

Use of isotope techniques in lake dynamics investigations

*Proceedings of a final Research Co-ordination meeting
held in Rehovot, Israel, 10–13 March 1997*



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FOREWORD

Lakes and surface water bodies represent an important component of the global water cycle. In many countries, they remain one of the most easily accessible freshwater resources. Lakes play an important role in regulating carbon, nitrogen and phosphorus cycles on continents. In addition, sediments accumulating in lakes and surface reservoirs are among the most valuable archives of past climatic and environmental changes on continents, providing a range of time scales from a single year to thousands of years.

Unfortunately, these valuable resources are under a continuous and increasing threat due to growing anthropogenic impacts, mostly in the form of (1) increasing pumping directly from these highly sensitive surface water resources, (2) sewage effluents and, (3) industrial pollutants being discharged directly into lake systems or into rivers and groundwater that form their catchment areas.

Indeed, the scarcity of water resources is becoming one of the major impediments to social and economic development and affects large arid and semi-arid areas. Rapidly growing population as well as unfavourable climatic events and recurrent droughts emphasize the ever growing need for intensive use of water resources for human agricultural and industrial purposes.

A large percentage of freshwater supplies are derived from groundwater resources which are being extensively exploited in many parts of the world. However, groundwater reserves suffer either from high pumping rates often at the limit of the natural recharge rate, or from human or naturally induced salinization and pollution. Furthermore, when the rate of water withdrawal exceeds the natural replenishment rate of aquifers, especially in arid and semi-arid areas, groundwater resources are effectively being mined. In order to limit the effects of this, the use of surface water reservoirs, either natural (lakes and ponds) or constructed dams and basins used for artificial recharge via infiltration have been developed. Human activities on catchment areas that cause accelerated erosion, salinization, widespread contamination of soil by agrochemicals accelerate processes such as the eutrophication of open water bodies, and contribute to deterioration of their water quality and aesthetic value.

Therefore, adequate knowledge of internal lake dynamics as well as quantification of transport and fate of pollutants in such systems is becoming a key issue in management of surface water resources in many parts of the world.

The contents of this technical document provide a cross section of different isotopically based methodologies that provide an important contribution towards a better understanding of the dynamics of lakes and surface reservoirs, as well as to better understand their vulnerability to pollution which thus may help to design adequate prevention and remediation strategies.

The IAEA officer responsible for this publication was L. Gourcy of the Division of Physical and Chemical Sciences.

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SUMMARY

The Coordinated Research Programme (CRP) on the "Use of Isotope Techniques in Lake Dynamics Investigations" was initiated in 1994. The programme was aimed at assessing the potential of environmental isotope techniques in studying the dynamics of lakes and related problems such as solute dynamics, sediment focusing, establishing the water balance components, and vulnerability of surface water bodies to pollution.

Five research contracts and three research agreements were awarded to the following Member States, respectively: Argentina, India, Israel, Kenya, the Slovak Republic, Switzerland, Turkey and the United States of America.

This publication is a compilation of the papers presented at the final Research Coordination meeting (RCM) held in Rehovot, Israel, from 10 to 13 March 1997, which brought the CRP to a successful conclusion. The meeting was organized by the IAEA in co-operation with the Weizmann Institute of Science, Israel. Preliminary results of the programme were presented at the first RCM held in Duluth, USA, organized jointly with the Large Lakes Observatory of the University of Minnesota in 1995.

The CRP enabled a number of isotope and geochemical studies to be carried out on small and large surface water bodies, with the general aim of better understanding of the dynamics of these systems under the growing anthropogenic influence. The programme also allowed free exchange of information among the most experienced groups from the developed countries and those teams from the developing world who are just starting to apply isotope techniques in lake investigations.

The IAEA recognizes the valuable collaboration of the participants in the CRP and their significant contribution to the overall success of the programme. It is expected that the results presented in this publication will serve as a valuable reference for future studies related to the assessment and management of surface water resources.

CRP — "Isotope techniques in lake dynamics investigations"

Main objectives

The Coordinated Research Programme (CRP) on the Use of Isotope Techniques in Lake Dynamics Investigations was launched with the aim of assessing the potential of environmental isotope techniques in studying the dynamics of surface water bodies and related problems, such as:

- dynamics of solutes;
- sediment focusing;
- establishment of the water balance components;
- vulnerability to pollution.

Both large surface water systems such as Lake Baikal, the Dead Sea, the Caspian Sea and Lake Turkana, and relatively small lakes, *i.e.* Lake Koycegiz, Lake Mar Chiquita and Lakes Naini were studied and discussed within the framework of the programme. In some cases, the work was already well advanced while in others; the CRP gave an impetus to initiate more comprehensive studies.

The projects implemented in the framework of the present CRP can be grouped into two general categories:

- *Methodological developments*

The methodological developments are related to the use of isotope techniques in (i) determining the different components of water balance and deciphering dynamics of surface water bodies on different spatial and temporal time scales, and (ii) deciphering part behavior of lacustrine systems from isotope proxy data preserved in sediments;

- *Case studies*

Case studies correspond to the application of isotope methods along with other geochemical tools to investigate specific characteristics of the given surface water system (e.g. water level fluctuations, internal mixing processes, salinization, fate of pollutants).

Overview

During the first IAEA consultants meeting on “Isotope Techniques in Lake Investigations” held in 1992 in Vienna Headquarters, the major problems were summarised as three key-questions mainly concerning the state of the-art in lake balance and lake dynamics studies:

- (i) *What is the input of isotope (tracers) in the system as a function of time? What are the losses by outflow, evaporation and sedimentation?*
- (ii) *What are the average concentration and the mean residence time of isotopes (tracers) in the lake?*
- (iii) *What is the significance of internal recycling?*

The main outcomes of the consultants meeting were the definition of four key-points to be investigated for the study of lakes through nuclear-related techniques:

- Lake balance (hydrological, chemical and isotopic balances), taking into account sampling at different time-scales (seasonal *and* long term records) of precipitation (input function), lake water along selected water columns, tributaries, surrounding aquifers, etc. It has to be noted that in lakes with periods of strong vertical mixing, the determination of mean concentrations may require only a small number of samples.
 - (a) Precipitation: stable isotope ratios such as $^{18}\text{O}/^{16}\text{O}$, $^2\text{H}/^1\text{H}$, and $^3\text{H}/^1\text{H}$.
 - (b) Evaporation rate estimation: $^{18}\text{O}/^{16}\text{O}$, $^2\text{H}/^1\text{H}$, $^3\text{H}/^1\text{H}$ and ^{36}Cl . All together with *in-situ* measurements, and meteorological data collection.
 - (c) Underground and surface inflow and outflow: $^{18}\text{O}/^{16}\text{O}$, $^2\text{H}/^1\text{H}$, $^3\text{H}/^1\text{H}$, ^{37}Cl , and $^{87}\text{Sr}/^{86}\text{Sr}$.
- Lake water dynamics
 - (a) Water movements and mixing: stable isotope ratios such as $^{18}\text{O}/^{16}\text{O}$, $^2\text{H}/^1\text{H}$, and $^3\text{H}/^1\text{H}$. All together with *in-situ* measurements, and chemistry (chemical composition of solutes).

- (b) Water-atmosphere exchanges, and estimation of segregation time of deep waters from any contact with the atmosphere: (i) $^3\text{H}/^3\text{He}$, (ii) rare gases such as ^3He , ^4He , ^{20}Ne , and ^{222}Rn , and (iii) anthropogenic compounds such as freons, and chlorinated hydrocarbons.
- Particle and solute dynamics
 - (a) Particle and solutes balances, particles deposition, vertical and horizontal transport, adsorption/desorption properties, re-suspension, soil erosion on the catchment, etc.: Nuclear Weapon Testing nuclides such as ^{137}Cs , ^{90}Sr , ^{10}Be , ^{210}Pb , ^{226}Ra , and U/Th series.
 - (b) Seasonal cycling of biological active tracers: $^{18}\text{O}/^{16}\text{O}$, $^{13}\text{C}/^{12}\text{C}$, $^{15}\text{N}/^{14}\text{N}$, ^{34}S .
 - (c) Redox processes, recycling of carbon and lake ventilation (deep waters): $^{13}\text{C}/^{12}\text{C}$, and $^{14}\text{C}/^{12}\text{C}$ on both TDIC (total dissolved inorganic carbon) and DOC (dissolved organic carbon).
 - (d) Changes of bottom conditions (e.g. methanogenesis) in association to the consumption of dissolved oxygen, NO_3^- , Fe^{3+} , etc.: $^{13}\text{C}/^{12}\text{C}$.
- Sediment dynamics
 - (a) Sediment focusing and sedimentation rate: different time scales (0-30 a.: Nuclear Weapon Testing nuclides; 0-100 a.: ^{210}Pb ; up to 500 a.: ^{32}Si ; up to 40,000 a.: ^{14}C , ^{10}Be ; above 40,000 a.: U/Th series).
 - (b) Sediment mixing and dispersive processes: short lived isotopes (^7Be , ^{228}Th , ^{234}Th).

In response to these key points, the major themes covered during the whole implementation of the CRP, as well as the results of scientific and technical investigations are as follows:

- **Lake dynamics**

Within this CRP, *Hohmann, Kipfer and Imboden* have determined the apparent age of bottom waters in Lake Baikal, the deepest and largest lake by volume on Earth, through combined ^3H - ^3He measurements. The ^3H - ^3He ratio of water gives an estimate of the residence time of deep waters, and thus allows investigation of their renewal. Maximum ^3H - ^3He ages found are in the order of 15, 17 and 10 years in the Southern, Central and Northern Basins respectively, with a mean renewal rate of about 10 to 15% a^{-1} . As a major result, the authors have also pointed out a decrease in the renewal time of deep waters, from 9.6 a in 1992 to 11 a in 1995.

The Caspian Sea project launched by the IAEA in 1995 aimed at assessing and establishing the water balance of the Caspian Sea as a prerequisite for the understanding of the water level fluctuations (2-m rise in almost 20 years). Up to now (results presented during the International Symposium on Water Resources, Vienna, 10–14 April 1999), the comparison/correlation of sea level fluctuations and freshwater inflow variations already observed has indicated the sea level variations is caused by changes in the river input in the water budget. The ^{18}O enrichment of deep water of the Central and Southern sub-basin with respect to surface water indicates that (1) deep water corresponds most probably to the previous lowstand (1950–1977) and (2) the present-day total inflow exceeded the evaporation by about 10% during the recent level rise. Moreover, the use of isotopic tools (mainly ^3H - ^3He which were detected in the whole water columns of the above mentioned sub-basins

indicating a quite intense water exchange/mixing) allowed the calculation of water residence time, indicating maximum “ages” of 20 to 25 years for deep water.

The reaction of terrestrial ecosystems, hydrological systems and landscapes to climate changes is clearly one of the most important aspects of global change research. The Caspian Sea can serve as the most characteristic example of the drastic and spectacular changes of such systems to hydroclimatic changes. The Caspian Sea has a drainage area that covers some 3.5 million square kilometers, from 62°N to 36°N, thus extending across several hydroclimatic regions. However, over geological time, the Caspian Sea has experienced important level fluctuations which had tremendous consequence firstly, on the natural environments of the neighboring regions. Hydroclimatic changes are reflected in continuous fluctuations of the sea level of this huge terminal lake, occurring on different time scales, the most recent one being the rise of almost 2.5 meters over the past 20 years, which has had disastrous consequences for the coastal regions of the riparian countries.

In such problems of hydroclimatic changes, the use of isotope techniques help in understanding how “surface water body” systems function at present, and how they functioned in the past, by:

- (1) studying the interrelationships between the lake/reservoir and its catchment area (drainage basin),
- (2) reconstructing the past climatic and environmental variations which have occurred at a local, regional and global scale.

- ***Lake water balance***

The study implemented by *Dapeña and Panarello* has focused on the hydrological and isotopic study of the endoreic Lake Mar Chiquita, Argentine Republic, a huge water body which has experienced during the last century (1890–1973) a growth in its size by 3000 km², and a corresponding decrease in salinity. The establishment of the lake water balance has confirmed that (i) the level drop is due to an increase in precipitation, and consequently, to different palaeoclimatic conditions, and (ii) lake outputs only correspond to evaporation losses, implying no downward leakage toward groundwater.

Bayari and co-authors presented the results of the study of Lake Koycegiz located in South Western Turkey. Lake Koycegiz is a meromictic lake, composed of two sub-basins (the Sutaniye sub-basin at the South, and Koycegiz sub-basin at the North, connected by a shallow 12m deep strait), and located on impermeable ophiolitic rocks, river deposits and karstified limestones. Environmental isotopic and chemical data reveal that Lake Koycegiz has a complicated mixing dynamics, mainly controlled by density-driven water flow from different origins, *i.e.* (1) rainfall and streamflow as low density waters and (2) high density thermal groundwater inflowing in the Southern sub-basin, this groundwater input being the major factor controlling the lake dynamics. Complete annual mixing cannot be achieved because of the density difference between mixolimnion and water inputs, and only about 60% of the mixolimnion in both basins is replenished annually. However, turnover times for mixolimnion and monimolimnions of both sub-basins have been estimated at ca 2, 5 and 3.5 years respectively.

Rao and co-authors have employed isotope techniques to study dynamics and sedimentation patterns of Lake Naini, India. One of the major results of the study is that the lake

groundwater system is a flow through type. Moreover, and in contrast to what was previously reported, the lake is not shallowing. A tritium- and water-balance coupled model was developed and allow for the estimation of lake and groundwater residence time, *i.e.* 1 and 13 to 37 years respectively.

- ***Development/assessment of isotopic techniques***

J. Gat presented the first set of ^{37}Cl measurements in the Dead Sea environment. The Dead Sea is being submitted to a continuous decline in water level, an increase in salinity and a massive precipitation of evaporites, all points considered as an irreversible evolution of its structure. Superimposed to changes in the hydrological regime of the Dead Sea from its original holomictic regime to short meromictic phases, halite precipitation as well as the re-introduction of the end-brines of the potash plant, have modified the chemical composition of waters, with the major consequence of inducing halite precipitation earlier every year.

Michalko and co-authors took their study sites, *i.e.* lakes, from the Vysoké Tatry Mountains, Slovakia, and obtained the first set of oxygen, hydrogen and sulphate sulphur stable isotope data in that area within this CRP. The isotope contents of water samples from the two sites have evidenced that (i) the isotopic enrichment of water from the Furkotska Dolina Valley system is related to an altitude effect without signs of evaporation, and (ii) the isotopic enrichment of water from the Strbské pleso lake is due to evaporation, due to either a longer residence time of water or by recharging it from last (climatic) phases of snow melt.

- ***Hydroclimatic changes and isotope techniques***

E. Odada presented some results on the isotopic composition of surface water samples taken from several East African Lakes. Generally, the evolution of stable isotope contents of lake water are considered as reflecting both water residence time and precipitation/evaporation ratio at a global scale. However, lakes from East Africa evolve differently, and one of the main results indicates that the modern stable isotope composition of lake surface waters seems to be an interplay between basin size (drainage area), altitude and local hydrological patterns.

Ricketts and Anderson made a detailed study of the relationships between hydroclimatic changes and the isotopic composition of inorganic carbonates found in Lake Turkana sediments (East Africa). The water level of Lake Turkana has fluctuated widely in response to variations in climatic conditions, dropping up to 20 m over the last 105 years. This study was initiated to compare the historic record of Lake Turkana level to several records of the isotopic composition of fossil carbonates, and to evaluate the use of the stable isotope composition of carbonates as a proxy for palaeo-lake level. This investigation evidenced that (i) the wide range of $\delta^{18}\text{O}$ values measured on inorganic carbonates could reflect the spatial variability in lake water isotopic composition rather than higher palaeotemperatures, (ii) the preliminary use of normalized/stacked data to define the palaeo-lake level curve for Lake Turkana was a much better estimation of the lake past fluctuations than any other lake level curve generated with non-normalized data.

Conclusion

The large amount of results gathered during this CRP over eight study sites located in seven countries and presented during the successive meetings confirms the great scientific and

socio-economic interest in using isotope techniques to investigate lake dynamics, lake groundwater/lake surface watershed interrelations, and sedimentation processes.

Among the new isotopic tools being applied in the framework of the CRP one should mention the use of the ^3H - ^3He technique to determine the ventilation rate of deep, large lakes. From the results established within this CRP, it turned out that the two largest and deepest lakes in the world, i.e. Lake Baikal and the Caspian Sea, are relatively well mixed. This surprisingly low apparent ages of deep water in both cases points to a high vulnerability to surface pollution and should be viewed as an important factor in designing proper management strategies for these unique systems.

Isotopic tools have also been successfully applied to relatively small lake systems studied in the framework of the CRP. Stable isotope measurements helped to determine the components of water balance and the source of salinity in the case of Lake Mar Chiquita, Argentina. Through the present CRP, it has been demonstrated that the value of an interdisciplinary approach, combining environmental isotopes with hydrochemistry and a classical hydrometric survey is indispensable for the determination of complex mixing patterns occurring in small lakes such as Lake Köycegiz, Southwest Turkey and Lake Naini, India.

Isotope techniques played an important role in extensive, ongoing studies of unique systems of global significance which are the Dead Sea and the Caspian Sea. These studies focused mainly on evolution and recent changes in the dynamics of these waterbodies, and the use of isotopic tools coupled with hydrological investigations allows for the deciphering of changes induced either by anthropogenic forcing or by climate changes.

As a conclusion, and although slightly emphasized in the contributions submitted to this volume, the role of lake sediments in deciphering past climatic and environmental changes on continents using isotope proxy data was extensively discussed during both meetings of the CRP. Furthermore, reconstruction of past behaviour of lacustrine systems and their response to external forcing, including climatic changes, always give a better understanding/knowledge of the functioning of these systems under the present-day conditions, and helps to make projections of their response to the ever growing anthropogenic impact more reliable.



ISOTOPIC STUDY OF THE "LAGUNA MAR CHIQUITA", CÓRDOBA, ARGENTINA AND ITS HYDROGEOLOGICAL AND PALEOCLIMATOLOGICAL IMPLICATIONS

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Abstract

This work presents the results obtained during the first stage of the investigations carried out in the Mar Chiquita lake (Córdoba Province, Argentine Republic) within the framework of the Coordinated Research Programme (CRP) on "Isotope Techniques in Lake Dynamics Investigations" of the International Atomic Energy Agency. The main objectives are to contribute to the study of this huge water body that in the past two decades increased its size almost three folds, to establish its water balance and to assess the influence of the climatic changes on the water budget. This water body is the final receptacle of a large closed basin formed mainly by the rivers Dulce, Suquía and Xanaes. During 1890-1973 it occupied 1800 to 2000 km² with a salinity of 310-250 g/L. At present, it has around 5000 km², a maximum depth of 10-12 m and a salinity rounding 42 g/L. The changes in salinity and size are related to an increase in precipitation which, at the same time, depends on different palaeoclimatic conditions. From a scientific point of view it is also important to study the lake hydrological balance, its groundwater input and output as well as the evaporation rate and the mean residence time. These latter considerations are the object of the present isotopic research. Future studies will consider a paleoclimatic approach.

1. INTRODUCTION

This work presents the results obtained during the first stage of the investigations carried out in the Mar Chiquita lake (Córdoba Province, Argentine Republic) within the framework of the Coordinated Research Programme (CRP) on "Isotope Techniques in Lake Dynamics Investigations" of the International Atomic Energy Agency. The main objectives are to contribute to the study of this huge water body that in the past two decades increased its size almost three fold, to establish its water balance and to assess the influence of climatic changes on the water budget.

The study of the Mar Chiquita Lake is of great importance since it is the major body of surface water in our country. Its geology and the chemical characteristics of its waters were studied by many researchers [1, 2, 3, 4, 5, 6, 7, 8]. The geochemical knowledge has a special scientific signification due to the influence the lake has over a great coastal environment.

The Mar Chiquita lake lies in a great plain in the Northeast of the Córdoba province, between 30° 20' and 31° 00' South latitude and 62° 10', 63° 10' West longitude. The lake has a tectonic origin, its a mean altitude is about 65 m a.s.l. and since 1973 it has had an area of about 5000 km² (Figure 1). Historic records show that at the beginning of the XXth century and towards 1950 the lake had a minimum size, while in 1982 it reached the maximum size, generally showing an inverse correlation between size and salinity. During 1890-1973 it occupied 1800 to 2000 km² with a salinity of 310-250 g/L. At present, it is 100-110 km from North to South, 90-95 km E-W, a maximum depth of 10-12 m and a salinity of about 42 g/L (Table I).



Figure 1 Map of South America, showing the research area

TABLE I: Some salinity historic records of the Mar Chiquita Lake.

