IAEA International Atomic Energy Agency

Water & Environment News

Newsletter of Isotope Hydrology Section
Issue No. 23, December 2007

ISSN 1020-7120

http://www.iaea.org/water

In this Issue

IAEA Water Resources Programme

Mr. Pradeep Aggarwal, IAEA Water Resources Programme Manager and Head, Isotope Hydrology Section briefing the media during the 51st General Conference of the IAEA, in Vienna.

(Photo Credit: K.M.Kulkarni/IAEA).

From the Section Head

This issue of the News focuses on several achievements in the IAEA's Water Resources programme during the year 2007. I am very pleased to note that we were able to facilitate specific improvements in the laser spectroscopy machine to obtain consistent analyses with desirable accuracy and precision for hydrological samples. This machine was demonstrated at the 12th IAEA symposium on isotope hydrology held in Vienna in May 2007. Additional highlights of the Symposium included a technical session on a boat cruise on the River Danube. Excellent food and weather were supplemented by two superb presentations related to river hydrology. This session was made possible by the generous financial contributions of Amex Export-Import GmbH, Dionex (Europe) Management AG, Eijkelkamp Agrisearch Equipment, GV Instruments GmbH, Labsco GmbH & Co., Los Gatos Research Inc. and Thermo Electron GmbH. I thank all of these partners and look forward to similar cooperation in the future.

It was great to have a very healthy participation of over 200 scientists in the Symposium. A demonstration of an automated sampler for remote collection of precipitation samples for isotope analysis also took place at the Symposium. Developed by the US Geological Survey and modified in cooperation with the IAEA, we hope to have this sampler made more widely available so that the deficiencies in the global isotope database may be eliminated. In this regard, I would like to note the publication of the Atlas of Isotope Hydrology – Africa. Most of the nearly 10 000 isotope data in this atlas were retrieved from IAEA archives and hopefully these can now be used for better assessing water resources. We are making all efforts to publish similar data from Asia and Latin America in the very near future.

Pradeep Aggarwal

Laser Spectroscopic Analysis of Stable Isotopes in Natural Waters—A Low-Cost, Robust Technique for the Use of Environmental Isotopes in Hydrological and Climate Studies

Applications of isotopes for understanding hydrological processes were essentially made possible by Nier's development of a dual-inlet mass-spectrometer in the late 1940s (Nier, 1947). Yet, the relatively high operational skill and cost of mass spectrometers used for measuring stale isotope ratios also has limited the more widespread use of isotopes by hydrologists in general although stable isotopes of oxygen and hydrogen in natural waters have proven to be effective tracers of the terrestrial water cycle. Less expensive and easy-to-operate spectroscopic methods using lasers have been developed for some time but have lacked the ability to provide results with sufficient precision necessary for hydrological applications. A laser spectroscopic machine has recently been developed that uses a cavity with high-reflectivity mirrors to generate path lengths of several kilometres, resulting in clear separation of different masses, promising measurements with the accuracy and precision required for hydrological samples. The performance of this laser machine, developed by Los Gatos Research, Inc., in California, USA, was tested with a number of secondary standards calibrated on the VSMOW scale and natural water samples.

Figure 1. The off-axis ICOS instrument manufactured by LGR Inc.

Theory of Operation

In laser absorption spectroscopy, a laser beam is directed through a gas sample and the mixing ratio (or mole fraction) of a gas is determined from the measured absorption using Beer's Law:

$$\frac{I_v}{I_o} = e^{-SL\chi P\phi_v}$$

(Iv is the transmitted intensity through the sample at frequency v; Io is laser intensity before entering the cell; P is gas pressure; S is absorption line strength; fv is the lineshape function of the transition (such that $\int \phi(v)dv \equiv 1$) L is the optical path length; and c is the mixing ratio.) Mixing ratio is then give as:

$$\chi = \frac{1}{SLP}\int_v \ln\left(\frac{I_o}{I_v}\right)dv$$

Unlike conventional multipass arrangements which are typically limited to path lengths less than two hundred meters, an Off-Axis Integrated Cavity Output Spectroscopy (off axis ICOS) absorption cell using high reflectivity mirrors results in effective optical path lengths that are several kilometres long, significantly increasing the measured absorption. For example, a cell length of 25 cm results in an effective path length of 2500 m. In addition, the path length depends only on optical losses in the cavity, and not on a unique beam trajectory (as in conventional multi-pass cells or cavity ringdown systems), the optical alignment is very robust allowing for reliable operation in the field.

Performance Testing

The instrument using off-axis ICOS, manufactured by LGR Inc., is shown in Figure 1. An auto-injector is used to deliver an approximately 1 µL volume of water into an evacuated absorption cell. The injection port is heated to about 80°C to ensure a quantitative transfer of volume from

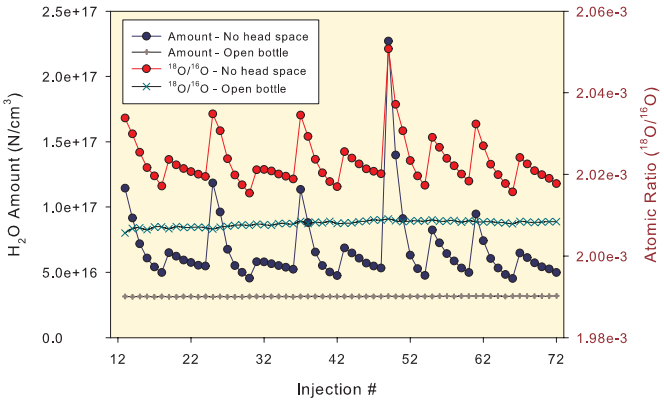

Figure 2. Variation in water amount have a large effect on atomic ratios.

the injector to the cell. The wavelength of a diode laser is tuned over selected H_2O, $^1H^2HO$ and $H_2{}^{18}O$ absorption lines near 1390 nm.

The integrated areas of the high-resolution absorption lines are combined with measured gas temperature to yield the molecular concentrations [H_2O], [$^1H^2HO$] and [$H_2{}^{18}O$], from which the atomic ratios $^2H/^1H$ and $^{18}O/^{16}O$ are determined directly and delta values are calculated using the atomic ratios of VSMOW-calibrated standards: A number of secondary standards calibrated on the VSMOW scale and natural water samples spanning a range of delta values were used to test the performance of the LGR instrument. Based

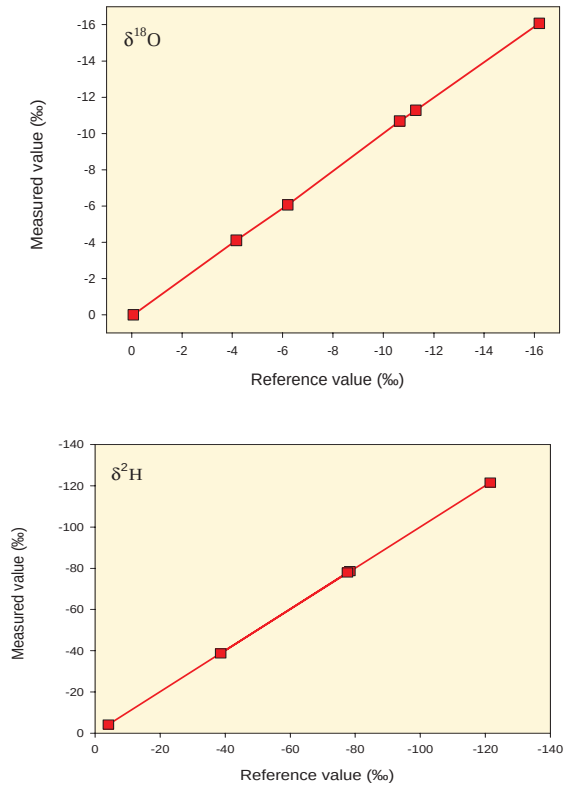

Figure 3. Accuracy of $\delta^{18}O$ and δ^2H measurements. Three of the measured samples were synthetic standards and natural water with dissolve salt concentration of 1000 mg/L.

on the initial set of tests (Aggarwal et al., 2006), it was determined that the amount of water introduced into the measurement cell had a large effect on calculated isotope ratios and produced measurements with large uncertainties. Figure 2 shows the results of repeated measurements on a single secondary standard, but from different sample bottles. In the first test, bottles were filled with no head-space and in the second, open or half-filled bottles were used. The no head-space configuration resulted in large variations in the six injections for each bottle, with the first injection (piercing a new septum) resulting in a higher water amount. The measured atomic ratios were directly correlated to water amount. With an open or half-filled bottle, pressurisation during injection was removed, resulting in small variations in water amount (<3%) and atomic ratios. With the water amount in an acceptable range, temperature variations of about 0.5°C had only a secondary effect on measured atomic ratios.

The operation of the laser machine was then modified by LGR Inc. to eliminate the water volume and temperature effects as much as possible. A modified machine with different sample injection and data analysis procedures was re-evaluated with secondary standards and natural samples. Results show that the instrument is capable of providing accurate results with a precision of approximately 0.1‰ for $\delta^{18}O$ and 1‰ for δ^2H in liquid water samples of up to 1000 mg/L dissolved salt concentration (Figure 3).

The IAEA is presently developing protocols for using this laser spectroscopic machine, including installation and operation manuals as well as data processing modules. Appropriate training courses also are being organized to provide IAEA member states with the ability to use this machine. Lastly, the provision of this machine through technical cooperation projects is being encouraged for routine operation in most member states. ■

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Learning about Best Practices in Aquifer Management in the USA

The IAEA Water Resources Programme supported a Study Tour/Aquifer Exchange, 16–26 April, 2007 in the USA together with the US Geological Survey (USGS) and GEF IW Learn to enhance the Management of Transboundary Aquifers.

Meeting with scientists, managers and policy-makers with real- life experiences combined with relevant field visits was a particularly effective approach for knowledge-sharing activities in the frame of cooperation among institutions. Various experts met, and case studies were presented highlighting the critical importance of a sufficient technical/ scientific understanding (good conceptual models, etc.) as a precursor to sound groundwater management as well as effective cooperation between countries.

