spring in situ measurement done for Bereketli, İkisu and Kisarna mineral springs and hot springs. Also, sampling studies were collected for oxygen-18, deuterium and tritium isotopes, in wet and dry seasons and analyzed in DSI.

3. GEOLOGICAL SETTING

The Liassic and Late Cretaceous aged volcanic-sedimentary rocks outcrop around the hot springs, and Late Cretaceous and Eocene aged volcanic-sedimentary rocks outcrop around the vicinity of Trabzon (Figs 2, 3). These units are given in the following:

Liassic aged Hamurkesen Formation [5] consists of basalt, andesite, dacite and pyroclastics rocks. Çatak Formation [6] contains sandstone, clayey limestone

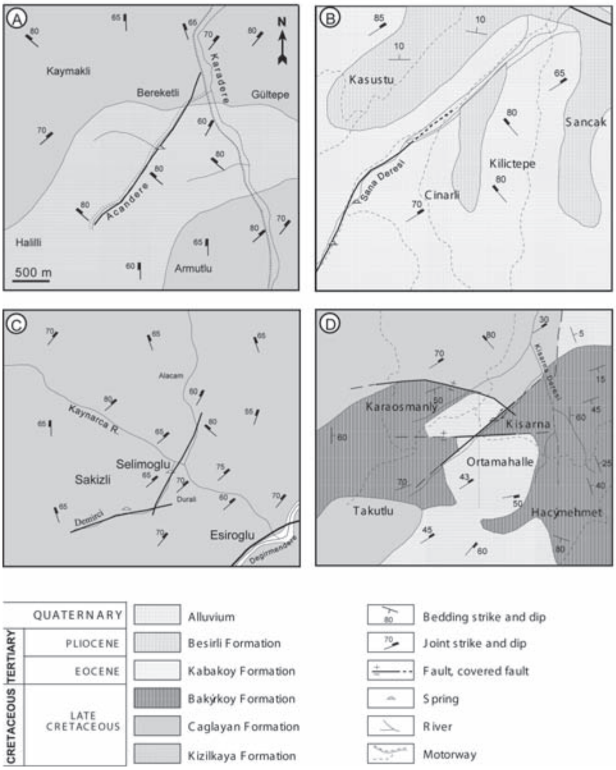

FIG. 2. Geological map of Trabzon mineral springs (A. Bereketli, B. İkusu, C. Selimoğlu-Durali, D. Kisarna).

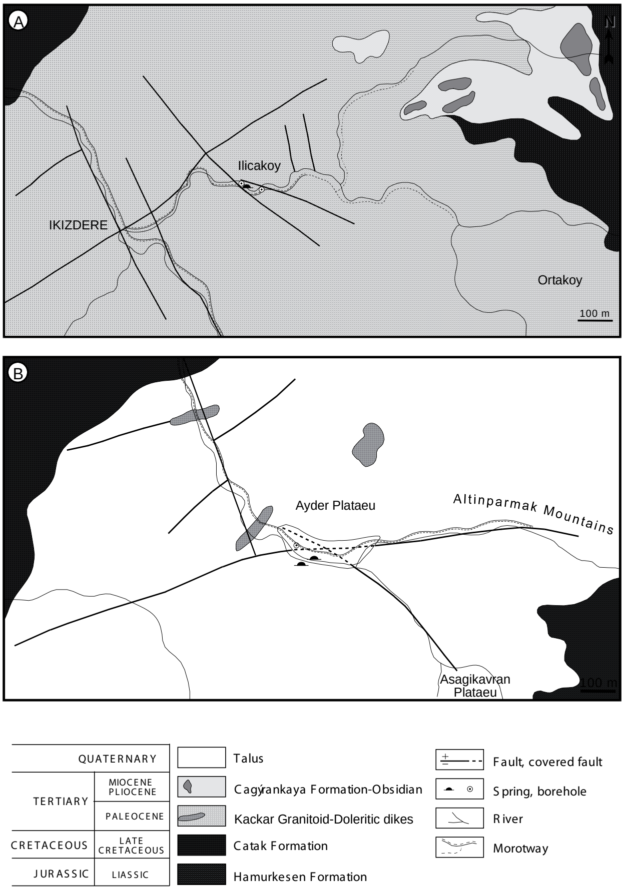

FIG. 3. Geological map of Ayder and Ilıcaköy hot springs (A: Ilıcaköy, B: Ayder).

and siltstone interbedded basaltic-andesitic rocks. Kızılkaya Formation [6] generally consisting of rhyodacite and dacite overlies conformably Çatak Formation. Çağlayan Formation [6] consists of basalt and basaltic pyroclastics. Bakırköy Formation [6] contains sandy limestone, clayey, marl and reddish limestone. Çatak, Kızılkaya, Çağlayan and Bakırköy Formations are Late Cretaceous units. Eocene aged Kabaköy Formation [6], consisting of sandstone, sandy limestone and marl interbedded basalts, andesite and pyroclastics overlies unconformably the Late Cretaceous aged formations.

The batholith of Kaçkar Granitoid-I intruded into Mesozoic rocks whereas Kaçkar Granitoid-II cut Cenozoic aged rocks [7]. In the Çağırankaya Plateau north-east of the Ilıcaköy andesite, andesitic pyroclastics and obsidian outcrop. This unit of Miocene-Pliocene age overlying unconformably the Late Cretaceous Çatak Formation is called Çağırankaya Formation. Pliocene Beşirli Formation [7] consisting of conglomerate and breccia overlies uncomformably Kabaköy Formation.

4. HYDROGEOLOGY

The volcanic rocks outcropping around the study area don't have the aquifer quality rocks as they have a low permeability. Water remaining in the fracture of these rocks can be seen leaking on the slopes. The formations having aquifer quality are the alluvium surfacing generally along the creek line in the shape of narrow bands. Although there is not any significant spring around the investigation area except the leaking waters from the fracture of volcanic rocks due to seasonal changes, mineral springs with not too high discharge can be viewed along the bottom of the valley. Though they can't be used because the ionic content of some of these is merely low and the others containing iron. Attributing to previous studies [3, 4, 8], in this study the springs having high ionic concentration and economical value were investigated. Those are Bereketli, İkisu, Selimoğlu, Durali and Kisarna mineral springs. Mineral springs in the investigation area are generally come to the surface in Late Cretaceous aged units, but hot springs are found in granitoids intruded into Mesozoic rocks. Mineral and hot springs reach to the surface mostly through discontinuities such as faults and fractures.

5. WATER CHEMISTRY

Among the investigated springs, mineral waters are classified as "cold waters" with the temperature of 14–15°C [9] and as " sixth class springs" with a discharge of 0.2–0.5 L/sec [10]. Bereketli and İkisu springs are classified as "fresh water" with a hardness degree of 20–21°Fr, Selimoğlu and Kisarna mineral springs are classified as "hard water" with a hardness degree of 25–29°Fr and Durali mineral spring are classified as "very hard water" with a hardness degree of 39°Fr [11]. All the springs are colorless, odourless, clear and gaseous. The values of springs differ for pH between 5.5–6.23, for EC 505–5070 µS/cm and for TDS 374–5098 mg/L. Among the hot springs, Ayder has 9.07 pH and 211µS/cm EC and Ilıcaköy has 6.5–6.78 pH and 4300–5500 µS/cm EC. The results obtained from chemical analyses of springs are given in Table 1. As the table checked, from meq/L values point, Ca the highest cation value in Bereketli, Selimoğlu and Durali springs while HCO_3 the highest anion

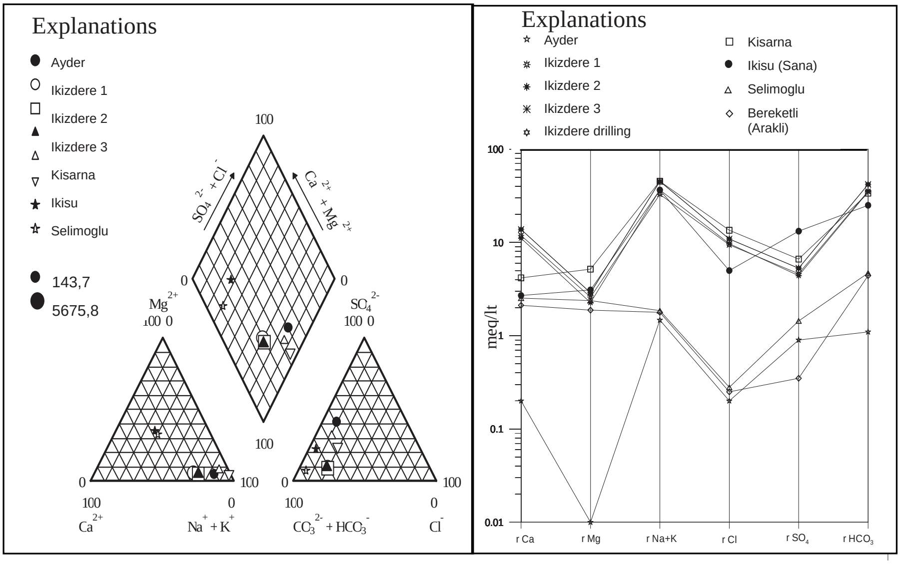

FIG. 4. Piper and Schoeller diagram of hot and mineral springs.

values. But in İkisu and Kisarna mineral springs Na is the highest cation value and HCO_3 is the highest anion value. Also in Ayder and Ilıcaköy hot springs Na is the highest cation value and HCO_3 is the highest anion value. Piper and Schoeller diagrams are used so as to determine chemical classifications of investigated springs. When the Piper diagram (Fig. 4) checked, it can be seen that mineral springs like Bereketli, Selimoğlu and Durali are carbonated and sulphated waters with Ca + Mg > Na + K value. İkisu and Kisarna mineral springs are salty and sodic waters with Na + K > Ca + Mg value. Furthermore, hot springs are also salty and sodic waters with Na + K > Ca + Mg value. When looked to the Schoeller diagram (Fig. 4), the lines connect the meq/L values of ions that belong to Bereketli, Selimoğlu and Durali springs passes parallel and close to each other. Durali and Selimoğlu show that these two springs originate from the same source. Kisarna and İkisu springs are parallel to each other except the Ca ion. While Ilıcaköy springs are parallel Kisarna and İkisu, Ayder spring has a very low ionic content.

TABLE 1. CHEMICAL ANALYSIS RESULTS OF INVESTIGATION WATERS.

	Hot Springs					Mineral Springs			
	Ayder Drilling	Ilıcaköy 1	Ilıcaköy 2	Ilıcaköy 3	Ilıcaköy Drilling	Kisarna	İkisu Şana	Selimoğlu Maçka	Bereketli Araklı
Temperature(°C)	57	20	30	24	63	15	19	15	14
pH	9.07	6.6	6.5	6.6	6.78	6.23	6.18	5.66	5.5
EC (μS/cm)	211	4500	4300	5500	4639	3890	5070	844	505
Ca (meq/L)	0.2	11.9	11.09	13.78	4.17	2.7	0.7	2.53	2.12
Mg (mg/L)	0.01	2.6	2.26	2.89	5.17	3.1	3.5	2.38	1.88
Na (mg/L)	1.43	28.77	32.62	40.13	40.87	23	47.5	1.8	1.75
K (mg/L)	0.04	4.04	3.91	4.88	4.36	13.4	19.8	0.06	0.03
HCO_3 (mg/L)	1.1	35.44	34.95	41.88	33.71	25	40.2	4.7	4.4
SO_4 (mg/L)	0.9	4.62	4.4	5.3	6.63	13.2	16.8	1.44	0.35
Cl (mg/L)	0.2	9.4	9.7	10.9	13.5	5	13.2	0.28	0.25
SiO_2 (mg/L)		37.8	35.98	40.93					
B (mg/L)		37	37	43	58	0.44	1.4	<0.1	<0.1

6. ENVIRONMENTAL ISOTOPES IN SPRINGS

In recent years natural isotopes in the water are being used for hydrogeological research. Generally in these studies tritium (^{3}H) and Carbon–14 (^{14}C) are used as radioisotope and oxygen–18 (^{18}O) and deuterium (^{2}H) are used as stable isotopes. ^{3}H and ^{14}C are being used for determining the groundwater age, while ^{18}O and ^{2}H are being used for determining the recharge area of groundwater and also indication of evaporation in the surface waters. Though stable isotopes ^{18}O and ^{2}H are used to calculate the probable recharging elevations, ^{3}H is utilized to determine the relative age and transit time of water system. The locations of samples of mineral and hot springs along with Global Meteoric Water Line (GMWL) are given in Fig. 5 [12]. According to GMWL isotopic transpositions are observed in Ilıcaköy hot springs, Ayder hot spring is mixing with surface or shallow waters and finally no change is observed mineral springs and surface waters (Fig. 5).

The relation between ^{18}O and ^{2}H as stable isotopes don't change due to specific fall regime. For this reason, with the help of deuterium excess of the samples, by determining the effect of various fall regimes, information could be gathered about the origin of the falls_through the recharge regions. Deuterium excess can be calculated with the equation $d = \delta D - 8 \times \delta^{18}O$ [13]. On the points where the deuterium excess has high values, marinal falls are dominant on the contrary and the points having low values continental falls are dominant [14] Results of oxygen-18, deuterium, tritium and deuterium excess values of investigated waters are given Table 2.

When Table 2 shows that the d_f values of mineral springs change between 11.19 and 18.98. The minimum d_f value is in Bereketli spring with a value of 11.19 and maximum is in Kisarna spring with a value of 18.98. In dry and wet seasons d_f values are different in Bereketli and İkisu springs. In dry seasons Bereketli and İkisu springs are mostly recharged by continental falls. In the springs affected from the same fall regime, the d_f values will be close to each other, and also tritium content will represent the transit time of water system. Due to deuterium — tritium relationship, relative transit time of water system can be maintained (Fig. 5). From the figure it can be seen that İkisu mineral spring has deep circulation like hot springs, but Bereketli, Durali and Kisarna mineral springs have shallow circulation with respect to them. Recharge elevation and transit time of the water system of the İkisu mineral spring is the longest considering oxygen-18 and tritium values. Although Kisarna mineral spring and İkisu mineral spring have the same recharge elevation Kisarna mineral spring has a shorter transit time of the water system.

TABLE 2. RESULTS OF OXYGEN-18, DEUTERIUM, TRITIUM AND DEUTERIUM EXCESS.

	Springs and surface waters	Date	δ^{18}O (‰)	δ^{2}H (‰)	d-excess (‰)	Tritium (TU)
Surface Waters	Değirmendere Creek Water	22.10.2003	–11.25	–78.13	11.87	11.30±0.90
	Şana Creek Water	20.09.2004	–9.05	–55.82	16.58	13.00±2.05
	Ayder Creek Water	19.09.2004	–12.75	–83.76	18.24	12.50±2.20
Mineral Springs	Bereketli (Araklı) M.S	21.07.2004	–9.34	–63.53	11.19	7.7±1.95
	Bereketli (Araklı) M.S	27.04.2005	–9.22	–59.35	14.41	
	İkisu (Şana M.S	21.07.2004	–11.02	–76.96	11.2	1.70±1.75
	İkisu (Şana) M.S	27.04.2005	–11.21	–73.08	16.6	
	Durali (Maçka) M.S	22.10.2003	–10.19	–68.94	12.58	7.30±0.75
	Kisarna M.S	22.09.2004	–11.10	–69.82	18.98	6.85±2.05
Hot Spring	Ilıcaköy (İkizdere) Hot Springs	19.09.2004	–12.70	–96.34	5.26	3.10±2.00
	Ayder (Çamlıhemşin) Hot Spring	19.09.2004	–14.22	–93.61	20.15	0.00±1.80

7. RESULTS

Various rocks that have evolved during Liassic to Quaternary outcrop in the study area. Hot springs reach the surface faults and fractures in granitoides that continue evolving along the Late Cretaceous and mostly settled through

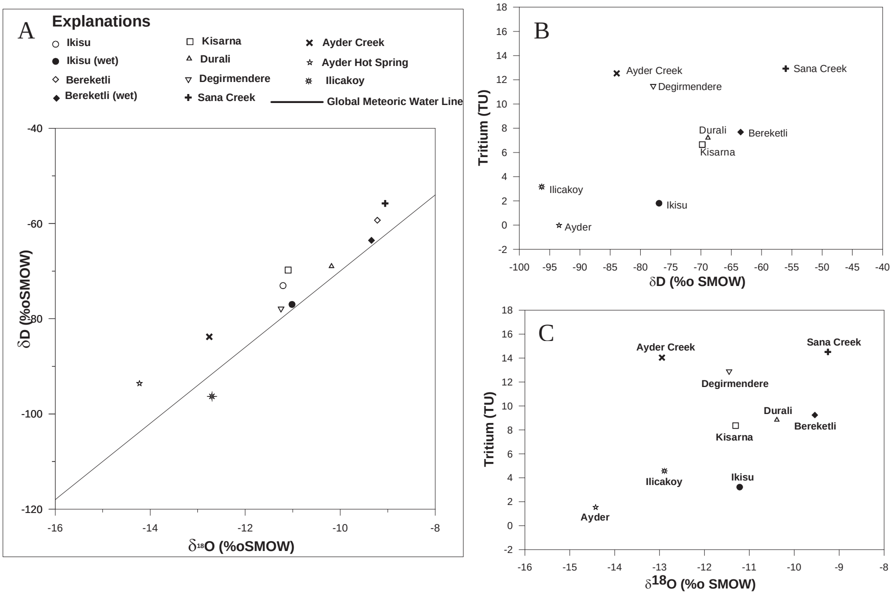

FIG. 5. In the investigated waters A. Relationship $\delta^{18}O$ – δDeuterium and Global Meteoric Water Line, B. Relationship δD – Tritium C. Relationship $\delta^{18}O$ – Tritium.

the end of Paleocene. Mineral springs reach the surface faults and fractures in Late Cretaceous aged basalt and basaltic pyroclastic rocks.