Year	Reference	TDS [g/L]
1911	Frank [3]	360.0
1912	Frank [3]	290.0
1915	Frank [3]	87.0
1923	Kanter [3]	137.0
1930	Frenguelli [5]	258.5
1953	Bertoldi de Pomar [5]	291.0
1970	D.P.H. [7]	269.5
1977	Durigneux [6]	78.7
1982	CIQAPA [7]	29.8
1986	Martinez [7]	28.7
1989	Martinez [7]	35.0
1991	Michelutti [13]	50.0
1994	Michelutti [14]	35.0
1996	Michelutti [15]	42.0

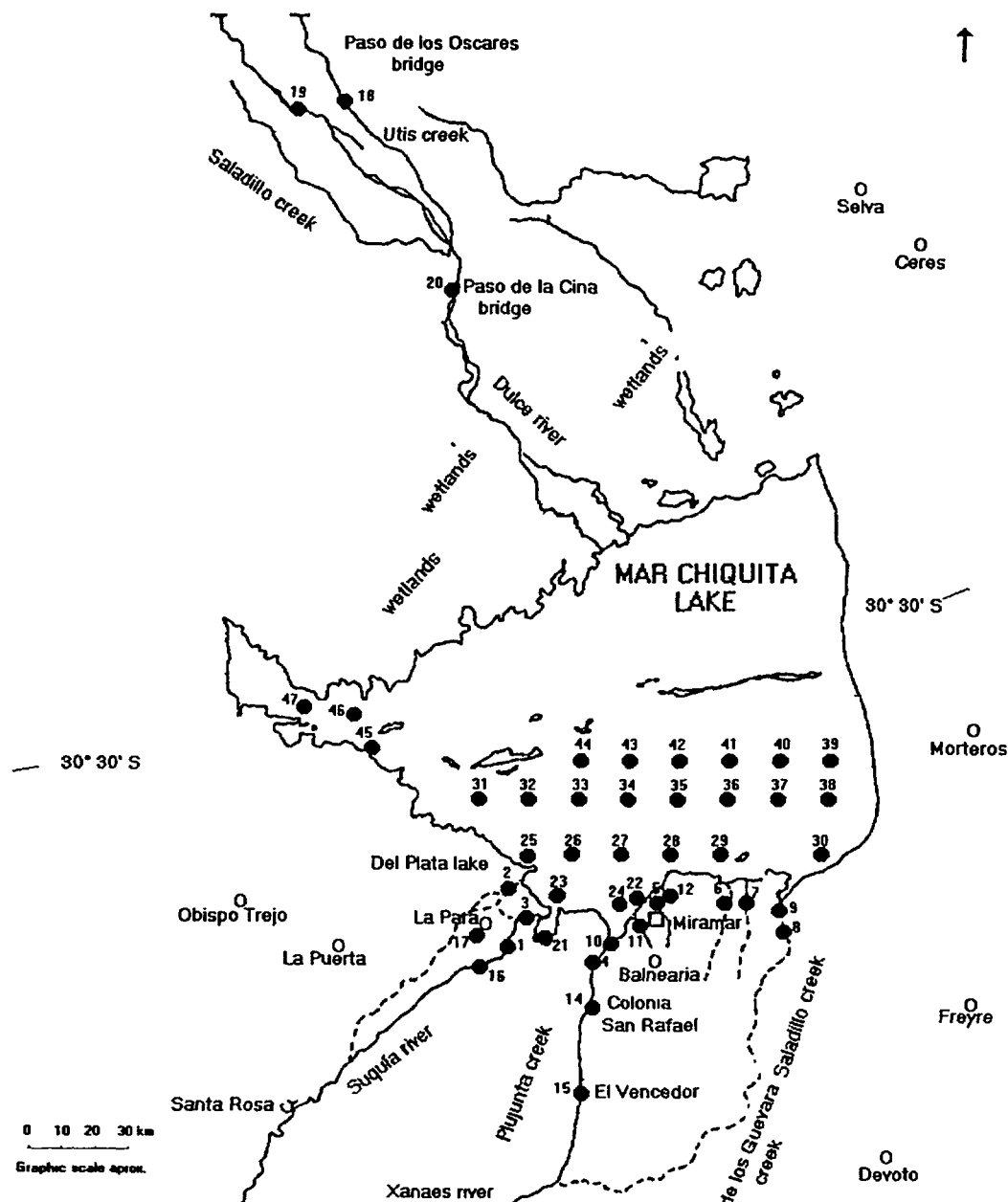


Figure 2. Schematic map of Laguna Mar Chiquita, main tributary rivers and sampling points.

This water body is the final receptacle of a large closed basin formed mainly by the rivers Dulce, Suquia (Primero) and Xanaes (Segundo) and a lot of temporary creeks (arroyos) (Figure 2).

The Dulce river originates in the Aconquija Mountain System at 5500 m a.s.l. (Tucumán and Salta provinces), it is then dammed at Río Hondo city and Los Quiroga town, it flows along a great plain for 600 km and finally reaches the North shore of the Mar Chiquita lake forming small temporary ponds and wetlands.

The Suquia and Xanaes rivers originate in the Sierras of Córdoba (to the SW of the lake) and reach the lake from the South, forming lowlands.

From a geological point of view it belongs to a big basin named the "Llanura Chaco Pampeana" province [9]. Both the outcrops in this area and the lake are in Quaternary sediments. In the post-Pliocene a fault system affected the area and the Selva-Tostado horst [10] rose. The scarp is around 30 m

high and thus acts as a barrier for the water flow (Figure 2). The age of the lake has been related to that of the Lujanense Stage (approximately 30 ka BP) [11].

Present climate is semi-arid to semi-humid. Precipitation (700-800 mm/year) falls mainly in summer decreasing from East to West. The mean summer temperature is 24.5°C and the mean temperature for the rest of the year is 11.5°C, which decreases from N to S [12].

The chemical composition of the lake water is of the sodium-chloride-sulphate type.

The changes in the salinity and size of the lake are associated with an increase in precipitation and are thus related to different paleoclimatic conditions. Figure 3 shows the annual discharge of the Dulce River since 1926. It is the main river carrying water into the lake. In this figure we can see the increase in discharge that occurred since 1973.

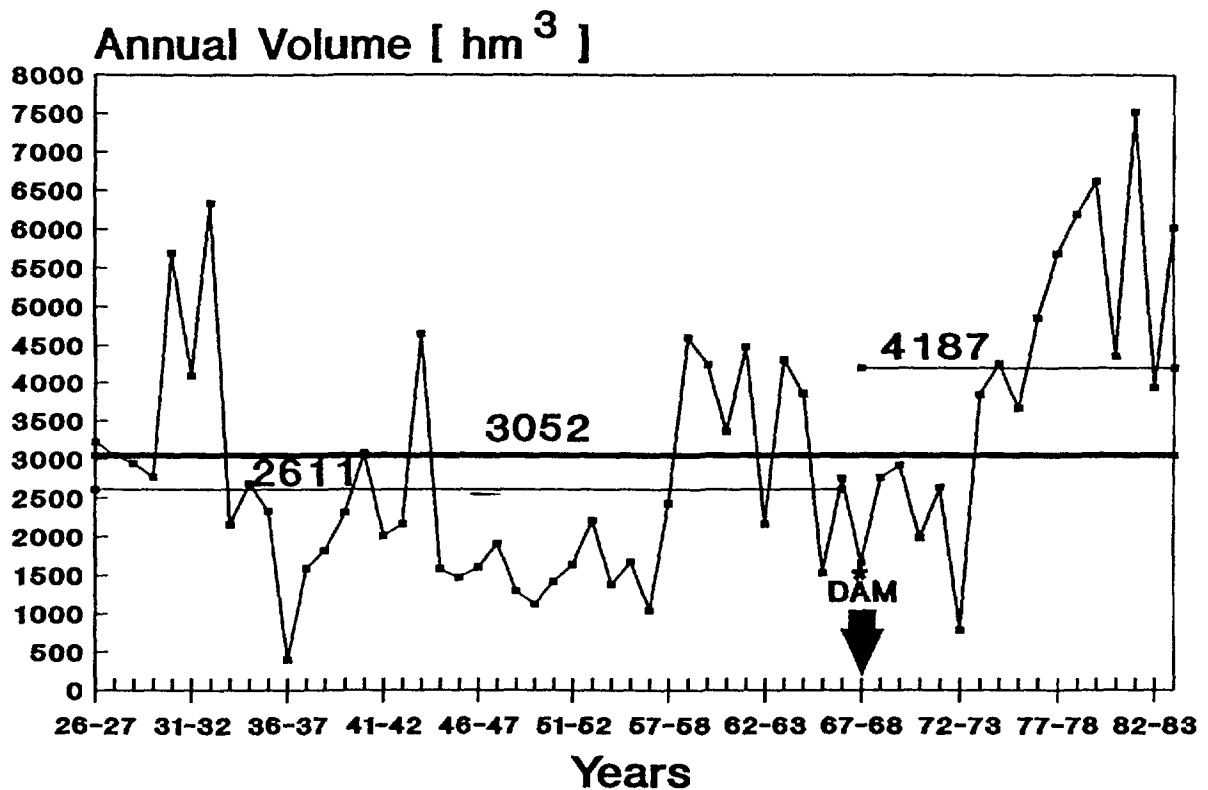


Figure 3. Annual discharge of river Dulce.

Martínez [7,8] studied the geochemistry of the lake. He concluded that the composition of its waters originated from the concentration by evaporation of the mean tributary water composition. The composition of the concentrated solution was then modified by equilibrium and redox chemical processes.

The high concentration of total dissolved solids results from the progressive accumulation of salt because of the deficit in the hydrological balance of the basin. The dissolved salts are carried mainly by the inflowing rivers, especially the Dulce [8]. In addition, a tributary of the Dulce, named Saladillo, brings salts from the Ambargasta salina during periods of high discharge. These salts are then carried by the Dulce River to the lake.

Therefore, the hydrodynamic of this lake is complex. Historic records of total dissolved solids show important variations with time (Table I) and are also associated with the changes in its volume.

From a scientific point of view it is also important to study the lake hydrological balance, its groundwater input and output as well as the evaporation rate and the mean residence time. These latter considerations are the object of the present isotopic research. Future studies will consider a paleoclimatic approach.

In order to obtain a local meteoric water line, a station located by the lake in Miramar has began collecting precipitation since March 1995. These data will be included in the balance when a better record is available. This station belongs to the Global Network of Isotopes in Precipitation (GNIP).

2. MATERIALS AND METHODS

In the first year, about 50 samples were analyzed for stable isotopes, tritium and major ions, comprising the lake and the associated rivers. The samplings done later were mainly of the tributaries.

Results are expressed in the usual way, *i.e.*

$$\delta = 1000 \frac{R_S - R_R}{R_R}$$

where:

δ : isotopic deviation $\delta^{18}\text{O}$ or $\delta^2\text{H}$, in per mil.

R_S and R_R : are the isotopic ratios ($^2\text{H}/^1\text{H}$, $^{18}\text{O}/^{16}\text{O}$) in the sample and the primary reference standard respectively.

The international standard is Vienna Standard Mean Ocean Water (V-SMOW) [16].

Isotopic analyses were done at INGEIS and the analytical errors are ± 0.1 and ± 1 per mille for $\delta^{18}\text{O}$ and $\delta^2\text{H}$, respectively.

3. RESULTS

Table II shows the isotopic values obtained from the superficial rivers, streams and groundwater. Only the Suquia, Xanaes and Dulce rivers are permanent, the rest of the streams are temporary, responding to precipitation, and highly evaporated (figure 4); so they can be neglected in the balance.

Figure 4 shows the isotopic values of the major superficial streams, groundwater, precipitation and lake and the global meteoric water line ($\delta^2\text{H} = 8\delta^{18}\text{O} + 10$).

The isotopic values, deuterium and oxygen-18 (Table III), measured all over the lake show uniformity within the laboratory analytical error *i.e.* $\delta^{18}\text{O} = 3.16 \pm 0.12$ per mille and $\delta^2\text{H} = 17.9 \pm 1.1$ per mille.

4. ISOTOPE BALANCE

An attempt to make an isotope balance using measured and estimated data was done. This is possible only in isotopically well-mixed lakes, in which evaporation has significantly raised the heavy isotope content with respect to inflow. The isotopic method is certainly useful in revealing and evaluating losses to groundwater, for which it is probably the best method available [17, 18, 19]. The mass and isotopic balances of a well-mixed lake are given by $dV = (I - Q - E) dt$, where V is the volume of the lake, I inflow

Table II: Deuterium and oxygen-18 content of surface water (sw) and groundwaters (gw)

I	I	II	II	III	III	TYPE	LOCATION
-3.1	-19			-4.7	-27	sw	1 - Suquia river, bridge route 17
		-1.7	-11			sw	2 - Suquia river (old river-course)
		-4.5	-24			sw	3 - Suquia river mouth
-1.8	-17	-6.1	-37	-4.8	-28	sw	4 - Xanaes river, bridge route 17
		-6.4	-40	-6.5	-41	gw	4 - Bridge route 17, 55/70m
1.6	8	-7.5	-48	-4.6	-30	sw	5 - San Antonio creek
2.3	7	-5.2	-28			sw	6 - Cañada I creek
-1.1	-13	-6.3	-37	-3.4	-25	sw	7 - Cañada II creek
-0.7	-12	-6.8	-44	-2.5	-17	sw	8 - Cañada Saladillo creek
-2.2	-17					sw	9 - Cañada Saladillo creek mouth
		-6.3	-34			sw	10 - Plujunta river
		-6.6	-41			gw	10 - Plujunta site, 55/70m
		-6.6	-39			gw	10 - Phreatic near Plujunta river 20m
2.3	8	-4.7	-33			sw	11 - San Jose creek
2.1	9	-5.3	-37			sw	12 - Cristale creek
		-6.5	-42	-6.7	-45	gw	13 - Miramar Station, 55/70m
		-5.4	-31			sw	14 - Xanaes River, San Rafael Colony
		-5.1	-30			sw	15 - Xanaes river, El Vencedor
		-4.1	-24			sw	16 - Suquia river, La Para Station
		-5.8	-37			gw	17 - La Para Station, 55/70m
1.3	1					sw	18 - Utis river
-2.1	-11					sw	19 - Dulce river, Paso de Oscares bridge
-1.5	-13			-2.3	-13	sw	20 - Dulce river, Paso de la Cina bridge
-1.0	-10			-2.3	-11	sw	20 - Dulce river, Paso de la Cina bridge
		-0.2	-1			sw	21 - del Plata lake near shore
		2.1	13			sw	22 - Mar Chiquita lake near shore

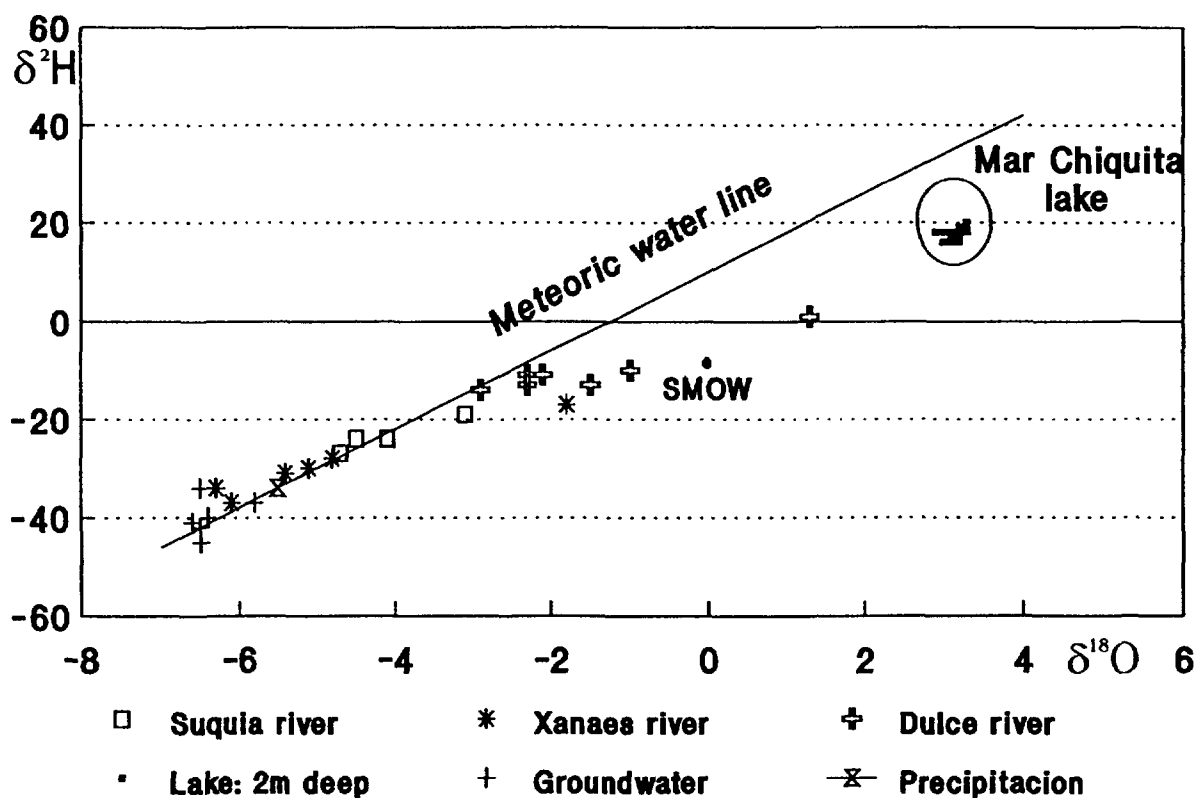


Figure 4. Deuterium and oxygen-18 plot of the Mar Chiquita system.

Table III: Deuterium and oxygen-18 content of Mar Chiquita Lake at a depth of 2 meters.

SAMPLE N° [1]	δ ¹⁸ O	δ ² H	SAMPLE N° [1]	δ ¹⁸ O	δ ² H
23 - LM1M	3.2	16	38 - LM17M	3.2	19
24 - LM2M	3.0	16	39 - LM18M	3.2	18
25 - LM3M	3.2	17	40 - LM19M	3.2	18
26 - LM4M	3.3	19	41 - LM20M	3.2	17
27 - LM5M	3.2	19	42 - LM21M	3.2	18
28 - LM6M	3.1	16	43 - LM22M	3.0	18
29 - LM7M	3.0	18	44 - LM23M	3.2	18
30 - LM9M	3.3	20	45 - LM33M	3.3	20
31 - LM10M	3.2	18	46 - LM34M	3.3	18
32 - LM11M	3.2	18	LM36M	3.1	18
33 - LM12M	3.1	18	LM37M	3.1	17
34 - LM13M	3.2	16	LM40M	3.2	17
35 - LM14M	3.1	17	LM41M	2.9	18
36 - LM15M	3.0	18	LM59M	3.3	18
37 - LM16M	2.9	18	LM60M	3.3	20
Averages			δ ¹⁸ O	δ ² H	
			3.16	17.9	
			0.12	1.1	

rate, Q outflow rate, E net evaporation rate, considering that the volume of the lake does not change significantly with time (steady state). So $dV/dt=0$ and $I=Q+E$. Then, by making $E/I=k$ and $Q/I=1-k$, being k the fraction of the inflowing water lost by evaporation, and writing this equation in isotopic terms, we obtain [17, 19] :

$$\delta_L = \frac{\delta_I (1 - h + \Delta\epsilon) + k (h \delta_a + \Delta\epsilon + \frac{\epsilon}{\alpha})}{(1 - k) (1 - h + \Delta\epsilon) + \frac{k}{\alpha}}$$

where:

δ_L , δ_a = isotopic composition of lake and atmospheric moisture,

δ_I = isotopic composition of inflow: rivers, groundwater and precipitation (La Suela and Santiago del Estero GNIP stations),

k = ratio of net evaporation against input fluxes = E/I ,

h = relative humidity,

$\epsilon = \alpha - 1 + \Delta\epsilon$ = total isotopic enrichment factor, resulting from the addition of the equilibrium ($\alpha - 1$) and kinetic enrichment factors ($\Delta\epsilon$),

$\Delta\epsilon$ = kinetic term [19]

$$\Delta\epsilon = 14.2 \frac{(x - h)}{x} 10^{-3}$$

α = isotopic equilibrium fractionation factor between liquid water and vapour.

x = water activity

The input values and the $\delta^{18}\text{O}$ used were:

Precipitation = 5200 hm^3 (800 mm/y over 6500 km^2)
Dulce river = 4440 hm^3 [20]
Suquia river = 347 hm^3 [21]
Xanaes river = 451 hm^3 [21]
Total = 10438 hm^3

$\delta_I = -3.8 \text{ ‰}$ (weighted value)

$\delta_a = -15 \text{ ‰}$

$\delta_L = 3.16 \text{ ‰}$

$h = 60\text{-}70\%$ (estimated 66 %)

$\Delta\epsilon = 0.004828$

$\epsilon = 9.86\text{‰}$ [22]

$x = 1$

The value obtained for k was: $k = E/I = 1.01$. This indicates that all the output is by evaporation and suggests that the lake is not leaking to groundwater, confirming its present steady state.