What best practices and other practical experiences emerged from a groundwater study tour/learning exchange sponsored by the IAEA together with GEF IW:LEARN and coordinated by the USGS? Representatives from three transboundary aquifer projects, the Guarani in Latin America, the Northwest Sahara and Iullemeden in Africa convened in the U.S. last April to review integrated management lessons and experiences at several sites. The importance of isotopic tools was emphasized in many of the examples presented.

With the overall goal of building capacities for transboundary aquifer management by learning about best practices and exchanging experiences and thereby setting the foundation for a network for future interaction and mutual benefit, the specific objectives of the exchange addressed:

- Technical aspects of water resources in support of groundwater management decisions (isotopic tools, monitoring networks, characterization, geo-databases, GIS) and aquifer development (recharge, permits, uses)
- Managerial aspects of (ground)water in order to ensure a sustainable water supply through discussion about several aquifers in differing climatic and hydro-geological settings-groundwater management models across governing boundaries, water management indicators, institutional arrangements, legal framework, permits, water uses and tradeoffs, policy direction;
- Public participation options advocacy and citizenship building strategies, user groups and stakeholder participation

Participants reflecting on the workshop emphasized a number of key observations:

- It is important to build and maintain groundwater monitoring networks – without data it is impossible to manage water resources.
- A good balance between scientists and decision-makers' roles in terms of water resources management has proven to be fundamental.
- Good management is based on reliable and a strong technical baseline. It is very difficult to manage without sufficient technical information.
- Isotopic tools are particularly important for characterizing aquifers due to the unique characteristics of groundwater.
- Integrated ground and surface water resources management should be emphasized.
- A strong water management process between the USA and Mexico was based on a history of common projects that provide mutual benefits as well as a cooperation system in the Boundary and Water Commission level strongly based on a technical assessment and support system.
- Despite desalinisation becoming a real option for water supply, groundwater management is less expensive.

According to Luiz Amore, Director of the Guarani Aquifer project, "US water agencies play an important role in education, participation and supporting decision making process on surface waters, in sharing waters from rivers and channels, and groundwater management trying to integrate land surface and soil use on groundwater availability and quality."

The Guarani's Brazilian national director, Julio Kettlehut stressed that, "A key lesson learned is the need for technical

information or data for doing any kind of water management. This looks obvious, but for me, the biggest difference between the US groundwater management systems and our countries' systems are related to the databases that the USA has. Most of our countries have legal and institutional systems established according to social and cultural aspects of each one, but in general we do not have enough gathered valuable data information."

"The most important empirical thing I learned in terms of transboundary water resources management is the value of trust between countries," said Robert Montes also of the Guarani Aquifer, "Trust allows the International Boundary and Water Commission (USA-Mexico) to manage more than 600 miles of land border, and the Colorado and Rio Grande rivers in an efficient way. A great example to follow."

This groundwater learning exchange began at the US Geological Survey Headquarters in Washington D.C., where participants learned about approaches to integrated water resource management, fundamental need for sound science and a good database in developing conceptual models as well as efforts in involving stakeholders. In El Paso, Texas the group visited the International Boundary Water Commission (IBWC) and exchanged views about transboundary water management. The IBWC emphasized the fundamental importance of developing trust based in part on a consistent transparent exchange of data. In Tucson, Arizona, presentations focussed on issues related to management in a water scarce region. Integrated groundwater/ surface water management and use, the need for sound technical information, good communication practices as well as water re-use and a visit to a well-functioning Artificial Recharge site in Tucson. The final stop in San Diego, California provided an opportunity to consider water management in areas of fast growing populations. The participants also visited a desalinization plant in San Diego (of brackish groundwater) which represents a growing option for water supply in California as well as in many parts of the world.

Exchange participants visiting the City of Tucson, Arizona Aquifer Recharge Facility.

The exchange helped in identifying and recognizing that there are very strong resemblances and comparisons between water resources management in arid areas in parts of the USA, such as Arizona and California, and the challenges faced in Northern Africa. Transboundary aquifer management in terms of technical and institutional capacities were also at the centre of the similitude between the regions the participants came from.

The study tour provided the basis for enhancing a network of groundwater professionals active in GEF supported groundwater projects that will be continue to be facilitated via the GEF IW Learn Programme.

The group used a blog to make information available on a daily basis. Several follow-up activities were recommended including a suggested meeting of all GEF supported groundwater projects to discuss issues directly related to the management of transboundary aquifers including TDAs and SAPs for transboundary aquifers, developing groundwater management plans etc. The IAEA and USGS are also considering a second exchange with participants from other groundwater projects (e.g. Nubian Aquifer, Nile Groundwater, etc.).

For some participants, the learning exchange resulted in changes to their management plans. For the Iullemeden Aquifer, the exchange contributed new knowledge to:

- Mathematical local models scheduled to precise the connection between Niger river and the aquifers and the type of management according to the water demands (consumption, livestock, plants, irrigated agriculture),
- The formulation of the Strategic Action Program after the adoption of the Transboundary Diagnostic Analysis by the three countries (Mali, Niger and Nigeria). ■

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For more information on IW:LEARN's learning exchange program please contact Janot Mendler (janot@iwlearn.org) or visit http://www.iwlearn.net/exchange. Groundwater exchange blogs as well as all presentations are available at http://www.iwlearn.net/groundwater.

Summary of the International Symposium on Advances in Isotope Hydrology and its Role in Sustainable Water Resources Management (IHS—2007)

The 2007 Symposium was an exciting meeting with abundant opportunities for participants to exchange ideas and learn about current applications and research in isotope hydrology and water resources management.

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. ■

Symposium in Pictures


Melk

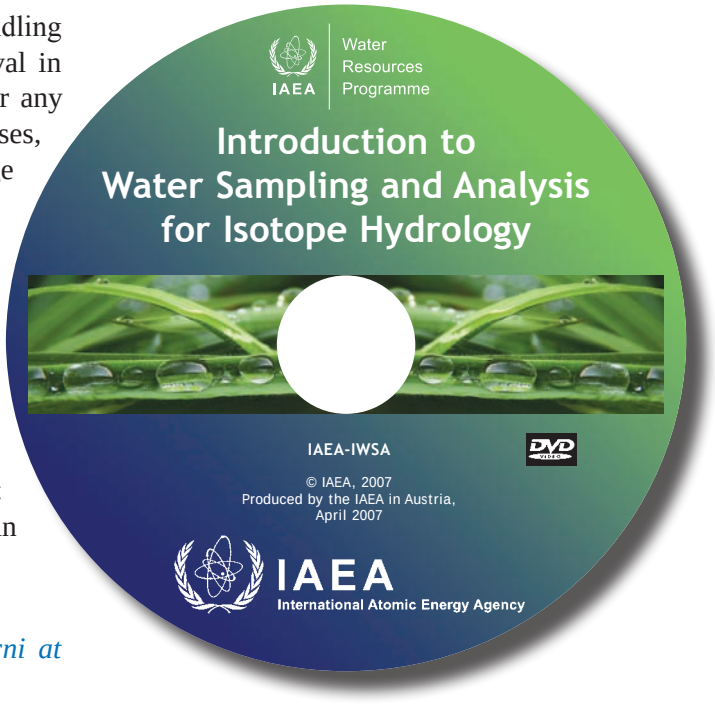

Requires
Integrated
flow


ADMIRAL TEGETTHOFF

Photo Credits. K.M. Kulkarni, D. Calma, L.Araguas, T.Vitvar and T.Chavez.

Introduction to Water Sampling and Analysis for Isotope Hydrology Video

Appropriate field sampling and the proper handling of water samples to the point of their arrival in laboratories for analysis is a prerequisite for any successful groundwater assessment. Yet, in many cases, simple mistakes are made due to a lack of knowledge of fundamental field sampling practices. This new video responds to this need by clearly demonstrating 'best practices' in collecting and handling samples in the field needed for utilizing isotopic techniques to support groundwater assessment activities. Field staff are often not involved in either planning of sampling campaigns or in assessing the data acquired. The wide distribution and use of this video should lead to improved abilities of field staff to conduct sampling appropriately and lead to better results in groundwater assessment activities. ■



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Atlas of Isotope Hydrology – Africa

At the core of all efforts for sustainable human development lies adequate supply of fresh water. With increasing populations and economic growth, it is imperative that we reach a balance between demand and availability of fresh water, protect available resources in rivers, lakes and aquifers, and prevent disputes over shared resources. Fresh water is a finite resource and, unlike many other strategic resources, fresh water has no substitute in most of its uses. Groundwater is an important resource for Africa, providing nearly two-thirds of drinking water on the continent, and an even greater proportion in northern Africa.

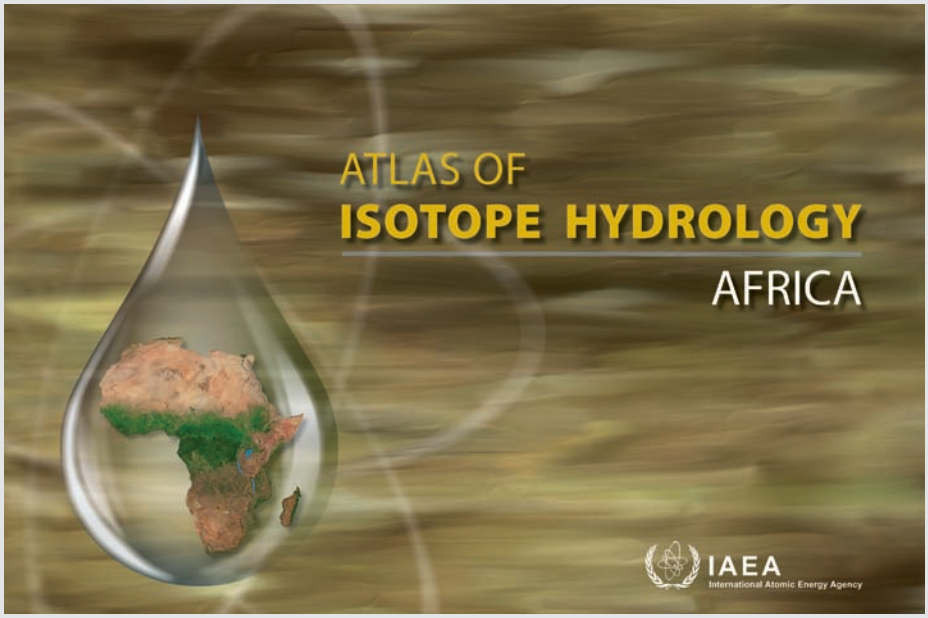
Despite the importance of groundwater for many societies, the world's groundwater resources are poorly understood and there is a lack of corresponding public concern about its protection, perhaps because the extent and availability of groundwater are not easily measured. Applications of isotopes in hydrology are based on the general concept of "tracing". Environmental isotopes are unique in regional studies of water resources to obtain temporally and spatially integrated characteristics of groundwater systems. Among the most important areas where isotopes are useful in groundwater applications include aquifer recharge and discharge processes, flow and interconnections between aquifers, and the sources, fate and transport of pollutants.