The Trabzon mineral springs have pH: 5.5–6.23, for EC: 506–5070 µS/cm, for TDS 374–5098 mg/L. Ayder hot spring has temperature 57°C, pH 9.07, EC 211µS/cm and TDS: 163 mg/L. Ilıcaköy springs have temperature 20–63°C, pH 6.5–6.78, EC 4300–5500 µS/cm and TDS 4012–4115 mg/L. Bereketli, Selimoğlu and Durali which are mineral springs, are in the classification of carbonated and sulphated waters with Ca + Mg > Na + K value. İkisu and Kisarna mineral springs are salty and sodic waters with Na + K > Ca + Mg value. But Ayder and Ilıcaköy are in class of $NaHCO_3$ water. Mineral springs are situated on the General Meteoric Water Line from the aspect of $\delta^{18}O$ – δD relationships. So, they are the springs with meteoric origin. Recharge elevation and transit time of the water system of the İkisu mineral spring is the longest considering oxygen-18 and tritium values. Although Kisarna mineral spring and İkisu mineral spring have the same recharge elevation Kisarna mineral spring has a shorter transit time of the water system. From the point of δD and Tritium relationship, mineral springs follows a shallow circulation. It is determined that Ayder and Ilıcaköy hot springs have a deeper circulation but the other mineral springs have partly deeper circulation. Ayder hot spring has a significantly higher altitude when compared to the others.

ACKNOWLEDGEMENTS

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ISOTOPIC AND GEOCHEMICAL TECHNIQUES APPLIED TO EFTENI AND DERDIN GEOTHERMAL SYSTEMS, NW TURKEY[1]

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Abstract

The Efteni and Derdin low-temperature geothermal areas are located in northwestern Turkey. Surface manifestations of relatively low-temperature springs (22–43ºC) emerge on the Düzce fault, a normal component dominated fault segment in the North Anatolian Fault System (NAFS). Ionic characteristics of the geothermal springs generally are Na > Mg > Ca and $HCO_3 > Cl > SO_4$. Isotopic and chemical evaluations show that there are two separate geothermal reservoirs in the area. Geothermometrical analyses applied to the Efteni and Derdin springs, representing these two separate reservoirs, reveal 113–135°C and 80–104°C respectively. Strong ^{18}O shift has been observed in the Derdin spring which has ~2 TU of tritium content indicating recent recharges. In the scope of this study, the thermal reservoirs and the physical processes that affect both springs are distinguished, and the hydrothermal structures of the springs are determined by chemical and isotopic analyses. Geothermometric equations, which are used to estimate reservoir temperatures, have been correlated using isotopic techniques and, in particular, dilution processes, such as surface water mixing, have been distinguished in the Derdin Spring.

1. INTRODUCTION

Efteni low-temperature geothermal area is located in the south-west of Düzce province, NW Turkey (Fig. 1). The area is characterized as an extremely tectonically active area. Large and frequent earthquakes are triggered by the influence of the westward motion of the Anatolian plate along the North Anatolian Fault (NAF). The last activity (Mw = 7.2) on November 12, 1999

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caused 845 fatalities in Düzce province and its vicinity. The study area is comprised of two distinct morphological units which have been formed by the Düzce fault which is a normal, component-dominated fault segment of NAF: (i). *The Ridge of Almacık block* comprises highlands to the south which have peak elevations ranging from 1500–1800 m asl. and (ii). *The Düzce plain* is a flat area to the north with altitudes ranging from 120–150 m asl. Surface manifestations of relatively low-temperature springs (22–43ºC) emerge on the active northern branch of NAF. The Efteni and Derdin geothermal areas have not been explored and reservoir rocks and reservoir temperatures have not been verified by exploratory drillings yet. In this study, hydrogeochemical and isotopic investigations of thermal springs have been carried out to evaluate reservoir lithologies, the origin and recharge mechanisms of the geothermal systems.

2. GEOLOGICAL AND HYDROGEOLOGICAL SETTINGS

The basement rock in the region is Precambrian Yedigöller formation which is mainly comprised of jointed and fractured metagranites, amphibolites and gneiss [1]. Lower Cretaceous Almacık Ophiolite Mélange is mainly composed of ultramafic rocks and Upper Cretaceous Akveren Formation overthrusting Eocene aged Yığılca and Çaycuma formations (Fig. 1). Unconsolidated Plioquaternary Karapürçek Formation and Quaternary alluvium unconformably overlie older formations. Metagranitic basement, volcanic and ultramafic rocks which outcrop mainly at the highlands of the area

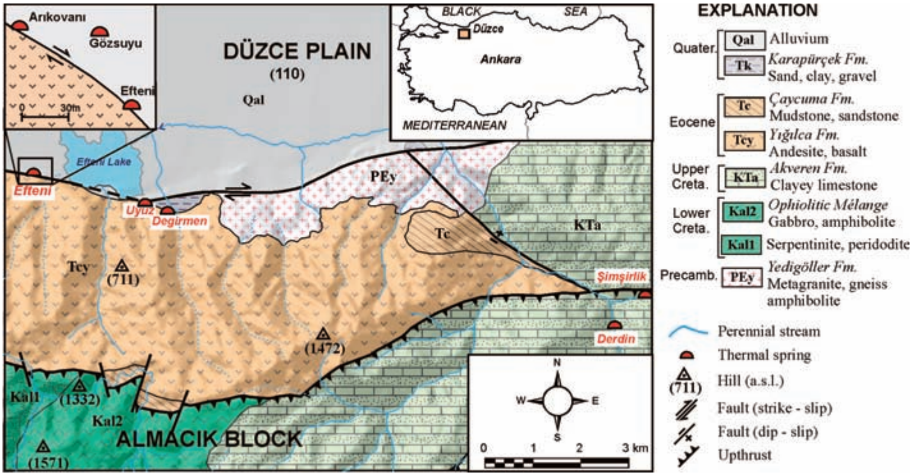


FIG. 1. Location and geological map of the study area (modified from [1]).

have low primary permeability. However, these brittle rocks have enhanced their secondary permeability by the development of joint and fracture systems due to active tectonics. Alluvium in the plain section of the Efteni geothermal area forms main cold groundwater aquifers. Akveren formation which is a sequence of mainly white, thick-bedded mudstones and clayey limestone has good cap rock characteristics due to its low permeability.

2.1. Thermal Manifestations

Efteni Spa Springs: the Efteni, Gözsuyu and Arıkovanı springs are the main thermal springs of the geothermal area. All the springs emerge upon contact with the Eocene volcanics and alluvium which are formed by the Düzce Fault to the south-west of Efteni Lake (Fig. 1). The Efteni spring has a flow rate of approximately 3.5 L/s whereas the others have less than 0.1 L/s.

Derdin and Şimşirlik Springs: the Derdin spring is located 17 km south of Düzce province. It has relatively high EC (7000 μS/cm) with 4 L/s. The spring emerges upon contact with the impervious Akveren formation and intrusive dacitic volcanics. Şimşirlik mineral water emerges at approximately 500 m south of the Derdin spring in a stream channel with a temperature of 18ºC and EC 3200 μS/cm. This is a typical seepage spring which emerges from several outlets with a total flow rate of 0.1 L/s.

Değirmen and Uyuz Springs: These springs emerge upon contact with the Eocene volcanics and Plioquaternary Karapürçek Formation (Fig. 1). The Değirmen spring has a flow rate of 0.5 L/s and a temperature of 25°C. The Uyuz spring is relatively cooler (23°C) and has a lesser flow rate (≈ 0.1 L/s). Both of the springs have low ionic concentration (EC ≈ 300–400 μS/cm).

4. GEOCHEMISTRY

The chemical compositions of water samples taken from the study area are given in Table 1. The thermal waters in the study area are sodium bicarbonate type. Chemical differences among the thermal waters can be shown in a semi-logarithmic Schoeller diagram (Fig. 2a). The diagram depicts two important findings regarding original relationships and mixing phenomena among the thermal waters.

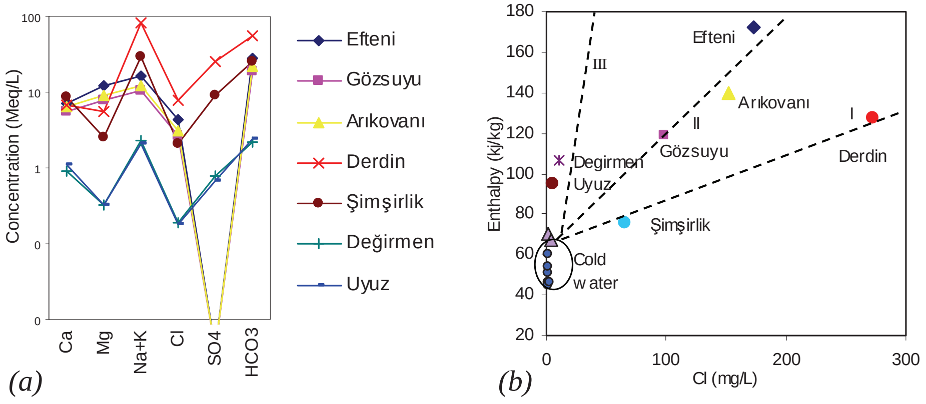
Firstly, there are at least two different reservoirs having distinct lithologies, these are represented by Efteni and Derdin springs. The similarity of the chemical composition of the Efteni spa springs, which are located very close to each other, is probably due to their origination from the same thermal aquifer.

This similarity can also be observed between the Derdin and Şimşirlik springs which have relatively higher ionic concentrations.

Another conclusion which can be made from the diagram is the similarity of the Değirmen and Uyuz springs which have lesser ionic concentration than the Derdin and Şimşirlik springs. This observation can be interpreted as showing that these springs have similar aquifer lithologies to the Derdin and Şimşirlik springs or that they have been diluted by young groundwaters during their ascent to the surface. As will be discussed in following sections, the Değirmen and Uyuz springs having relatively lower ionic concentration and high tritium content show that they represent the intermediate groundwater flow system in the area. They have no connection with the thermal reservoirs of the Efteni or Derdin springs and they may be warmed up due to the high

TABLE 1. CHEMICAL AND ISOTOPIC ANALYSES OF THERMAL SPRINGS IN THE STUDY AREA.

Sample	Efteni	Gözsuyu	Arıkovanı	Derdin	Şimşirlik	Değirmen	Uyuz
pH	6.31	6.45	6.21	6.42	6.4	7.89	7.81
EC (μS/cm)	3000	2000	2400	7000	3200	400	350
T (°C)	42.8	29.3	30	31	18	25	23
Ca (mg/L)	174	95	105	124	138	31	28.5
Mg (mg/L)	134	85	113	68	28	4.5	4.5
Na (mg/L)	385	220	305	1945	657	52.5	43.1
K (mg/L)	13	8.1	10.9	48.5	23	0.23	0.26
Cl (mg/L)	149	84.6	126.12	270.8	65	8.75	5.9
SO_4 (mg/L)	–	0.6	–	1220.2	421.3	46.6	27.9
HCO_3 (mg/L)	1808	1043	1369	3654	1669	173	170
$\delta^{18}O$ (‰ SMOW)	–11.21	–10.29	–10.70	-8.30	–10.59	–10.19	–10.73
δD (‰ SMOW)	–75.61	–71.17	–71.86	-70.03	–67.44	–66.98	–67.89
^3H (TU)	0.06±0.28	3.52±0.30	2.81±0.29	1.96±0.28	5.76±0.34	4.53±0.31	2.96±0.29



(a) *(b)*

FIG. 2. a) Schoeller diagram, b) Chloride- enthalpy diagram of the thermal waters.

geothermal gradient in the area. Consequently, low mineralized springs are representative of the Eocene volcanics of the area. The geochemical similarity between the Derdin spring and the Değirmen and Uyuz springs is reasonable considering the geological structure of the area. As can be seen from the geological map (Fig. 1) we have an Upper Cretaceous aged clayey limestone unit overthrusting Eocene volcanics. This geochemical similarity indicates the continuity of Eocene volcanics below the Upper Cretaceous unit.

Geothermal fluids are examined for possible mixing processes through conservative components such as Cl and Enthalpy. The Cl-Enthalpy diagram (Fig. 2b) indicates that there are two different mixing lines between the thermal springs. The Efteni spa springs coincide with mixing line (I) whereas the Derdin and Şimşirlik springs are on the mixing line (II). However, the Değirmen and Uyuz springs (which have lower Cl concentration when compared to other thermal manifestations) coincide with a different mixing line. It can be concluded from this observation that there is no hydraulic connection between the Değirmen (also Uyuz) spring and the Derdin springs. Consequently, the comparison of conservative components of the springs indicates that the chemical similarity between these springs is due to similar mineral-water interaction in different portions of the Eocene volcanics.

4.2. Geothermometry Applications

The temperatures of the two thermal reservoirs have been estimated by geothermometric equations. Cation geothermometers gave very wide temperature ranges (30–250 °C) and the position of thermal waters in the

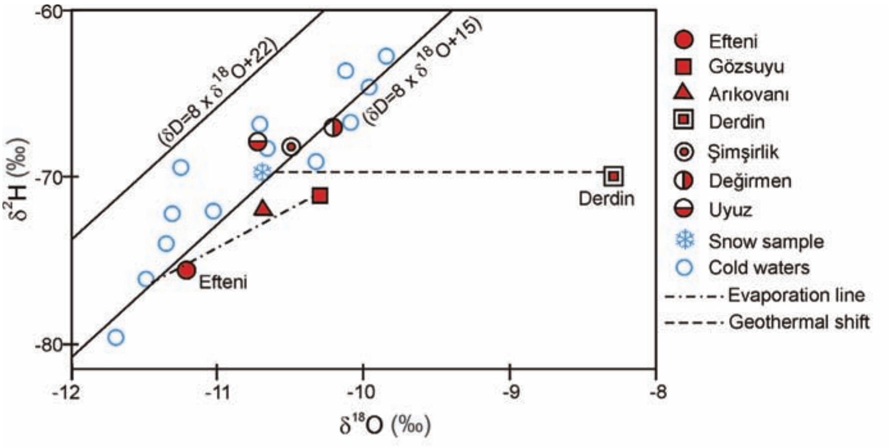


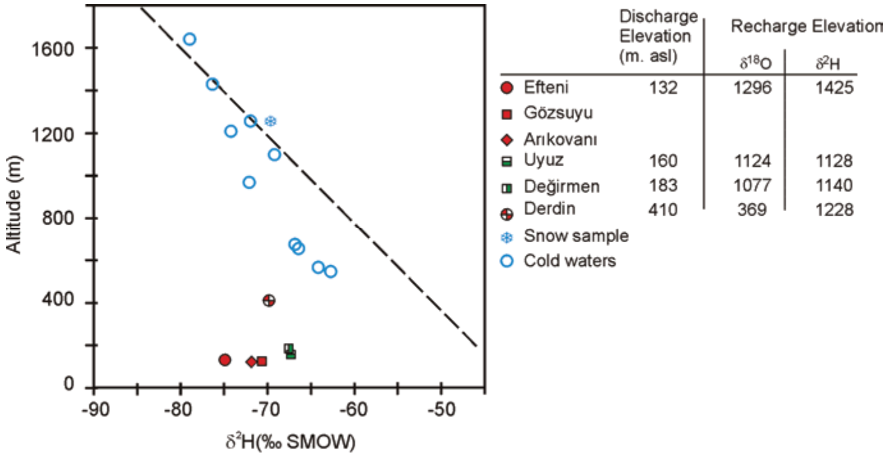
FIG. 3. $\delta^2H - \delta^{18}O$ diagram of the thermal and cold waters of the study area.

Na-K–Mg diagram proposed by [2], indicates that the chemical equilibrium has not yet been attained between rock and fluid in these reservoirs. Silica geothermometers are assumed to be more applicable. Quartz geothermometers derived relatively high temperatures but less than 180ºC. Reference [3] concluded that geothermal waters equilibrated with chalcedony below 180ºC but with quartz at higher temperatures. The reservoir temperatures of the Efteni and Derdin springs are estimated as 113–135ºC and 80–104ºC respectively, based on chalcedony geothermometers. Reference [4] calculated the reservoir temperature of the Efteni spring as 90–110ºC by the mineral equilibrium approach and concluded that the intersection of mineral saturation curves (albite, microcline, illite, epidote, chalcedony) indicate that the lithology of reservoir rock/rocks of the Efteni geothermal area are of magmatic or volcanic origin.

5. ISOTOPE HYDROLOGY

Stable isotopic ^{18}O and ^{2}H analyses were carried out to determine the origin of the thermal waters and the recharge area of the geothermal reservoirs. The Local Meteoric Water Line (LMWL) was obtained using the isotopic composition of cold water samples located at different altitudes of the Almacık ridge (Fig. 3). The equation of LMWL is the same as that for [5] the Marmara Region (NW Turkey): $\delta D = 8 \times \delta^{18}O + 15$.

Nevertheless, some water samples are present between the LMWL and the Eastern Mediterranean MWL [6]. Except for the Derdin spring, thermal



	Discharge Elevation (m. asl)	Recharge Elevation	
		δ^{18}O	δ^2H
● Efteni	132	1296	1425
■ Gözsuyu			
◆ Arıkovanı			
⊟ Uyuz	160	1124	1128
◫ Değirmen	183	1077	1140
⊕ Derdin	410	369	1228
❄ Snow sample			
○ Cold waters			

FIG. 4. δ^2H vs altitude relationship of the thermal and cold water springs of the study area.

waters are closed to the LMWL and this suggests that geothermal waters are meteoric in origin. A clear δ^{18}O shift from the LMWL due to isotope exchange by progressive water-rock interaction has been observed only in the Derdin spring.