Variations in the isotope contents of air moisture and in the humidity values significantly affects the k value. Thus, it will be important to make a record of these parameters, together with temperature, by means of thermographic and hydrographic stations located in and around the lake.

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ISOTOPE STUDIES ON DYNAMICS AND SEDIMENTATION IN LAKE NAINI, INDIA

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Abstract

Understanding hydrodynamics of a water body like a lake is a prerequisite for planning and managing its use. In the present study, isotope techniques are employed to study the dynamics and sedimentation pattern of Lake Naini, in India. From the study a few observations are made: (i) the Lake is a warm monomictic one; (ii) the presence of a centrally submerged ridge in the Lake plays a vital role in the intermixing of the Lake's two sub-basins; (iii) the Lake-Groundwater system is a flow-through type and (iv) the Lake is not shallowing at a rate reported by earlier investigators and has different depositional zones with constant/varying sedimentation rates. A Tritium and Water Balance Model is developed to estimate the water retention time of the Lake and also the groundwater residence time between precipitation and input to the lake.

1. INTRODUCTION

Lakes, among the various hydrological environments, are usually well suited for studies using isotope techniques. Lakes, in fact are systems which, although complex, are generally accessible at all points for tracer injections, sample collection and in-situ measurements. An Advisory Group Meeting organised by IAEA in 1977 [1], summarised the major problems in physical limnology and attempted to indicate solutions which are practicable with isotope methods.

In the present study, environmental isotope (namely $\delta^{18}\text{O}$, δD and ^3H) levels and conventional physical & chemical parameters (like Temperature [T in $^{\circ}\text{C}$], Dissolved Oxygen [DO in mg.L^{-1}], and Electrical Conductivity [EC in $\mu\text{S.cm}^{-1}$]) are employed to study dynamics of Lake Naini, in the State of Uttar Pradesh, India. Also environmental ^{137}Cs and ^{210}Pb dating techniques are employed to estimate the recent sedimentation rate and pattern in the lake. The study was carried out in collaboration with the National Institute of Hydrology at Roorkee.

2. ABOUT THE SYSTEM

2.1. Morphometry & Hydrography

Crescent shaped lake Naini (Fig. 1) is a tectonically formed sub-tropical and eutrophic lake situated at an altitude of about 1937 m above mean sea level [latitude $29^{\circ}24'$ N & longitude $79^{\circ}23'$ E] in the Nainital district of Kumaun Himalayas. The lake is divisible into Mallital (Northeast) basin and Tallital (Southwest) basin due to presence of a submerged transverse ridge running east-west about 8 m below the lake surface. Maximum and average depth of the lake are 27.3 and 18.5 m respectively; the surface area and volume being 465, 000 m^2 and 8.5 Mm^3 respectively. Catchment area of the lake is about 4.9 km^2 and from conventional techniques it is believed that the groundwater contribution to the lake is substantial. The lake, in addition being a tourist spot, is the only source of drinking water to the Himalayan city, Nainital.

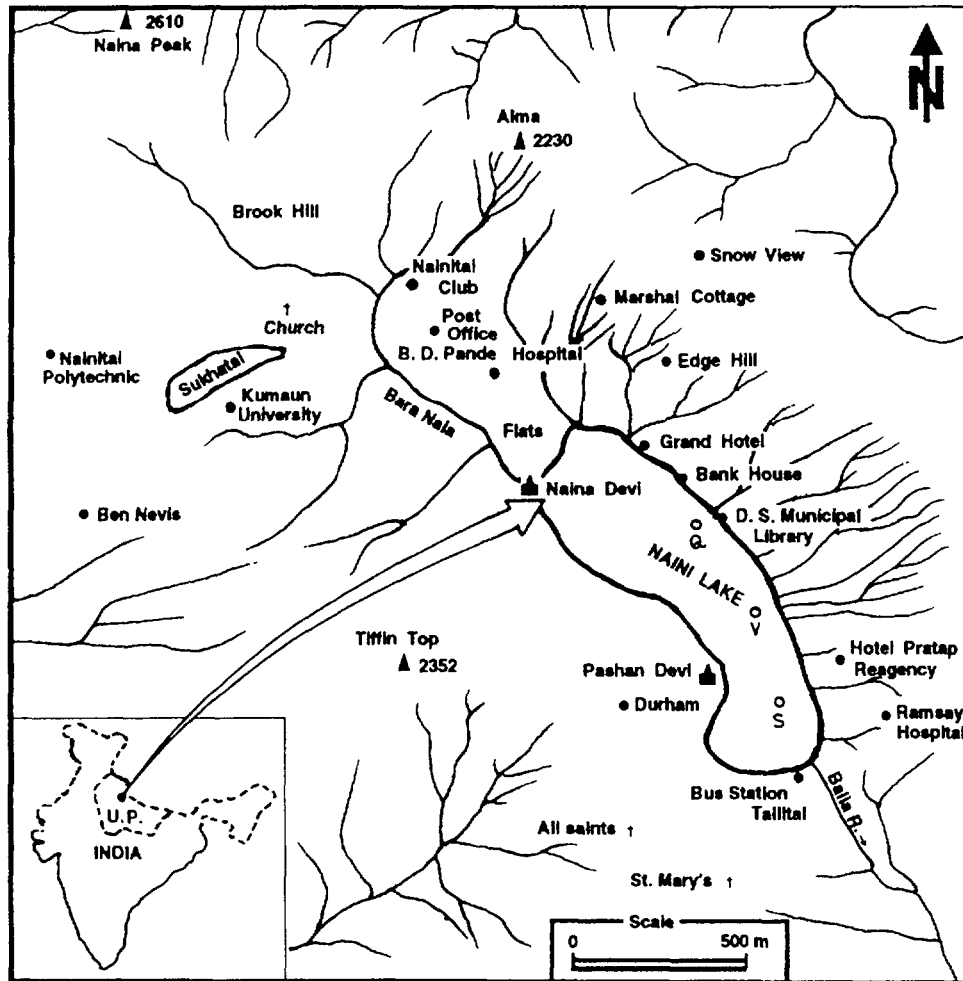


Fig.1: Location map of Lake Naini [with core sampling stations indicated]

2.2. Meteorology

The annual rainfall in the catchment of Lake Naini ranges from 2200 to 2500 mm. The monthly maximum rainfall is about 630 mm in August and the minimum is 3 mm in March. Besides rainfall there are occasional snowfalls in and around the lake basin during winter, varying between 20 to 60 mm in recent years. To know the nature of influence of different hydrometeorological parameters (like water level, rainfall, relative humidity, water & air temperature, wind velocity & direction etc.) on the dynamics and sedimentation pattern of the lake, a Data Acquisition System (DAS) with 13 sensors has recently been installed at the lake site by the National Institute of Hydrology, Roorkee.

2.3. Geomorphology and geology of the catchment area

The Nainital Hill forms a synclinalorium which is cut diagonally by a fault called Naini Fault (Fig. 2) into two parts. The north-western part is made up exclusively of argillaceous limestone and marlites whereas the south-western part comprises of dolomite with limestone and black carbonaceous slates [2]. It is believed that the sub-recent rotational movements were responsible for blockade of a stream called Balia, in its upper reaches, resulting in the formation of lake Naini. The lake (also other lakes in this region) is related to neotectonic movements on the Main Boundary Thrust and with the genetically related faults.

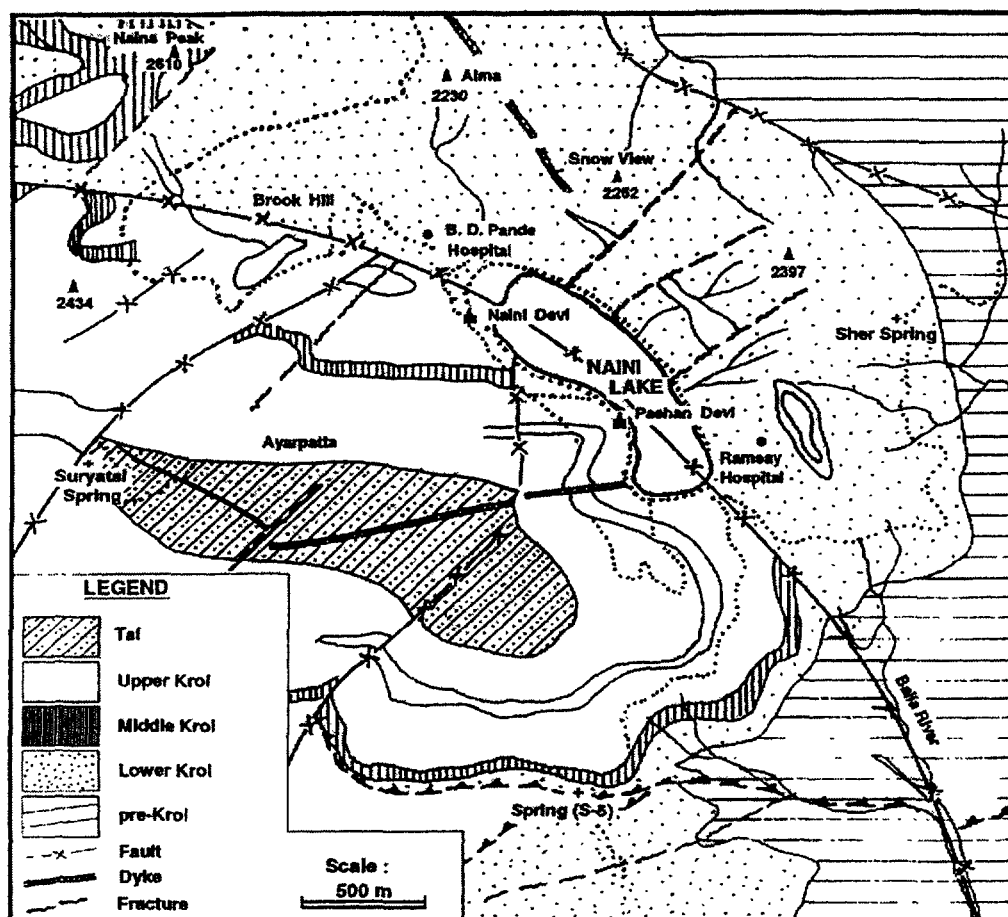


Fig. 2: Geology map of Lake Naini and its surrounding

3. SAMPLING & ANALYTICAL TECHNIQUES

3.1. Water sampling

Using a depth water sampler a reconnaissance water sampling programme was carried out in May'94 and water samples from different depths and locations of the lake for environmental isotope analysis (δD , $\delta^{18}O$ and 3H) were collected, and in-situ measurement of physical & chemical parameters like T, DO and EC made. Subsequently a series of water sampling programmes were carried out during Oct. & Dec.'94 and Feb., Mar., May, Jun., Aug., Sep., in Figs. 3a and 3b respectively and Nov.'95 at selected locations & depths of the lake, ground water, streams and from the springs within and outside the catchment for the analysis of the above parameters. A few monthly rain samples were also collected near the lake and at different altitudes in its catchment for the isotope analysis. The water sampling locations in the lake and in its catchment are shown.

3.2. Analysis of water samples

Deuterium analysis of the water samples was carried out on the hydrogen gas obtained by quantitative reduction of water with granulated zinc at about 450°C [3]. For the determination of oxygen-18 in the water samples, the most commonly used technique of CO_2 equilibration method was employed. In this method, the isotopic exchange at 25°C, between the water samples and CO_2 of known oxygen - 18 content is carried out [4]. The overall precision of the measurement is ± 0.2 and ± 1 ‰ (at 1 σ criterion) for $\delta^{18}O$ and δD respectively. All values are relative to V-SMOW. For the measurement of tritium in the water

samples, the liquid scintillation counting technique, subsequent to electrolytic enrichment, was employed. The overall measurement error is about ± 0.5 Tritium Units (TU) at 1σ criterion (equivalent to 0.12 Bq.L^{-1}).

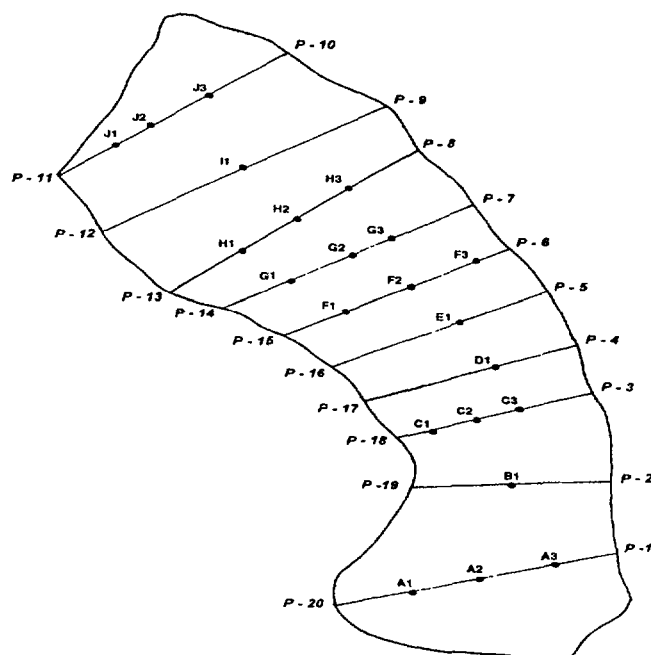


Fig. 3a: Water sampling locations in Lake Naini

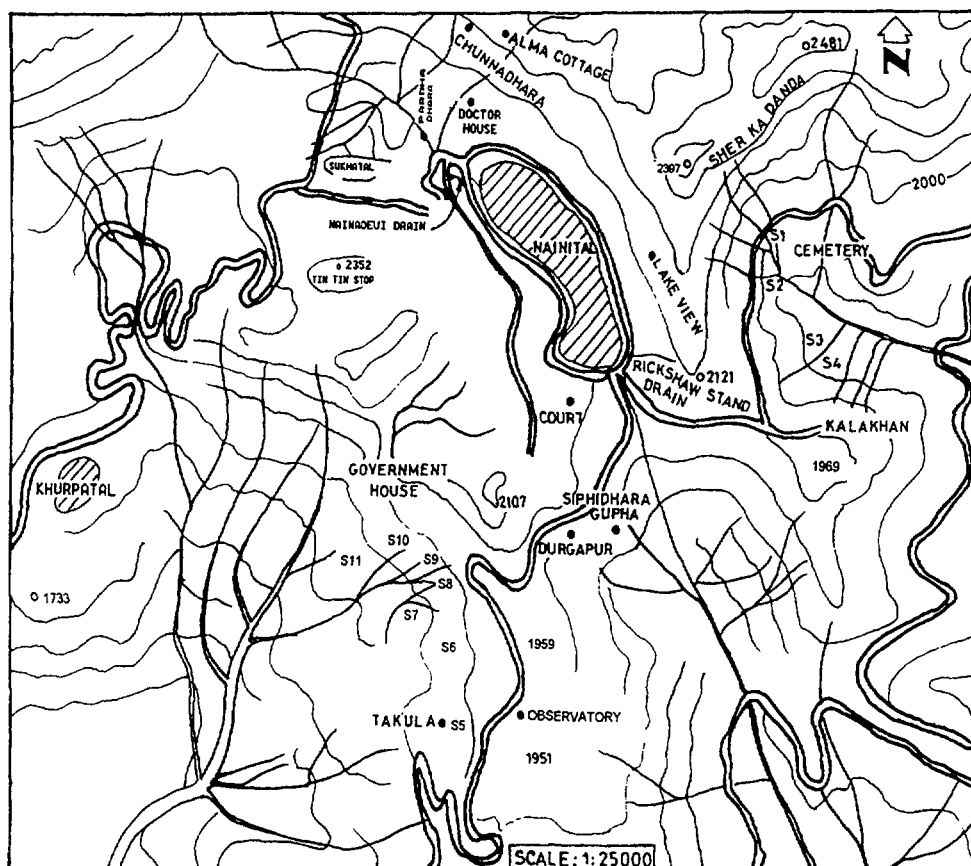


Fig. 3b: Water sampling locations in the catchment

3.3. Core sampling

Core samples were collected at different locations in the lake using a gravity corer, its outer and inner diameter being 6.0 and 5.2 cm respectively. Most of the sampling stations (ref. Fig.1) are from the eastern side of the lake since a large number of gullies loaded with considerable amount of sediments join the lake basin at those stations. The length of the cores obtained ranged in size from 15 to 60 cm. With the help of an adjustable piston rod with silicone packing, the obtained cores were extruded vertically and sliced at 2 cm intervals. Sliced core sections were stored in the laboratory. Measurements were made of the bulk density before drying samples in an oven at a temperature slightly above 100°C for about 7 to 8 hours prior to analysis. The dry unit weight, water content, and porosity were also estimated after drying. The textural composition of the core samples was mainly clay and silt. The clay mineralogy assemblage of this lake mainly consists of montmorillonite, illite, kaolinite, and chlorite besides the mixed layer minerals, which are typical high altitude clays [5].

3.4. Analysis of core samples

The determination of ^{210}Pb content is based on the α - measurement of its grand-daughter, namely ^{210}Po , which is assumed to be in secular equilibrium with its parent. The basic radiochemical procedure involves adding of ^{208}Po as a yield tracer, leaching the sediment samples with aqua-regia, the residual solids are filtered off and the solution is dried and converted to chloride with concentrated HCl. The final solution is taken in 0.5 M HCl. Polonium nuclides are then spontaneously deposited on silver planchettes by adding ascorbic acid in the HCl solution prior to α counting using Si surface barrier detector connected to a multichannel analyser. The standard counting error of measurement is generally less than 10 % in the upper sections of the cores and slightly higher values at the deeper sections since the counting time is kept constant for the entire core sections. As the supported ^{210}Pb results from the decay of ^{226}Ra present in the sediment core with which it is in equilibrium, estimation of ^{226}Ra activity is determined directly by α counting. The ^{137}Cs activity in each section is determined by gamma counting of the oven-dried samples using high purity Germanium detector coupled with a 4096 channel analyser system. A ^{137}Cs standard, having essentially the same geometry and density is used. The samples are counted for about 500 min to obtain a good statistical accuracy. The detection limit for ^{137}Cs by this method is about 0.25 mBq.g⁻¹ and the standard counting error is less than 10 % in the core sections.

4. ISOTOPIC RESULTS

4.1. Lake

From the monthly δD and $\delta^{18}\text{O}$ values of the lake water samples, it is observed that the surface water samples showed highly enriched isotopic values compared to the bottom samples. This is due to evaporation of water at the surface of the lake. Also a clear seasonal variation in the stable isotopic values of lake water samples were observed.

4.2. Precipitation & altitude effect

From fig.4, it can be seen that the δD and $\delta^{18}\text{O}$ values of the precipitation fall close to Global Meteoric Water Line (GMWL). It is known that there is an altitude effect in the δD and $\delta^{18}\text{O}$ values of precipitation [6]. This is in the range - 0.2 to - 0.7 ‰ per 100 m for $\delta^{18}\text{O}$. Figs. 5a and 5b show the δD and $\delta^{18}\text{O}$ values of precipitation samples as a function of altitude (h, in meters) and the relationships obtained are:

$$\delta^{18}\text{O} = - (4.0 \times 10^{-3}) h - 3.07 \quad (1)$$

$$(n = 12, r^2 = 0.85, \text{ significant at } 0.05 \text{ level}) \text{ and}$$

$$\delta D = -(3 \times 10^{-2}) h - 28 \quad (2)$$

($n = 12$, $r^2 = 0.75$, significant at 0.05 level)

Thus the altitude effect is -0.4‰ and -3.0‰ per 100 m for $\delta^{18}\text{O}$ and δD respectively.