This Atlas of Isotope Hydrology focuses on Africa. Data from nearly 10 500 isotope records gathered from about 80 IAEA projects in 26 African countries from 1973 to 2007 are included. For each country, a digital elevation map is provided that shows major water bodies, locations of stations in the IAEA global network of isotopes in precipitation (GNIP) and the project study areas. Summary pages for each project include a higher resolution map of the study area, and data tables and plots for median and mean $\delta^{18}O$ and $\delta^{2}H$, average annual precipitation and air temperature, tritium values, and radiocarbon in groundwater.

The Isotope Hydrology Information System (ISOHIS), maintained by the Isotope Hydrology Section of the IAEA, has been the source of the hydrological and isotope information used in the compilation of this Atlas of Isotope Hydrology – Africa. The isotope information presented in the Atlas can be downloaded through the online application WISER from the internet site: http://www.iaea.org/water.

The isotopic information presented in this unique Atlas is expected to be a valuable reference to scientists, practitioners and policy makers engaged in the field of hydrology. ■

For further information, please contact K.M. Kulkarni at k.m.kulkarni@iaea.org or L.Araguas at l.araguas@iaea.org



Publication No.: STI/PUB/1302
August 2007
ISBN 978-92-0-107207-8
Price: € 110

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News in Brief

Awards/Recognitions and Publications

- An exhibit prepared by the IAEA WRP won an innovation award during the GEF International Waters Conference in Cape Town, South Africa held from 31 July–3 August, 2007. As a side event to the Conference, the Innovation Marketplace Exhibit served as a venue for exchange of ideas, information and knowledge. The IAEA had a booth entitled Isotopes–Water's Key, introducing the IAEA/UNDP/GEF Nubian Aquifer Project along with highlighting the scientific role of isotopic techniques. A 'water tasting event' was also held at the booth as a side event for the Conference with water coming from Libyan Arab Jamahariya, Australia and Austria. The objective of providing water of different ages was to highlight challenges in groundwater assessment and the special role of isotopes.

New Staff Member

- Mr. Ahmed Ragab Allam joined the the IAEA as the Project Manager for the joint IAEA/UNDP/GEF Nubian Shared Sandstone Aquifer Project in August 2007. Mr. Allam works collaboratively with the Water Resources Programme and the Division for Africa. Formerly, he was Director General of the Egyptian Water Resources & Irrigation Mission in Uganda. His interests include water resources management, especially groundwater management. He has been involved in facilitating cooperation with international waters, working in Uganda and Sudan as well as in various activities related to Nile River Basin cooperation.

Departing Staff Member

- Mr. Andy Garner left the Isotope Hydrology Section as of 30 November, 2007 to begin a new position within the IAEA as Programme Coordinator for the Department of Nuclear Sciences and Applications. Mr. Garner was Water Resource Management Specialist involved in facilitating various programme activities supported by the IAEA involving the management of transboundary waters including two new initiatives, for the Nubian Sandstone Aquifer System (NSAS) and for the Nile River Basin, both in collaboration with the United Nations Development Programme (UNDP) and the Global Environmental Facility (GEF.) He also worked on building partnerships in the water sector and enhancing communication and outreach activities.

Meetings

- First coordination meeting on the regional project RER/8/012 "Isotope Methods for Management of Drinking Water Resources in Water Scarcity Areas" was held at the IAEA headquarters from 25–29 June 2007. National and regional scale water related activities and technical themes of common concern to the TC European region were discussed during the meeting. Possible joint activities on the transboundary water resources and creating a network between institutions in the region were also analysed.

- Under the IAEA/UNDP/GEF Nubian Aquifer Project a modelling meeting was held from 21–24 August, 2007, where representatives from Chad, Egypt, Libyan Arab Jamahariya and Sudan participated. This was a consecutive meeting resulting from the SADA/SAP Training Course and SADA planning meeting previously held in March, 2007 in Khartoum, Sudan. The meeting was held with great success and further consultations on the project were carried out. During the meeting modelling techniques were reviewed and introduced as tools that provide a system for decision-making under the implementation of the project and that complement the analysis for the preparation of the Shared Aquifer Diagnostic Analysis (SADA). Previous modelling and available data on the Nubian Aquifer was reviewed and the discussions were held on the options, needs and approaches for a new, comprehensive and improved model.

- A Technical Meeting entitled The Application of Isotope Techniques for Water Quality Assessment and Management–Focusing on Nutrient Management in Rivers was held in Vienna, Austria during 8–10 October, 2007. With a dozen participants, the meeting's main objective was to present papers that will be compiled

for an IAEA publication (a 'guidebook') on isotope techniques for nutrient management in rivers, and to discuss ideas and synthesis papers for the publication.

Training Course

- IAEA Regional Training Course on Application of Isotope Techniques in Hydrology was held at the Center for Ecotoxicological Research of Montenegro, Budva, Montenegro during 5–14 November, 2007. The main purpose of the course was to provide participating young professionals with adequate practical training in methodologies on the application of isotope techniques in hydrology, data interpretation and groundwater modelling. Practical demonstration of isotopic sampling was also offered. The course was part of efforts supported by the IAEA through technical cooperation projects for addressing country specific water resource management issues.Twenty-two trainees from Albania, Croatia, Cyprus, Hungary, The Former Yugoslav Republic of Macedonia, Lithuania, Malta, Republic of Moldova, Montenegro, Serbia and Tajikistan, 3 external lecturers and two IAEA staff participated in this activity.

Cooperation

- The IAEA Isotope Hydrology Section participated in the 2007 Joint Danube River Survey (JDS). Last summer, three ships completed an over 2400 km journey in almost 50 days along the River Danube. From the headwater area of the Danube above Regensburg, Germany to the Black Sea, the trip was the world's biggest river research expedition in 2007. The mission was to conduct a survey of the biological, geochemical, and hydrological status of river water, habitats, and sediments at 95 sampling points along the main Danube stem and its 11 large tributaries. The expedition attracted international collaboration of all Danube countries and included an on-board research team of 18 scientists from 8 countries. The IAEA Isotope Hydrology Section cooperated with the International Commission on the Protection of the Danube River (ICPDR) in the river research expedition, to conduct a series of isotope surveys at over 100 locations. In addition, an on-board radon detector was used to map ^{222}Rn concentrations in the river. The isotope studies will be used to understand such issues as groundwater input to the river, role of tributaries and human impact in the spatial evolution of Danube water quality and quantity.

New Developments/Forthcoming

- A new IAEA/UNDP/GEF joint initiative entitled Mainstreaming Groundwater Considerations into the Integrated Management of the Nile River Basin has been approved and is due to be launched and begin activities in the first quarter of 2008. The project objective will be to enhance national and regional capacity to add a 'groundwater dimension' to joint management of the Nile Basin by means of filling an information gap about the role of groundwater and its contribution to water balances in lakes, rivers, and wetlands. It will complement other projects in the region and will bring support and coordination from regional institutions and will ensure a common understanding of groundwater issues and analysis among the riparian countries.■

Editor's Note

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Radon and Radium Isotopes as Tracers of Coastal Mixing and Submarine Groundwater Discharge

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1. Introduction

Subsurface discharge of water from coastal aquifers, called submarine groundwater discharge (SGD), has been recognized as an important component of hydrological cycle. This discharge includes meteoric water from land drainage as well as sea water that has entered coastal aquifers. We follow Burnett et al. (2003) in defining submarine groundwater discharge as any and all flow of water on continental margins from the seabed to the coastal ocean, regardless of fluid composition or driving force.

SGD is increasingly being recognized as an important factor in the understanding and sustainable management of coastal fresh water aquifers in many highly populated areas of the world. In addition, SGD is a significant pathway for communication of materials between the land and the sea. SGD is known to supply essential nutrients and trace metals to coastal oceans. In some cases SGD may result in contamination of the near-shore marine environment from land-based activities. Additionally, SGD may remove certain components (e.g., uranium) from seawater during circulation through coastal aquifers. Thus, SGD and related processes may be important as both a source and a sink in geochemical cycles. As we learn more about SGD and subterranean aquifers, we recognize how significant these processes are to the coastal ocean.

Estimation of SGD is complicated due to the fact that direct measurement over large temporal and spatial scales is not possible by conventional means. Measurement of a range of isotopic tracers at the aquifer–marine interface and in the coastal ocean provides the possibility to produce integrated flux estimates of discharge not possible by non-nuclear methods. Many researchers have applied a variety of methods to estimate SGD (see Burnett et al., 2006 for review). A large spread of global estimates for SGD fluxes illustrates the high degree of variability and uncertainty of present estimates. It should be noted that estimates based on water balance considerations and some models usually include only the fresh water fraction of the total hydrologic flow. Recirculated seawater and saline groundwater fluxes are often volumetrically important and may increase these flows substantially.

In cases of fresh water fluxes chemical anomalies such as salinity are useful for estimation of SGD. However, in cases of brackish and saline SGD fluxes, which in many cases have more impact on the coastal environment, isotopes have distinct advantages over chemical techniques. Investigations using a combination of stable, long-lived, and short-lived radioisotopes along with other complementary techniques allow various aspects of coastal hydrology to be studied.