The recharge areas of thermal springs are estimated via the stable isotopic composition-altitude relationship between a snow sample (1260 masl) and cold water springs having low ionic concentrations (Fig. 4). Regression equations computed from δ^{18}O and δ^2H against altitude are:

$$\text{Altitude (m)} = -370 \times \delta^{18}\text{O} - 2741 \ (R^2=0.86) \text{ and}$$
$$\text{Altitude (m)} = -39.7 \times \delta^{2}\text{H} - 1546 \ (R^2=0.95)$$

The average recharge elevations of thermal springs computed from the above mentioned equations are given in Fig. 4. Due to ^{18}O enrichment in the Derdin spring, the recharge elevation based on the δ^{18}O-altitude relationship computed lower than the discharge elevation. By ignoring geothermal shift in the Derdin spring, the average recharge area altitudes calculated from δ^{18}O-Altitude and δ^2H-Altitude relationships, reveal that the thermal springs are recharged mainly from the highland parts of the Almacık mount which has peak elevations ranging between 1500–1800 m.

Tritium concentrations of the cold water samples are close to the tritium concentration of recent precipitations (~10 TU). The low tritium content of the Efteni spring shows that the thermal aquifer is recharged by groundwater having a relatively long residence time (>55 years) which represents a deep

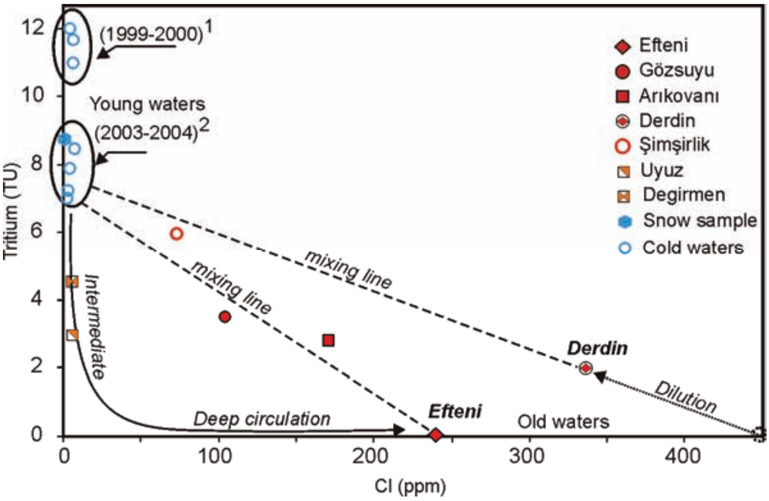


FIG.5. Tritium – Cl diagram of the thermal and cold waters of the area ([1] previous data from Ref. [7], [2] recent data).

circulation groundwater flow system in the study area. The Derdin spring has relatively high tritium content (~2 TU) compared to the Efteni spring, indicating recent recharges. The contradiction between tritium content, which is indicative of recent recharge, and strong ^{18}O shift in the Derdin spring, is a reflection of the mixing process between young waters and thermal waters.

Groundwater circulation systems in the area are classified in their groups according to the chloride concentration and tritium content of cold and thermal waters (Fig. 5). A deep circulation groundwater flow system is represented by the Efteni spring with its relatively high chloride concentration and low tritium content. A shallow circulation system is represented by cold waters having low ionic concentration and tritium content close to recent precipitations. Finally, an intermediate groundwater flow system is represented by the Değirmen and Uyuz springs which have tritium and chloride concentrations between old and young groundwaters.

Similar mixing lines have been constructed in Tritium-Cl graph. The Arıkovanı and Gözsuyu springs are on the mixture line between the Efteni spring and cold waters. Similarly the Şimşirlik spring is between the Derdin spring and cold waters. The most important conclusion from Fig. 5 concerns the dilution process in the thermal waters of the Derdin spring. This reveals that the geothermal shift in the Derdin spring should be stronger than observed and the reservoir temperatures based on silica concentrations are underestimated due to dilution and probable silica polymerization.

6. CONCLUSIONS

Although the reservoir temperature of the Efteni spring computed higher than the Derdin spring, ^{18}O enrichment due to water-rock interaction at high temperatures was observed only in the Derdin spring. Nevertheless, the presence of tritium, which is indicative of recent recharge, concludes that the Derdin spring is affected by a mixing process and the geothermal shift in this spring should be stronger than observed. This shift could be related to the carbonate rich rocks of the Akveren formation. However this formation is hydrogeologically impervious and the chemical features of the Derdin spring do not reflect a carbonate aquifer. In particular, the Schoeller diagram illustrates that this spring resembles springs having low ionic concentrations discharging into Eocene volcanics.

Underestimation of reservoir temperatures via silica geothermometers for Derdin spring is probably due to dilution process observed in Tritium–Cl graph. Actually, there are two distinct processes which affect silica concentration by mixing of young waters. These processes are; decreasing silica concentration due to the mixing of cold fresh waters and silica polymerization due to an instantaneous fall of temperature. Reservoir rocks of two geothermal reservoirs in the area represented by Efteni and Derdin spring are probably Precambrian metagranites (Yedigöller formation) and Eocene volcanics respectively. Consequently, both the reservoirs having silicate rocks but ^{18}O enrichment observed in Derdin spring is due to high reservoir temperature. From this point of view, reasons of this higher reservoir temperature estimated in Derdin spring are:

(a) Reservoir of Efteni spring is covered by Eocene volcanics which do not have good cap rock characteristics. Presence of young waters having low ionic concentration but relatively high discharge temperature in Eocene volcanics reveals relatively high thermal conductance.

(b) Reservoir of Derdin spring covered by impervious Akveren formation (clayey limestone) which has good cap rock characteristics. This features of Akveren formation leads conservation of high reservoir temperatures by the geological time.

Chemical and isotopic features of Efteni and Derdin springs suggest the existence of two distinct thermal aquifers in the study area. The geothermal waters are mainly Na–HCO_3 type waters. Reservoir temperatures were estimated via geothermometry applications as 113–135ºC. Stable isotopic composition shows that the geothermal waters are mainly of meteoric origin. Clear ^{18}O shift of Derdin spring from LMWL is probably due to ^{18}O isotope exchange by water- rock interaction. Average recharge area altitudes of thermal springs calculated from ^{18}O-Altitude and ^{2}H relationships reveal that the thermal springs are recharged mainly from the highland parts of the Almacık mount.

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ISOTOPIC EVALUATION OF GEOTHERMAL WATERS IN KONYA REGION (TURKEY)

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Abstract

Konya region (Turkey) has three important geothermal subregion. These are Cihanbeyli, Beysehir-Seydisehir-Ilgin and Ismil-Eregli subregions. Geothermal waters in the region have temperature between 19.8–51°C, discharge between 0.1–130 L/s and total mineralization range from 852 to 5110 mg/L. The isotopic analysis evaluated according to ^{18}O/^{2}H, ^{18}O/TU, Cl/TU, pH/EC and Giggenbach diagrams. The geothermal water aquifers are recharged from higher altitudes and they are hardly affected by recent precipitations and these waters reveal meteoric origin. They have more negative δ^{18}O and δ^{2}H values and lower ^{3}H contents compared to cold waters. The reservoir rock temperature is 250°C, and water depths are ranging from 500 to 1000 m. The waters are heated from volcanism and geothermal gradient.

1. INTRODUCTION

Konya region, located in Middle Anatolia, has significant number of thermal spring (Fig.1). Some studies have been carried out in this area [1-11]. Temperature, electrical conductivity and pH values of these water were measured by using WTW mark portable analysis equipment. Samples are collected from these waters for hydrochemical and isotopic analyses.

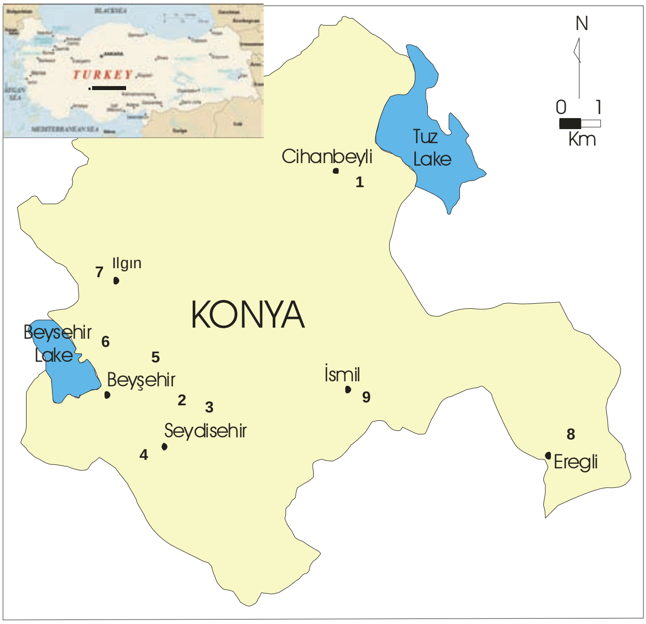

FIG. 1. Location map of the study area and the samples.

2. GEOLOGY

Geological features are compiled from previous studies. The basement of C-subregion is Middle Triassic-Upper Jurassic aged Ballıklı Tepe formation formed dolomitic limestone. Ballıklıtepe formation located around Cihanbeyli thermal water. Upper Cretaceous aged Koçkaya formation formed sandstone, calsiturbidite, shale intercalation, serpantinite and volcanic sandstone with tectonic contact. Upper Miocene- Pliocene aged İnsuyu formation came with unconformability on Koçkaya formation. Upper Miocene-Pliocene aged Çaltepe andesites observed around of Karadağ and cutting İnsuyu formation. Çaltepe andesites are covered by Tuz lake formation. Plioquaternary aged Cihanbeyli formation came with unconformity. Travertine is located an upper part of the area.

BSI-subregion has Cambrian aged Çaltepe formation formed dolomite, dolomitic limestone and limestone. Upper Cambrian-Lower Ordovician aged Seydisehir formation formed metasandstone and shale came over Çaltepe formation. Triassic aged Pınarbaşı formation and Middle Triassic aged Tarasçı formation came over Çaltepe formation with conformity. Upper Triassic aged

Sarpyardere formation, Jurassic aged İçerikışla formation Upper Miocene-Pliocene aged Katrangediği formation came over young formations. Upper Miocene- Pliocene aged İnsuyu formation formed limestone and marl and Quaternary aged travertine came over Katrangedigi formation.

Upper Eocene-Oligocene aged Sivritepe anhydrite located in IE-subregion. Kurtulmuştepe formation came over Sivritepe anhydrite with conformity. Miocene aged Kızılöz formation formed sandstone, claystone and conglomerate. İnsuyu formation came over this formation. Quaternary aged alluvium and travertine came over all formations.

3. HYDROGEOLOGY

Exploitation of geothermal energy depends on heat source, reservoir, cover rocks and water supply. Meteoric waters going down through the fissures and fractures by the effect of gravity and heated by geothermic gradient. Heated waters rise through the faults acting as hydrothermal channels due to hydrostatic pressure, fissures, density contrast between hot and cold water, expansion etc. and form hot and mineralized springs at the surface. Hydrochemical features are given in Table 1.

3.1. Defining hydrochemical analysis results

The thermal waters of C-subregion are classified as “F–Ca–Na–SO_4–HCO_3–Cl hot and mineralized waters” according to [12]. The thermal waters of IE-subregion classified as “Ca–Mg–Na–SO_4–HCO_3 hot and mineralized water” and “I–F–Na–Cl hot and mineralized water”. The thermal waters of BSI-subregion classified as “Ca–Mg–SO_4 hot and mineralized water” and “Na–Ca–HCO_3 hot and mineralized water” except Ilgin spa, “aquatherm”. The whole thermal waters classified according to Piper diagram [13] in 1st region except sample 9. So, these waters are named “Ca + Mg > Na + K” and “carbonate and sulphate water”. The thermal waters are “immature waters” properties according to Giggenbach diagram. The reservoir rock temperature calculated by geothermometers is 250°C and water depths are ranging from 500 to 1000 m. According to Giggenbach diagram [14] geothermal fields of Konya region plot into the immature fields (Fig. 2). The thermal waters on Schoeller diagram [15] show lines combining anions and cations are approximately parallel.

TABLE 1. ANALYSIS RESULTS OF THE GEOTHERMAL WATERS IN KONYA REGION.

Sub region	Water samples No./name	T (°C)	pH	EC (µS/cm)	Hard. (Fr)	Ca	Mg	Na	K	Cl	SO_4	CO_3	HCO_3
						mg/L							
C	1. Cihanbeyli	20.4	6.8	5110	222	888	0.0	631	17.1	560	2289	0	536.8
BSI	2. Kavakkoy drill-1	51	6.3	3180	108	424	4.8	313	8.4	210	226.7	0	1512
	3. Kavakkoy gazlı spring	19.8	6.3	4130	158	576	33.6	402	84.1	260	302.9	0	2293
	4. Ilica spring	29.3	7.2	852	40	140	12	17.4	4.8	25	46.8	0	439.2
	5. Koskkoy spa	35.7	7.1	1224	74	192	62.4	29.3	2.9	20	594.5	0	195.2
	6. Cavus spa	28	6.3	1337	79	264	31.2	20.8	6.9	20	245.5	0	683.2
	7. Ilgin spa	41.3	6.4	1005	42	140	16.8	43.3	11	25	127.7	0	439.2
IE	8. Akhuyuk spring	31	6.4	4760	242	640	196	1262	933	35	5849	0	268.4
	9. Ismil	42.9	6.4	3820	83	420	105	320	22	410	810	0	1050

3.2. Isotopic Analysis

Water samples are plotted close to the LMWL in $\delta^{18}O-\delta^{2}H$ plot (Figs 3 and 4). This result shows that the waters are of meteoric origin. Thermal waters have high ^{3}H value but cold waters have low ^{3}H value. In other words, the hot waters are having long term deep (>50 year) hydraulic cycle and cold waters have shallow hydraulic cycle. It can be said that the mineralized waters are mixture of hot and cold waters (Table 2, Fig. 2).

Water samples approach to Antalya Meteoric Water Line (AMWL = GMWL + 16) above Global Meteoric Water Line [16]. This samples increase proportional with recharge area. According to d_{excess} = +10 to +16, groundwater recharge from Mediterranean rain. According to the ^{18}O–TU graph (Fig. 5), 1, 2, 3 and 4 numbered samples are recharge at higher altitude and have deep circulation. The others are deep circulating waters recharged from low altitude. Three different circulation systems were found according to Cl/TU graph (Fig. 6). Samples 5, 6 and 8 are reflecting deep circulation system; sample 1 is affected wide apart process with impression of surface water and cold groundwater (Fig. 6). Waters are connate water and deep circulation in the pH/EC graph, except samples 4, 5 and 6 (Fig. 7).

TABLE 2. ISOTOPE VALUES OF THE SAMPLES.

Sub region	Water samples No./name	01/2005			10/2005		
		$\delta^{18}O$ (‰)	δD (‰)	3H (TU)	$\delta^{18}O$ (‰)	δD (‰)	3H (TU)
C	1. Cihanbeyli	–8.69	–63.45	5.45 ± 2.06	–9.54	–65.01	1.20 ± 1.05
	2. Kavakkoy drill-1	–10.21	–65.16	4.50 ± 2.10	–10.36	–63.42	1.20 ± 1.15
	3. Kavakkoy gazlı spr	–10.20	–64.75	4.15 ± 2.00	–10.29	–62.83	0.80 ± 1.10
BSI	4. Ilica spring	–10.10	–62.87	4.45 ± 2.05	–10.13	–60.10	0.95 ± 1.15
	5. Koskoy spa	–10.45	–67.81	2.20 ± 2.00	–10.67	–64.40	0.80 ± 1.15
	6. Cavus spa	–10.69	–69.91	0.55 ± 2.00	–10.77	–66.80	0.15v1.15
	7. Ilgin spa	–10.15	–69.30	2.40 ± 1.95	–10.61	–68.58	0.00 ± 1.10
IE	8. Akhuyuk spring	–9.98	–9.98	0.90 ± 2.00	–9.71	–8.80	0.00 ± 1.10
	9. Ismil	–	–	–	–9.06	–58.55	0.00 ± 1.10

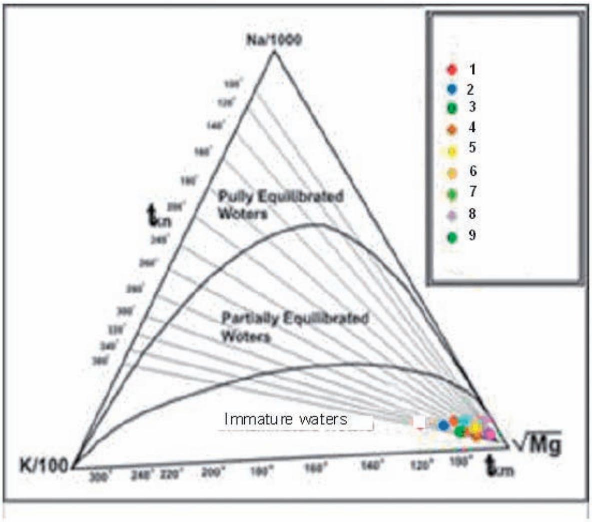

FIG. 2. Giggenbach diagram of the samples.