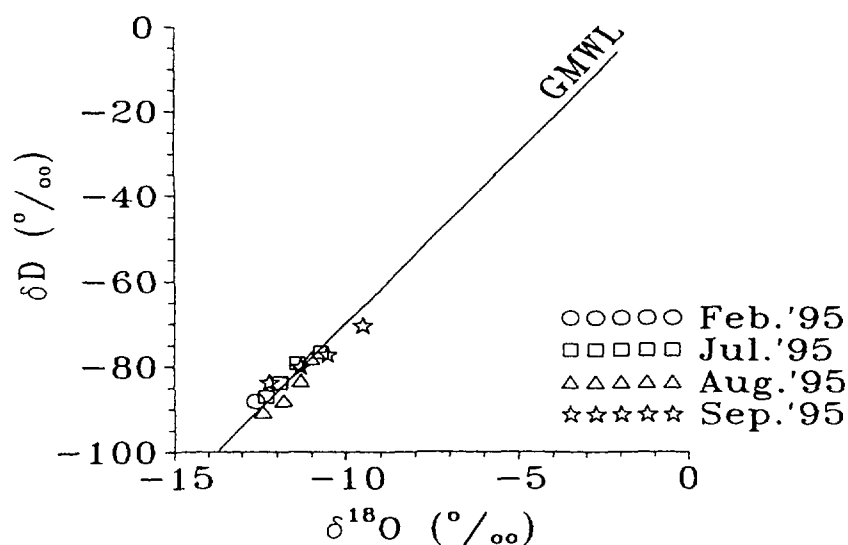


Fig. 4: δD Vs $\delta^{18}\text{O}$ plot of rainwater

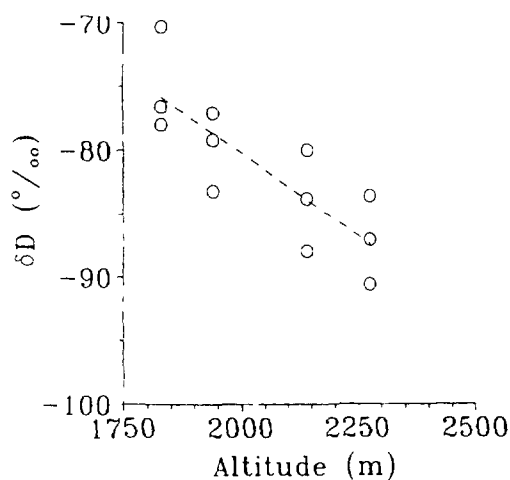


Fig. 5a: Variation of δD values in rainwater with altitude

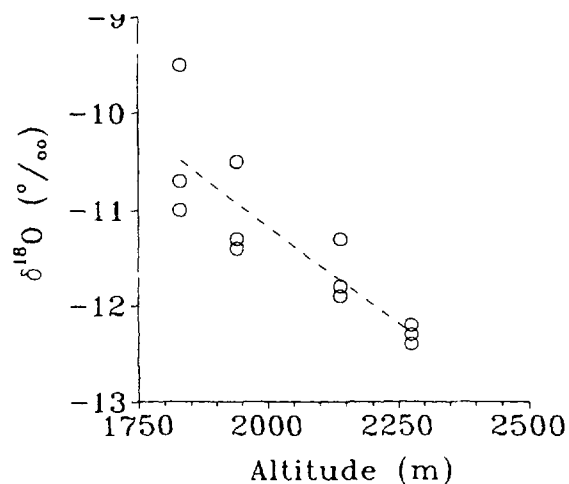


Fig. 5b: Variation of $\delta^{18}\text{O}$ values in rainwater with altitude

5. DISCUSSION

5.1. Lake dynamics

The water dynamics of lakes (i.e. mixing and transport of water) is of interest for planning their usage for domestic and industrial purposes, flood control or power generation. In the latter two cases, knowledge of flow dynamics of the lake helps to predict how the outflow rate, or the capacity of the lake will be affected by changes in the inflows. Whenever the water is to be used for irrigation or for drinking, the concentration dynamics of

conservative and/or non-conservative pollutants is of interest. The concentration dynamics will describe the outflow response to change in inflow concentration of a given substance.

A conservative (inert) component is not degraded (physically, chemically or biologically) during its passage through the lake, while non-conservative components undergo a process of loss or accumulation. The concentration dynamics of inert soluble matter is a general property of the lake, being determined by the flow, mixing pattern and the residence time distribution in the lake. The concentration dynamics of a specific non-conservative component is obtained by superimposing its kinetics of loss (or accumulation) on the concentration dynamics of inert soluble matter. Dynamics of Lake Naini is thus a prerequisite for more quantitative applications like water balance studies, determination of water retention time etc. In the following section a few observations on the dynamics of lake Naini is made from the spatial and temporal distribution of all the parameters under discussion.

The (monthly) depthwise distribution of environmental isotopes (δD and $\delta^{18}O$) along with in-situ physical & chemical parameters of the lake water are shown in Figs. 6a to 6f. From the figures, it is clearly seen that the change in the in-situ physical & chemical parameters as well as the isotope contents with depth show correlative trends. The lake is stratified for 7 to 9 months a year (usually from March/April to October/November). The stratification builds up quickly in March and is very strong in summer. During the stratification periods, the metalimnion (i.e. the region of relatively rapid change of density) is seen at a depth of 3 m during the months of March/April to June/July and at a depth of 6 m during the remaining periods of the stratification. The winter overturn is during November and since then the lake is well mixed for 3/4 months (i.e. from November/December to February/March). During the well mixed condition the whole water mass or just parts of it circulate if there is enough wind. The EC of lake waters, during stratified periods and during the well mixed periods, is more or less constant. Therefore it appears that the stratification seen here is, by and large, a thermally induced one and not one induced by solute concentration. The vertical distribution of all the above parameters (ref. Figs. 6a to 6f) indicates a higher levels at a few deepest points. This may be due to the groundwater recharge (in the form of underwater springs) at those points & depths. Most of the inferred groundwater recharges are seen near the submerged ridge in the centre, through the major fractures are in the north-east of the lake boundary, along the existing fault plane and near the existing dyke in the south-west sub-basin (ref. Fig. 2).

The isotopic composition of hypolimnion does not remain constant during the period of stratification and the δ values of hypolimnion and those of the epilimnion are not correlated well. This probably indicates the water retention time of the lake is very short and lack of correlation between the δ values of hypolimnion and epilimnion indicate independent inflow components to the two regions. The uniform tritium content of the lake during the reconnaissance survey in May 1994 (i.e. about 11.2 ± 0.5 TU) gave a clear indication, in advance, that the stratification seen during that period could be a seasonal and the lake is expected to be well-mixed during winter.

The presence of the submerged transverse ridge about 8 m below the lake surface has an important control on the dynamics of the lake. Its presence inhibits the mixing of deeper waters of Mallital with Tallital and thus the two sub-basins of the lake exhibit differential behaviour. This is confirmed by the slight variations in the levels of all the tracers under discussion, particularly at deeper depths (ref. Figs. 6a to 6f).

The stratification in the lake has profound consequences on the physical, chemical and biological phenomena in the lake. For example, aeration occurs in the epilimnion, while in the hypolimnion anaerobic conditions prevail. In lakes the vertical component of water transport is of greatest interest in the understanding of mass flux and mass balance. Traditionally, vertical transport is expressed by the generalised Ficks' law with a vertical turbulent diffusion coefficient. Since no satisfying theory exists to calculate the coefficient from basic hydrodynamic principles, field data on temperature or chemical tracers are commonly used to

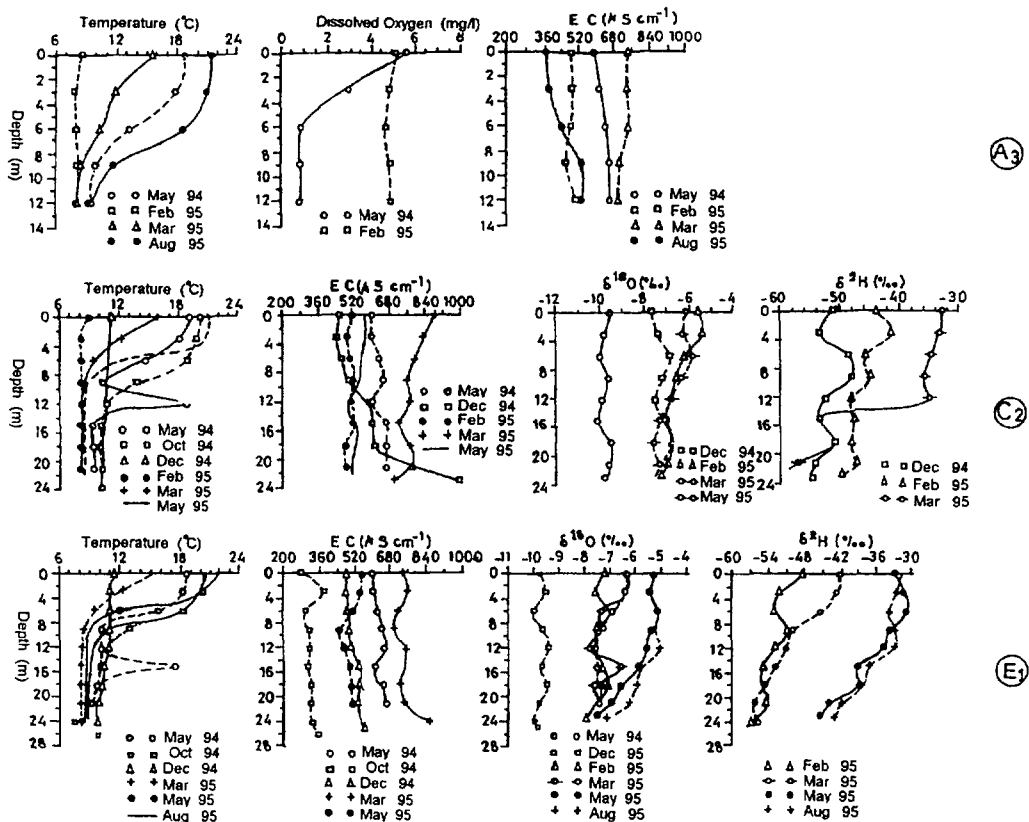


Fig. 6a to 6c: Monthly depthwise distribution of environmental isotopes and in-situ physical & chemical parameters of the Lake waters at locations A3, C2 and E1, respectively

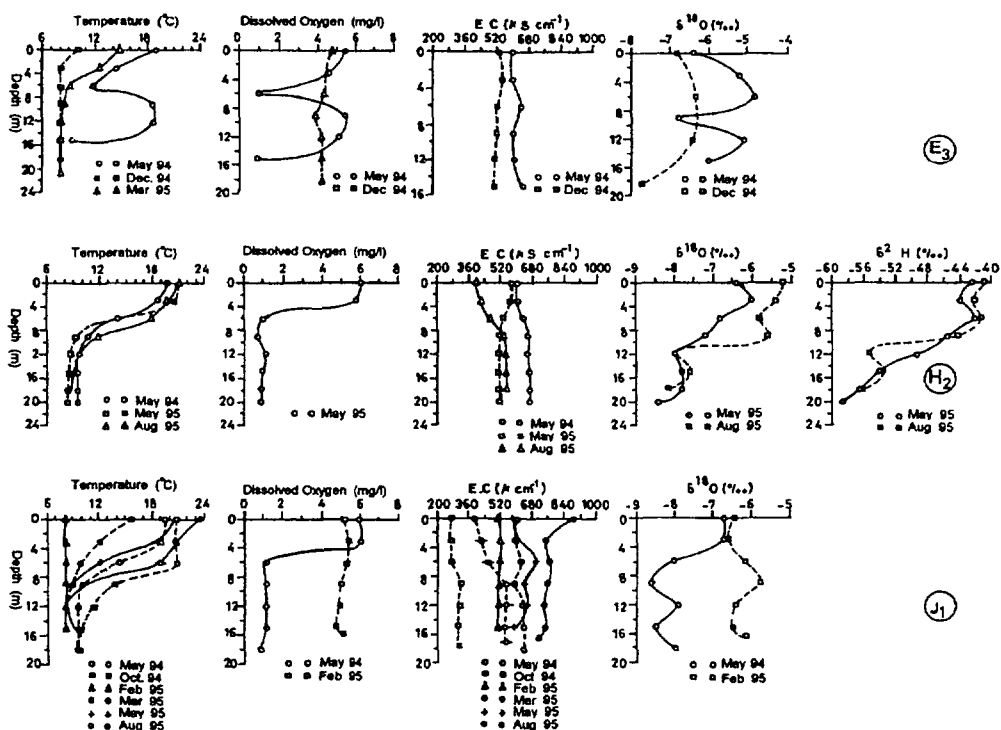


Fig. 6d to 6f: Monthly depthwise distribution of environmental isotopes and in-situ physical & chemical parameters of the Lake waters at locations E3, H2 and J1, respectively

determine vertical eddy diffusivity [7]. Therefore, assuming that the change in depth of the thermocline in Lake Naini is predominantly governed by wind induced mechanical stirring, the following hydraulic parameters of the Lake Naini are obtained from the record of periodic vertical temperature structure of the lake based on a methodology suggested by Blanton [8]: (i) an approximate value of the vertical diffusion coefficient (K_z) is about 0.1 to 0.05 $\text{cm}^2.\text{s}^{-1}$; (ii) the rate of entrainment, which indicates the mixing process in the epilimnion is about 1.3×10^{-3} to $6.7 \times 10^{-5} \text{ cm.s}^{-1}$ and (iii) an empirical value of the mean static stability, a parameter which is a measure of the resistance to an exchange- supporting force, such as wind, during the period of stratification is in the range of 9×10^{-5} to $1.5 \times 10^{-3} \text{ s}^{-2}$.

5.2. Determination of Water Retention Time of the Lake and Residence Time of its sub-surface input using a Tritium- Water- Balance Model

The injection of tritium (^3H , half-life ~ 12.43 a) into the atmosphere via thermonuclear bomb tests carried out during early 1950's and '60s has provided a useful tracer for investigating hydrological balances, water residence times, and mixing in lakes, rivers, and oceans [9 & 10]. Tritium from these tests was rapidly incorporated into precipitation and became part of the hydrologic cycle. Thus, tritium levels in precipitation compiled by the International Atomic Energy Agency [11] from the World Meteorological Organisation monitoring network for the peak fallout years can be used as a quantitative function of tritium input for hydrological studies. In this study an attempt is made to calculate hydrological properties such as water retention time (T) of Lake Naini and residence time of its groundwater τ using the (fallout) tritium balance and (conventional) water balance equations.

5.2.1. Formulation of the Tritium- Water- Balance Model

The volume of water contained in Lake Naini changes as a function of inputs and outputs. The inputs consist of direct precipitation (I_P) and inflow of stream water (I_S) and ground water (I_G), and the outputs consist of evaporation (O_E) and outflow as groundwater (O_G) or stream water (O_S). Therefore the lake water balance is given by:

$$\frac{dV}{dt} = I_P + I_S + I_G - O_E - O_G - O_S \quad (3)$$

where $\frac{dV}{dt}$ is the rate of change of lake volume, either in units of m.a^{-1} or $\text{m}^3.\text{a}^{-1}$. Since the measured tritium content of the lake in 1994 was fairly uniform (i.e. about 11.2 ± 0.5 TU) throughout the lake, the lake can be considered isotopically well mixed (i.e. the tritium content of the outflow components of groundwater and stream water are equal to that of the lake, (T_L); usually this is a case for a water body wherein mixing is fast relative to the residence time of water). Assuming that the Lake Naini has been at hydrological steady state (i.e., the inputs and outputs have been balanced) during the past four decades, the corresponding tritium balance of Lake Naini would be:

$$\frac{dT_L}{dt} = T_P.I_P + T_S.I_S + T_G.I_G - T_E.O_E - T_L.O_G - T_L.O_S - T_L.\lambda.V \quad (4)$$

where T_i represents the respective tritium content of the above water balance component (in Tritium Units, TU) and last term being the decay term (where λ is the radioactive decay constant of tritium [0.0557 a^{-1}]). In Lake Naini, O_S refers to the sum of quantity of water that

is being pumped out from the lake for drinking purpose and that which is being released through an existing sluice gate during the periods of incessant rains. T_l is defined by [9] as:

$$T_E = \frac{\alpha \cdot T_S - h \cdot T_A}{\alpha_k (1 - h)} \quad (5)$$

In Eq. 5, h is the relative humidity, T_A is the tritium content of the water vapour over the lake, α is the equilibrium fractionation factor for tritium between liquid and vapour phases (~ 0.9), T_S is the tritium content of the lake surface water, and α_k is the kinetic fractionation factor (~ 1.1). The change produced by evaporation and molecular exchange can be positive or negative, depending on the relative tritium content of the lake water and precipitation.

Eq. 4 is divided by volume, V to give

$$\frac{dT_L}{dt} = T_P \cdot K_{IP} + T_S \cdot K_{IS} + T_G \cdot K_{IG} - T_E \cdot K_{OE} - T_L \cdot K_{OG} - T_L \cdot K_{OS} - T_L \cdot \lambda \quad (6)$$

where K_{IP} , K_{IS} , and K_{IG} are the ratio of volume rate of water that enters the lake as direct precipitation, stream water, and groundwater, respectively, to that of the lake volume and K_{OS} , K_{OG} , and K_{OE} being the fractions that leave the lake as stream water, groundwater, and evaporation, respectively. For a steady-state system (i.e. no increase or decrease of volume with time), the Water Retention Time (T) is defined as the inverse of sum of either K_{IP} , K_{IS} , and K_{IG} or of K_{OS} , K_{OG} , and K_{OE} [12]. Since the lake volume is assumed to be a constant (i.e. hydrologic steady state), from eq.3 it can be obtained that:

$$K_{IP} + K_{IS} + K_{IG} = K_{OS} + K_{OG} + K_{OE} \quad (7)$$

In addition, the tritium content in the water vapour over the lake is assumed to be in equilibrium with local meteoric water, (i.e. $T_A = \alpha \cdot T_P$, which is a reasonable assumption for a mid-continental, temperate-zone setting [13]). Tritium measurements in water vapour and local precipitation in the arid Dead Sea region of Israel have shown this approximation to be valid [10]. Even tritium in water vapour over the ocean has been shown to be in equilibrium with precipitation rather than with the ocean water [14]. Now assuming piston-flow of groundwater:

$$T_{G,t} = T_{P,t-\tau} \cdot e^{-\lambda \tau} \quad (8)$$

where $T_{G,t}$ is the tritium content of the groundwater at any time, t and $T_{P,t-\tau}$ is the tritium content of the precipitation at a time $t - \tau$ (where τ is the residence time of groundwater). Now discretising the eq. 6 in a time step of one year (chosen based on the availability of hydrological and isotopic data of the lake) it becomes:

$$T_{l,t} - T_{l,t-1} = T_{P,t} \cdot K_{IP} + T_{S,t} \cdot K_{IS} + T_{P,t-\tau} \cdot e^{-\lambda \tau} \cdot K_{IG} - \frac{\alpha \cdot T_{l,t} - h \cdot \alpha \cdot T_{P,t}}{\alpha_k [1 - h]} \cdot K_{OE} - T_{l,t} \cdot K_{OG} - T_{l,t} \cdot K_{OS} - T_{l,t} \cdot \lambda \quad (9)$$

Since the catchment of Lake Naini is small, for practical purposes it can be assumed that $T_{S,t} = T_{P,t}$ (i.e. the stream waters entering the lake undergo negligible change in their tritium content during their travel from the catchment to the lake in the form of atmospheric exchange). Therefore the above equation can be rearranged to get:

$$T_{l,t} \cdot \left(1 + \frac{\alpha \cdot K_{OE}}{\alpha_k [1 - h]} + K_{OG} + K_{OS} + \lambda \right) = T_{l,t-1} + T_{P,t-\tau} \cdot e^{-\lambda \tau} \cdot K_{IG} + T_{P,t} \cdot \left(K_{IP} + K_{IS} + \frac{h \cdot \alpha \cdot K_{OE}}{\alpha_k [1 - h]} \right) \quad (10)$$

Using Eq. 7, the most difficult water balance components, namely K_{OG} and K_{IG} , in the above equation are expressed in terms of T as $K_{OG} = \frac{1}{T} - K_{OS} - K_{OE}$ and $K_{IG} = \frac{1}{T} - K_{IS} - K_{IP}$ respectively.

$$T_{L,t} \left(1 - K_{OE} \left[1 - \frac{\alpha}{\alpha\kappa(1-h)} \right] + \frac{1}{T} + \lambda \right) = T_{L,t-1} + T_{P,t} \left(K_{IP} + K_{IS} + \frac{h\alpha \cdot K_{OE}}{\alpha\kappa(1-h)} \right) + T_{P,t-\tau} \cdot e^{-\lambda\tau} \left(\frac{1}{T} - K_{IS} - K_{IP} \right) \quad (11)$$

5.2.2 Model output

Now for a known value of K_{IP} , K_{IS} , K_{OE} , h , α , and $\alpha\kappa$, the tritium content of Lake Naini in 1994 is calculated using the above equation for different values of T , pre-1953 tritium content of the lake, and τ . The values of T_P , for the period 1953 to 1987, were reconstructed from the nearest available IAEA-WMO precipitation network stations, namely Kabul and New Delhi. An explanation of the development and use of this correlation is available in IAEA Technical Bulletin #206 [15]. For the periods before 1953 and after 1988, a T_P value of 5 to 15 TU was assumed. Changing the pre-1953 tritium content of the lake from 0 to 20 TU results in a change of less than 0.5 TU in the model calculated tritium content of the lake in 1994. So the uncertainty in the pre-1953 tritium content of the lake and in the pre-1953 T_P values does not significantly affect the results.