2. Use of Radium Isotopes to Estimate SGD

Within the decay series of uranium and thorium are four radium isotopes (Figure 1). All derive from decay of thorium parents, which are tightly bound to particles. Due to a reduction in the adsorption coefficient of radium with increasing salinity (Li et al., 1977), radium daughters are mobilized in the marine environment. Sediments thus provide a continuous source of Ra isotopes to marine waters at rates set by the decay constants of the Ra daughters. Measurements of the Th isotope activities in the sediments and the distribution coefficient of radium between the sediments and water provide a means of quantifying the potential input of each Ra isotope to the water. With half-lives ranging from 3.66 days (^{224}Ra) to 11.4 days (^{223}Ra) to 5.7 years (^{228}Ra) to 1600 years (^{226}Ra), this quartet of isotopes can provide powerful constraints on processes occurring in estuaries, salt marshes, and the coastal ocean.

Salty groundwater contacts more sediment surfaces than do surface waters, therefore groundwaters usually have high activities of Ra. As salty groundwater flushes through the sediments, Ra is transferred to the coastal ocean. Once lost from the sediments, the Ra isotopes regenerate at different rates. The long lived ^{226}Ra requires 1600 years to regenerate 50% of its activity, but ^{228}Ra regenerates 50% of its activity in 5.7 years. Because the sediments retain Th but not Ra, they serve as a constant source of Ra to marine waters. Surficial coastal aquifers that are continuously flushed with salt water have low activities of ^{226}Ra. Deeper aquifers that are flushed less efficiently often have higher ^{226}Ra.

The discovery of high activities of ^{226}Ra in the coastal ocean that could not be explained by input from rivers or sediments coupled with measured high ^{226}Ra in salty coastal wells led to the hypothesis that submarine groundwater discharge

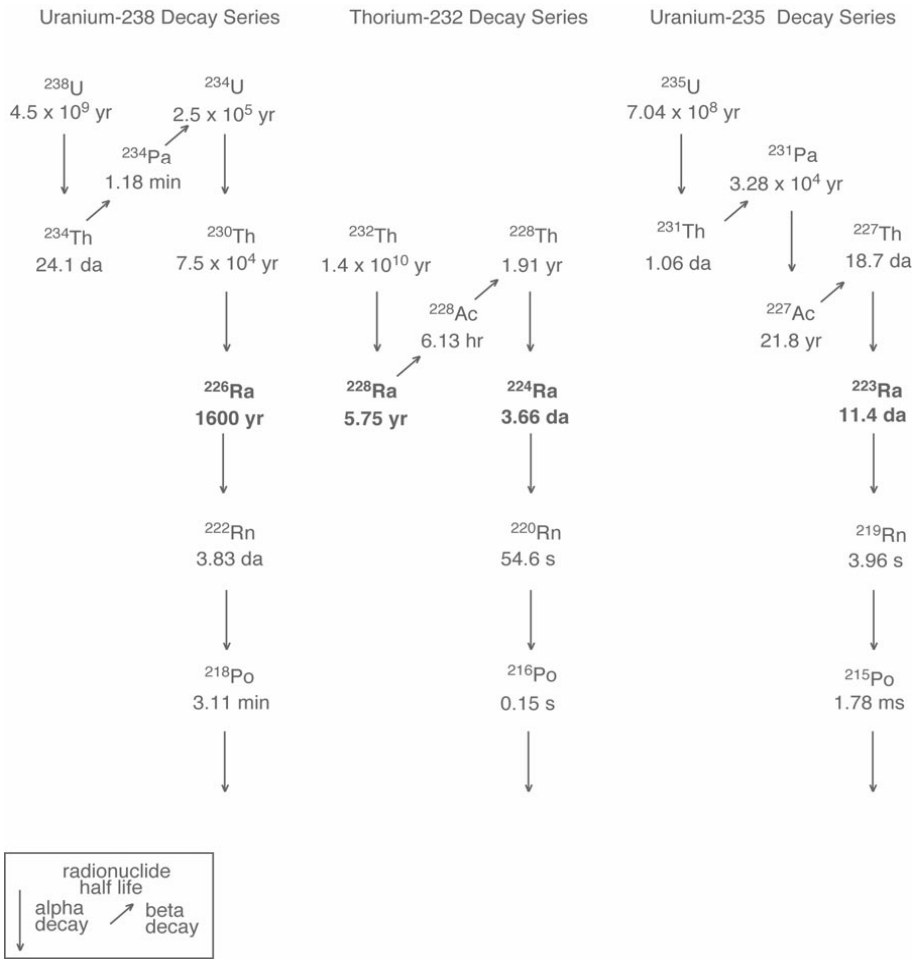

Figure 1. Isotopes of the uranium and thorium decay series.

(SGD) was responsible for the elevated activities (Moore, 1996). Earlier, similar reasoning had been used to deduce a large SGD flux to the Swanatee River (Burnett et al., 1990). The excess ^{226}Ra in a salt marsh was also explained by SGD (Rama and Moore, 1996). Since then excess ^{226}Ra has been a diagnostic tracer of SGD in the coastal ocean (Moore, 1997; Moore and Shaw, 1998; Moore, 1999; ; Krest et al., 2000; Charette et al., 2001; Kelly and Moran, 2002; Moore et al., 2002; Crotwell and Moore, 2003; Moore, 2003; Kim and Hwang, 2002; Kim et al., 2003; Krest and Harvey, 2003; Moore and Wilson, 2005; Hwang et al., 2005; Moore et al., 2006; Moore, 2006).

The two short lived Ra isotopes, ^{223}Ra and ^{224}Ra, provide additional evidence of groundwater input. Rama and Moore (1996) used the four Ra isotopes to determine that groundwater input to the North Inlet salt marsh occurred where tidal creeks were cut into deeper aquifers rather than through muddy surficial sediments. The short-lived isotopes may also provide a means of estimating the residence time of estuarine and coastal waters (Moore, 2000a; 2000b; Moore et al., in 2006). The residence time is important because it provides the time scale available for components to accumulate in the water column.

2.1. Measurement of Radium Isotopes

Ra isotope measurements are made by filtering 20–400 L of surface water or 1–20 L groundwater into plastic buckets. The sample volume is recorded and the water is pumped through a column of manganese coated acrylic fiber (Mn fiber) to quantitatively remove Ra (Moore, 1976). Each Mn fiber sample is partially dried with a stream of air and placed in closed loop air circulation system described by Moore and Arnold (1996). Helium is circulated over the Mn fiber to sweep the ^{219}Rn and ^{220}Rn generated by ^{223}Ra and ^{224}Ra decay through a 1 L scintillation cell where alpha particles from the decay of Rn and daughters are recorded by a photomultiplier tube (PMT) attached to the scintillation cell. Signals from the PMT are routed to a delayed coincidence system pioneered by Giffin et al. (1963) and adapted for Ra measurements by Moore and Arnold (1996). The delayed coincidence system utilizes the difference in decay constants of the short-lived Po daughters of ^{219}Rn and ^{220}Rn to identify alpha particles derived from ^{219}Rn or ^{220}Rn decay and hence to determine activities of ^{223}Ra and ^{224}Ra on the Mn fiber. The expected error of the short-lived Ra measurements is 10%. Because counts are only recorded in coincidence, the background of this system is extremely low.

After the ^{223}Ra and ^{224}Ra measurements are complete, the Mn fiber samples are aged for 2–6 weeks to allow initial excess ^{224}Ra to equilibrate with ^{228}Th adsorbed to the Mn fiber. The samples are measured again to determine ^{228}Th and thus to correct for supported ^{224}Ra.

After these measurements are completed, the Mn fibers are leached with HCl in a Soxhlet extraction apparatus to quantitatively remove the long lived Ra isotopes. The Ra is coprecipitated with $BaSO_4$. The precipitant is aged for 2 weeks to allow ^{222}Rn and its daughters to equilibrate with ^{226}Ra. Alternately the Mn fiber can be ashed or compressed into a standard geometry and measured directly after the ingrowth period (Dulaiova and Burnett, 2004). The samples are measured in a gamma ray spectrometer to assess the activities of ^{226}Ra and ^{228}Ra (Moore, 1984). The expected error of the long-lived Ra measurements is 7%.

Standards are used to calibrate the efficiency of the counters. For ^{224}Ra the standard is prepared by adsorbing ^{232}Th in equilibrium with its daughters onto a column of Mn-fiber. For ^{223}Ra, the standard is ^{227}Ac in equilibrium with its daughters. These standards are prepared with activities similar to that of samples. They are treated just as the samples described above in the delayed coincidence system. For ^{226}Ra, a standard solution having an activity about 10–100 times the sample activity is precipitated with $BaSO_4$ as described above. For ^{228}Ra the standard is a solution of ^{232}Th with daughters in equilibrium. This is treated the same way as the ^{226}Ra standard.

2.2. Interpretation of Radium Isotope Data

a. Separating Sources of SGD

Moore (2003) used the ^{228}Ra/^{226}Ra AR to distinguish groundwater derived from the upper Floridan Aquifer (UFA) vs the surficial aquifer (SA) in samples collected on the Gulf coast of Florida near the Florida State University Marine Lab (30°N). He found that most surface water samples fell along a mixing line having a ^{228}Ra/^{226}Ra AR = 2.5, indicating a surficial aquifer source (Figure 2). However, some offshore samples fell off this trend and toward a sample from an artesian well in the UFA. Springs in the area were also influenced by the UFA source. Moore (2003) used a 3-endmember mixing model to assess the relative amounts of water from the open Gulf, the offshore UFA, and the nearshore SA in the surface water samples.

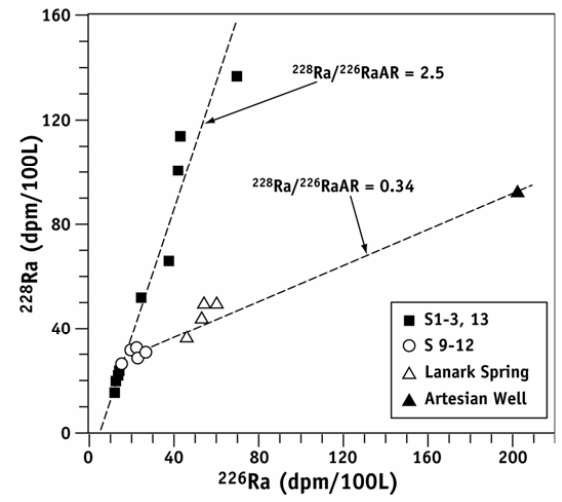

Figure 2. Samples collected near the FSU Marine Lab (Moore, 2003) show large radium enrichments. Nearshore surface water samples (shown as squares) fall on a trend having a ^{228}Ra/^{226}Ra mixing ratio = 2.5. Most samples collected offshore (also shown as squares) fall on the same trend. Some samples collected offshore (circles) have lower salinity and fall below the trend for the other offshore samples. These lower salinity samples fall near a mixing line that includes samples collected near a submarine spring (open triangles) and an onshore artesian well from the Florida aquifer (triangles). The mixing ratio for these samples is 0.34. These data illustrate the use of the long-lived Ra isotopes for differentiating signals derived from the surficial and the Floridan aquifers.