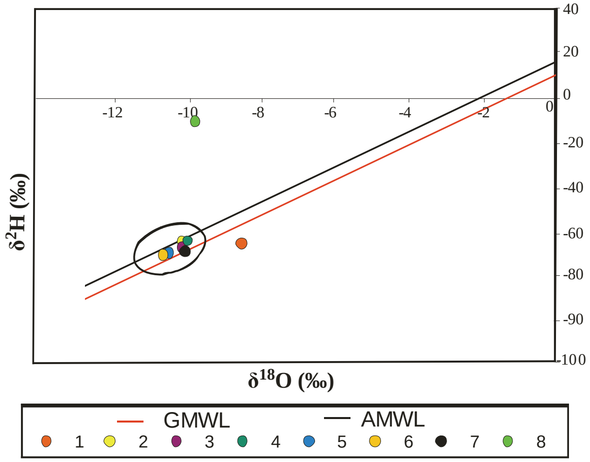

FIG. 3. $^{18}O/^{2}H$ plot of the samples(01/2005).

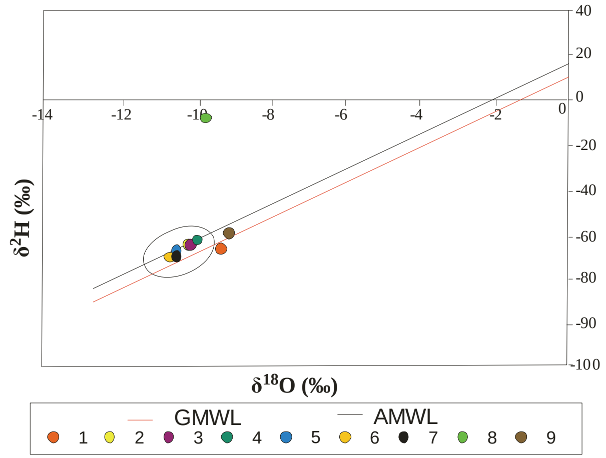

FIG. 4. ^{18}O/^{2}H plot of the samples (10/2005).

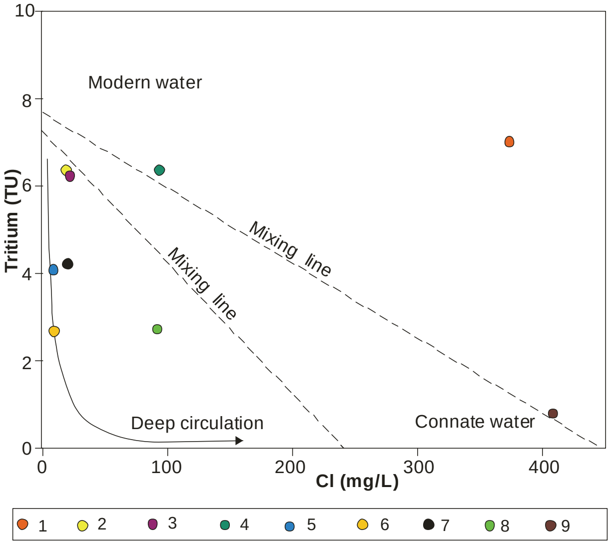

FIG. 5. Chloride/Tritium plot of the samples(01/2005).

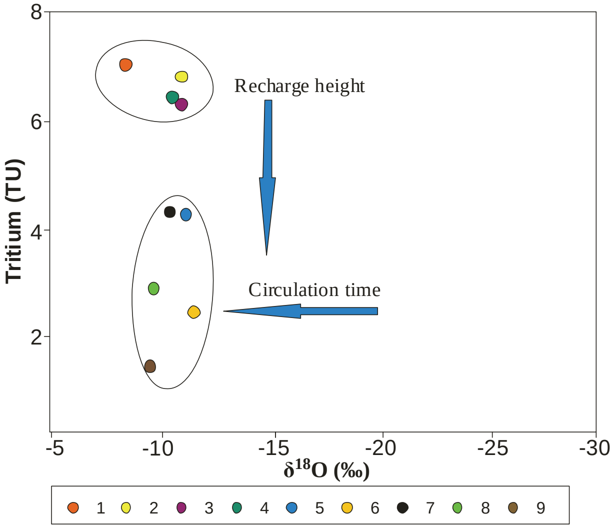

FIG. 6. Tritium/^{18}O plot of the samples (01/2005).

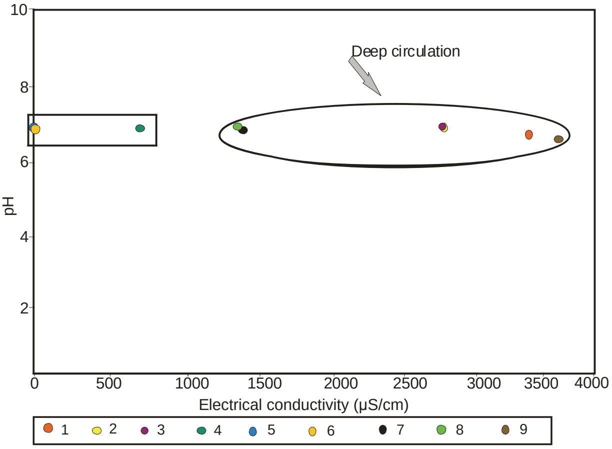

FIG. 7. pH/EC plot of the samples (01/2005).

4. CONCLUSIONS

1. Each geothermal water has different geological, hydrogeological and physicochemical properties.
2. In the scope of whole studies, hot and mineralized waters around C-subregion have temperature range from 17.5 to 29°C, discharge is 1.2 L/s and total mineralization range from 4587 to 5139.5 mg/L. Thermal waters around the IE-subregion have temperature between 18–42.9°C, discharge between 0.45–2 L/s and total mineralization between 5207–35449 mg/L. BSI-subregion's thermal waters has temperature range from 19.8 to 51°C, discharge between 15 to 130 L/s and total mineralization between 852–4130 mg/L.
3. The waters are of meteoric origin and immature according to the $\delta^{18}O - \delta^{2}H$ plot and Gigenbach diagram.
4. Some samples have high altitude and deep circulation according to the ^{18}O–TU graphic and some waters are connate water and deep circulation according to the pH/EC graphic. Three different circulation systems were found according to Cl/TU graphic.

ACKNOWLEDGMENTS

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ISOTOPIC AND HYDROCHEMICAL PROPERTIES OF HOT AND MINERALIZED WATERS IN SW KONYA GEOTHERMAL FIELD (TURKEY)

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Abstract

The study area is located at southwest part of Konya (Central Anatolia). The basement formation of the area is Çaltepe, deposited from Early Cambrian through Middle Cambrian. Seydişehir Formation which is composed of alternating slate, sandstone and metasandstone overlies conformably the overthrown Çaltepe Formation and is Upper Cambrian-Lower Ordovician in age. Seydişehir Formation is conformably underlined by Neocene in age Tarasçı Limestone. Alluvium is Quaternary-Present in age.

The hot and mineralized waters located in the study area around Ilıcatepe and Kavakköy villages have a temperature range between 31°C and 46°C, flow rate between 1.42 and 5 L/s and a total dissolved mineral between 2218–3500 mg/L. Aquifer of these waters are the porous limestone and dolomitic limestone of the Çaltepe formation. The travertine cones occur as a result of water activity. The waters classified according to the AIH standards are Ca, Na, HCO_3, and B bearing hot and mineralized water.

The oxygen and hydrogen isotope compositions of geothermal waters reveal meteoric origin. They have more negative $\delta^{18}O$ and $\delta^{2}H$ values, and lower ^{3}H contents compared to cold waters. The geothermal water aquifers are recharged from higher altitudes and are hardly affected by recent precipitations.

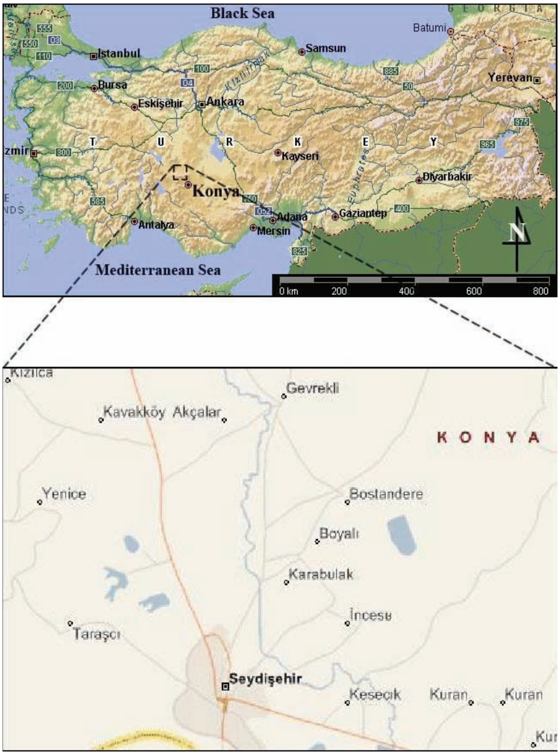

FIG. 1. Location map of the study area.

1. INTRODUCTION

Konya has important potential of hot and mineral waters in Inner Anatolia region (Fig. 1). The temperatures and discharges of hot and mineral waters in Seydişehir region are suitable for thermal tourism. Some studies have been carried out in this area [1–3, 5, 7–12]. Temperature, electrical conductivity and pH values were measured by using WTW portable analysis equipment. Samples were collected from these waters for hydrochemical and isotopic analyses.

2. GEOLOGY

Lower-Middle Cambrian Çaltepe formation, comprising of limestone and dolomite forms the basement rock in the study area. Seydişehir formation conformably overlies Çaltepe formation and is composed of metasandstone, shale and phyllite. Pinarbaşi and Taraşa formation, mostly carbonates, disconformably on the Seydişehir formation. The sequence continues with

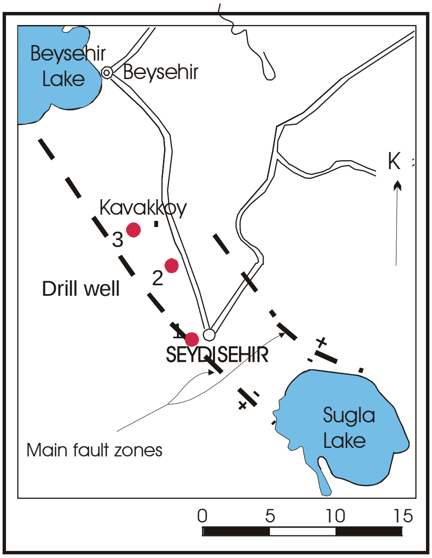

Fig. 2. Fault directions of the study area.

detritics Sarpyardere and İçerikışla formation. Travertine and alluvium partly cover all above mentioned formation.

3. HYDROGEOLOGY

Exploitation geothermal energy depends on heat source, reservoir, cover rocks and water supply. Meteoric waters going down through the fissures and fractures by the effect of gravity are heated by geothermic gradient (Figs. 2 and 3). Heated waters rise through the faults acting as hydrothermal channels due to hydrostatic pressure, fissures, density contrast between hot and cold water, expansion etc. and form hot and mineralized springs at the surface. Hydrochemical features are given in Table 1.

4. SPRINGS AND DRILLINGS

Hot and mineral water rise to the surface by means of springs and drillings in the study area. Springs are located along the NW–SE fault (Fig. 2). Temperature of springs is 18.5–34°C, discharge is 0.1–3 L/s, pH is 6.7–7.1, EC is 852–4130 μS/cm and total mineralization is 706–3555 mg/L. Temperature of drillings is 43.3–51°C, discharge is 40 L/s (artesian) and depth is 317 m.

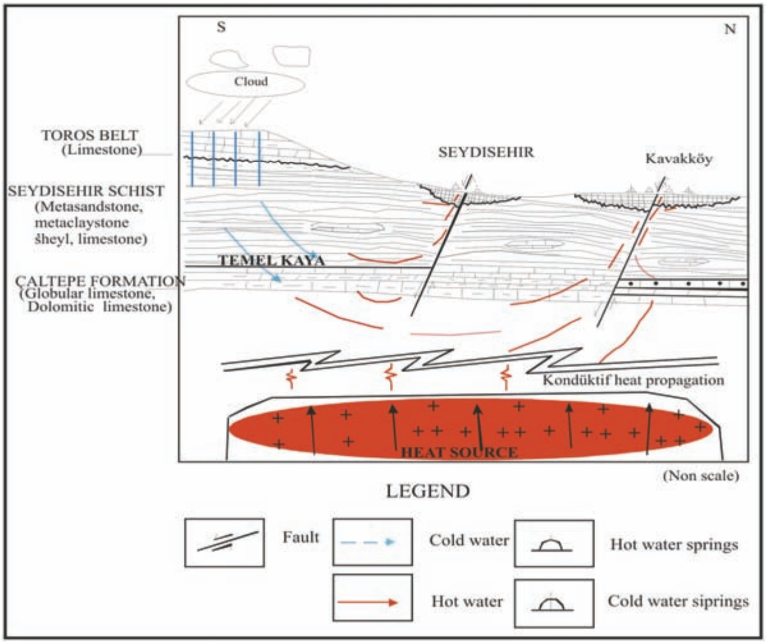

FIG. 3. Geothermal model of the study area.

4.1. Hydrochemical analysis

The thermal waters of Seydişehir district are classified as “Ca–Mg–SO_4 hot and mineralized water” and “Na–Ca–HCO_3 hot and mineralized water”. The thermal waters have “immature waters” properties according to Giggenbach diagram [6] (Fig. 4). The reservoir temperature calculated by using geothermometers as 250°C and water depths are ranging from 500 to 1000 m.

4.2. Isotopic Analysis

The relationship between ^{18}O and ^{2}H is linear. This result shows that the waters are of meteoric origin. Thermal waters have high ^{3}H value but cold waters have low ^{3}H value. In other words, the hot waters are having long term deep (>50 year) hydraulic cycle and cold waters have shallow hydraulic cycle. It can be said that the mineralized waters are mixture of hot and cold waters (Table 2).

TABLE 1. HYDROCHEMICAL RESULTS (mg/L; EXCEPT NOTED) OF THE WATERS.

Water samples No./name	T(°C)	pH	EC (µS/cm)	Hard. (Fr)	Ca	Mg	Na	K	Cl	SO_4	CO_3	HCO_3
1. Kavakkoy drill-1	51	6.3	3180	108	424	4.8	313	8.4	210	226.7	0	1512
2. Kavakkoy gazlı spring	19.8	6.3	4130	158	576	33.6	402	84.1	260	302.9	0	2293
3. Ilica spring	29.3	7.2	852	40	140	12	17.4	4.8	25	46.8	0	439.2
4. Kavakköy drill-2	43.3	6.9	3760	242	297	79.1	297	86	214	47	0	2016

TABLE 2. ISOTOPE CONTENTS OF THE SAMPLES.

Water samples No./name	01/2005			10/2005		
	δ^{18} (‰)	δD (‰)	^{3}H (TU)	δ^{18}O (‰)	δD (‰)	^{3}H (TU)
1. Cihanbeyli	–8.69	–63.45	5.45 ± 2.06	–9.54	–65.01	1.20 ± 1.05
2. Kavakkoy drill-1	–10.21	–65.16	4.50 ± 2.10	–10.36	–63.42	1.20 ± 1.15
3. Kavakkoy gazlı spr	–10.20	–64.75	4.15 ± 2.00	–10.29	–62.83	0.80 ± 1.10

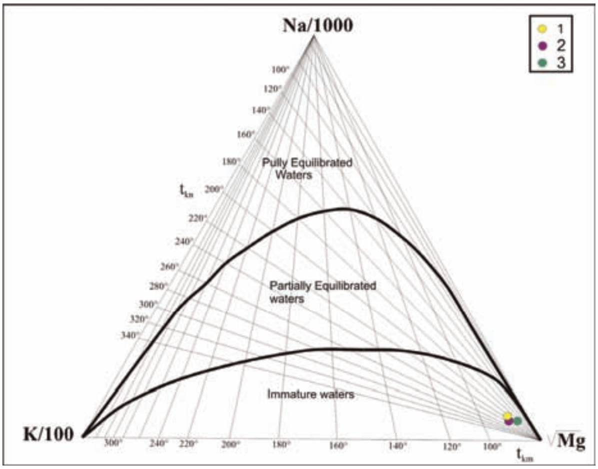

FIG. 4. Giggenbach diagram of the samples.

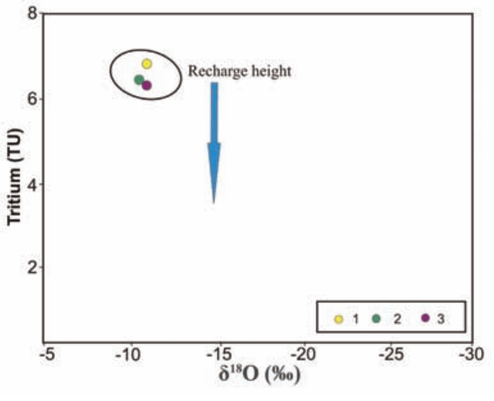

FIG. 5. ^{18}O/^{3}H plot of the samples (01/2005).

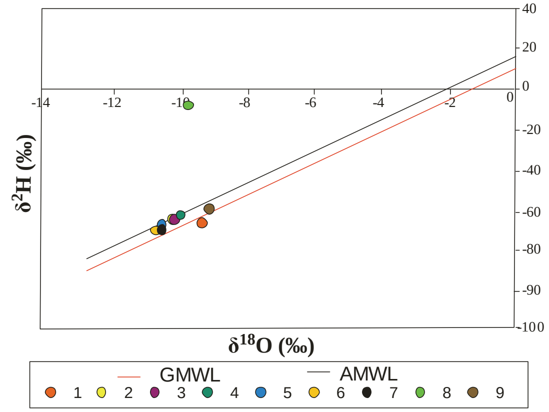

FIG. 6. ^{18}O/^{2}H plot of the samples(01/2005).