The tritium content that would be present in lake Naini water in 1994 were computed using the model for different values of T and τ . If the value of WRT ~ 25 years, the amount of water entering the lake is less than that lost by evaporation, indicating that the Lake Naini is a terminal lake. This solution is not possible, so calculations were carried out only for WRT less than 25 years and found that for a single value of τ , the calculated tritium content of the Lake in 1994 does not change beyond a WRT of 2 years. It was also observed that the model calculated tritium value of the Lake water in 1994 (for different values of τ) would match the measured value of 11.2 ± 0.5 TU in 1994 only when the WRT is about 1 year.

Therefore, for a T of 1 year, the model calculated tritium content of Lake in 1994 for different values of τ is shown in Fig. 7. As seen from the figure, the calculated tritium content

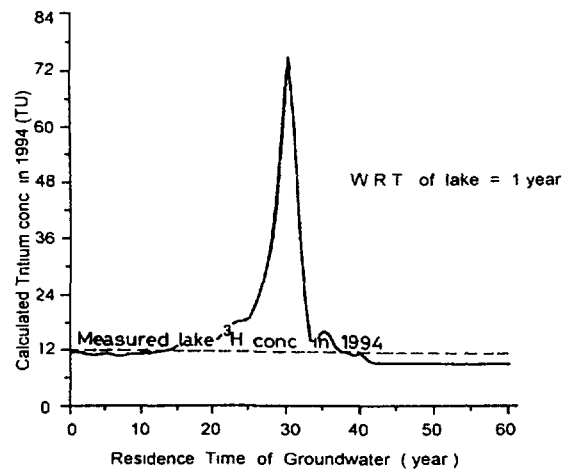


Fig. 7: Model calculated tritium content of the Lake in 1994 for WRT = 1 year and different values of groundwater residence time

of Lake in 1994 reaches as high as 76 TU for a τ of 30 years and a lower value of 10.3 TU for a τ above 42 years. The measured tritium content of 11.2 ± 0.5 TU in 1994 lake waters matches only for τ of 0, 13 and 37 yrs. Since one of the u/s springs in the Lake catchment measured a tritium value of 9.2 ± 0.5 TU and the lake tritium level is lower than the present day precipitation of about 14.2 ± 0.7 TU, τ cannot be zero. Therefore the τ could be either 13 or 37 years. This ambiguity in the interpretation of the τ is mainly due to the variable tracer (tritium) input function. Therefore for springs with a constant outflow, at least two tritium levels determinations taken in a large time span are required to estimate the age of its water. Or this ambiguity can also be overcome to certain extent by a proper hydrogeological interpretation of the isotopic data. However, the lower value appears more acceptable from the local hydrogeology. The model calculated yearwise tritium content of lake Naini with its τ being 13 years and 37 years (WRT being 1 year) is shown in Fig. 8.

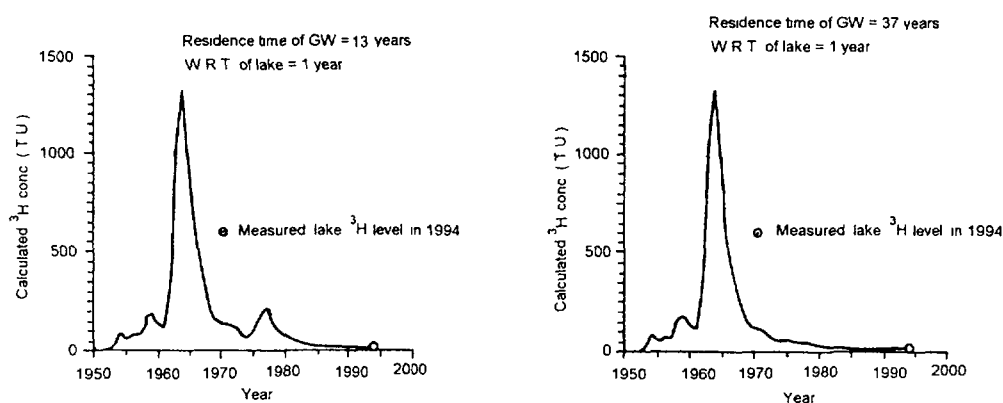


Fig. 8: Model calculated yearwise for a) WRT = 1 year and groundwater residence time of 13 years, b) for WRT = 1 year and groundwater residence time of 37 years

5.3. Estimation of recent sedimentation rate and pattern of lake Naini using environmental ^{137}Cs and ^{210}Pb dating technique

In tracing the history of man's impact on the environment it is evident that in many places the period of greatest impact lies within the last 150 years. Lake sediments provide a basis for reconstructing many aspects of this impact, for estimating rates of change, and for establishing a baseline in environmental monitoring programmes [16]. In such studies the establishment of accurate chronologies of sedimentation is of vital importance not only for dating events but for determining sediment accumulation rates also. Furthermore, sedimentation rates based on palynological or stratigraphy methods often provide only historical averages involving many meters of sediment. Such measures not only lack the necessary accuracy and detail, but may not adequately reflect the rates within the upper 20 cm or so of sediment where significant sediment water exchanges are occurring at the present time [17]. Application of radiometric methods to sedimentary geochronology has enjoyed considerable success [18]. In the present study, environmental ^{210}Pb and ^{137}Cs dating techniques are employed to determine the recent sedimentation rates and pattern in Lake Naini.

A few selected core sample, namely samples collected from locations V and S [in Tallital basin] and Q [in Mallital basin] in the lake, (ref. Fig. 1), were analysed for ^{210}Pb and ^{137}Cs . The depth profiles of (total) ^{210}Pb and ^{137}Cs in the core samples, and also the available porosity and water content profiles are shown in Fig. 9. There are three different models; CONSTANT FLUX and CONSTANT SEDIMENTATION RATE [CFCS], CONSTANT FLUX [CF] and CONSTANT INITIAL CONCENTRATION [CIC], that are being widely

used for dating ^{210}Pb deposits with or without significant mixing during deposition [19]. However none of the models is universally applicable. In practice the type of model to be used is usually decided on the depthwise distribution of (total) ^{210}Pb concentration [19]. The estimated sediment accumulation rates in Lake Naini at different locations, both in linear and mass units, obtained from ^{137}Cs and ^{210}Pb dating techniques, are given in table 1, along with the ^{210}Pb model used. From the table, it appears that the lake is not shallowing at a rate reported by earlier investigators [20 & 21]. The possibility exists that Lake Naini is subsiding approximately at the same rate it receives the sediments [5]. It seems that the Lake has different depositional zones with constant/varying recent sedimentation rates. The sedimentation rate at Tallital basin is comparatively higher than at Mallital basin. In a study to know the factors affecting distribution of lead and other trace elements in sediments of Lake Michigan, it was observed that organic matter is more important in the complexation of lead

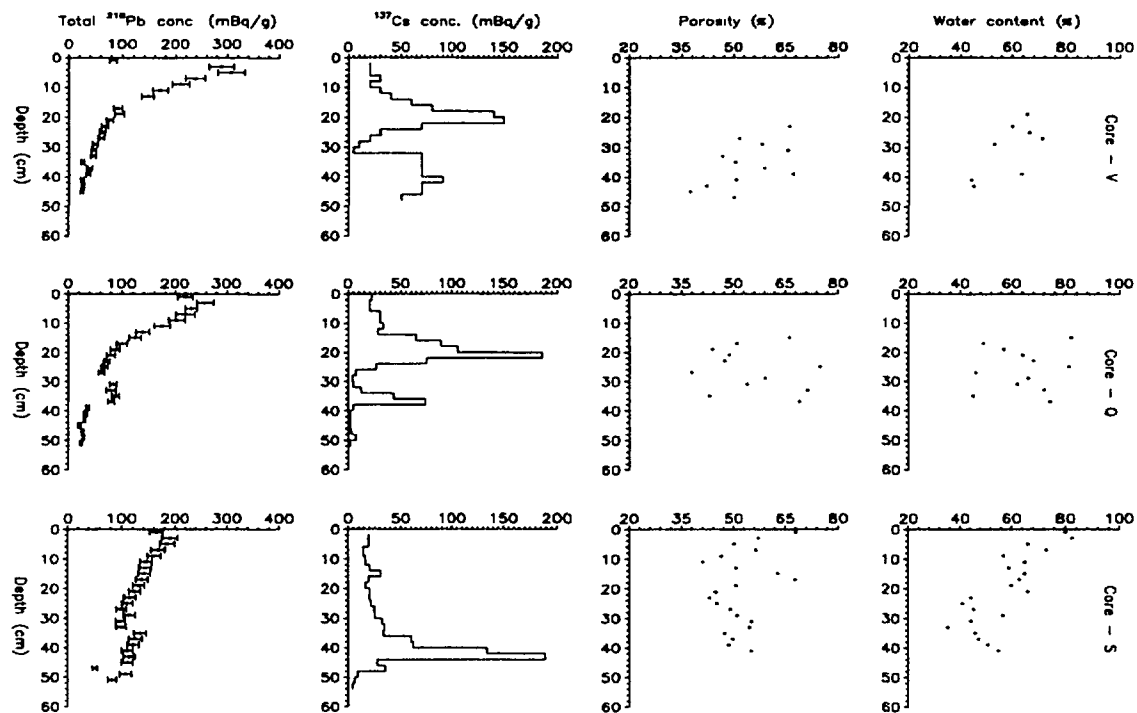


Fig. 9: Depthwise distribution of ^{210}Pb , ^{137}Cs , (available) porosity and water content in the core samples.

in lake water and sediments than absorption on clay of hydrous oxides [22]. On the other hand, the dominant mechanism of ion-exchange with the clay component of sediment and soil results in the removal of ^{137}Cs from the water column [23]. Therefore, the observed spatial distribution of superficial (i.e. top 2 cm core section) ^{137}Cs and (total) ^{210}Pb in the sediments of lake Naini may reflect patterns of deposition of two major sedimentary components, namely clay and organic carbon respectively.

An attempt was also made to use the textural properties of the lake sediments (like porosity and water content) to identify and assess the possible effect of sediment focussing, slumping, inhomogeneity in the sediment composition etc. on the obtained ^{210}Pb (and ^{137}Cs) profiles (ref. Fig. 9). Sediment focusing is a process whereby water turbulence moves sedimented material from shallower to deeper zones of a lake. According to Hakanson's scheme [24], the 50% water content of surficial sediments in a lake sediment core marks the transition between zone of erosion and transportation, and 75% water content of surficial sediments marks the transition between zone of transportation and accumulation. However as it can be seen from Fig. 9, the surficial water content in the obtained core sediments of lake

Table 1. Sedimentation rates and inventories of ^{210}Pb and ^{137}Cs in Lake Naini.

Sampling station (water depth in m)	average sedimentation rate					superficial inventory *		
	^{210}Pb		^{137}Cs					
↓	model used	linear (cm.a^{-1})	mass ($\text{g.cm}^{-2}.\text{a}^{-1}$)	linear (cm.a^{-1})	mass ($\text{g.cm}^{-2}.\text{a}^{-1}$)	total ^{210}Pb	^{137}Cs	ratio
V (24)	CFCS	0.48 ± 0.40	0.112 ± 0.010	0.60 ± 0.07	0.140 ± 0.016	0.30	0.12	2.46
Q (20)	CF	0.64 ± 0.18	0.150 ± 0.041	0.70 ± 0.03	0.168 ± 0.007	1.06	0.16	6.62
S (20)	CF	1.24 ± 0.44	0.289 ± 0.104	1.35 ± 0.05	0.315 ± 0.018	1.53	0.26	5.87

* surficial inventories are in Bq.cm^{-2}

Naini is above 75% and therefore there is no sediment focusing taking place in the sampling location of the lake.

The porosity profile for homogeneous sediments with uniform compaction usually show an exponential decrease with depth [25]. But in Lake Naini, the profiles are not exponential type. Also the lake bottom slopes gently at the sampling locations and do not favour any major slumping. This probably indicates that the non-monotonic ^{210}Pb profiles (at locations Q and S) and/or lower sediment-water interfacial ^{210}Pb concentration (at all locations) in lake Naini is the result of the actual change in the sedimentation rate with varying sediment composition and dissimilar histories of deposition taking place at those sampling stations.

6. CONCLUSION

Thus from the present study a few conclusions are made: (i) the lake is a warm monomictic lake and the two sub-basins show a differential behaviour; (ii) it seems that the lake-groundwater system is a flow through type; (iii) the WRT of the lake is about 1 year; (iv) the possible age of groundwater is 13 or 37 years and (v) the lake is not shallowing at a rate reported by earlier investigators and has different depositional zones with constant/varying sedimentation rates.

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THE DEAD SEA: A MODEL OF A DESICCATING TERMINAL SALT LAKE

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Abstract

The continuing decline in the water level of the Dead Sea and the commensurate increase in salinity and precipitation of evaporates results in an irreversible evolution of the structure of the sea. The Dead Sea has been switching from its holomictic regime to short meromictic phases of up to 4-year duration, following the particular rainy winters of 1980 and 1992. The massive precipitation of halite in recent years, as well as the re-introduction of the end-brines of the potash plant, is changing the ion composition of the Dead Sea waters. This necessitates the adjustment of the equation-of-state of the brine and the solubility curve of halite. One consequence is that the onset of halite precipitation during the summer occurs earlier and earlier in the annual cycle. New isotopic measurement of $\delta^{37}\text{Cl}$ of the brine and evaporate deposits and of $\delta^{18}\text{O}$ in dissolved oxygen in the water column have yielded new information on geochemical processes in the Dead Sea system. A systematic monitoring of the oxygen and hydrogen isotopes in the Dead Sea waters has, unfortunately not been continued in recent years and should be encouraged for the future.

1. INTRODUCTION

The Dead Sea represents the ultimate, highly mineralized, terminal lake of the Jordan River system whose water balance is under extreme anthropogenic stress. The resultant everchanging situation of the lake and, in particular, the changing water level, increase in salinity, precipitation of salts and the exposure of new coastal land areas have provided the major motivation for research. (Fig. 1).

An intensive measurement campaign of hydrographic and other parameters, during the years from 1975 to the beginning of the nineties have established the general pattern of behavior. Many of the findings were published in the literature and summarized in the book "The Dead Sea - the Lake and its Setting (T. Nieni, Z. Ben-Avraham. and J.R. Gat, editors) just now published by Oxford Press [1].

Compared to the rather intensive research effort during these 15 years, lack of funding has curtailed field operations in recent years. A minimal record of the ever-changing lake system has, however, been provided by Anati and coworkers [2] through periodic hydrographic monitoring of the water column at the deepest part in the center of the lake (bottom at -729, MSL) off Ein-Gedi.

2. HYDROGRAPHIC DEVELOPMENT OF THE LAKE

The hydrographic development is being triggered by the decline of the surface water level, which resulted in the historic termination of the centuries-long meromictic state by an overturn of the water column early in 1979 [3]. Fig. 2 shows the position of the surface level during the recent years. The general trend is a secular drop of about 60 cm per year of the lake

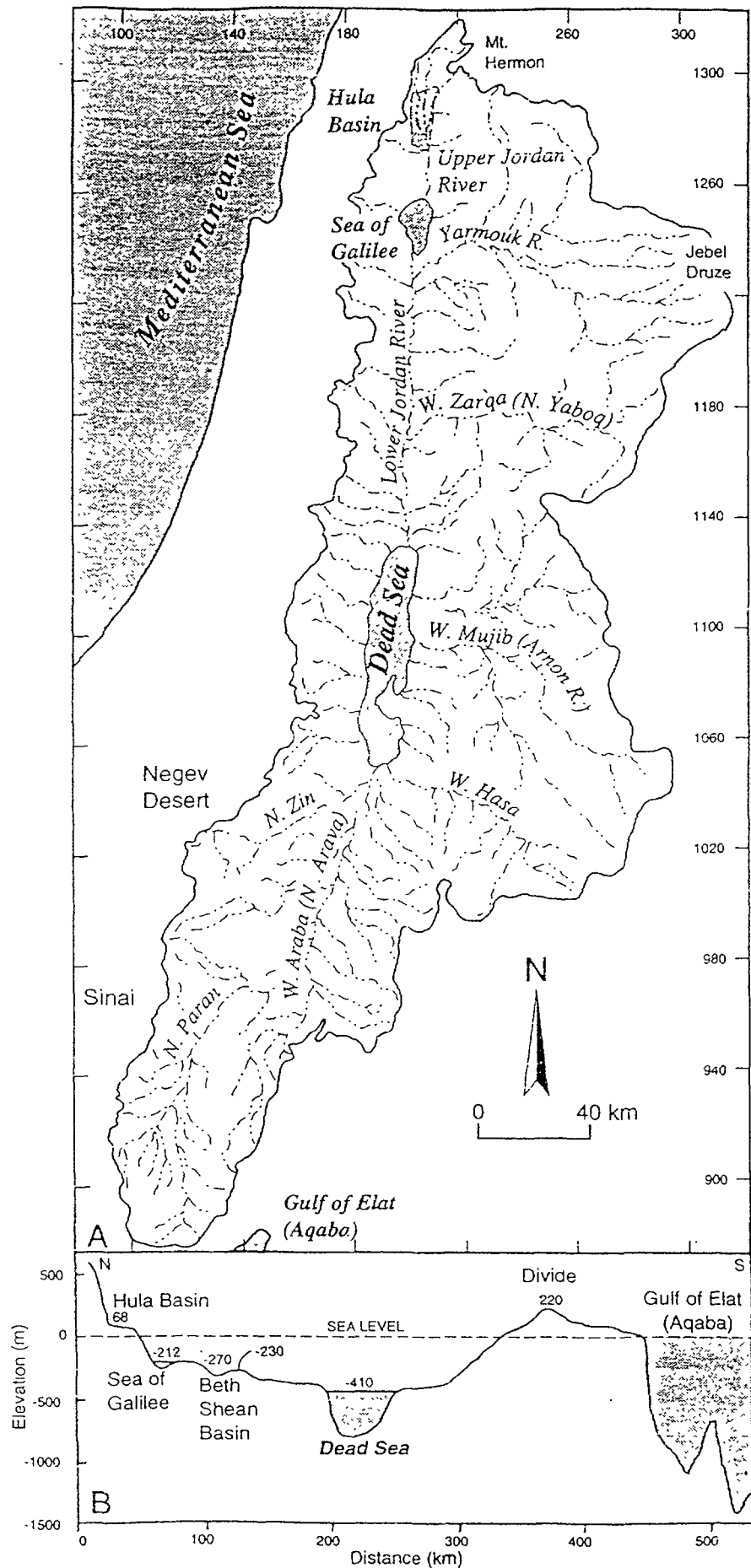


Fig. 1: Location plan and section

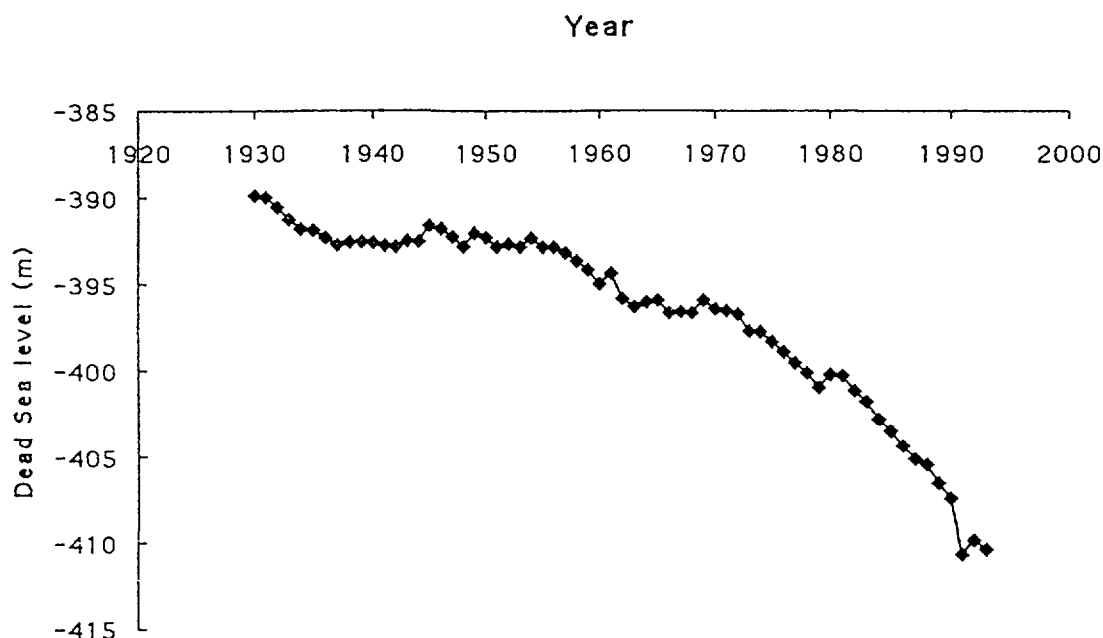


Fig. 2: Hydrograph of the Dead Sea level since 1929

surface level. In 1980 and 1992, following relatively large amounts of freshwater inflows the lake level rose. Apart of these two special years, the levels dropped even faster, 80 cm per year with very little variability of <2%.