A result of the model was the presence of a significant and variable UFA component in the surface water.

The following equations are used to establish the 3-end-member mixing model.

$$f_o + f_{ns} + f_{os} = 1.00 \quad (1)$$

$$^{226}Ra_o f_o + {}^{226}Ra_{ns} f_{ns} + {}^{226}Ra_{os} f_{os} = {}^{226}Ra_m \quad (2)$$

$$^{228}Ra_o f_o + {}^{228}Ra_{ns} f_{ns} + {}^{228}Ra_{os} f_{os} = {}^{228}Ra_m \quad (3)$$

where

f is the fraction of ocean (*o*), nearshore SGD (*ns*), or offshore SGD (*os*) end-member,

Ra_o is ^{226}Ra or ^{228}Ra activity in the ocean end-member,

Ra_{ns} is ^{226}Ra or ^{228}Ra activity in the nearshore SGD end-member,

Ra_{os} is ^{226}Ra or ^{228}Ra activity in the offshore SGD end-member,

Ra_m is measured ^{226}Ra or ^{228}Ra activity in the sample.

These equations may be solved for the fractions of each end-member.

$$f_{NS}=\frac{\left(\frac{^{228}Ra_M - {}^{228}Ra_0}{^{228}Ra_{OS} - {}^{228}Ra_O}\right) - \left(\frac{S_M - S_0}{S_{OS} - S_O}\right)}{\left(\frac{^{228}Ra_{NS} - {}^{228}Ra_O}{^{228}Ra_{OS} - {}^{228}Ra_O}\right) - \left(\frac{S_{NS} - S_O}{S_{OS} - S_O}\right)} \quad (4)$$

$$f_{OS} = \frac{S_M - S_O - f_{NS}(S_{NS}-S_O)}{S_{OS} - S_O} \quad (5)$$

$$f_O = 1.00 - f_{NS} - f_{OS} \quad (6)$$

A similar result was obtained from samples collected on the southern coast of Sicily (Moore, in 2006). Springs from a limestone aquifer discharging on the beach and just offshore had much lower $^{228}Ra/^{226}Ra$ AR than did shallow wells on the beach. Samples collected in the nearshore zone as well as samples collected in seepage bags fell between the isotopic composition of these sources. Again the 3-endmember model was able to resolve these sources.

b. Evaluating Coastal Ocean Exchange Times and SGD Fluxes

To evaluate the balance of radium in the coastal ocean, the exchange rate or residence time of the water must be known. Moore (2000a) used the short-lived Ra isotopes to estimate exchange rates. The model used was a one-dimensional advection–dispersion model. The change in concentration or activity (A) with time (t) as a function of distance offshore (x) for a radioactive tracer with decay constant (λ) may be expressed as a balance of advection, dispersion, and decay

$$\frac{dA}{dt} = K_h \frac{\partial^2 A}{\partial x^2} - \omega \frac{\partial A}{\partial x} - \lambda A \quad (7)$$

If net advection, ω, can be neglected, this reduces to

$$\frac{dA}{dt} = K_h \frac{\partial^2 A}{\partial x^2} - \lambda A \quad (8)$$

where K_h is the dispersion coefficient. In this case the boundary conditions are

$$A = A_i \text{ at } x = 0$$
$$A \to 0 \text{ as } x \to \infty$$

If K_h is constant and the system is steady state,

$$A_x = A_0 \exp\left[-x\sqrt{\frac{\lambda}{K_h}}\right] \quad (9)$$

where

A_x = activity at distance x from coast
A_0 = activity at distance 0 from coast
λ = decay constant

A plot of ln ^{223}Ra or ln ^{224}Ra as function of distance from the coast may be used to estimate K_h if the exchange is dominated by dispersion rather than advection and if the system is steady state.

$$\ln A_x = \ln A_0 - x\sqrt{\frac{\lambda}{K_h}} \quad (10)$$

In this case the slope,

$$m = \sqrt{\frac{\lambda}{K_h}} \quad (11)$$

The long-lived Ra isotopes are used to assess the relative roles of advection and dispersion. Decay of ^{226}Ra and ^{228}Ra may be neglected over the time scale of shelf water exchange. Figure 3 is a plot of the distance averaged activity of ^{226}Ra and ^{228}Ra as a function of distance offshore for repeated occupations of offshore transects in the South Atlantic Bight reported by Moore (2000a).

For ^{226}Ra, the data within 50 km of the coast fit a line with a slope of -0.219 dpm·100L^{-1}·km^{-1} having r^2 = 0.951; for ^{228}Ra the slope is -0.319 dpm·100L^{-1}·km^{-1} with r^2 = 0.959. These excellent linear correlations are strong evidence that the distributions within 50 km of the coast are controlled by dispersion with negligible net advection.

There is clearly a break in slope at 50 km offshore for both isotopes. Two processes could cause this change. Advection of water from the southwest could interrupt the profile. Such advection is consistent with the wind pattern during this cruise (Moore et al., 1998) and the flow of the Gulf Stream. The break in slope could also be produced by more rapid mixing of water in the 50–100 km region or to a large eddy transporting Ra from another area. Because of these possibilities the mixing can only be determined for the inner 50 km.

During the same cruise, activities of ^{223}Ra and ^{224}Ra were measured. These results were distance averaged for repeated

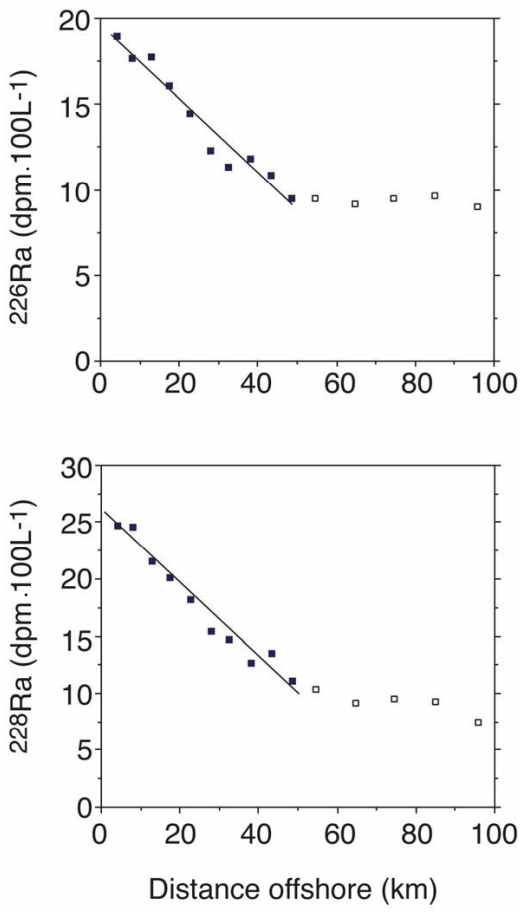

Figure 3. The distance averaged distribution of the long-lived Ra isotopes across the continental shelf of South Carolina (Moore, 2000a).

transects as described above. Figure 4 shows the activities of the ln transforms of ^{223}Ra and ^{224}Ra as a function of distance from shore. For ln ^{223}Ra, the distribution within 50 km of shore has a slope of -0.0439 dpm·100L^{-1}·km^{-1} with $r^2 = 0.973$. The distribution of ln ^{224}Ra over the same interval has a slope of -0.0724 dpm·100L^{-1}·km^{-1} with $r^2 = 0.986$. Using equation 10 and its assumptions, the value of K_h derived from ^{223}Ra is 31.5 km^2·d^{-1} (360 m^2·s^{-1}); for ^{224}Ra equation 10 yields K_h = 36.2 km^2·d^{-1} (420 m^2·s^{-1}). The differences in these estimates may be due in part to differences in the time and space scales of eddy mixing. The longer lived ^{223}Ra looks at a larger scale than ^{224}Ra. However, it is encouraging that in this experiment the estimates from the two short lived isotopes are very similar.

We may use the estimates derived here to calculate the flux of ^{226}Ra and ^{228}Ra from the coast to the ocean as described by Moore (2000a). The flux of a conservative tracer can be estimated from the product of the offshore concentration gradient and K_h. The ^{226}Ra gradient is -0.219 dpm·100L^{-1}·km^{-1} or -2.19 × 10^9 dpm·km^{-3}·km^{-1}. For K_h = 34 km^2·d^{-1} (the average of the two estimates), the offshore ^{226}Ra flux is 7.5 × 10^{10} dpm·km^{-2}·d^{-1}. This Ra is transported offshore in the 10 m deep surface layer; therefore, the offshore flux is 7.5 × 10^8 dpm·km^{-1}·d^{-1}.

The total flux for the 80 km coastline from Charleston, SC, to Winyah Bay, SC, is 6 × 10^{10} dpm·d^{-1}. If this flux can be scaled to the 320 km coastline of the entire study area, the flux would be 2.4 × 10^{11} dpm·d^{-1}. The ^{228}Ra data indicate an offshore flux of this isotope for the entire study area of 3.5 × 10^{11} dpm·d^{-1}. Based on the ^{226}Ra data used here and an assumed 30 day residence time for waters of the inner shelf, Moore (1996) estimated that the ^{226}Ra flux from this coastline was 2.1 × 10^{11} dpm·d^{-1}.

To use the flux of the long-lived Ra isotopes to estimate SGD, we must know the Ra activity in the source water that supplies the SGD. Salty groundwater along this coast has a ^{226}Ra activity in the range 2–10 dpm·L^{-1} with most values in the range 4–8 dpm·L^{-1}.