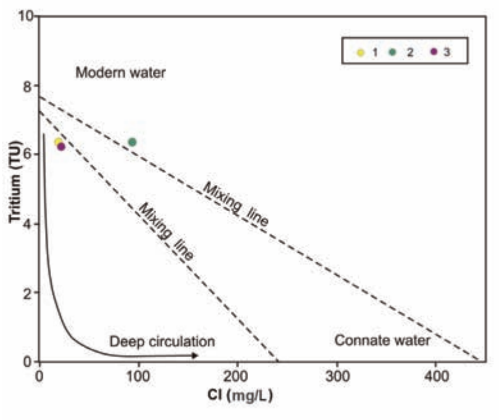

FIG. 7. Chloride–tritium plot of the samples (10/2005).

Water samples approach the Antalya Meteoric Water Line (AMWL = GMWL+16) over the Global Meteoric Water Line [4]. This samples increase proportional with recharge area. According to approach of skew +10 to +16, groundwater are recharged from Mediterranean rain of far past and change to territorial rains (Fig. 5 and 6). According to the ^{18}O–TU diagram 1, 2, 3 and 4 numbered samples receive recharged at high altitude and have a deep circulation. The other waters are characterized by deep circulation recharging from low altitude. Three different circulation systems were found according to Cl/TU graphic. Samples 1, 2 and 3 are reflecting deep circulation system; sample 1 is affected by (surface water and cold groundwater (Fig. 7). These are

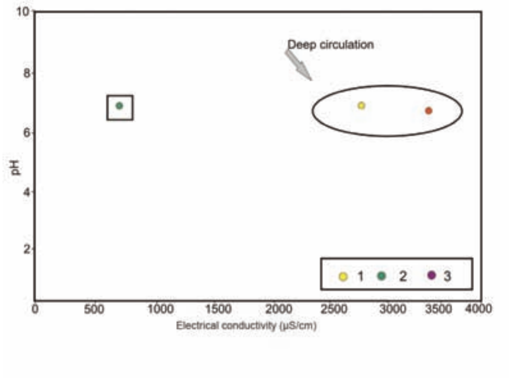

FIG. 8. pH/EC plot of the samples (01/2005).

connate showing deep circulation in the pH/EC graphic, except samples 4, 5 and 6 (Fig. 8).

5. CONCLUSIONS

1. Temperature of springs is 18.5–34°C, discharge is 0.1–3 L/s, pH is 6.7–7.1, EC is 852–4130 µS/cm and total mineralization is 706–3555 mg/L Temperature of drillings is 43.3–51°C, discharge is 40 L/s (artesian) and depth is 317 m.
2. Thermal waters plot between SMWL–MSRWL, indicating high altitude of recharge and deep circulation, according to the isotopic analysis.
3. Some samples were recharged at high altitude and undergo deep circulation according to the ^{18}O–TU graphic. Some waters are connate and shown a deep circulation according to the pH/EC graphic. Three different circulation systems were found according to the Cl/TU plot.
4. It is necessary to increase the geothermal waters temperature and discharge with drillings to use in thermal tourism. The springs should be prevented from contamination by applying protection zones.

ACKNOWLEDGMENTS

This investigation was made possible through the financial support of Selcuk University Scientific Research Project (BAP Project Number: 2004/045).

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HYDROGEOCHEMICAL AND ISOTOPIC EVALUATION OF THERMAL AND MINERALIZED WATERS OF TERME-(KIRŞEHIR) AND KOZAKLI (NEVŞEHIR), AREAS, TURKEY

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Abstract

In the Central Anatolian Region, two neighboring cities of Kırşehir and Nevşehir have significant thermal and mineral water potentials. The Kırşehir massive and Cenozoic magmatic units are exposed around Terme and Kırşehir areas. Around Kozaklı (Nevşehir), the Kırşehir massive is overlain by thick salt layers such as gypsum type evaporitic rocks of Oligocene age. Thermal and mineral waters are mostly manifested through the normal faults. Lower parts of Oligocene deposits in Kozaklı are composed of conglomerate and sandstone. Thermal and mineral waters that form aquifer in fractures of marble and schists of the Kırşehir massive are accumulated via buried faults in Oligocene conglomerate and sandstones which comprise another aquifer with warmer temperature. On the contrary, in the Kırşehir area, faults that cut the Pliocene cover within the marble and massive pebbly schists transport the water to the surface. In Kırşehir-Terme, springs have discharge temperature of about 41°C, but temperature reach 60°C in the bottom hole. Temperature of waters in the Kozaklı area is 90–98°C while it exceeds 100°C in the bottom hole. The water types of Kırşehir and Kozaklı area are $Ca–HCO_3$ and Na–Cl, respectively. Environmental isotope results (^{18}O, ^{2}H, ^{3}H, ^{13}C) indicate that thermal waters have a meteoric origin and some of rainwater is percolated downward along fracture and faults and heated at depth and then rises to the surface along fractures and faults which act as hydrothermal conduit.

1. INTRODUCTION

The Kırşehir and Nevşehir cities in the Central Anatolia are characterized by significant potential of thermal and mineral waters (Fig 1). In the Kırşehir city, the Terme springs within the N-S extending Kılıçözü valley are manifested at an elevation of 980 m. The Kozaklı-Nevşehir geothermal area 75 km from the east of Kırşehir extends along a NW-SE trend at southeast of the town center.

Thermal springs are issued along a valley in the Nevşehir Kozaklı resort area of 1.5 km length and 200 m width. Waters of these springs are used for heating and balnelogical purposes. By this time, several works have been conducted in the Kırşehir and Kozaklı geothermal areas. The aim of this study is to investigate hydrogeochemical and isotopic characteristics of thermal waters in the Kırşehir and Nevşehir regions and to determine their origin.

2. GEOLOGY

2.1. Kırşehir Terme Resort

The rocks of the Kırşehir Massive are the oldest unit around the Kırşehir Terme resort and surroundings. The basement is comprised by Paleozoic metamorphic schist and marbles which are interbedded with white colored quartzites with thickness of a few ten cm. The thickness of metamorphic schists is more than 1000 m. They are cut by granites of Paleocene age [1] . The Eocene conglomerate and sandstones unconformably overlie the older units. At

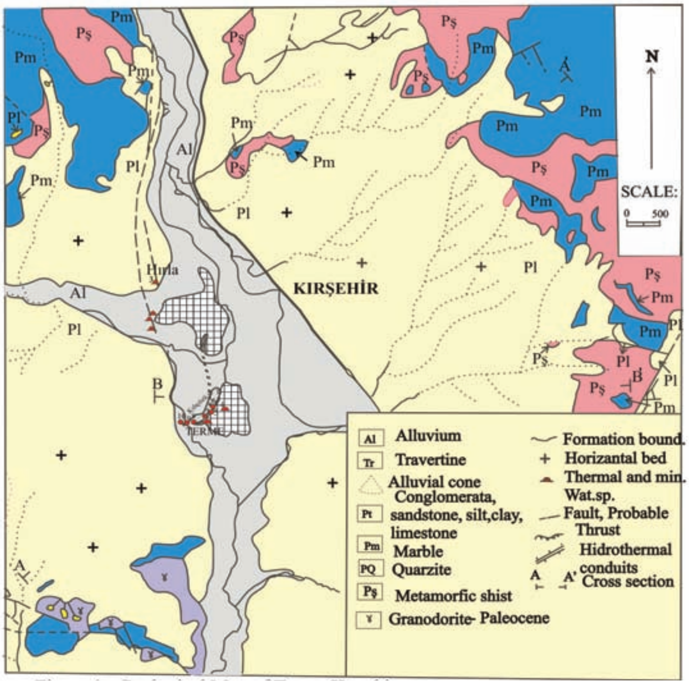

FIG. 1. Geological map of Terme-Kirşehir

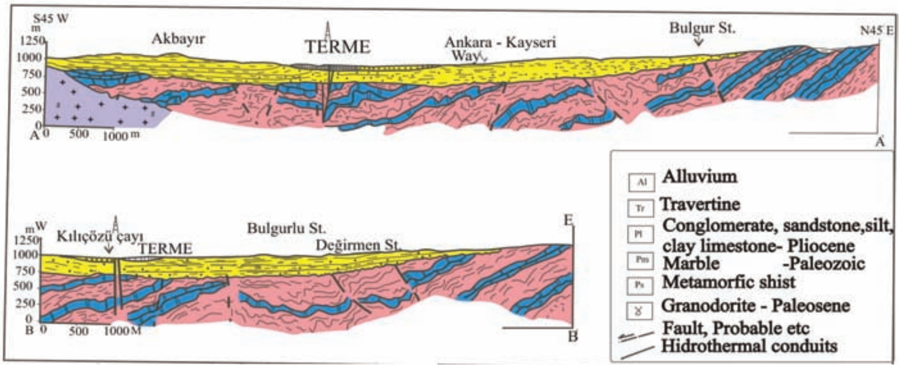

FIG. 2. Geological cross-section.

north and western parts of the area, they are covered with horizontal bedded Pliocene conglomerate, sandstone, clay and limestone. Quaternary alluvium and travertines are widely exposed in the area (Fig. 1, 2).

2.2. Nevşehir-Kozaklı Resort

Since Kozaklı geothermal field is very close to the center of Kozaklı town, the geothermal potential and economic use of thermal waters in this field have been subjected to various works [2–11] . The geology of the area was revised from previous works (Fig. 3). The metamorphic schists at the basement are not exposed around the Kozaklı resort and they are observed at higher elevations of the area. It is believed that metamorphic rocks could be found below the Oligocene units around the Kozaklı area. The Oligocene and Miocene units are the oldest rocks exposing in the study area. The Oligocene-Miocene formation above the Lutetian and older units comprises the N-NW part of the area. The Oligocene-Miocene formation [5] is represented by red colored claystone, conglomerate and sandstone at the lower levels and by multi-colored clays and marls together with gypsiferous and salty units to the top. This unit is unconformably overlain by Miocene tuffite, conglomerate and marl and Pliocene lacustrine limestone, marl, tuffite and clayey limestones. Quaternary alluvium and travertines are found at the upper most part. The Erciyes volcanism which was started in the Neogene time was very effective in formation of thermal and mineral waters in the study area. The activity of volcanism was probably continued during the Pliocene [12] .

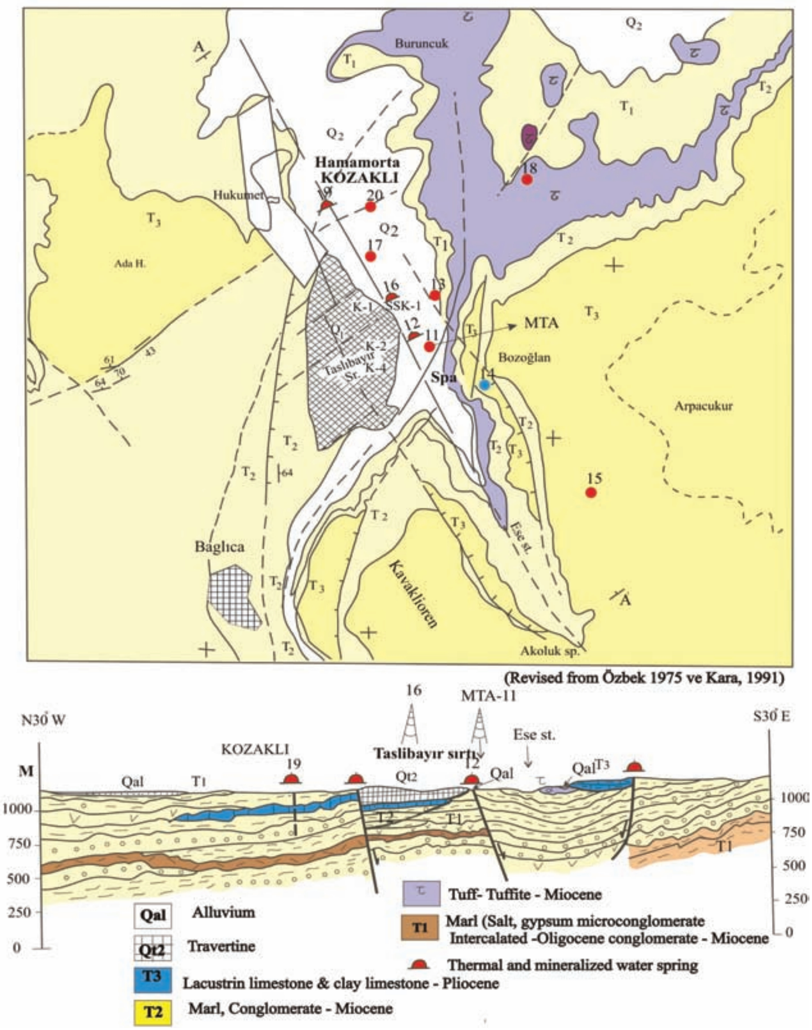

FIG. 3. Geological map and cross-section of Kozaklı Area.

3. HYDROGEOLOGY

3.1. Kırşehir-Terme Resort

The metamorphic schists of the Kırşehir Massive exposing around the Terme resort are mostly impermeable. Permeability is enhanced by fractured-controlled karstification and fracture and fissures in marbles. Thus, marbles comprise the primary aquifer where substantial amount of hot water can be stored. The Eocene conglomerate and sandstones are loosely cemented and have high efficient porosity. Conglomerate and sandstones at the contact between Pliocene lacustrine deposits and metamorphic schists and marbles are characterized by high porosity and permeability values [13] . Since thermal and mineral waters issuing through the normal faults are over saturated with respect to calcite, this hydrothermal conduit has been completely plugged by carbonate precipitates. These long-lasting events have given rise to gradual decreasing of spring discharges and extinction of some. The presence of Tertiary intrusion and Pliocene volcanism in and around the study area resulted in geothermic gradient to fall below the normal value of 33 m. The meteoric waters are heated by geothermic gradient during percolation. These heated waters are accumulated within fractures, fissures and karstic voids of marbles which comprise the pressured aquifers. Waters which are heated upon percolation downward rise to the surface via suitable fractures, fissures and karstic voids and, form the Terme springs (Fig. 1,2). These waters rising to the surface for a long geological period are over saturated with respect to calcite; they form the Terme Stone at the surface. Some of these waters rising through the faults buried under the marbles and Tertiary formations facilitate formation of a hot water aquifer of 25–37°C within the base conglomerates and alluvium of the Pliocene lacustrine deposits. In the Kırşehir-Terme area, MTA has opened more than 12 hot water wells since 1994. Depth of these wells is between 164 and 500 m, discharge is 30–185 L/s and temperature is 44–60°C.

3.2. Nevşehir-Kozaklı Resort

Fractures and fissures within the marbles of the Paleozoic Metamorphites and of the Eocene limestones exposing around the Kozaklı springs provide secondary porosity and thus an aquifer character for these rocks. Limestones also comprise the aquifer of the Kozaklı hot water springs. Oligocene clayey-marl levels have a low porosity and therefore, they act as cap rock. Depending on their secondary porosity, the Pliocene conglomerate and limestone levels are of aquifer character. Thermal waters are manifested along NW-SE and NE–SW extending normal faults and their adjacent secondary ones (Fig. 3). In the Kozaklı geothermal area, more than 20 wells were drilled by MTA, government and private organizations and depth of these wells ranges from 50 to 205 m. Most of these wells are of artesian type. During the summer season, water is pumped from the wells. Waters have a temperature range of 80–98°C and their discharge is 2–40 L/s. Waters with temperature greater than 90° produced from a well of maximum 150 m depth may indicate the presence of still cooling magma chamber in the Kozaklı area.

4. MATERIALS AND METHODS

The study was conducted in three stages as field observations, sampling and analyses. During the field work, the geology map of the hot springs area was prepared. In order to determine hydrochemical and isotope characteristics of the hot springs, waters of production wells in Kırşehir and Kozaklı areas were sampled in August 2005. A total of 10 samples were collected from each area. The chemical analyses of water were performed at the Hacettepe University Water Chemistry Laboratories and Canada Acme Laboratories. The tritium analyses were conducted at the Hacettepe University Water Chemistry Laboratories and stable isotope analyses (^{18}O, ^{2}H and ^{13}C) were carried out at Ottawa University G.G. Hatch Stable Isotope Laboratories. Temperature, pH and EC measurements were done at sampling sites. Precision of analyses are ±0.15‰ for ^{18}O, ±2‰ for ^{2}H and ±0.2‰ for ^{13}C.