Following the overturn observed in February 1979 a very weak stratification was established during summer 1979 by virtue of a temperature balance which scarcely overbalanced the inverse salinity gradient [4]. An imminent overturn in the fall of 1979, which would have established a monomixis, was prevented by the early onset of freshwater inflows of the 1979/80 rainy season. A further overturn only took place in Dec. 1992.

From that time to the present, the Dead Sea entered a phase in which it switches from one mixing regime to another. Hutchinson [5] defines a "meromictic" lake as one in which part of the deep water is stabilized, and a "holomictic" lake as one which can go freely through annual circulation periods. A new and more precise definition of these regimes became necessary then for the case of the Dead Sea, which was formulated by Anati as follows: a period is defined as "meromictic" if it is longer than one seasonal cycle; it begins with the onset of a stable stratification, and terminates with the first overturn. A "holomictic" period is a non-meromictic period which comes between meromictic periods. According to this definition, it begins with an overturn and terminates with the onset of a stable stratification.

The bars at the bottom of Fig. 3 indicate these changes of regime. According to this definition, the 1979-1980 holomictic period is revealed as considerably shorter than a whole holomictic year as it was previously considered to be. During the two decades represented in Fig. 3, the Dead Sea has been switching from holomictic to meromictic at particularly rainy winters, staying then meromictic for a typical period of four years.

Judging from these two decades of Dead Sea hydrography since 1977, the combined contribution of rain, floods, springs, and minor rivers runoff, has been almost negligible in comparison with the Jordan river surges which followed the openings of the Degania dams.

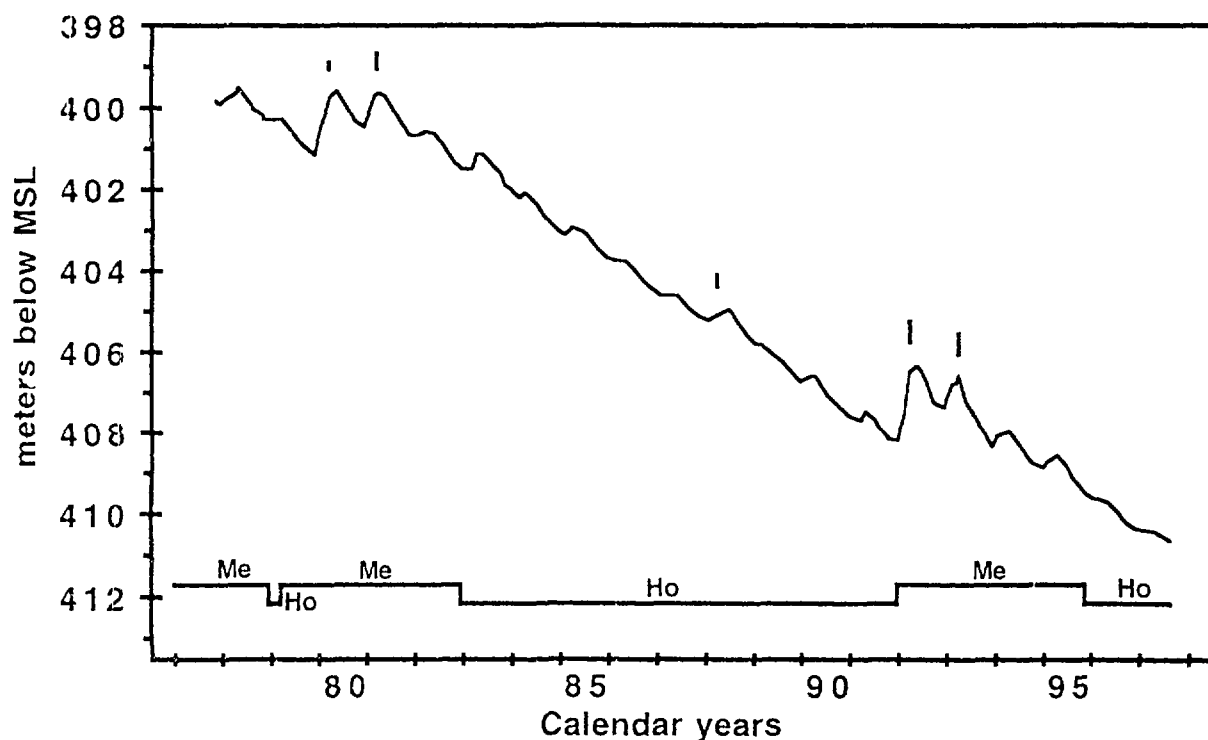


Fig. 3 Surface levels of the Dead Sea. Bars at bottom signify the mixing regime which operates: HO - holomictic; ME - meromictic; vertical dashes on top show timing and magnitude of floods due to opening of the Degania Dam at Lake Kinneret.

The five vertical dashes shown in Fig. 3 represent the five strongest surges during the period, their lengths being proportional to the amounts of water released. It can be seen that the changes into a new meromictic period depend mostly on the amount of fresh water released through the Degania dams, that is on the amounts of winter rains in the northern catchment area, rather than in the local vicinity.

Until 1995, all recorded overturns were documented, or estimated to have occurred, in early to mid-December. Similarly, the lowest stability of the water column in meromictic years has always been registered in early to mid-December. The first recorded exception to the rule occurred in 1995; the Dead Sea water column overturned in mid-November (In 1996, the paucity of data did not permit an accurate estimate of the date of overturn). It is not to be excluded that the high salt concentration attainable with the present ionic composition, brings about a preconditioning favorable to double diffusive mixing (DDM) at an earlier stage (say May, rather than July-August). This, in turn, would accelerate the deepening and weakening of the pycnocline, causing an early (and therefore wann) overturn. If future evidence will eventually point at this kind of strong warming-up trend in the deep water mass of the Dead Sea, in addition to the documented (weaker) warming up due to increasing salinities, this might corroborate this hypothesis.

The Dead Sea thermohaline structure in the summer of 1996 is described by Ran Weinstein and David A. Ariati as follows: Since the overturn of November 1995, four cruises have been conducted in the Dead Sea, three of them at the deep station of Ein-Gedi 320 and one at the shallower station of Ein-Gedi 120. The conclusion from analyzing the data collected in those cruises is that the vertical stability of the Dead Sea water column is very fragile, because of

destabilizing salinity gradient, and apparently, we can expect an overturn of the Dead Sea before winter.

The thermocline is very sharp just below 21 in. The temperature difference between the epilimnion and the hypolimnion is 11.5°C; that gives the column stability of 5 su. This difference is seasonal and it builds during spring and summer. This year (1996) the temperature structure is maintaining the stability of the water column.

The detailed salinity structure of the uppermost 40 m shows that there is an unstable structure resulting from poor inflow of fresh water during the winter, and evaporation of surface water that increase the concentration of salinity below the surface.

2. SALINITY

The chemistry of the Dead Sea waters, and in particular its mineral load, is its most notable attribute. Aptly, the Hebrew name for the Dead Sea is the "Salt Sea". Many studies were concerned with explanation of the particular ion composition of the brine.

Zak summarizes the situation as follows: the waters of the present-day Dead Sea are a Ca-chloridic brine, with over 330 g/l dissolved ions, and with unique high Br content of about 5 g/l. The same brines occur as interstitial water in formations adjacent to the lake, as do a number of other brines known from springs and boreholes around the lake. All these brines are derived from three basic types: 1) Diagenetic type brine, originally evaporated seawater of the Gulf of Sedom and later modified by Mg/Ca exchange into Ca-Mg-Na-K-Cl-Br water (with $\text{Ca}^{2+} > \text{HCO}_3 + \text{SO}_4^{2-}$, which has obtained its Ca by exchange of its original (marine) Mg with the Ca of carbonate sediment of the Dead Sea Group and of the surrounding pre-rift Cretaceous and older carbonate rocks, and which has lost most of its original sulfate by precipitation with this sequestered Ca; 2) Meteoric waters, dilute to mesohaline, whose composition has seawater affinity (airborne seasalts); 3) Metamorphic brine, the result of incongruent alteration and dissolution of hydrous evaporate minerals of the Dead Sea Group, which represent phases of desiccation of the successive marine and lacustrine water bodies.

The Dead Sea, which reaches a depth of about 325 m, may be regarded as an outcrop of brine, partly fossil, partly of recent derivation, which pervades both the Dead Sea Group and the downfaulted Mesozoic formations flanking and underlying it.

The waters of the open lake, the Dead Sea brine *sensu stricto*, maintain their composition by mixing processes with the above solutions combined with multiple progressive and regressive evaporation cycles, with periodic precipitation of halite, and occasionally of carnallite. The processes also take place along hydraulic pathways created by the Rift's marginal faults, which provide porosity and moreover enable brines to sink to depths of geothermal heating. The evolution of the Dead Sea brines can be considered a characteristic model for the hydrochemistry of continental rift-basins, temporarily connected with the ocean.

The relative ionic composition of the Dead Sea brine changes through the years, and therefore the equation of state of its waters [$r = f(T, S, P)$] also changes through the years, and must be revised periodically. It was assessed in 1980 [6], and then again in 1990 [7]. Although the rate of salt deposition has not been measured since 1992, indirect evidence points to a substantial increase during the present holomictic period of 1995-97. This massive salt deposition, combined with the reinjection of extremely dense "end brines" to the main water

body, is expected to have changed the relative ionic composition of Dead Sea brines at an enhanced rate, and the latest assessments of the equation of state may well deserve being updated already. The same can be said of other properties: saturation, heat capacity, viscosity, etc.

The change of salt composition affects not only its equation of state, but also that of the solubility of the evaporitic salt and foremost that of halite. In a multicomponent solution such as the Dead Sea brine, solubility is not only a function of total salinity and of temperature, but also of the ion composition. The effect of components other than NaCl, especially of the alkaline earth cations Mg and Ca, is to decrease the thermodynamic activity of the Na and Cl ions, and thus one witnesses a salting out effect. Indeed in the Dead Sea brine the halite solubility is only about one third of that of pure NaCl solution. Thus every time that massive halite deposition occurs, the NaCl solubility line is shifted in temperature-salinity space, and the onset of halite precipitation occurs earlier in each annual cycle.

The detailed and accurate prediction of this effect on the pattern of evaporate deposition is of concern but has not been fully resolved.

In addition to the geochemistry of major ions, some minor components have come to attention. Recently the mass balances of nitrogen and phosphorus have been addressed by Nissenbaum and Stiller. In the Dead Sea the very limited biota provides the opportunity of studying long-term mass balance of nutrients while decoupling geochemical factors from biological effects. Average ammonia in the water column rose from about 5.9 - 6.7 mg N L⁻¹ in the pre-1979 overturn period to 7.5 mg N L⁻¹ in 1981 and 8.9 mg N L⁻¹ in 1991. This increase could not be accounted for by the decrease of lake volume due to the decline in lake level. In 1977, during the destratification process, the water below 150 m depth still retained the same ammonia values as in the lower water mass during the stratified stage, indicating that the isolation of the deep waters still persisted. Following the 1979 overturn, the dissolved ammonia concentration became fairly homogeneous. Calculation of the quantity of inputs of ammonia from surface sources, such as runoff, perennial saline and fresh water springs and the Jordan River are shown to be of secondary importance as compared with diffusion from the sediments. Pore waters from the sediments in the deepest part of the lake showed increasing concentration of ammonia with depth, of up to 58.5 mg N-NH₃ L⁻¹ at 45 cm depth. However, calculation of the 1981 and 1991 nitrogen inventories showed that there must be an additional source of ammonia. It is tentatively assumed that the oxygenation of the entire water column after the 1979 overturn, and especially during the 1982-1991 monomictic stage resulted in mineralization of much of the dissolved organic nitrogen reservoir. Nitrate and nitrite are very low in the Dead Sea (about three orders of magnitude less than ammonia) and it can be shown that the nitrate load is compatible with recent, pollution-derived, sources. Dissolved and particulate phosphorous concentrations in the lake are quite low, at about 35 mg P L⁻¹ dissolved phosphate, and 30 to 50 mg P L⁻¹ for particulate phosphate. The dissolved phosphate distribution in the water column is fairly homogeneous, except for somewhat higher values near the sediment-water interface. Particulate phosphate, on the other hand, shows greater vertical, spatial and temporal variability. Mass balance calculations showed that the two major sources of phosphate are diffusion from the sediments (mostly) and phosphate introduced by the Jordan River. The mean residence time of dissolved phosphate is about 60 years. The exact mode of its removal is unknown, but co-precipitation with authigenic aragonite seems a plausible mechanism.

3. GAS EXCHANGE

Gases are another chemical component whose geochemistry is strongly affected by the high salinity so that freshwater studies have little relevance to the Dead Sea story. Dissolved oxygen was scrutinized by Shatkay et al. [8]. They concluded that the oxygen profiles in the Dead Sea follow the hydrographic structure of the water column, as determined by the physical variables (namely salinity, temperature and density), but also suggest the presence of chemical processes, such as oxygen reduction in the deeper part of the water column. It seems that the dominant source of reducing material is allogenic organic matter, brought in mainly by floods during the winter months.

From the data so far accumulated, it is evident that gas exchange rates are high only during winter months when strong winds and higher energy wave regime conditions prevail. At other times (especially during summer months), the deduced piston velocities are extremely low, lower even than the values found in the laboratory for conditions of diffusive transport across a fully developed boundary layer. Possibly this might indicate the presence of organic films at the water surface, which inhibit gas transfer across that interface. As a result the Dead Sea is mostly undersaturated with respect to DO, and thus seems to be a 'permanent sink' for incoming atmospheric oxygen.

A more recent study on the isotopic composition of dissolved oxygen by Luz and Barkan, who found a 7‰ enrichment in $\delta^{18}\text{O}$ (O_2) in the deep waters relative to the surface waters, suggests that there occurs bacterial oxidation in the deep waters of the Dead Sea. Their reasoning is based on a decline in the O_2/Ar ratio, from which an isotopic discrimination of -18‰ is calculated which is typical for bacterial oxygen consumption.

4. ISOTOPIC MEASUREMENTS

The measurements of the stable isotope composition of the Dead Sea waters, which were reported in detail in two papers in the past [9,10], were unfortunately not continued systematically.

However, some new measurements of other isotopic tracers were conducted, foremost on chlorine isotopes. An abstract of this work by Stiller and coworkers [11] which was accepted in Applied Geochemistry for publication in 1998 reads as follows:

This study presents the first set of $\delta^{37}\text{Cl}$ measurements in the Dead Sea environment. $\delta^{37}\text{Cl}$ values for the meromictic (long-term stratified) Dead Sea water column prior to its complete overturn in 1979 were -0.47‰ SMOC for the UWM (Upper Water Mass) and +0.55‰ SMOC for the LWM (Lower Water Mass). The $\delta^{37}\text{Cl}$ values for the pre-overturn Dead Sea cannot be explained by the prevailing model on the evolution of the Dead Sea during the last few centuries and require corroboration by more measurements. The 1979 overturn wiped out almost completely the isotopic differences between the UWM and LWM. Even so, chlorine isotope data could be used to decipher physical processes related to the overturn such as incomplete homogenization of the deep water mass. Inputs into the lake, comprising fresh waters (springs and the Jordan River) and saline springs gave a range of -0.37‰ to +1.0‰ with the fresh water sources being more enriched in $\delta^{37}\text{Cl}$. Based on the $\delta^{37}\text{Cl}$ measurements of the End-Brine (the effluent from Dead Sea evaporation ponds) and of recent Dead Sea halite, the chlorine isotopic composition of the originating brines have been estimated. They gave a

narrow isotopic spread, + 0.01‰ and +0.07‰ and fall within the same range with Dead Sea pore water (+0.13‰) and with the post overturn Dead Sea (-0.03‰ and +0.16‰). Rock salt from Mt. Sdom gave a value of -0.59‰ indicating its formation at the last stages of halite deposition from evaporating sea water. The hypersaline En Ashlag spring gave a depleted $\delta^{37}\text{Cl}$ value of -0.32‰, corresponding to a residual brine formed in the very latest stages (including bishofite deposition) of sea water evaporation.

The most telling use of environmental isotopes in recent years, related to the Dead Sea system, has been in the study of the Coastal hydrological regime. As the lake level drops and the lake-shore line recedes, it is accompanied by a restructuring of the freshwater-saltwater interface zone. Furthermore, the new coastal lands (the terra nova) which were saline bottom sediments of the Dead Sea are now exposed to flushing by fresher waters, whether by rain, surface floods or upwelling of water from shallow water table. Yehieli and coworkers have pursued these processes in which are summarized in the cited publications [12] and which are schematically represented in Fig. 4.

Stable isotopes in plant waters of new plants which are invading the terra-nova have been used to advantage by Yakir and Yehieli [13] to study the pattern of water usage. It was found

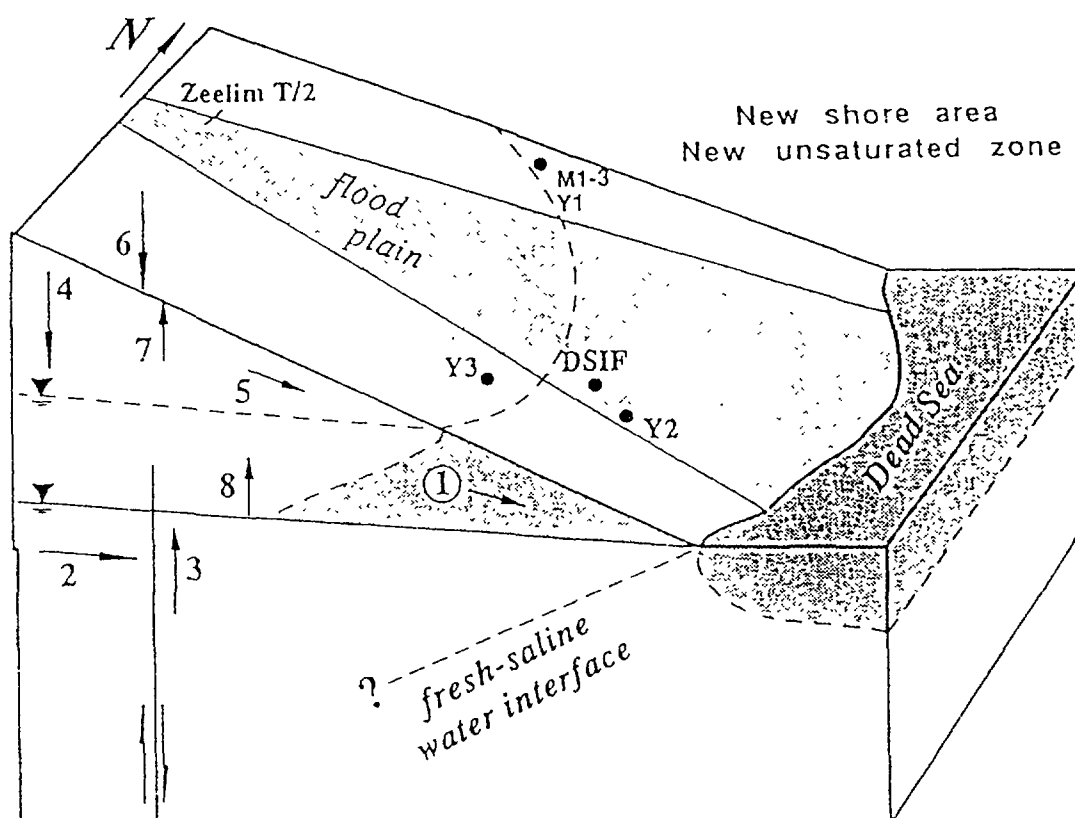


Fig. 4: Conceptual model describing the different water transport mechanisms in the study area (broken line denotes the former ground-water and Dead Sea levels): 1) drainage of residual Dead Sea solutions as a result of the receding of the Dead Sea in the last few decades; 2) transport of groundwater originating in the west; 3) upflow of water through fault plane; 4) percolation of rainwater and floodwater; 5) lateral flow in the unsaturated zone; 6) adsorption of air moisture by the saline surface sediments; 7) evaporation; and 8) capillary rise.

that the plants appear to ignore the more saline water pockets in the soil zone (which are marked by enrichment of heavy water isotopes and preferentially use up fresh water lenses which can be related to recent floodings of the area.

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STABLE ISOTOPIC COMPOSITION OF EAST AFRICAN LAKE WATERS

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Abstract

The investigation of stable isotopic composition of East African lake waters was conducted by scientists from the Department of Geology, University of Nairobi as part of the International Decade for the East African Lakes (IDEAL) project and in close collaboration with the scientists from Large Lakes Observatory of the University of Minnesota and the Isotope Hydrology Laboratory of the IAEA in Vienna. The Research Contract was part of the IAEA Co-ordinated Research Programme on Isotope Techniques in Lake Dynamics Investigations, and was sponsored by the Agency.