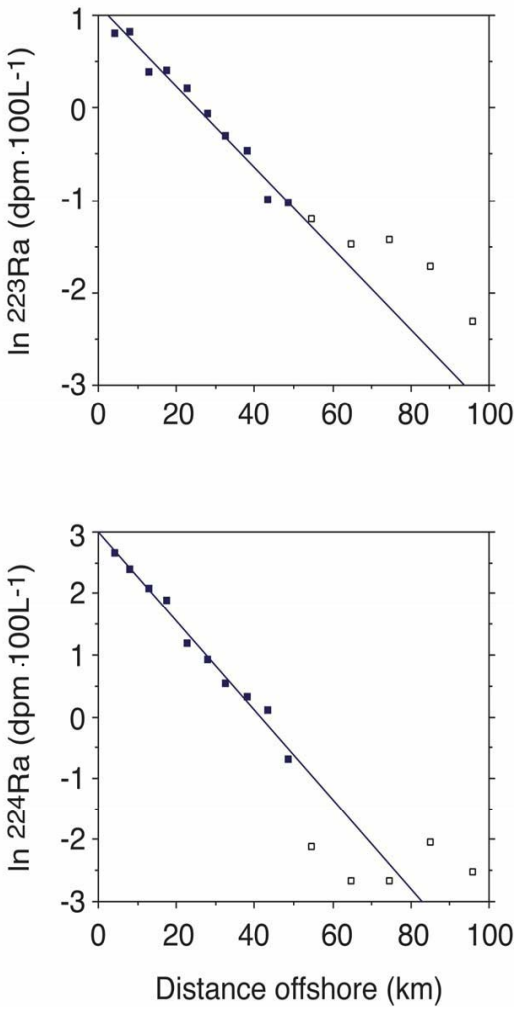

Figure 4. The distance-averaged distribution of the ln transform of the short-lived Ra isotopes across the continental shelf of South Carolina (Moore, 2000a).

If we take 6 dpm·L^{-1} as the average, the SGD flux may be calculated by dividing the ^{226}Ra flux by the average ^{226}Ra in the groundwater. This yields a flux of 3.5×10^{10} L·d^{-1} or 400 $m^3 \cdot s^{-1}$.

c. Evaluating Fluxes of Other Components

If we know the composition of other components in the SGD, estimating their fluxes once the SGD flux is known is trivial. However, in making the SGD flux based on ^{226}Ra we had to take the average ^{226}Ra that had been measured in coastal wells. Another approach is to look for relationships between Ra and other components in the groundwater. If such relationships are found, the component/Ra ratio in the groundwater can be multiplied by the Ra flux to yield the component flux. Such an approach was used by Moore et al. (2002) to estimate nitrogen and phosphorus fluxes to coastal waters, They found strong relationships between total dissolved nitrogen (TDN) and ^{226}Ra and totaldissolved phosphorus (TDP) and ^{226}Ra used these relationships to determine TDN and TDP fluxes. Figure 5 shows the relationships measured in monitoring wells off the South Carolina coast.

Assuming that the water supplying excess ^{226}Ra to the coastal ocean is similar to these well waters, we use the nutrient-Ra correlation to estimate the nutrient flux (Figure 5). For example the total dissolved phosphate (TDP) to ^{226}Ra ratio is 0.93 µM·dpm^{-1}. To support a ^{226}Ra flux of 1.5×10^{11} dpm·d^{-1}, the accompanying TDP flux is 1.4×10^5 moles·d^{-1}. The total dissolved nitrogen (TDN)/^{226}Ra ratio is 26.4 µM·dpm^{-1}, thus the TDN flux would be 4.0×10^6 moles·d^{-1}.

d. Evaluating Estuary Residence Times

Moore (2000b) developed a model to estimate the ages of water masses in the coastal ocean. This model assumed that radium was only added to the water near the shoreline; after the water left the coast and lost contact with the bottom, radium additions ceased. This model is not applicable to estuaries and salt marshes where radium additions from sediments and groundwater are continuous. To use radium isotopes to estimate ages in these systems, Moore et al. (in 2006) used a different approach. A similar approach was developed by Hwang et al. (2005). Assume the system under study is in steady state, that is radium additions are balanced by losses. Additions include radium fluxes from sediment, river, and groundwater; losses are due to mixing and, in the case of ^{223}Ra and ^{224}Ra, radioactive decay.

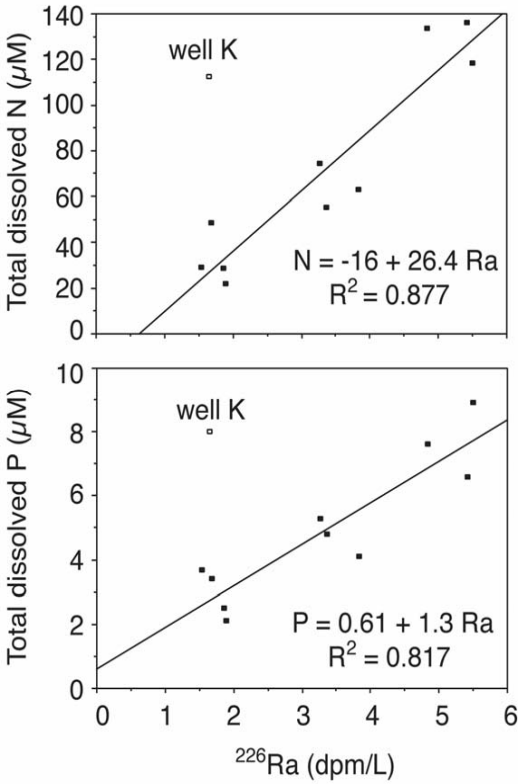

Figure 5. The concentrations of total dissolved nitrogen and phosphorus display strong correlations with ^{226}Ra in samples from monitoring wells off the South Carolina coast (Moore et al., 2002).

Write an equation for the ^{224}Ra balance:

$$F\ ^{224}Ra = I\ ^{224}Ra\ (\lambda_{224} + 1/\tau) \quad (12)$$

where F ^{224}Ra is the total flux of ^{224}Ra to the system, I ^{224}Ra is the inventory of ^{224}Ra in the system, λ_{224} is the decay constant for ^{224}Ra, and τ is the apparent age of water in the system. We can write a similar equation for ^{228}Ra; but, because the half-life is 5.7 years, the effect of decay can be ignored.

$$F\ ^{228}Ra = I\ ^{228}Ra\ (1/\tau) \quad (13)$$

Now divide equation 12 by equation 13.

$$F\ (^{224}Ra/^{228}Ra) = I\ ^{224}Ra\ (\lambda_{224} + 1/\tau)/\ I\ ^{228}Ra\ (1/\tau) \quad (14)$$

This equation can be rearranged and solved for τ:

$$\tau = [F(^{224}Ra/^{228}Ra)\text{-}I(^{224}Ra/^{228}Ra)]/I(^{224}Ra/^{228}Ra)\lambda_{224} \quad (15)$$

In this case F (^{224}Ra/^{228}Ra) is the ^{224}Ra/^{228}Ra activity ratio (AR) of the flux into the system, I (^{224}Ra/^{228}Ra) is the

$^{224}Ra/^{228}Ra$ AR in the system, and λ_{224} is the decay constant of ^{224}Ra (0.19 d^{-1}). Here we use the $^{224}Ra/^{228}Ra$ AR because the time scale is appropriate to the ^{224}Ra half-life. In cases where ages are expected to be on the order of weeks, a similar equation based on ^{223}Ra would be more appropriate. This model is quite sensitive to the value selected for the $^{224}Ra/^{228}Ra$ AR of water entering the system. This can be determined by finding areas of discharge via infrared imaging or other techniques and measuring shallow groundwaters at these sites. Another approach is to collect as much data as possible from shallow permeable sediments and plot ^{224}Ra vs ^{228}Ra to determine the average activity ratio.

2.3. Summary of Radium Studies

There are good reasons why radium is closely linked to SGD studies. Because radium is highly enriched in salty coastal groundwater relative to the ocean, small inputs of SGD can be recognized as a strong radium signal. In many cases this signal can be separated into different SGD components using the two long-lived Ra isotopes. The short-lived Ra isotopes are useful in evaluating the residence time or mixing rate of estuaries and coastal waters. Such estimates coupled with distributions of the long-lived Ra isotopes enables a direct estimate of radium fluxes. At steady state these fluxes must be balanced by fresh inputs of Ra to the system. If other sources of Ra can be evaluated, the Ra flux that must be sustained by SGD can be evaluated. By measuring the Ra content of water in the coastal aquifers, the amount of SGD necessary to supply the Ra is determined. SGD fluxes of other components are determined by measuring their concentrations in the coastal aquifer or by determining relationships between the component and Ra and multiplying the component/Ra ratio by the Ra flux.

3. Use of Radon

Natural ^{222}Rn ($t_{1/2}$ = 3.83 days, Figure 1) provides a means of determining SGD pathways and fluxes into the coastal zone. The ^{222}Rn activities in groundwater are often 2–4 orders of magnitude higher than the activity in seawater. The radon tracing method is an excellent qualitative tool for identifying areas of spring or seepage inputs in most coastal environments. Radon measurements can also be used to quantify SGD. The utility of ^{222}Rn as a tracer of SGD has been demonstrated in a wide range of environments from coastal embayments to the coastal ocean (Burnett et al., 1996; Cable et al., 1996a; Corbett et al., 2000). The very large enrichment of ^{222}Rn concentration in groundwater over surface waters, its unreactive nature, and short half-life make ^{222}Rn an excellent tracer to identify areas of significant groundwater discharge. The approach for quantifying SGD using ^{222}Rn is similar to radium (^{226}Ra), except for a few key differences (Fig. 11): (1) ^{222}Rn loss to the atmosphere must be accounted for in many situations, (2) there is no significant source from particles in rivers, and (3) decay must be accounted for owing to its relatively short half-life. Using the steady state flux by difference approach, this equation is:

$$F_{SGD} = \frac{\left[\frac{(A - A_{ocn})z_{wc}}{T_w}\right] - \left[\phi D_s\left(\frac{\partial A_{sed}}{\partial z_{sed}}\right)\right] + \left[e_g(A - A_{atm})\right] + \left[\lambda A\right]z_{wc}}{A_{gw}} \quad (16)$$

3.1. Measurement of Radon

Radon samples may be collected in the field and measured in the laboratory or it may be measured directly in the field. For lab measurements, samples (0.5 to 20 L) are drawn into evacuated vessels and kept sealed. Most laboratory procedures use a gas circulation system in which a carrier gas (helium or nitrogen) is passed through the sample to flush the radon through a moisture trap and into a cold trap where it is adsorbed. The cold trap is evacuated and then warmed so that radon will be passes into a counting chamber. The counting chamber consists of a cylinder having silver-activated zinc sulfide on the inside. After allowing the ^{222}Rn daughters to reach secular equilibrium (about 2 hours), the chamber is attached to a photomultiplier tube (PMT). Alpha particles from decay of ^{222}Rn and its daughters activate the zinc sulfide causing emission of light. The PMT converts these emissions into electrical pulses that are amplified and scaled. Later the sample can be measured again to assess the activity of ^{226}Ra. Excess ^{222}Rn is the initial measured ^{222}Rn minus the ^{226}Ra activity.