5. HYDROGEOCHEMISTRY

5.1. Water Chemistry

In semi-logarithmic diagram of thermal and mineral waters, the lines connecting the mili-equivalent values of ions are almost parallel indicating that waters are of similar origin (Fig.4). According to Association of International Hydrogeologists (AIH) [14] , the Kırşehir hot waters are “Ca, Na, HCO_3, Cl, CO_2 thermal and mineral waters”. High content of CO_2 gas in waters facilitates travertine deposition. Interaction between water and rock is closely related to thermodynamic instability of minerals in an environment of water and gas under varying pressure and temperature conditions [15] . The presence of CO_2 gas, chloride and fluoride indicates that they have endogenic origin. In this respect, these waters are of mixed origin. EC values of springs in the Kırşehir area are lower than those of the Kozaklı hot waters (1650–3560 µS/cm) and ranking of ions is as rCa>rNa+K>rMg; $rHCO_3$>rCl>rSO_4. Na and Cl are the dominant ion pair in the Kozaklı hot waters. Except for samples no. 19 and 20, ranking of cations is rNa+K>rCa>rMg and except for samples no. 11, 12 and 13, ranking of anions is rCl>r SO_4>r HCO_3 and that of samples no. 16, 17 and 18 is rCl>r HCO_3 >r SO_4. The Cl and SO_4 contents of the Nevşehir Kozaklı waters are higher than those of Kırşehir waters. However, EC and Cl contents of Kozaklı geothermal waters are higher. The Kozaklı hot waters are of Na–Cl–SO_4 type and, since pH values are close to neutral character, sulfate is most probably derived from dissolution of sulfide minerals by deeply circulating waters. Although the Kozaklı thermal and mineral waters have high chloride concentrations, their boron content is generally low. The highest B content (606 ppb) was determined in sample no. 15 from the Güneş thermal well. High SO_4, Cl and Na concentrations of the same water may be indicative of high ion dissolution capacity of water. In addition, fluid circulating within the sedimentary rocks may also dissolve boron derived from decomposition of organic materials. Constant Na but varying K concentrations of Kozaklı thermal and mineral waters may be attributed to the fact that geothermal fluid, as it rises to the surface, is in ion exchange with lithologic units.

5.2. Evaluation of Isotope Data

In this section, oxygen-18 (^{18}O), deuterium (^{2}H), tritium (^{3}H) and carbon-13 (^{13}C) contents of water samples collected from springs and wells in the study area are examined and groundwater circulation system, recharge-discharge characteristics of aquifers and their hydrogeological features are investigated. The relation between isotopic composition of studied waters and meteoric water line ($\delta^{2}H = 8 \times \delta^{18}O + 10$) [16] representing the worldwide precipitation is given in the $\delta^{18}O$–$\delta^{2}H$ graphic. Examination of this graphic reveals that thermal waters are plotted on the global meteoric water line (Fig. 5). In this respect, thermal waters in the study area are of meteoric origin and some of precipitation is percolated downward through fractures, fissures and faults and heated at depth and then rises to the surface via faults and effective fractures that act as hydrothermal conduits. These waters with the same recharge area are closely plotted in the $\delta^{18}O$–$\delta^{2}H$ graphic. Regarding their $\delta^{18}O$ ratios, thermal waters show a slight negative shift from the local meteoric line. Interaction

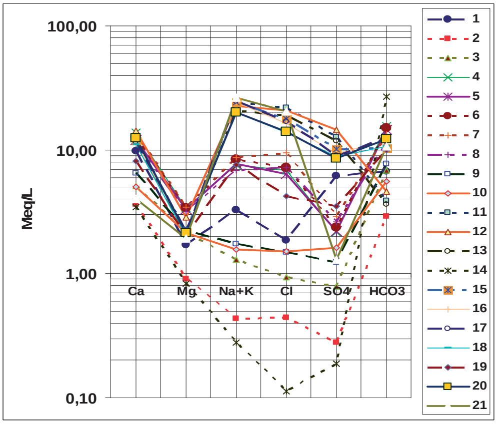

Fig.4. Schoeller diagram.

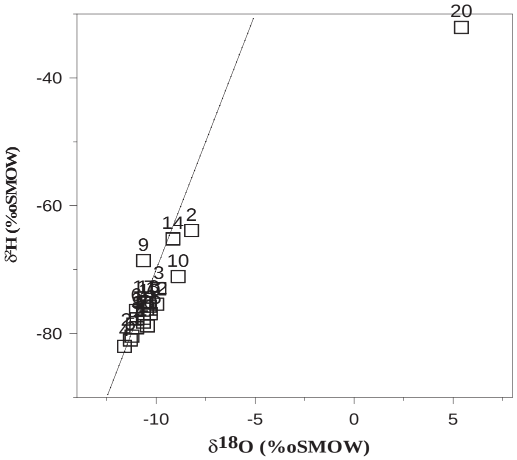

Fig. 5. Plot of δ^{18}O versus δD.

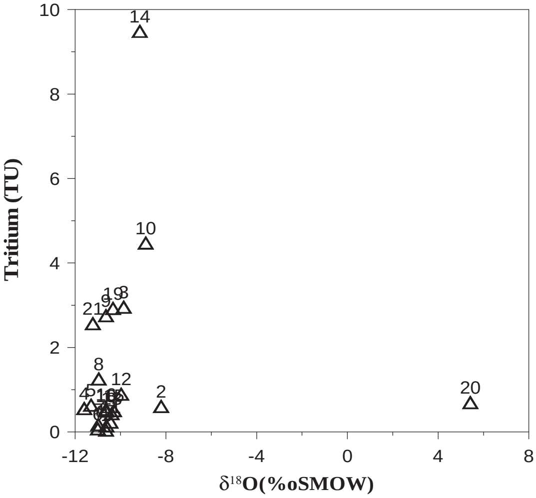

Fig. 6. Plot of δ^{18}O versus tritium.

between thermal waters and CO_2–rich rocks may result in enrichment of ^{16}O isotope and depletion of ^{18}O isotope. Mixing with cold waters may also show a variation in O–18 values. In addition, interaction with different lithologies and manifestation of hot waters at higher elevations could also affect the δ^{18}O ratio [17]. Sample collected from Kozaklı city bath well (sample no. 20) is shifted from the meteoric water line. Considering their O–18 contents, cold waters seem to be affected from young precipitation and therefore, they are young

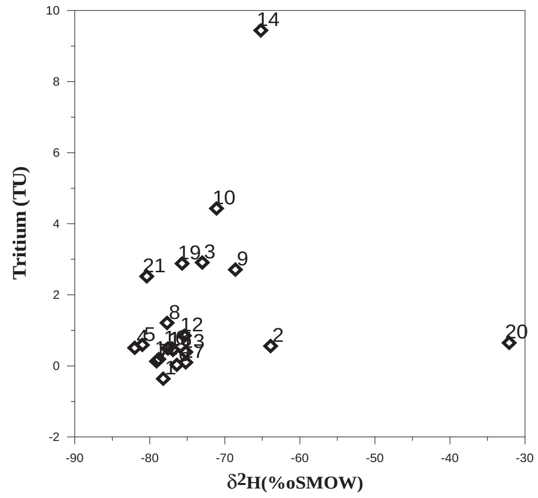

Fig. 7. Plot of δD versus tritium.

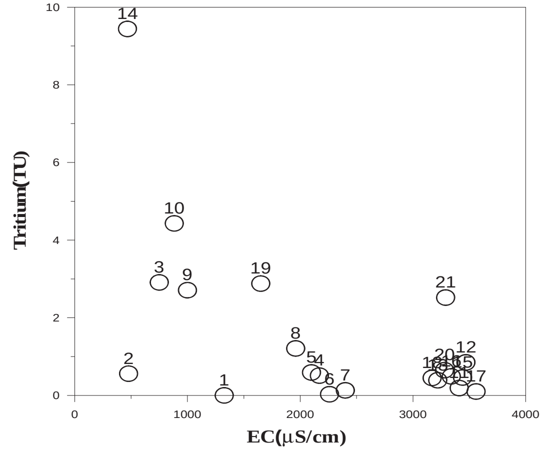

Fig. 8. Tritium versus EC(μS/cm).

waters. These waters haven been subjected to evaporation. The oxygen-18 – tritium relation reflects the relation between recharge elevation and residence time of waters. Cold waters are recharged from lower elevations (Fig. 6, 7). On the other hand, since thermal waters have similar limit values regarding their oxygen-18 and tritium contents (plotting close to each other), they might be recharged from the same or higher elevations. In the EC–^{3}H graphic, hot waters are represented by high EC values since they have longer residence

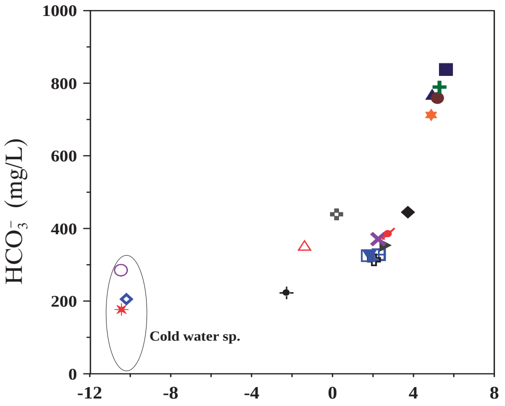

Fig. 9. HCO_3 versus $\delta^{13}C$ (‰ PDB).

time but their ^3H values show a decrease (Fig. 8). Dissolved inorganic carbon C_{DIC} and $\delta^{13}C_{DIC}$ values of groundwaters are related to alteration reactions in aquifer or soils. $\delta^{13}C_{DIC}$ values of Ş. Mustafa fountain (sample No. 2) and Terme Üçgöz fountain (sample No. 10) are –10.13 and –10.46‰, respectively. Kozaklı Altın water in the Nevşehir region has a $\delta^{13}C_{DIC}$ value of –10.43‰ (Fig. 9). $\delta^{13}C_{DIC}$ ratios of these waters are controlled by CO_2 accumulated in soil or underground voids. The ^{13}C represented by $\delta^{13}C_{DIC}$ values of 5.29 and 5.61‰ in samples 6 (well no T6) and 7 (well no T12), respectively, is derived from marine carbonates or metamorphic CO_2. In this respect, carbon in the studied waters may reflect different origins. It is believed that carbon in high temperature waters is derived from dissolution of marine carbonates [18]. However, carbon in low temperature waters has an organic origin. In Kozaklı and Kırşehir hot waters, HCO_3–$\delta^{13}C_{DIC}$ relation was also examined (Fig.9). As HCO_3 concentrations of the Kozaklı and Kırşehir waters decrease, $\delta^{13}C_{DIC}$ values also decrease. On the other hand, this is not the case for the thermal waters, that is, as HCO_3 concentrations of the thermal waters increase, $\delta^{13}C_{DIC}$ values also increase. In addition, $\delta^{13}C_{DIC}$ values of all cold and thermal waters in the investigation area are conformable with their EC values.

6. RESULTS

Marbles of the Kırşehir Massive are the reservoir rocks of the Kırşehir Terme springs while Eocene limestones above the Paleozoic metamorphites comprise the reservoir rock in the Kozaklı geothermal field. Thermal waters are manifested as spring groups along NW-SE and NE-SW trending normal faults and their secondary faults. Chemical characteristics of the Kırşehir and Kozaklı thermal waters are very similar. Springs in the Kozaklı area are represented by higher total ion concentrations and EC values. Cl and SO_4 concentrations of the Kozaklı waters are greater than HCO_3 content. Cold waters in both fields are of Ca-HCO_3 type. Environmental isotope results indicate that thermal waters have a meteoric origin and some of rainwater is percolated downward along fracture and faults and heated at depth and then rises to the surface along fractures and faults which act as hydrothermal conduit. $\delta^{18}O$-tritium data yield that thermal waters are recharged from higher elevations in comparison to cold waters. Based on $\delta^{13}C_{DIC}$ values, carbon in waters have multiple sources. It is thought that carbon in high-temperature waters is derived from dissolution of marine carbonates while carbon in low-temperature waters is sourced from an organic pool. There is a fair positive correlation between HCO_3 concentrations and $\delta^{13}C_{DIC}$ values of thermal waters.

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STUDY OF THE KHOY GEOTHERMAL AREA BASED ON ISOTOPE AND CHEMICAL INVESTIGATIONS

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Abstract

Major thermal and mineral springs originate along the main Qutur fault zone which aligns along the valley of the same name. The actual outflow sites of these waters are situated at the valley flanks near the bottom of the valley and are accompanied by remarkable travertine deposits. The local spring outflow location seems to be determined by the intersection of (i) the local sedimentological bedding planes (of a strata of higher hydraulic conductivity) and (ii) minor faults of transversal orientation to the Qutur fault. According to the results of this study it is concluded that in the Khoy geothermal area two water systems are interacting (Fig. 4), (i) the recent waters of actual recharge in the high mountain areas as the Almalu Spring Nr. 8 and (ii) the deep thermal and mineral waters within a deep aquifer which is contained within tectonic fault zones (as the Qutur fault). This deep groundwater is influenced by a high influx of CO_2 of deep origin and the mixing with a deep seated highly mineralized HCO_3 rich formation water. The Qutur River itself is considered in this conceptual model to represent the main natural discharge level. Based on this conceptual model the hot highly mineralized thermal water is ascending to the surface by the buoyancy effect through tectonically induced active fault zones where an interaction with the uprising CO_2 also takes place.

1. INTRODUCTION

The Khoy geothermal system is located in a very active tectonic zone to the northwest of Iran, 30 to 40 km from the Turkish border and about 30 km southwest of the city of Khoy (Fig. 1). The investigation of the geothermal resources of the Khoy area NW Iran started with an initial reconnaissance study in 1997 [1]. Within the IAEA TC project “Characterization of the Khoy Geothermal Area” a new sampling activity of the naturally occurring springs and the accessible observation boreholes for isotope and hydrochemical analyses were carried out in July 2002 and were followed by two additional sampling activities in October 2002 and June 2003 [2]. Based on the previous study [1] the scope of the currently presented second study was: (i) to include selected cold springs at high altitudes which probably represent the conditions of groundwater recharge of the thermal groundwater system, (ii) to include hot and moderately warm springs with high CO_2 contents and (iii) to sample also the Qutur River at two locations, one upstream and another one downstream of the Khoy geothermal area in order to clearly identify the deep thermal system and its mixing components in the outflowing mineral and thermal waters.

2. GEOLOGICAL AND TECTONIC OVERVIEW

They main thermal and mineral natural springs are observed along an approximately 2 km long segment of the north bank of the Qutur Chay (Qutur River) which flows in a valley formed by a fault. Travertine sediment deposits are present at the outflow of thermal and cold mineral springs. These types of sediments are situated at the lowland parts of the flanks and around the river at the bottom of the valley. As consequence of the tectonic structure, geological formations of different origin join each other. The oldest formations are mesozoic or even older metamorphic rocks overlain by igneous rocks of Cenozoic and Quaternary age. These rocks are outcropping along faults of several distinct systems. The Cenozoic sedimentary formations consist of siltstone, conglomerate and limestone units as well as some non-consolidated alluvial deposits. These represent old Qutur River bed sediments. Based on drillings and gravity investigations a granitic batholith is supposed to exist at a depth of 200 meters below the riverbed. According to the observed structures several horst and graben systems exist which are oriented parallel to the Qutur Valley and filled with clastic sediments.

3. HYDROGEOLOGY

Major thermal and mineral springs are outflowing along the Qutur along its main fault zone. The spring locations seem to be determined by the intersection of the main fault with i) local sedimentological bedding planes (of stratas of higher hydraulic conductivity) and ii) with minor faults of transversal orientation to the Qutur fault, cross cutting the adjacent rocks. The spring outflow sites are frequently surrounded by travertine deposits. However, such deposits also exist at dry places, at the same or slightly higher altitudes than the observed outflow zones. These deposits were formed during an earlier period with higher located outflow sites and were dried out as a result of the recent hydraulic situation. According to the given morphologic situation, the Qutur River represents the area of discharge of the local groundwater flow system. If this would be also the case with respect to the thermal aquifer which is feeding the observed springs, this would be quite plausible from the hydrogeological point of view, but in complete disagreement to the postulated conceptual model of the previous study [1]. The solution of this fundamental question regarding the conceptual model of the existing flow systems was one of the main targets of the present study and will also influence further geothermal exploitation possibilities in the area.

4. DISCUSSION OF THE RESULTS OF CHEMICAL AND ISOTOPE ANALYSES

4.1. CO_2 contents of the analyzed waters

Based on the field measurements during the sampling activity of July 21–22, 2002 at the locations presented in table 1, it can be noticed that the amount of CO_2 in all water samples yield CO_2 contents which largely exceed the equilibrium concentrations with respect to atmospheric CO_2 (about 300 mg/L vol.) as well as with respect to the saturation with soil CO_2 (maximum value corresponds to about 2 vol% equivalent to a concentration in water of 39 mg/L. An exception are the samples of cold water from springs No. 7 and No. 8 situated at higher altitudes in the recharge area (outside of the Qutur Valley) as well as samples No. 9 and No. 10 from the Qutur River itself. These observations now indicate that all hot and mineralized waters are influenced by tectonically induced CO_2 ascending from depth by fault zones and connected fracture systems [3].

TABLE 1. SAMPLING SITES AND RESULTS OF FIELD MEASUREMENTS (TITRATION) OF THE SAMPLING ACTIVITY OF 21-22 JULY 2002.

Location No.	Location Description	Altitude (m a. s. l.)	Water Temp. (°C)	CO_2 (mg/L)	HCO^{3-} (mg/L)	O_2 (mg/L)
1	A.E.O-Well	1436	17.2	1056	3220.8	0.0
2	Dareh-Khan- Spring	1460	17.3	1755.6	2000.8	0.0
4	Kooroglee-Spring	1648	48.6	220	1470.1	1.8
5	Warm Spring	1445*	56.2	400.4	1415.2	0.0
6	Cold Spring	1445	18.1	1276	5185	0.0
7	Koochak-Spring	2695	5.0	17.6	237.9	10.0
8	Almaloo-Spring	1987	12.0	22	323.3	7.8
9	Qutur River upstream	1711	20.3	22	280.6	3.3
10	Qutur River downstream	1438	20.9	44	317.2	3.6

4.2. O_2 contents of the analyzed waters

Shallow cold groundwater normally contains dissolved oxygen in concentrations close to equilibrium with atmospheric conditions, dependending on the temperature and altitude of the zone of recharge. Within the area studied the waters of the cold spring Almalu (Nr. 8) and Koochak (Nr. 7) reflect best such conditions of recharge [3]. The Qutur River water sampled upstream and downstream of investigated thermal area yielded lower oxygen concentrations reflecting a deficit to oxygen equilibrium saturation. This is due to oxygen consumption by the decomposition of organic matter contained in river waters. For the thermal spring water of the locations No. 1, 2, 5 and 6, no measurable oxygen results, which is quite common for groundwater of longer residence time because the oxygen originating from the recharge area is consumed by water rock interaction processes along the flow path (e.g. by oxidation of pyrite, H_2S, etc.). The small amount of oxygen measured at spring Nr. 4 (1.8 mg/L) most probably results from the sampling conditions (uptake during outflow and cooling).