Water and grab sediment samples were obtained from East African Lakes during the month of January and February, 1994 and July/August 1995. Water samples were analysed for oxygen and deuterium isotopic composition at the IAEA Laboratories in Vienna, Austria. In this final paper we report the results of the study of oxygen and deuterium isotopic composition from the East African lake waters.

Introduction

Since 1990, we have observed that most if not all lakes in East Africa had a rapid decrease in lake level. Rocky shorelines in Lake Baringo for example indicate a decrease of at least 1 metre during this period. Lakes Elmenteita and Nakuru have almost run dry. Whether the current trend in lake levels in East Africa is a local response to current drought conditions in sub-Saharan Africa or to global warming is subject to speculation. This situation provided a unique opportunity to monitor and study the changes in the isotopic composition of the lake waters as well as the chemical and ecological responses of small lakes to these changes.

Objective

The primary objective of this project is to study temporal changes in the chemical and isotopic composition of lake waters induced by climate change in the tropics, and the ecosystem response to these changes. The other objective was to establish a lake water sampling programme in East Africa covering different climatic setting, altitude, mean annual temperature, rainfall and chemistry (Table 1, Fig. 1) in order to investigate seasonal variability in isotopic composition of precipitation in the region.

Methods

Lakes that were sampled (Fig. 1) were selected to cover a wide latitudinal as well as altitudinal, range (Table 1). This selection was done with the aim of trying to establish an evaporation/precipitation gradient as well as a temperature gradient. In each lake, between one and three grab sediment samples were obtained using an Ekman dredge. Surface water samples were obtained coincidentally with the grab samples. The waters were filtered with a .45m filter paper and three 250 ml portions were saved to be later analysed for major anions, cations and isotopes. Field titrations were also performed to determine alkalinities. Measurement of water temperature pH, conductivity and total dissolved solids (TDS) were also carried out.

Water samples were analysed for oxygen and deuterium isotopic composition at the International Atomic Energy Agency Laboratory in Vienna, Austria. Sediment samples were analysed at the University of Minnesota, and at the University of Nairobi.

Results

The deuterium and ^{18}O content of lake waters in East Africa is presented in Table 2. The result is reported in conventional delta notation (δ) as parts per thousand deviation of the isotope ratios $^2\text{H}/^1\text{H}$ or $^{18}\text{O}/^{16}\text{O}$ relative to the standard V-SMOW (Vienna Standard Mean Ocean Water). The deuterium excess, defined as $\delta = \delta^2\text{H} - 8\delta^{18}\text{O}$, describes the location of individual data points on the plot with respect to the so-called Global Meteoric Water Line (GMWL) defined by the equation $\delta^2\text{H} - 8\delta^{18}\text{O} + 10$. Using this equation the $\delta^{18}\text{O}$ and δD values of lake waters in East Africa was plotted in Figure 2. The range of $\delta^{18}\text{O}$ values of the lake waters is from -3‰ to 12‰ while δD varies from about -16‰

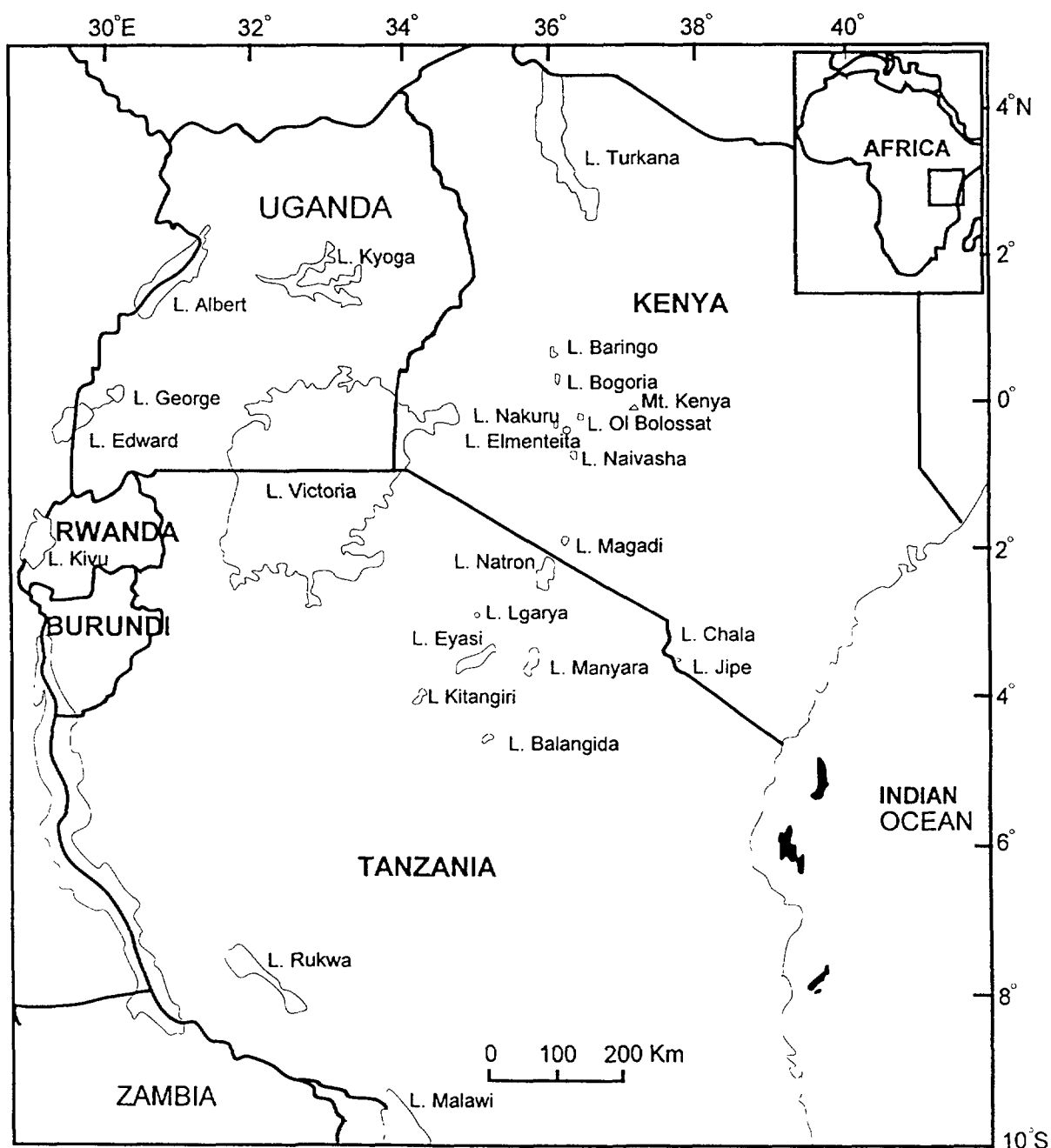


Fig.1 Location map for the East African Lakes of this study

Table 1 Description of East African lakes sampled in this study

Lake	Altitude	Latitude	Longitude	Lake Area (Km ²)	Zm (m)	Z(Mean) (m)	Vegetation
Turkana (16GC)	375	2°50'N	36°28'E	7500	110	31	Semi arid, shrubs
Jipe	701	3°35'S	37°45'E	30	-	~3	Savanna
*Chala	838	3°19'S	37°41'E	5	~100	-	Open forest
*Katwe+	895	0°08'S	29°52'E	2.45	2.45	0.33	-
Edward+	913	0°25'S	29°30'E	2800	120	-	Open forest
Kitagata+	925	0°03'S	29°58'E	-	-	-	-
Baringo	975	0°38'N	36°05'E	160	4	-	Savanna
*Nyamusigire+	975	0°17'S	30°02'E	4.4	4.9	-	Forest
*Kamweru+	1160	0°15'S	30°07'E	0.3	33.5	22.7	Forest
*Nkugute+	1220	0°19'S	30°06'E	1.05	58	20	Farms, forest patches
Manyara	1235	3°35'S	35°50'E	400	-	-	Savanna
*Nyabikere+	1265	0°30'N	30°20'E	-	40	-	Farms, forest patches
Nyibulita+	1327	0°31'N	30°19'E	-	65	-	Farms, forest patches
*Katanda+	1340	0°29'N	30°16'E	0.4	146	-	Forest
*Saka+	1520	0°42'N	30°14'E	0.01	8.5	2.7	Open forest, grasses
Babati	1540	4°15'S	35°44'E	5	-	-	Farms, ~50% forest
Singidai	1540	4°47'S	34°45'E	10	~4	-	Savanna
Kindai	1540	4°51'S	35°44'E	3	-	-	Savanna
*Duluti	1600	3°23'S	36°47'E	1	-	-	Forest
Nkunga	1840	0°07'N	37°36'E	~1	-	-	Forest
Small Momela	1850	3°14'S	36°54'E	~0.5	-	-	Open forest
Naivasha	1880	0°46'S	36°21'E	175	~5	-	~90% farms, grasses
Oi Bolossat	2320	0°09'S	36°26'E	40	~2	-	~90% farms, grasses
*Rutundu	3079	0°19'S	37°28'E	1	~10	-	Alpine

to -70‰ (Table 2). The plotted $\delta^{18}\text{O}$ and δD values relative to SMOW of meteoric waters is shown in Figure 2.

Discussions

The lakes sampled in this research contract range in altitude from 360 m to 3,000 m (Table 1, Fig. 1). The altitudinal distribution of these lakes provide two major climatic gradients; a precipitation/evaporation gradient and a temperature gradient. These climatic gradients should be reflected in the isotopic and chemical composition of the lake waters in East Africa. The results obtained in this work clearly indicate that lake waters from East Africa behave differently, perhaps due to excessive evaporation that characterises this region.

The isotopic composition of precipitation in the East African region reflects the regional circulation pattern (Rozanski, 1995). The region experiences recurrent events of extremely low deuterium and $\delta^{18}\text{O}$ isotope composition of precipitation, often persisting for more than one month, which most probably are associated with unusually strong convective activity within the air column, associated with passage of the intertropical convergence zone (ITCZ). In general, isotopically depleted waters are associated with the rainy seasons (Table 2).

Table 2 Values of Isotope (δD , $\delta^{18}O$) in East African lakes in this study

Location	Sample Code	delta (O-18)	delta (H-2)
L. Manyara	A1/1	-2.44	-8.9
L. Manyara	A1/2	-2.42	-10.9
L. Momela	A2/1	3.92	23.7
L. Momela	A2/2	2.69	24.4
L. Singindai	A3/1	7.32	47.6
L. Singindai	A3/2	7.19	45.6
L. Babati	A4/1	4.16	25.4
L. Babati	A4/2	4.37	25.9
L. Kindai	A5/1	6.01	37.2
L. Kindai	A5/2	6.00	36.2
L. Duluti	A6/1	3.42	18.7
L. Duluti	A6/2	3.58	19.2
LT95-1WS	A7/1	5.70	36.4
LT95-1WS	A7/2	5.70	40.9
LT95-2WS	A8/1	5.41	38.8
LT95-2WS	A8/2	5.69	39.9
LT95-3WS	A9/1	5.73	39.9
LT95-3WS	A9/2	5.72	41.0
TURK R.-5WS	A10/1	-0.60	3.5
TURK R.-5WS	A10/2	-0.68	2.7
LT95-5WS	A11/1	6.01	41.3
LT95-5WS	A11/2	6.05	41.2
Omo R.-6WS	A12/1	-0.81	3.0
Omo R.-6WS	A12/2	-0.89	-1.9

Location	delta (O-18)	delta (H-2)	d-excess
L. Edward, 0 m	4.04	29.7	-2.6
L. Kifuruka, 0 m	5.80	32.1	-14.3
L. Saka, 0 m	1.87	17.3	2.4
L. Katanda 0 m	6.65	39.2	-14.0
L. Kamweru 0 m	3.25	22.3	-3.7
L. Nkugute, 0 m	3.40	25.0	-2.2
L. Nyanabunta, 0 m	5.45	35.0	-8.6
L. Nyabikere, 0 m	0.83	13.9	7.3
L. Kitagata, 0 m	6.16	34.8	-14.5
L. Nyambusin, 0 m	6.84	39.4	-15.3
L. Nyantonde, 0 m	4.64	28.1	-9.0
L. Nyantonde 10 m	4.59	32.3	-4.4
L. Nyantonde, 20 m	4.52	27.8	-8.3
L. Nyantonde, 30 m	3.15	23.4	-1.8
L. Nyantonde, 60 m	3.28	23.7	-2.5
L. Nyantonde 150 m	3.68	21.8	-7.6

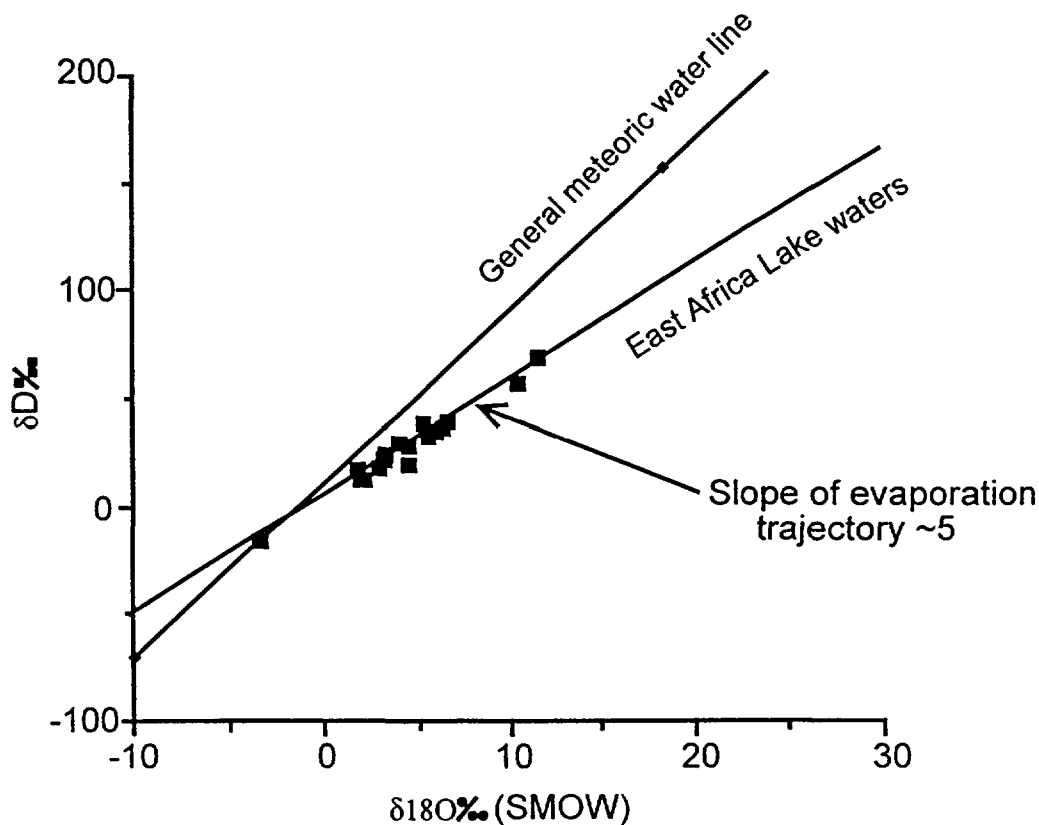


Fig.2 Plot of $\delta^{18}\text{O}$ and δD values relative to SMOW of meteoric waters of this study.

In lakes with seasonally dry climate, the oxygen isotopic composition of a lake's water is mainly the result of evaporative evolution and residence time of the water body (Beadle, 1974; Gat, 1981; Gonfiantini, 1986). This does not seem to be the case in East Africa. The isotopic composition of the lake waters studied in this contract seems to be an interplay between basin size, altitude and hydrology. However, further research is required in order to have a better understanding of the physical and chemical factors that cause the observed variability in the isotopic composition of lake waters in this region.

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STABLE ISOTOPES IN LAKES OF THE HIGH TATRA MOUNTAINS, WESTERN CARPATHIANS, SLOVAKIA

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Abstract

Data of oxygen, hydrogen and sulphate sulphur stable isotopes from the lakes of the Vysoké Tatry Mts., acquired in the framework of IAEA No. 8675/RB project "Stable isotopes in lakes of High Tatra mountains, Western Carpathians, Slovakia" represent the first set of this kind information on the territory of Slovakia. Moreover a complete set of chemical composition of waters was taken and compared to preceding results and contemporary state of acidification was evaluated. Values of studied chemical compounds respond to their source - initial precipitation waters and bedrock character with influence of biochemical processes. Acidification is due to inactive geological background (granites), high contribution of SO_x and NO_x from atmospheric deposition and low buffering ability of soil. Acidification of lakes is lowered from 1980 and is approaching to level before acidification, probably as consequence of industry crisis in Eastern Europe after 1989. Water samples from the Furkotska dolina valley water system follow the MWL with natural trend of increasing content of heavy isotopes with lowering altitude. In depth profiles of single lakes' isotope composition does not change - due to natural conditions during sampling campaigns (spring and fall homothermy?), all waters are meteoric in origin without signs of evaporation. Water of the Strbské pleso lake is enriched to heavy isotopes, all samples fit an evaporation line. This could be explained by longer residence time of water, or by the recharging from the last phases of the snowmelt. Sulphate sulphur isotope ratios from lakes are the same and they are identical with these of snow packs.

1. INTRODUCTION

Mountain lakes formed in the Vysoké Tatry (High Tatra) Mts. were chosen for intended research of IAEA No. 8675/RB project "Stable isotopes in lakes of High Tatra

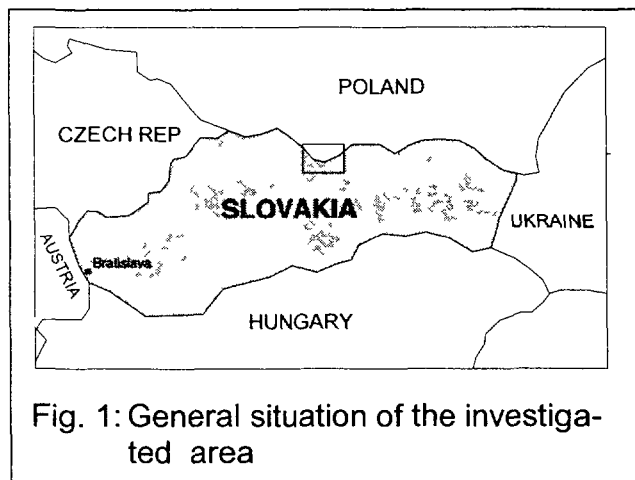


Fig. 1: General situation of the investigated area

Mts., Western Carpathians, Slovakia". Vysoké Tatry Mts. are the highest part of Western Carpathians and whole Carpathian arc as well. They form natural border between Slovakia on the south and Poland on the north (Fig. 1.). Acquired data of oxygen, hydrogen and sulphate sulphur stable isotopes from the lakes of the

Vysoké Tatry Mts., represent the first set of this kind information on the territory of Slovakia. Moreover a complete set of chemical composition of waters was taken and compared to preceding results and contemporary state of acidification was evaluated.

2. NATURAL CONDITIONS OF THE INVESTIGATED AREA

2.1 Geomorphology

Main ridge of the Vysoké Tatry Mts. is in the form of an arc shaped to the south. It is some 26,5 km long, its mean altitude is 2279, mean altitudes of summits is 2357 and saddles 2179 m. a. s. l. Highest summits on the main range are Ladvový štít (Ice peak) with 2627 and Lavinový štít (Avalanche peak) with 2606 m. a. s. l.. Placement of highest summits (Gerlachovský štít 2654, Lomnický štít 2634 m. a. s. l.) on southern side-ridges which are separated by deep valleys, forms typical asymmetric structure of the Vysoké Tatry Mts.. Studied lakes are situated in such valley - Furkotská dolina valley and Strbské pleso lake in between Furkotská dolina and Mlynická dolina valleys (Fig. 2).