Field measurements of ^{222}Rn are usually done with a solid-state alpha detector in a commercial radon-in-air monitor. The radon is purged from the sample, dried, and then passed into the detector. Alpha decays are recorded as a function of their energy, so the instrument is specific for each isotope in the decay chain. Burnett et al. (2001) developed a continuous radon monitor that allows much easier and unattended analysis of radon in coastal ocean waters. The system analyses ^{222}Rn from a constant stream of water delivered by a submersible pump to an air–water exchanger where radon in the water phase equilibrates with radon in a closed air loop. The air stream is fed to a radon-in-air monitor to determine the activity of ^{222}Rn. More recently, an automated multi-detector system has been developed that can be used in a continuous survey mode to map radon

activities in the coastal zone (Dulaiova et al., 2005). By running as many as six detectors in parallel, one may obtain as many as 12 readings per hour for typical coastal ocean waters with a precision of better than 10–15%.

3.2. Interpretation of Radon Data

a. Assessment of Atmospheric Evasion

Atmospheric evasion is usually quantified using local wind speed measurements applied to theoretical gas exchange models (e.g., Macintyre et al., 1995). Dulaiova and Burnett (2006) showed recently that one can also make experimental estimates of ^{222}Rn exchange with the atmosphere by looking at the respective slopes of ^{222}Rn and ^{224}Ra in surface waters away from a common source (Figure 12). The isotopes ^{222}Rn and ^{224}Ra have very similar half-lives and are affected in the same manner by mixing processes but only radon will emanate to the atmosphere. One can thus estimate the radon air-water exchange rate from the difference in the slopes of the ^{222}Rn and ^{224}Ra horizontal distributions. Estimated gas exchange velocities (k) based on their results from the Gulf of Thailand agreed well with some theoretical models developed for lakes, estuaries and coastal systems.

b. Evaluation of SGD

Cable et al. (1996a) provided the first example of ^{222}Rn being used to quantify SGD to the coastal zone. Working in the northeastern Gulf of Mexico, they used a four box sub-pycnocline model (Figure 6) to evaluate the flux. The strong pycnocline that develops in the summer time allowed the authors to look at fluid flow from the sediments into the bottom boundary layer without having to correct for the air-sea loss of ^{222}Rn. Using this approach, they estimated that diffuse SGD in a 620 km^2 area of the inner shelf was equivalent to ~20 first magnitude springs. Cable et al. (1996b) also investigated SGD near a submarine spring in the same study region. In a transect across the spring outflow, they observed a ^{222}Rn increase of 10–50 fold over background activities. In addition, they found a strong correlation between seepage rate (as measured by seepage meters along shore-normal transects) and ^{222}Rn and CH_4 inventories in the water column along a nearby shoreline.

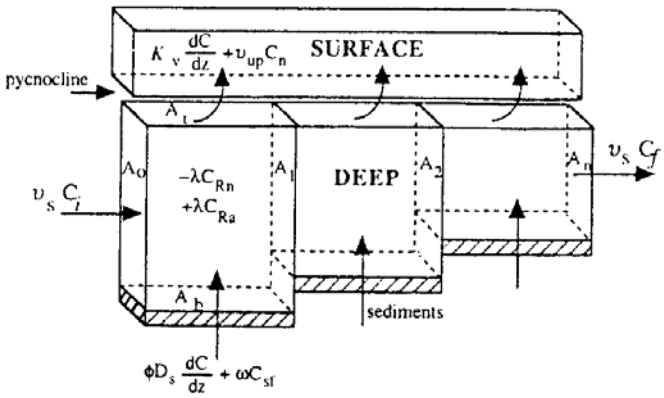

Figure 6. Four box model used to evaluate SGD by Cable et al. (1996b). An incremental mass balance of ^{222}Rn in the sub-pycnocline water column was applied using this box model, which allows the sub-pycnocline water column to change with distance up the continental shelf. Sources and sinks considered for ^{222}Rn were (1) total advective-diffusive benthic input processes [ωC_{sf} ; ϕD_s (dC/dz)]; (2) horizontal transport ($\upsilon_s C_i$; $\upsilon_s C_f$); (3) radon production and decay (± λC); and (4) loss across the pycnocline [K_v (dC/dz) + $\upsilon_{up} C_n$].

In Chesapeake Bay, Hussain et al. (1999) observed an inverse ^{222}Rn variation with salinity, which they suggested was consistent with a lower salinity groundwater component entering near the head of the bay. Using a similar box model approach, they estimated that ^{222}Rn-derived SGD rates to Chesapeake Bay were on the order of 10% of the riverine flux of fresh water to the bay. ■

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Nubian Modelling Meeting

In the frame of the joint IAEA/UNDP/GEF Nubian Aquifer System Project, representatives from the four participating countries met during 21–24 August in Vienna, Austria. The objective of the meeting was to review and introduce modelling techniques into the decision support system for project implementation. Previous modelling and data were reviewed and options and approaches for a new and improved model were discussed.

This modelling meeting was in line with the previous Shared Aquifer Diagnostic Analysis / Strategic Action Programme (SADA/SAP) Training Course and SADA planning meeting held last March in Khartoum, Sudan.

The modelling is thus a tool to be used with the SADA, which is a technical fact-finding analysis. Previous modelling and data used, along with their corresponding analysis was presented, agreement on the modelling code to be used by all countries was reached, arrangements for national modelling teams and a nubian modelling team were made, and finally, further work on the Nubian Aquifer Regional Information System (NARIS) was agreed as a main need for further modelling efforts to be effective. Plans were made for the nubian modelling team to meet again in the following months in order to be trained on the modelling software chosen as well as to work on the further development of the Nubian Aquifer Conceptual Model. ■

Isotope Hydrology Activities in the Asia and the Pacific Region

By Manzoor Choudhry, Pakistan Institute of Nuclear Science and Technology (PINSTECH), Islamabad

The global overview of water availability versus population stresses the continental disparities, and in particular, pressure put on the Asia which supports more than half the world's population with only 36% of the world's water resources. Presently, over 1.1 billion people lack access to improved water supply and the Asia has the highest share of people unserved by water supply –65%. Over 2.4 billion people lack access to improved sanitation and the Asia has 80% of them. From the point of sustainability of resources, surface- and groundwaters are facing serious threat of pollution due to disposal of industrial effluents, domestic sewage, landfill leachates, agricultural activities and seawater intrusion in almost all of the IAEA's Member States in Asia.

Geogenic release of toxic elements (like arsenic, fluoride, manganese, etc.) into groundwater threatens millions of people in Bangladesh, China, India, Myanmar, Pakistan, Thailand and Vietnam. Fluoride contamination has been noticed in parts of India, Pakistan Thailand and Vietnam. Fast growth of population, with expanding urban areas and industries, has resulted in rapid increase in water demand. To meet these requirements, large amount of groundwater is being abstracted. On the other hand, urbanization and industrialization has reduced groundwater recharge. As a result of over-exploitation and reduction in recharge, aquifers are getting depleted and hydraulic gradients have altered favouring induced infiltration from the contaminated surface water and seawater intrusion. The IAEA, through its Water Resources Programme, has been assisting its Member States to address variety of issues by encouraging local, national and regional authorities to adopt a more collaborative and comprehensive approach towards collection of hydrological data and by introducing them to isotope techniques which improve capabilities of water resources development and management practices including mitigation options. In the recent past the IAEA's regional projects on water resources were planned according to the needs of the region. The project RAS/8/084, Access to Clean Drinking Water started in 1999–2000 project cycle and was later upgraded as a model project. Major objectives of the project were: to promote the use of isotope techniques for addressing the problems related to fresh drinking water, and to develop and verify groundwater flow and pollutant transport models for selected aquifer systems in the region. Under the project RAS/8/097, Isotope Techniques for Groundwater Contamination Studies in Urbanized and Industrial Areas, carried out during 2003–2006, groundwater quality issues using isotope geochemical techniques in selected urbanized and industrial areas were studied. Under this project, a subproject on Geogenic Contamination of Groundwater focused on arsenic contamination of groundwater in different countries.

Water is a precious resource in Mongolia. (Photo courtesy: L. Janchivdorj/Mongolia).

In these regional projects, twelve countries from the region, viz., Bangladesh, China, India, Indonesia, Republic of Korea, Malaysia, Mongolia, Pakistan, Philippines, Sri Lanka, Thailand, Vietnam, participated and undertook national studies with the active involvement of the end-user departments. The IAEA supported activities of the projects by arranging regional events like review meetings, training courses, workshops and seminars as well by fielding expert missions and providing isotope analytical services, equipment and materials. In the framework of these projects, various hydrological aspects like recharge mechanism, groundwater dating, interaction between various water bodies, origin, flowpath, scale and geometry of pollution, salinization mechanisms of groundwater, effect of landfills on groundwater, geogenic contamination as well as groundwater modelling were undertaken by the researchers in the Member States.