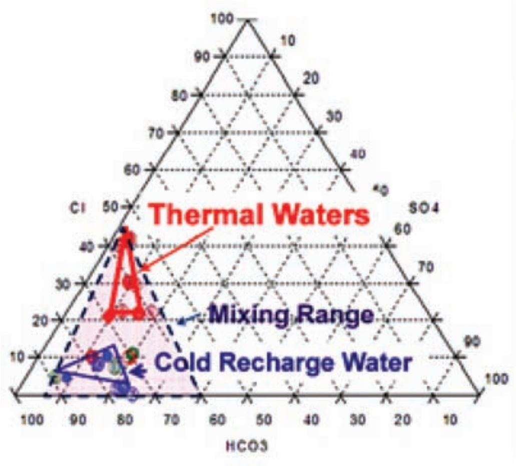

FIG. 1. Piper-type diagram of the anion concentrations (in meq%) of the Khoy thermal and mineral groundwater and of the Qutur River (samples of July 2002 and October 2002).

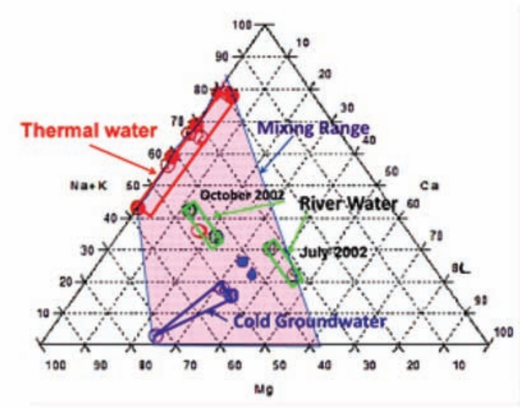

FIG. 2. Piper-type diagram of the cation concentrations (in meq%) of the Khoy thermal and mineral groundwater and of the Qutur River (samples of July 2002 and October 2002).

4.3. Characterisation of the investigated waters based on the main ion concentrations

For the water No. 7 Koochak-Spring and No. 8 Almaloo-Spring which are most representative of recharge conditions a characterisation as Mg–Ca-–Na–

HCO_3 type results. For the Qutur River samples No. 9 and 10, from up- and downstream of the investigated geothermal area, a characterisation as Ca–Mg–Na–HCO_3 to Mg–Ca–Na–HCO_3 type results (samples of July 2002, or October 2002 respectivelly).

For the thermal water and the low temperature mineralized waters a different characterisation as Na–Mg–HCO_3–Cl–SO_4 type results. But in considering processes of water rock interaction as hydrolysis of minerals of plutonic rocks such as mica, feldspars, and the dissolution and oxidation of pyrites an evolution from the cold recharge waters No. 7 and No. 8 to the higher mineralized thermal waters would be possible. A further uptake of CO_2 of tectonic origin is increasing the water-/ rock- interaction processes. The increase of sodium can be explained by water rock interaction processes such as hydrolysis as well as by ion exchange such as the exchange of calcium by sodium.

Therefore, according to this chemical characterization, the cold, low mineralized spring water (represented by Nr. 7 and 8), originating from the higher locations within the catchment area may be considered as original end member of the recharge type groundwater, whereas the higher mineralized thermal and mineral waters are thought to result from evolution by mixing processes with the recharge type groundwater and ongoing processes of water rock interaction.

4.4. Characterisation of the Khoy waters according to isotope signatures

4.4.1. *δ^2H and $\delta^{18}O$ isotopic composition of the investigated waters of the Khoy area*

The results of analyses of δ^2H and $\delta^{18}O$ of the water of the 3 sampling instances of July 2002 to July 2003 as well as the results reported of the 2007 sampling activities [1] were used in the following interpretation.

Since the linear relationship with respect to altitude of groundwater recharge is nearly worldwide well established for both stable isotope ratios of the water, δ^2H and $\delta^{18}O$ it is applied to get information about the recharge altitdes of involved groundwater [4]. In the case of the Khoy waters the $\delta^{18}O$ ratio is probably much more affected by water rock interaction processes due to geothermal conditions (oxygen isotope exchange with rock minerals) than the δ^2H ratio. Therefore under such circomstances the relationship between the δ^2H values with respect to the altitude of the corresponding sampling sites for the investigated waters of the Khoy area is more adequate [6, 7]. Within the Khoy area an indicative relationship of the δ^2H values to the altitude of recharge exists for the cold, low mineralized springs at high altitudes such as Nr. 7 Koochak spring, Nr. 8 Almalu spring and the corresponding altitude of

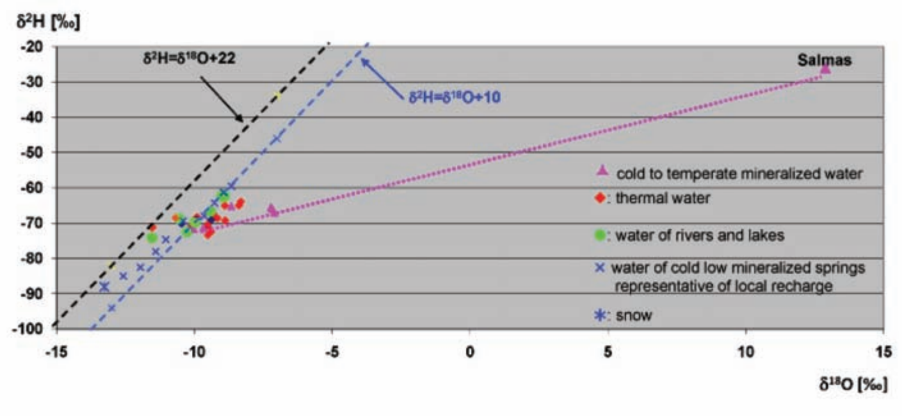

FIG. 3. Diagram of the relationship of δ^2H to $\delta^{18}O$ for the investigated waters of the Khoy area, sampling periods July 1997, July 2002 October 2002 and July 2003 (including the highly mineralized Salmas water).

a snow sample (of the 1997 sampling campaign reported in [1]. If now it is assumed that this relationship represents the recent recharge conditions of the Khoy area with respect to altitude, the resulting recharge altitude of the Khoy thermal waters would be in the range of 1800 to 2000 m a. s. l.

The same range of altitude also results for the samples of the Qutur River, which is quite plausible since it is fed by surface and groundwater of the same catchment area.

According to the diagram of δ^2H versus $\delta^{18}O$ presented on Fig. 3, the cold low mineralized ground waters as well as the water samples of the Qutur River are aligned along but slightly above the GMWL. As already mentioned the surface waters of the Averin Lake and river are situated above the GMWL showing a deuterium excess, d in the range of 15 to 20‰. Most of the samples of thermal waters on Fig. 3 are situated below the GMWL. They can be aligned mainly by horizontal lines to points representing cold low mineralised spring water which reflect the recent recharge conditions. Therefore the δ^2H and $\delta^{18}O$ values of these thermal waters can be explained by a recharge under recent conditions but influenced by an oxygen isotope exchange process with the aquifer rock minerals under higher temperature conditions or with gasous CO_2 under low to moderate temperature conditions.

Now a special situation of evolution is presented by the high mineralized, cold to moderately warm mineral waters which are situated also below the GMWL. The δ^2H and $\delta^{18}O$ values of these waters align nearly perfectly on a straight line leading to the Salvas spring water, which presents most probably a formation water or even a hydrothermal fluid. Therefore this straight line probably represents a mixing line towards the values of the Salvas spring water as mixing end-member. Such waters as represented by the sample of the Salvas spring with a $\delta^{18}O$ value in the positive range are considered to correspond to Giggenbach's defined "Andesitic Waters" [8]. More commonly these waters are named "formation waters" or "hydrothermal waters" if originating from geothermal areas. These waters have completely lost their meteoric signatures by the water rock interaction processes and are reflecting more closely isotope signatures of the minerals of the corresponding rock environment along their flow path or deep reservoir.

4.4.2. Relationship of d^2H, $d^{18}O$ values the cold mineralised waters to the CO_2 /carbonate system

If the $\delta^{18}O$ values of the investigated cold to moderately warm highly mineralized waters are compared to their corresponding HCO_3 concentrations an enrichment with respect to $\delta^{18}O$ with increasing HCO_3 concentration is revealed. This fact was also recognised in CO_2 and HCO_3 rich waters in Western Turkey [9, 12]. But since a linear relationship to increasing δ^2H values with increasing HCO_3 concentration also exists it seems to be not only one but two processes which are interacting: (i) the increase of the $\delta^{18}O$ values by isotope exchange with the CO_2/HCO_3 – system, and (ii) an ongoing mixing with highly mineralized water of huge, unusual high HCO_3 concentration.

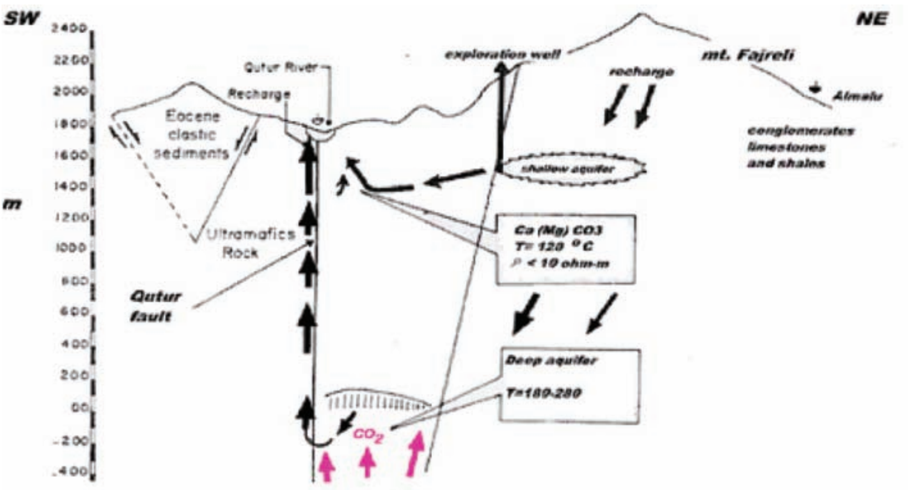

FIG.4. Schematic conceptual model of the interrelations of the cold groundwaters and thermal waters.

5. CONCLUSIONS

In the presented Khoy geothermal area two water systems are interacting (Fig. 4), (i) the recent waters of actual recharge in the high mountain areas as the Almalu Spring Nr. 8 and (ii) the deep thermal and mineral waters within a deep aquifer which is contained within tectonic fault zones (as the Qutur fault) which is dominated by a high influx of CO_2 of deep (probably thermo-metamorphic) origin and the mixing with a deep seated highly mineralized HCO_3 rich formation water. The Qutur River itself is considered in this conceptual model to represent the main natural discharge level. Based on this conceptual model the hot highly mineralized thermal water is ascending to the surface by the buoyancy effect through tectonically induced active fault zones where an interaction with the uprising CO_2 also takes place.

In the lower levels of the valley, a gradual mixing process between the cold low mineralized water and the ascending hot highly mineralized water takes place up to a complete replacement of the cold water in the deepest parts of the valley. Therefore based on the stable isotope data an actual recharge seem to exist, so that sustainable exploitation of this geothermal reservoir seems to be possible as long as the extraction rate does not exceed the natural recharge. As a rough estimate this rate will be about equal to the actual flow rate of the Qutur River, in the range of 0.5 to 1 m^3/s or less.

ACKNOWLEDGEMENTS

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ORIGIN OF THE THERMAL WATERS OF STABIO (SWITZERLAND) AND SIRMIONE (ITALY) BASED ON ISOTOPE AND CHEMICAL INVESTIGATIONS

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Abstract

The study areas are located in Southern Switzerland near the Swiss boundary to Italy and in Northern Italy, at Garda Lake. The thermal waters of Stabio and Sirmione as well as the mineral water of Salo were investigated with hydrochemical and isotopic methods in which tritium, stable isotopes as well as ^{36}Cl, Radon and Uranium were measured. The results of these investigations clearly indicate that the waters of Stabio and Sirmione have a different origin than the normal shallow groundwater arising from the present day meteoric water cycle. Both areas may be linked to deep tectonic fault zones and induced flow systems. Furthermore, its chemical composition reflects a strong influence of water rock interaction processes and/or of mixing components of original deep sedimentary brine with a shallow groundwater. Interaction with the uprising CO_2 also takes place.

1. INTRODUCTION

The water of the Salo mineral spring was first investigated in the context of an earthquake of Magnitude M = 5 which happened in November 2004 [1],

[2]. The groundwaters of this area including the thermal water of Sirmione were further investigated in the frame of a Bachelor study in 2006 [3]. Both areas are well known spa resorts, Sirmione situated at a semi-Island at Lake Garda and Stabio in the southernmost Switzerland close to the Italian border. In both places the thermal water is mainly used in the health resorts in inhalation therapy.

2. GEOLOGICAL AND TECTONIC OVERVIEW

2.1. Overview of the Salo/ Sirmione area at the Southern edge of Lake Garda

The Salo mineral spring is situated at the south eastern shore of Lake Garda. The shore along Lake Garda mainly consists of quaternary glacial and

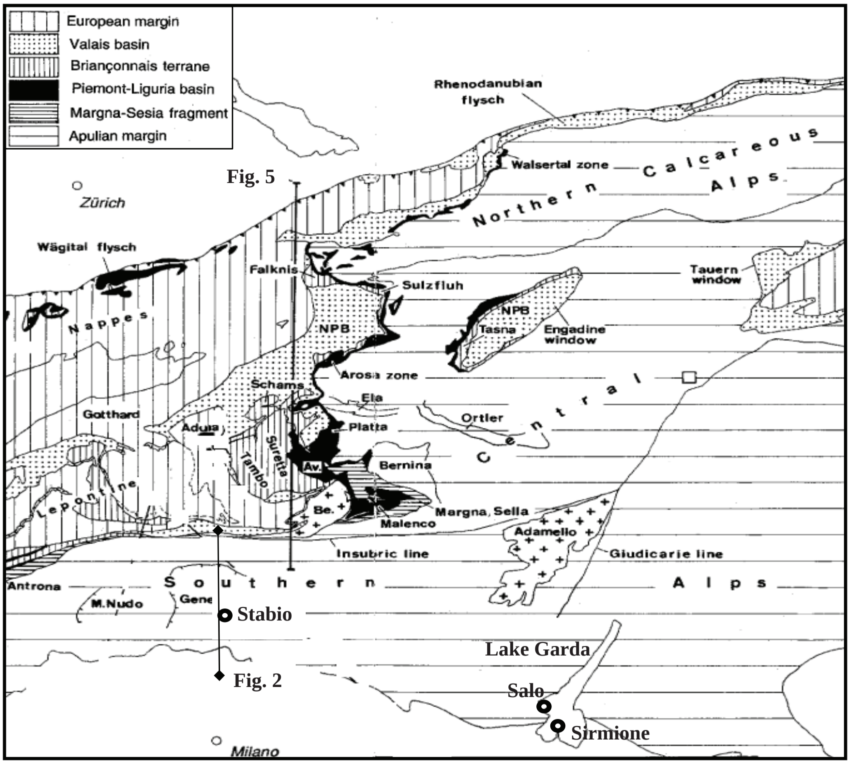

FIG. 1. Geological map of the Alps, from the Molasse Bassin in the North up to the Po Pain in Northern Italy. The present-day position of the major paleogeographic/tectonic units of the Alps are indicated as: Av.: Avers Buendnerschiefer; Be.: Bergell intrusion; modified after [4].

fluvial deposits from the Wurm period. From the tectonic sketch map on Fig. 1 [8] it follows that the eastern shore line of the Lake Garda is following nearly exactly a NE–SW oriented fault zone which is aligned almost parallel to the Giudicaria Fault zone. As deduced from measured CO_2 soil gas concentrations it is assumed that the Salo Mineral spring (Fonte Tavina) is also situated in such a fault zone.

The small semi island of Sirmione is situated on the middle part of the Southern shore of Lake Garda. On the shore at its end the Sirmione thermal spring of sub-lacustrine type emerges. The outflowing water has a temperature of 50°C. According to measurements on the outcropping cretaceous limestone rocks the captured spring outflow can be situated on a fault line parallel to the eastern shore line of Lake Garda.

2.2. Overview of the Stabio area

The Stabio village is located within the most Southern part of Switzerland, near the border to Italy. The geology of this area is characterized by its situation south of the Insubric Line belonging to the zone of the Southern Alps. Within this area E-W trending deep fault zones (acting sliding planes within the over-thrusted slices of the deep basement) are deduced from recent seismic investigations (Geotraverse Project). But these deep structures are not evidenced in the observed near surface geolocical structure as shown by the detailed cross section in Fig. 2.

The near surface geology is characterized by tertiary and quaternary (Messinien) deposits (consolidated and non consolidated clastic sediments) which present basin fillings above the tectonically sliced bedrock (Fig. 2).