Impact of the projects

1. Based on the isotope hydrological studies carried out under these projects, the respective authorities in the Member States got benefited and consequently formulated policy decisions for management of their water resources. For example:

- In the Philippines, an isotope study confirmed earlier observations of the terrain classification study performed by the Mines and Geosciences Bureau delineating the potential groundwater recharge areas in the study area. Consequently, resolution was adopted for implementation of watershed management and protection policies (DENR AO 23, Series of 2005) which provided for more efficient and holistic watershed management programme. Subsequently, the City of Davao Executive Order (No. 22, Series of 2005) was issued delineating groundwater protection zones.
- Through the findings of isotope studies of landfill sites, the Malaysian Government expressed concern over unmanaged dumpsites that could contaminate drinking water. The Government has decided to close down many open dumpsites and set up a committee to address the landfill related problems.
- Local government in Jakarta, Indonesia made a new regulation called '*Prokasih*' (meaning river clean programme) that must be followed by the management of 13 river basins in Jakarta district. All industries in Jakarta and vicinity now must submit a six-monthly reports on actions taken on treatment of their effluents to Environment Department.
- In Sri Lanka, a secretariat to promote rainwater harvesting has been formulated at the Ministry of Urban Development and Water Supply.

2. The end-user departments in the Member States are now convinced about the importance of integration of isotope techniques with other methodologies in addressing their hydrological problems. In Bangladesh, China, India, Indonesia, Republic of Korea, Malaysia, Pakistan and Vietnam more funds are being allocated for hydrological investigations using isotope techniques. Bangladesh, Thailand, Philippines Sri Lanka and Vietnam, realising the necessity of isotope analytical facilities, have established/ are establishing isotope laboratories.

Pollution of surface water by urban waste in Bangladesh (Photo courtesy: Nasir Ahmed/Bangladesh).

3. These projects contributed to the collection of a significant amount of isotope and chemical data which could be useful for future hydrological studies. Although a large quantity of isotope and chemical data have been generated through the previous projects and research contracts, its proper archival has not been attempted to in the Member States. Realizing the value of earlier isotope data for regional models and for assessment of possible impact of climate change on water resources, Isotope Hydrology Section of IAEA and the counterpart organizations in the Member States, have started collection of isotope data. In order to develop a database on Asian region, a new project RAS/8/104 entitled Assessment of Trends in Freshwater Quality Using Environmental Isotopes and Chemical Techniques for Improved Resource Management has been started. The project aims at compilation of old data from previous studies while collecting new data from the ongoing or new studies for the benefit of policy makers and researchers. Recently, Isotope Hydrology Section of the IAEA has brought out an Atlas of Isotope Hydrology – Africa. The atlases on Asia and The Pacific as well as on Latin America are in various stages of preparation. In this regard, assistance and cooperation of researchers who had undertaken the past studies will certainly benefit the compilation of data for Isotope Hydrology Atlas – Asia and The Pacific. ■

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Meetings in 2007

- Second Coordination Meeting under TC RAS8103 on Use of Isotopes and Geochemical Techniques in the Study of Artificial Recharge in Groundwater (ARASIA3). Dubai, UAE, 29 January – 1 February, 2007.
- Technical Coordination Workshop for the Regional Project RLA/8/041 Application of Isotopic Tools for Integrated Management of Coastal Aquifers (Desarrollo de Herramientas para la Gestión Integrada de Acuíferos Costeros. Fase I). Vienna, Austria. 26 February – 1 March, 2007.
- Regional Training Course on Shared Aquifer Diagnostic Analysis (SADA) and Strategic Action Programme (SAP) Documents. Khartoum, Sudan. 24–29 March, 2007.
- Technical Coordination Workshop of Counterparts of National Technical Cooperation Projects on Water Resources Vienna, Austria. 16–19 April, 2007.
- IAEA/GEF IW:Learn/USGS Study Tour Best Practices in Groundwater Assessment Management and Public Participation. El Paso, Texas; Tucson, Arizona; San Diego, California, USA. 18–26 April, 2007.
- International Symposium on Advances in Isotope Hydrology and its Role in Sustainable Water Resources Management,(IHS–2007). Vienna, Austria. 21–25 May, 2007.
- 6th Meeting of the Scientific Steering Committee of GNIP. Vienna, Austria. 21–22 May, 2007.
- Consultants Meeting on the Use of Isotopes in the Assessment of River-Aquifer Interactions: A Case Study of the Tri-Country Austrian-Slovak-Hungarian part of the Danube Basin. Belgrade, Serbia. 7–8 June, 2007.
- Research Coordination Meeting on Isotope Age and Composition of Streamflow as Indicators of Groundwater Sustainability. Vienna, Austria. 1–5 October, 2007.
- Technical Meeting on The Application of Isotope Techniques for Water Quality Assessment and Management, Focusing on Nutrient Management, in Rivers. Vienna, Austria. 8–10 October, 2007.
- Research Coordination Meeting on Optimization of Irrigation Water Use Efficiency by Using Isotope Techniques to Evaluate Water Flux Below the Root Zone in Flood and Drip Irrigation. Vienna, Austria. 26–30 November , 2007.
- Research Coordination Meeting on Moisture Isotopes in the Biosphere and Atmosphere (MIBA); Vienna, Austira, 3–7 December, 2007.
- Consultants Meetings on Water Isotope Measurement by Laser Spectroscopy; 3–7 and 10–14 December, 2007.

Meetings in 2008

- 2nd Research Coordination Meeting on Isotopic Techniques for Assessment of Hydrological Processes in Wetlands, Vienna, Austria. 14–18 April, 2008.
- 2nd Research Coordination Meeting on Geostatistical Analysis of Spatial Isotope Variability to Map theSources of Water for Hydrology Studies. Vienna, Austria. 6–9 October, 2008.
- Meeting of the GNIP Scientific Steering Committee. Vienna, Austria. 9–13 June , 2008.
- Coordination and Operational Requirements for Isotope Hydrology Laboratory Networks. Vienna, Austria. 8–10 September, 2008.
- Regional Workshop to Review the Use of Isotopes in Water Resources Management. Vienna, Austria. 13–16 September 2008.
- Workshop for Project Development/Formulation. Vienna, Austria. 3–7 November, 2008.
- Review and Synthesis of Isotope Data from Various Aquifers. Oregon, USA. 27–31 October, 2008.

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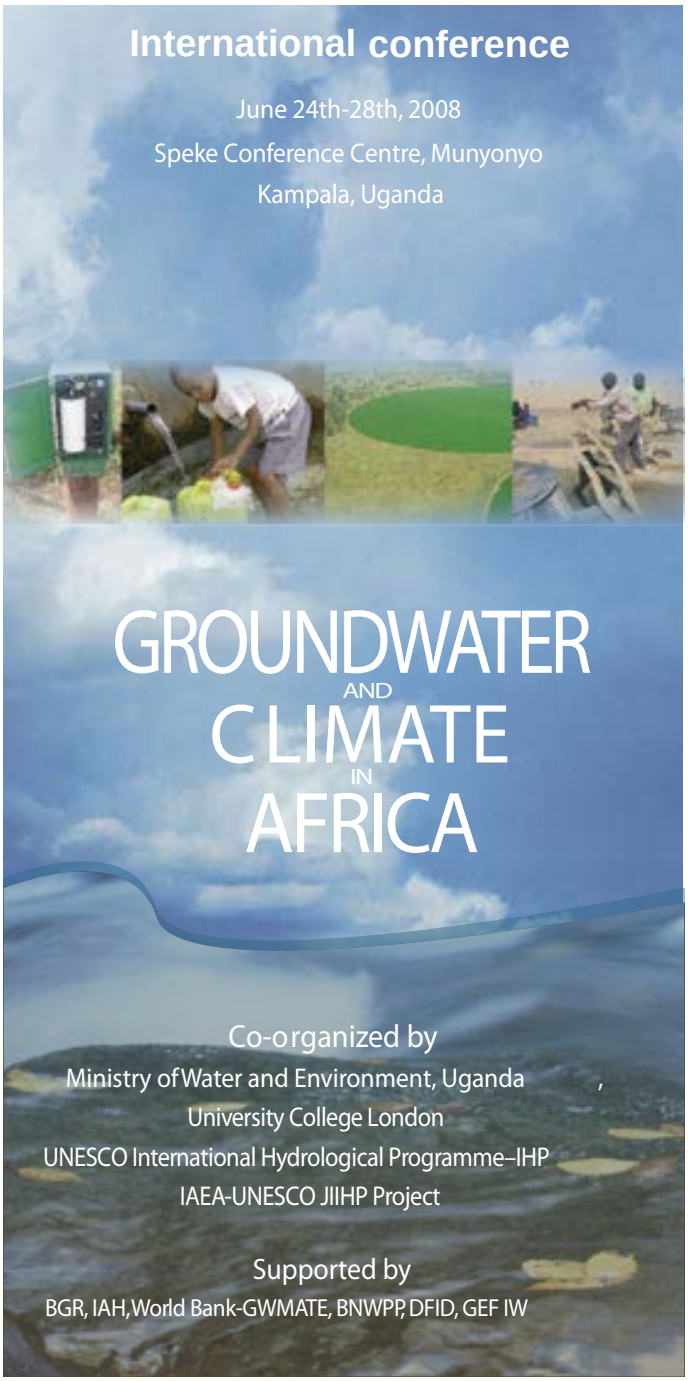
Groundwater & Climate in Africa - an International Conference

Current monitoring and assessments of the impacts of climate variability and change on water resources commonly exclude groundwater. This omission is of particular concern in Africa where current usage and future adaptations in response to climate change and rapid population growth, place considerable reliance upon groundwater to meet domestic, agricultural, and industrial water demands.

The conference seeks to bring together water and climate scientists from research/academic institutions, government departments, and private sector as well as representatives from international agencies, donors and consortia in order to share knowledge and expertise, and thereby improve current understanding of the impact of climate and development on groundwater resources in Africa.

Presentations of case studies from outside Africa are welcome. Presenters are encouraged, however, to articulate clearly the generic aspects of their study that might inform research and policy in Africa. ■

For further information, please visit http://www.gwclim.org or alternatively, please contact the Conference secretariat: info@gwclim.org



IAEA International Atomic Energy Agency

Water and Environment News No. 23 December 2007

The Water and Environment News are prepared twice per year by the Isotope Hydrology Section, Division of Physical and Chemical Sciences, Department of Nuclear Sciences and Applications.

International Atomic Energy Agency
Wagramer Strasse 5, P.O. Box 100,
A-1400 Wien, Austria

Printed by the IAEA in Austria,
December 2007

07-50271