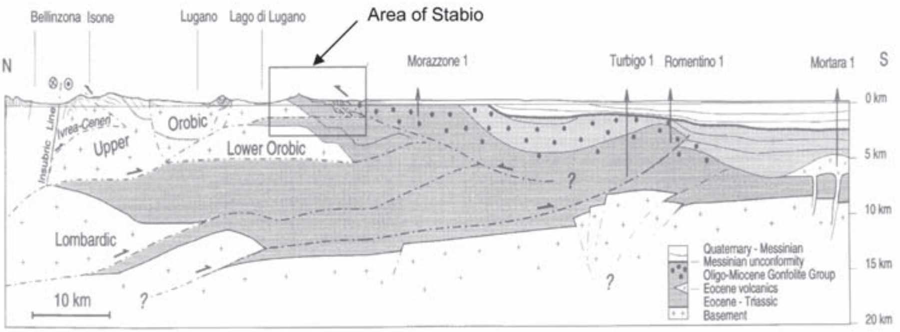

FIG. 2. North-South cross section of the area South of the Insubric Line of Fig. 1 (after [7]).

At Stabio, near the location of the two thermal wells of the spa site, the adjacent hard rock consisting of dolomite limestone is outcropping as indicated by the cross section of Fig. 2. This outcrop belongs to a NE-SW striking tectonic structure interpreted as a tectonically squeezed anticline. This structure is also coinciding with an NE-SW trending fault zone almost parallel to the Giudicarie Line. The Giudicarie Line itself originates as a split off from the Insubric Line continuing at the North Eastern Ending of the Adamello Granitic Massiv (intrusion) in NE–SW direction.

3. HYDROGEOLOGY

3.1. Hydrogeology of the Stabio area

The Hydrogeology of the stabio area is characterised by fluvio- lucustral to glacial sediments which follows a SW to NE direction along the river Laveggio which is flowing from SW to NE into the lake of Lugano. The quaternary infillings along the Lavegio valley are about 1 to 2 km large and nearly up to 200 m deep and consist mainly of alternate layers of gravel, sands and silty gravels. In a deep borehole, approximately 99 m, situated around 4 km north east of Stabio the dolomitic bed rock was touched after crossing the non consolitaded quaternary deposits at a depth of 94 m below surface and drilled through for about 5 m to an end depth of 99 m [6, 9]. At the emplacment of the Stabio therme, the bedrock of dolomitic limestone is outcropping (Cross sections of Fig. 2 and Fig. 5). It belong to a NE-SW trending tectonic structure of an overthrusted anticline which has its Northern end at the village of Stabio, in the vicinity of the Stabio spa location. At the beginnig of the spa history of Stabio at the end of the 19th century the thermal water with its characteristic smell of H_2S was outflowing at several locations around the spa building. About 50 years later two boreholes were drilled near the former spring sites to a final depth of about 25 to 50 m. The water in the spa borehole inside the building had in April 2006 temperature of 17°C (without pumping).

3.2. Hydrogeology of the Salo/Sirmione area at the Southern ege of the Lake Garda

Around Lake Garda the flat part of the shore consists of quaternary glacial and fluvial deposits mainly from the last glaciation period. Along the steeper parts of the surrounding hills the consolidated rocks of upper Permian to Neocene are protruding [8]. The eastern shore line of the Lake Garda follows almost exactly a NE–SW oriented fault zone which is aligned almost parallel to the Giudicaria Fault zone. The Salo mineral springs at the Western Sea shore of Lake Garda appear at the contact zone between the non consolidated glacial deposits along the lake shore and the steeper slope consisting of consolidated rocks.

The present NE–SW trending fault zone which is supposed to exist according to the geological map [8] crossing through the site where the mineral spring cropped up could only partly be confirmed by systematic sections of measurements of soil CO_2 concentrations [3].

On the middle part of the Southern shore of Lake Garda the small semi island of Sirmione is situated. On the shore at its North-Eastern end, the Sirmione thermal spring of sub-lacustrine type emerges. According to measurements on the outcropping cretaceous limestone rocks the captured spring is out flowing of the lake floor at the shore of the peninsula at the crossing of a NE–SE trending fault line.

4. DISCUSSION OF THE RESULTS OF CHEMICAL AND ISOTOPE ANALYSES

4.1. Radioelement concentrations of the analyzed themal and normal groundwater

Enhanced Radon concentrations appears for the thermal waters of both areas. This well known fact is one of the main reasons for its use in inhalation therapy. As represented on Fig. 3 the concentrations of ^{222}Rn are highest for the Stabio thermal water (91.8 Bq/L), whereas the highest ^{226}Ra concentrations are measured for the Sirmione water with 750 Bq/L. The total uranium (^{238}U + ^{234}U) concentrations are much smaller in all waters. Its maximum concentration is reached for the Stabio spa water (StB) with 10 Bq/L. As also recognised in other studies [9], there is no correlation to be observed between the concentrations of ^{222}Rn with respect to ^{226}Ra nor with respect to ^{238}U + ^{234}U for both other isotopes.

The comparison of the ^{222}Rn with the fluoride concentration yields a positive correlation.. This trend is consistent with the measured values of the normal shallow groundwater within the quaternary deposits of the Salo area and of the Salo mineral water up to the waters with higher Radon concentrations as the Sirmione and the Stabio thermal water. For the Salo mineral water also somewhat enhanced CO_2 concentrations result.

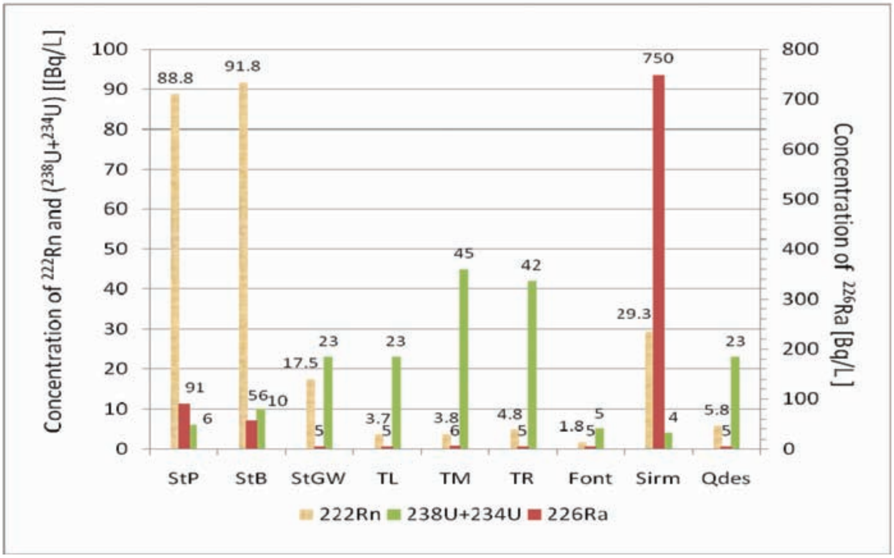

FIG. 3. Radioelement concentrations of the investigated waters of the Stabio and Sirmione/Salo areas.

4.2. Chemical composition of the analyzed themal and normal groundwater

According to the chemical composition the cold groundwaters of both areas are of similar Ca–Mg–HCO_3 type. The thermal waters of both areas are of Na–HCO_3–Cl type.

From the presentation of the anions and cation concentrations in the extended Piper diagram of Fig. 4 a characterisation in quite distict three groups results. One group is formed by the cold normal groundwater of the Salo and Stabio area as also of the Salo-Tavina mineral water. These waters are characterized as Ca–Mg–HCO_3 type. Both thermal waters of Stabio and Sirmione belong to the Na–HCO_3–Cl type. These thermal waters of the two different locations are separated in the rhombic representation, which reveals considering the cation composition somewhat higher Ca and Mg concentrations but lower Na concentrations for the Stabio thermal water than the Sirmione thermal water. When looking at the anion concentrations, the Stabio thermal water shows higher HCO_3 but lower chloride and sulphate concentrations compared to the Sirmione thermal water. Considering these 3 resulting quite distinct water types, different origin and chemical evolution is deduced. A mixing process between these two types of thermal waters with the shallow cold groundwater and mineral water seems to be probable, but both the Stabio

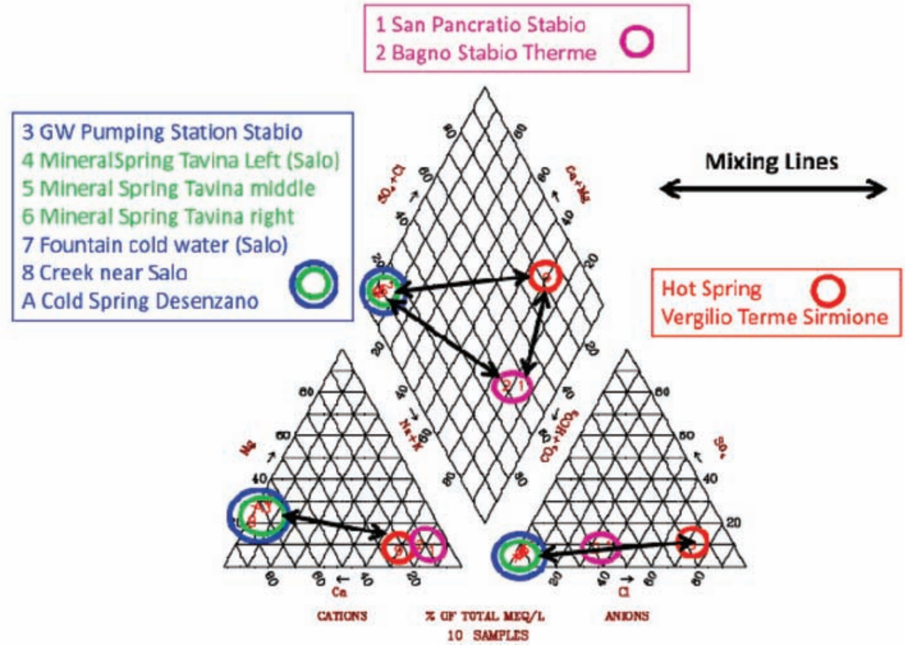

Fig. 4. Piper-type diagram of the anion and cation concencentrations in [meq/L].

and the Sirmione thermal water seem to represent individual end members. Because of their high concentrations of total dissolved solids as well as of Chloride, Fluoride and sodium concentrations an evolution from a deep basin brine is presumed.

4.3. Composition and concentration of analyzed gases in the sampled waters of Stabio

Enhanced concentrations of CH_4 (19 to 29 mL/kg), CO_2 (7 to 10 mL/kg) and of Ethene (0.007 to 0.012 mL/kg) result for the Stabio termal water. These gas occurrences are interpreted as signatures of the presence of a hydrocarbon reservoir as known to exist in the sedimentary deposits of the Po plain. According to [3], these gases reflect, by their reported range of $\delta^{13}C$ values > –48‰ to –52‰, typical gases originating from source rocks producing wet gases together with liquid petroleum [10] Also evidences of minor oil seeps were reported by [11] after blasting in a quarry close to the Stabio spa.

4.4 Characterisation of the Stabio waters according to the isotope signatures

For the Stabio thermal area more information about isotope results were available due to a more intense study needed for a new valorisation of the curative aspects and touristic potential of this area in Southern Switzerland.

- *δ^2H and δ^{18}O isotopic composition of the investigated waters of the Stabio area*

  The results of analyses of δ^2H and δ^{18}O of the thermal water of Stabio are about 5‰ for ^{2}H and 0.8‰ for ^{18}O lower than for the normal shallow groundwater of the area. This difference may indicate (i) an origin of the thermal water from infiltration areas situated higher (at about 1600 m altitude compared to 400m altitude for recharge of normal groundwater, as a resultby of the altitude relation published in [12] for Southern Switzerland) or (ii) even an infiltration during changed climatic conditions.

- *δ^{13}C and 14C of dissolved TDIC* of *the investigated waters of the Stabio area*

  For the Stabio thermal water δ^{13}C- values in the range of –1.54 to –1.44‰ may indicate either a complete exchange of the TDIC with the CO_2 of thermo — metamorphic origin (by the complete decomposition of carbonate rocks) or even of CO_2 of (earth) mantle origin, wheras the δ^{13C} value of TDIC of –12.7‰ of the normal cold groundwater reflect recharge conditions (with contact of the infiltrating water with soil CO_2 and dissolution of carbonate rocks with a δ^{13}C value of 0 ‰.

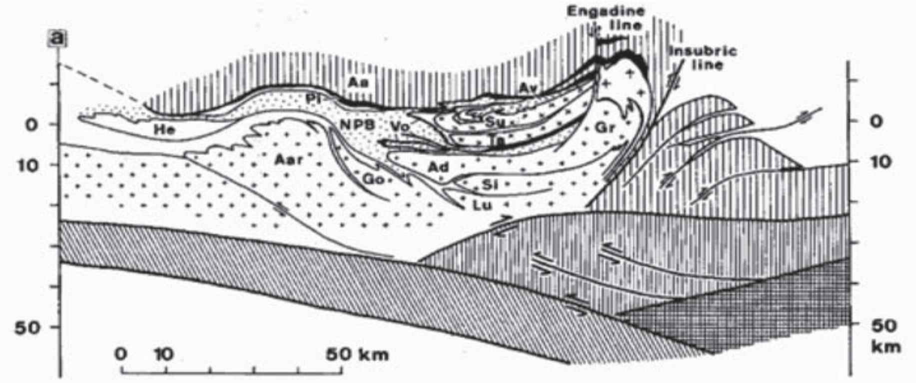

Fig. 5. Tectonic cross-section according to N–S transect Graubünden (trace on tectonic map above), as resulting from the deep seismic investigations in the frame of the Geotraverse Project [4].

The results of ^{14}C analyses ot the TDIC with 7.95 and 26.0 pMC for the thermal water wells of Stabio and of 85.21 pMC carbon for the normal shallow cold groundwater reflect clearly an ongoing mixing process between the shallow normal groundwater and an uprising deep water along tectonic faults. This interpretation is also in aggrement with the results of the tritium analyses with values of 1.1 ± 0.7 and 3.1 ± 0.7 TU for the Stabio thermal water of the two wells compared with a value of 9.4 ± 1.1 TU of the normal cold groundwater.

TABLE 1. RESULTS OF ^{36}CL ANALYSES OF THE THERMAL, MINERAL AND NORMAL GROUNDWATER OF THE SIRMIONE/SALO (LAKE GARDA) AND STABIO AREAS AND ADDITIONAL ELEMENTS DETECTED IN THE CHEMICAL ANALYSES (n.d.: NOT DETECTED).

Sample	^{36}Cl/Cl	Error	Cl	Li	Sr	Br	F	NO3
Location	(10^{-12})	^{36}Cl/Cl (%)	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
Salo Mineral Water 1	0.270	4	6.93	0.10	n.d.	n.d.	0.24	24.90
Salo Mineral Water 2	0.267	4	7.16	0.10	n.d.	n.d.	0.29	24.95
Salo Mineral Water 3	0.289	4	7.21	0.10	n.d.	n.d.	0.32	25.02
Salo Fountain (spring)	0.924	4	1.52	n.d.	n.d.	n.d.	n.a.	9.08
Salo Creek	0.543	4	2.16	n.d.	0.44	n.d.	0.76	11.59
Sirmione Thermal water	0.011	20	916.17	0.94	3.97	5.02	4.21	n.d.
Salo-Desenzano spring	0.656	4	2.36	0.10	n.d.	n.d.	n.d.	19.31
Stabio thermal 1	0.022	14	147.65	0.23	0.51	0.75	7.44	n.d.
Stabio thermal 2	0.019	15	231.84	0.24	0.60	1.21	5.56	n.d.
Stabio cold Groundwater	0.119	5	9.80	0.10	0.33	n.d.	0.14.	16.82

4.5 Characterisation of the waters of the Stabio and Sirmione area based on the $^{36}Cl/Cl$ isotopic ratio and chloride concentration of the investigated waters of the Sirmione/Salo and Stabio area

From the $^{36}Cl/Cl$ ratios and chloride concentrations of cold, mineral and thermal groundwaters of both areas (Table 1) the following informations result: All cold and mineral waters suggest an origin close to actual recharge conditions. By inserting the $^{36}Cl/Cl$ ratios and chloride concentrations of the thermal waters of Sirmione and Stabio in the diagram represented in [13] the corresponding data points show a position within the range of waters of tectonic active zones in Western Turkey. These waters are intepreted in [13] as a result of mixing processes between deep seated highly mineralized brines (formation water) and groundwater of the recent recharge.

5. CONCLUSIONS

South of the Insubric Line deep fault zones are deduced from recent seismic investigations (Geotraverse Project). The results of the isotope and geochemical investigations of the waters of the areas of Sirmione /Lake Garda and Stabio presented here agree well with this new tectonic model (according to N–S cross-section of Fig. 5): Ascending deep hot and highly mineralized water as well as CO_2 of probably thermometamorphic (or even mantle) origin is mixed at shallow depth with groundwater of recent recharge.

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In many parts of the world, surface water and groundwater resources are at risk because of indiscriminate use, rapidly growing populations, increasing agricultural demands, and the threat of pollution. These risks are often compounded by a lack of understanding about local conditions governing the occurrence, distribution and movement of surface and groundwater resources. Historically, the IAEA has played a key role in advancing isotope techniques and in promoting the use of isotopes to address water resource sustainability issues worldwide. The quadrennial IAEA symposia continue to be an important component of the IAEA's mission in water resources management. The 12th symposium in the series was convened from 21 to 25 May 2007 in Vienna with the objectives of: reviewing the state of the art in isotope hydrology; outlining recent developments in the application of isotope techniques to water resources management; and identifying future trends and developments for research and applications. These proceedings — in two volumes — contain the presentations made at the symposium. A CD-ROM containing the complete text of these proceedings is attached to the inside back cover of the second volume.

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