2.2 Geology

From the geological point of view the Tatry is a relatively highly elevated block, almost completely lined by overlying sediments of the Central Carpathian Paleogene Basin. Southern and central parts are covered by the Mesozoic sediments. Scarcely Mesozoic outcrops are present inside the Paleogene and Quaternary sediments, to the south of the Tatry block.. The lowermost structural unit incorporated in the Tatry block is called the

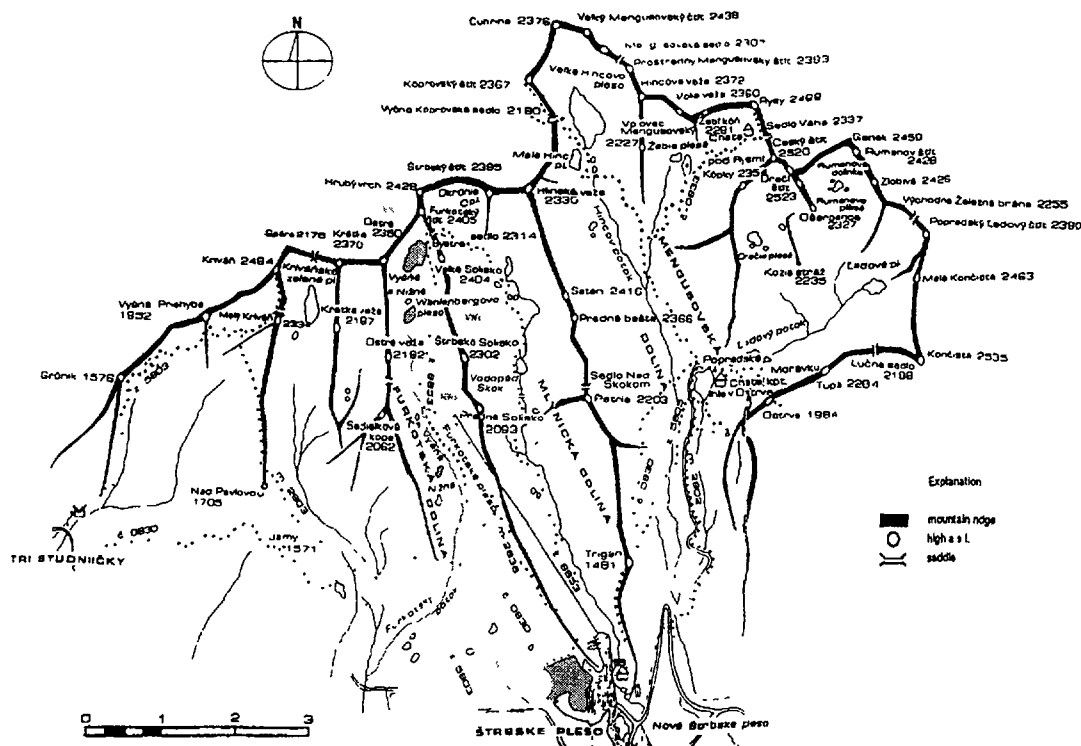


Fig. 2: Detailed situation of the investigated area

Tatricum. This unit is formed by the crystalline basement and by the Permian - Mesozoic sequences. The basement prevailing consists of the granitoids and metamorphic rocks. The basement comprises several tectonic slices made by both the Alpine and pre-Alpine events. The lowermost basement unit is formed by complex of mica schists and gneisses, overlaid by granitoids and migmatites in the south-western part of Tatra Mts. region. The upper basement unit of Tatricum is formed by a complex of granitoids which are underlain by migmatites and amphibolites. The cover of the granitoid intrusion consists of the metamorphic rocks.

The oldest formation of the Tatricum cover unit (Tatric Permian - Mesozoic sequences) is conglomerate which is believed to have started its deposition already in Permian. Younger Mesozoic formations consist of various limestones, dolomites, marls and sandstones. Abundant fossils (pelecypods, brachiopods, ammonites, crinoids, foraminifers etc.) prove their deposition in the marine environment. However, there are some exceptions. Shallow marine even continental sediments are present in the sequences in the western part of Tatra Mts. region. Here its continental origin proved by the occurrence of the tracks of *Coelurosaurichnus tatricus* on the bedding planes [8].

The Tatricum is overlaid by the Fatricum. The Fatricum in the Tatry region is represented by a very complicated nappe structure - Krizna nappe - which only consists of

the Mesozoic sequences ranging in age from the Lower Triassic to Lower Cretaceous. A complicate internal structure of the Krizna nappe can be seen on the western slopes of Tatra Mts. There are small-scale nappes, thrust slices and duplexes.

The Choc nappe represents the upper unit called Hronicum, which overlies the Fatricum. The Choc nappe occurs in a form of the two partial nappes in a Tatra Mts. region.

The Upper Cretaceous - Lower Eocene sediments are missing in the Tatry region. It is presumed that the erosion of the Palealpine structures took place during this time period. A presence of the outcrop with Eocene transgressive sediments overlying directly the crystalline basement indicates how intensive this erosion was. It is believed that the erosion took place during the whole Late Cretaceous - Early Paleogene time period.

Thickness of Quaternary sediments and the area they cover is given by direct relationship to the Pre-Quaternary base. Existing geophysical data (supported by the hydrogeological borehole logging results) revealed that the major thickness is concentrated in the area of the 1.5 - 4.0 km belt along the southern edge of the Vysoke Tatry Mts.. Boreholes had proven the thickness up to 400.0 m. In the S and SE direction, towards the Poprad and Biely Vah river valleys, the Quaternary thickness are gradually reduced. Quaternary sediments are including many genetic types - glacial (würm, riss and mindel period), glaciofluvial, fluvial and polygenetic accumulations with very variable granulometric compositions. According to their age, we can distinguish members ranging from late Pleistocene up to Holocene. Basement in the studied area is practically built only from granitoids with Quaternary mainly glacial sediments.

2.3. Climate

Main influence on climatic conditions has slope exposition to prevailing western, North-Western winds. Southern winds influence is not so important because of the influence of the Nizke Tatry (Low Tatra) mountains (main ridge altitude is near 2000 m. a. s. l.) rain shadow from the south. Mean annual temperature on the Vysoke Tatry Mts. main ridge oscillate from -2 to -4 °C, in Strbske pleso altitude level from +3 to +5 °C. Amount of precipitation highly depends on slope exposition. Total year amount of precipitation moves from 1000 to 3500 mm. Snow cover lasts on the slopes of the Vysoke Tatry Mts. meanly 140 - 180, on the ridge to 240 days per year. Mean evaporation is about 400 - 500 mm per year.

2.4. Hydrogeology

Groundwater in granitoids of the Vysoke Tatry Mts. is bound to fissures of various origin, first of all fissures of the weathered zone and sub-surface expansion up to the 50 m of the depth. Bedrock aquifer is closely connected with overlaying Quaternary deposits, and the mutual exchange of groundwater between them is constantly going on. To distinguish the "pure granitoids" groundwater runoff in this area, discharge gaging on the Beliansky potok stream were established on the Tri studnický station in the period of 1977 - 1980 [3]. Average specific groundwater runoff in these climatic and hydraulic conditions, not too much influenced by presence of Quaternary sediments, was calculated as $7.8 \text{ l.s}^{-1}.\text{km}^{-2}$ using Foster method and $6.8 \text{ l.s}^{-1}.\text{km}^{-2}$ using Kille's method. Minimal (base) specific flow was ranging from $1.2 \text{ l.s}^{-1}.\text{km}^{-2}$ to $4.2 \text{ l.s}^{-1}.\text{km}^{-2}$ in the same period.

The most important aquifers on the territory of the Central part of the Vysoke Tatry Mts. are glacial and glacial-fluvial deposits. For glacial-fluvial sediments, transmissivity proven by pumping tests was ranging from $4.40 \cdot 10^{-5} \text{ m}^2.\text{s}^{-1}$ up to $6.52 \cdot 10^{-5} \text{ m}^2.\text{s}^{-1}$. Permeability of all genetic types of Quaternary sediments is connected with their granulometric composition. Permeability coefficient of glacial-fluvial sediments is therefore ranging from $4.93 \cdot 10^{-7} \text{ m.s}^{-1}$ to $9.75 \cdot 10^{-2} \text{ m.s}^{-1}$. The thickness of glacial-fluvial deposits is usually 25 - 35 m, in tectonic depressions 40 - 80 m, but the permeability there is influenced by higher content of pelitic components. Permeability coefficient of glacial sediments is ranging from $1.84 \cdot 10^{-8}$ to $1.98 \cdot 10^0 \text{ m.s}^{-1}$. Transmissivity from pumping tests ranging from $1.57 \cdot 10^{-4} \text{ m}^2 \cdot \text{s}^{-1}$ up to $9.93 \cdot 10^{-3} \text{ m}^2.\text{s}^{-1}$. For their permeability, the granulometric composition of the filling between the stony material is important.

The groundwater regime gaging [3] had shown that the lowest values of both discharges and groundwater levels are present in January - February period in lower altitudes and in March - April period in higher altitudes. The highest levels are then reached in May - July or July - August respectively. Based on gaging in the 1975 - 1980 period, the prognostic natural groundwater resources were calculated for the central part of the Vysoke Tatry Mts.. Total area of outcropped crystalline rocks in the central part of the Vysoke Tatry Mts. represents 150.5 km^2 . 15.5 km^2 is represented by the Mesozoic carbonates present in "islands" along the mountain edge and the rest - 312.9 km^2 is covered by thick Quaternary deposits.

From the groundwater protection point of view is important, that classical pollution sources are influencing the chemical composition of the Vysoke Tatry Mts. groundwater only in limited way. The major pollution sources there are mainly liquid and solid waste as

the result of presence of tourist centres and tourist activities, negative impacts of traffic on roads and forest exploration activities. Because of the limited buffering ability of crystalline rock environment, noticeable are also influences of emissions transported by air masses and precipitated over the area. Self-purification and filtration ability of the major aquifers, present in the Vysoke Tatry Mts. region, is generally very low.

2.5. Hydrology

Continental main water divide between (Black and Baltic sea) pass across western bank of the Strbske pleso and Solisko ridge to the main ridge. Furkotska dolina water system (Fig. 2) belongs to Black Sea watershed and Mlynicka dolina valley to Baltic Sea watershed. Water flow of streams is quick (about 2 m.s^{-1}) and lowest discharge is during winter (December - March), highest in June - combined influence of snow thawing and high precipitation period in high altitudes.

Table I Basic characteristic of the largest Vysoke Tatry Mts. lakes (modified from [4])

Lake	altitude [m a.s.l.]	exposition	surface area [ha]	depth [m]		Period	
				max.	mean	thaw	freeze
Morskie Oko	1393	N	34,93	51	28	V - VI	X
Wielki Staw z Pieciu Stawow	1664	N	34,35	79	38	V - VI	X - XI
Czarny Staw nad Morskim Okiem	1580	N	20,64	76	38	V - VII	X - XI
Velke Hincovo pleso	1965	S	20,08	53	23		
Strbske pleso	1350	S	19,76	20	6	IV - V	XI
Czarny Staw Gasienicowy	1620	N	17,94	51	21	V - VII	X - XI
Czarny Staw z Pieciu Stawow	1722	N	12,69	50	22		
Vysne Wahlenbergovo pleso	2157	S	5,18	21		VII - VIII	IX - X

During glacial period a lot of lakes were formed in the Vysoke Tatry Mts. Their number is about 138 now. The most of them (88 %) is in the area over the forest line. Small lakes with surface to 1 ha and maximal depth (up to 2 m) are prevailing. Second group is formed by lakes with surface area 1 - 10 ha and maximal depths from 2 to 10 m. In the Vysoke Tatry Mts. there is only 6 lakes larger than 15 ha and 6 lakes with maximal depth bigger then 50 m (Tab.I).

Majority of lakes has not visible surface inflow, water is recharging into them from Quaternary sediments, with the exception of lakes that were created on streams. Outflowing water deepened surface channels in bedrock - beginning of fluvial net. Moraine lakes characteristic outflow is inside of moraine. Strbske pleso represent specific phenomena – it is so named “dead ice” lake.

3. SAMPLE PROCESSING

Samples for chemical and isotopic analyses were taken in two campaigns - in June (5-6th) and September (25-26th). Samples were taken from rubber boat from the surface level and from every five meters. When this was not possible (frozen or shallow lake), more samples were taken to characterise whole water profile. Temperature and conductivity were measured on the boat in 3 l water volume sampling vessel. This probably could influenced measured temperature especially during September sampling of Vysne a Nizne Wahlenbergovo pleso lake because of bad weather. Vysne Wahlenbergovo pleso lake was found in June frozen and in September half frozen, Nizne Wahlenbergovo pleso lake was completely frozen in September. For sulphur isotope analyses about 50 litres of water samples were taken from the surface of lakes. Samples for oxygen and hydrogen isotopic composition were taken into 50 ml glass bottles with sealing cup and to analyses stored in refrigerator.

Ratio of $^{18}\text{O}/^{16}\text{O}$ (water) was measured on CO_2 equilibrated with the water in a special equilibration device that was connected on line with a MAT 250 mass spectrometer. The unknowns are measured against an internal standard calibrated against SMOW. Reproducibility of preparation method ($n = 48$) was better than $\pm 0.07\text{‰}$.

Hydrogen gas for isotope analyses was produced by a zinc reduction technique. Approximately 5 μl of a water sample are reduced under vacuum with 150 mg of zinc at 490 °C during 30 minutes. The obtained results are normalised to internationally accepted standards (V-SMOW, SLAP) and reported in the usual δ -notation. The standard deviation calculated from replicate δD analyses of a sample was generally better than $\pm 1\delta$.

Sulphate sulphur from waters was precipitated with BaCl_2 (hot, acidified with HCl) as BaSO_4 and converted into H_2S by reaction with hot mixture of HCl , H_3PO_4 a HI . Such H_2S was purged by nitrogen via zinc acetate, resulting in precipitation of ZnS . Subsequently, a mixture of ZnS/CuO reacts gradually under temperatures 320 °C and 770 °C. SO_2 was storage in glass ampoules for measurement. Measurement was characterised by reproducibility of $\pm 0.3 \text{‰}$. Calibration of laboratory standard was carried out by IAEA international standards (NZ1 and NZ2) and recommended comparison materials (NBS122 and NBS127).

4. RESULTS AND DISCUSSION

In the spring (June 5-6th) and fall (September 25-26th) periods were the lakes and streams in High Tatra Mts., chosen for the research, sampled for isotopic (hydrogen,

oxygen, and in fall also sulphate sulphur) and chemical composition. This was first attempt to check stable isotope composition of water of these lakes. There was some basic information on chemical composition of water and evaluation of acidification of lakes [1], [2], [5], [9], [10]. For research were chosen different types of lakes in different altitudes and differently influenced by geogenic and anthropogenic factors. We chose water system in Furkotska dolina valley with: the uppermost Vysne (Upper) Wahlenbergovo pleso lake (VW), Nizne (Lower) Wahlenbergovo pleso lake (LW), Vysne Furkotske pleso lake (VF), stream between Vysne Wahlenbergovo pleso lake (VW) and Nizne Wahlenbergovo pleso lake (NW) - VWs and stream under the Nizne Wahlenbergovo pleso lake (NW) - NWs. The Strbske pleso lake (SP) lake vicinity is the main tourist and sports (especially winter sports) centre.

Results of performed analyses, both isotopic and chemical, are given in enclosed Tables III, IV and V. Vertical profiles of the chosen parameters (T, TDS, Na, Cl) of individual lakes (Fig. 3) and the altitudinal profile of the Furkotska dolina valley lakes including Strbske pleso lake as the lowest point (Fig. 4) are shown. In the reality SP lake is not connected to the Furkotska dolina water system. Results of snow pack analyses [6] as the source water representative are enclosed for comparison.

Sampling was organised to admit characterisation of the chemical and isotopic composition of the lake, stream and initial water (mainly after snow melting). Chemical parameters of VW water (Tab. III, IV, V) are in good concordance with chemical composition of snowpack - main input of the water into the lake - and inactive bedrock

Table II Contemporary and preacidificated alkalinity values of lakes. Ca + Mg, Cg, A - concentrations from single years, AP₁, AP₂ - calculated estimates preacidification alkalinities, DA₁, DA₂ differences between AP₁ - A and AP₂ - A, all in meq/l, (1980 values are taken from [9]).

Year	Locality	Ca + Mg	A _{p1}	Ca	A _{p2}	A	D _{A1}	D _{A2}
1980	Strbske pleso	201	173	141	163	121	52	42
1980	Vysne Furkotske pleso	203	185	170	199	32	143	167
1980	Vysne Wahlenbergovo pleso	126	103	116	133	-6	109	139
1980	mean	177	154	142	165	40	101	116
1996	Strbske pleso	243	212	165	192	171	42	8
1996	Vysne Furkotske pleso	131	109	116	132	118	-9	15
1996	Vysne Wahlenbergovo pleso	100	75	80	88	57	18	32
1996	Mean	157	132	120	138	115	17	18

Table III: Results of the water isotope analyses with basic site and water characteristic

No.	Locality	Altitude [m a s l]	Date	Depth [m]	T air [°C]	T water [°C]	pH	Conduct. [μS cm ⁻¹]	O ₂	δ ¹⁸ O _{H2O} SMOW [‰]	δD _{H2O} SMOW [‰]	d ³⁴ S _{SO4} CDT [‰]
1	Vysne Wahlenbergovo pleso	2145	05 06 96	0,0		0,3	5,22	16		-13,79	-94,3	
2	Vysne Wahlenbergovo pleso	2145	05 06 96	1 0		1,0	5,56	16		-13,88	-98,7	
3	Vysne Wahlenbergovo pleso	2145	05 06 96	2 0		3,2	5,55	13		-13,98	-98,8	
4	Vysne Wahlenbergovo pleso	2145	26 09 96	0,0	-2,0	1,6	5,85	13	8,8	-12,22	-85,3	4,5
5	Vysne Wahlenbergovo pleso	2145	26 09 96	4,0	-2,0	2,1	5,87	13	8,4	-12,11	-84,2	
6	Vysne Wahlenbergovo pleso	2145	26 09 96	10,5	-2,0	2,2	5,80	12	8,6	-12,19	-84,4	
7	Vysne Wahlenbergovo pleso	2145	26 09 96	15,0	-2,0	2,3	5,82	14	8,3	-12,13	-85,4	
8	stream under VW pleso (VWs)	2075	05 06 96	0,0		1,2	6,65	10		14,04	-98,0	
9	stream under VW pleso (VWs)	2075	26 09 96	0,0	0,0	1,6	5,80	13	11,1	-12,47	-86,2	
10	Nizne Wahlenbergovo pleso	2053	05 06 96	0,0		3,6	6,78	13		-13,40	-96,2	
11	Nizne Wahlenbergovo pleso	2053	05 06 96	3,0		4,3	6,00	15		-13,40	-91,4	
12	Nizne Wahlenbergovo pleso	2053	05 06 96	6,3		4,4	5,57	14		-13,26	-85,5	
13	Nizne Wahlenbergovo pleso	2053	26 09 96	0,0	0,5	0,9	5,85	15	10,8	-12,21	-85,2	4,3
14	stream Furkota (NWs)	1800	06 06 96	0,0		17,2	5,92	21		-13,18	-90,6	
15	stream Furkota (NWs)	1800	25 09 96	0,0	2,0	4,2	6,05	18	10,1	-11,58	-80,4	4,7
16	Vysne Furkotske pleso	1750	06 06 96	0,0		10,6	6,10	34		-13,20	-89,2	
17	Vysne Furkotske pleso	1750	25 09 96	0,0	1,0	4,5	5,93	18	8,3	-11,36	-75,9	
18	Strbske pleso	1350	06 06 96	0,0		17,0	6,42	37		-7,45	-65,1	
19	Strbske pleso	1350	06 06 96	4,5		11,1	6,12	33		-7,51	-61,3	
20	Strbske pleso	1350	06 06 96	9,0		6,7	6,32	39		-7,16	-56,0	
21	Strbske pleso	1350	06 06 96	13,5		6,4	5,72	39		-7,16	-56,4	
22	Strbske pleso (bottom)	1350	06 09 96	17,9		6,3	6,05	40		-7,16	-62,2	
23	Strbske pleso	1350	25 09 96	0,0	3,6	8,1	6,50	30	8,5	-7,03	-60,1	4,8
24	Strbske pleso	1350	25 09 96	5,0	4,0	8,0	6,55	30	8,9	-7,00	-59,8	
25	Strbske pleso	1350	25 09 96	10,0	3,5	8,0	6,41	30	8,0	-6,98	-60,9	
26	Strbske pleso	1350	25 09 96	18,0	3,5	6,1	6,05	39	3,5		-60,5	

Table IV Results of waters chemical analyses - basic components

No.	Locality	Altitude [m a.s.l.]	Date	Depth [m]	COD	TDS [mg l ⁻¹]	Ca [mg l ⁻¹]	Mg [mg l ⁻¹]	Cl [mg l ⁻¹]	SO4 [mg l ⁻¹]	NO3 [mg l ⁻¹]	HCO3 [mg l ⁻¹]
1	Vysne Wahlenbergovo pleso	2145	05 06 96	0,0	0,08	7,06	1,28	0,06	0,45	2,05	0,90	1,47
2	Vysne Wahlenbergovo pleso	2145	05 06 96	1 0	0,33	7,81	1,43	0,07	0,40	1,90	0,65	2,44
3	Vysne Wahlenbergovo pleso	2145	05 06 96	2 0	0,65	6,80	1,15	0,05	0,45	1,55	0,60	1,95
4	Vysne Wahlenbergovo pleso	2145	26 09 96	0,0	1,09	17,50	1,95	0,32	0,16	4,60	1,60	5,50
5	Vysne Wahlenbergovo pleso	2145	26 09 96	4,0	0,59	18,60	2,03	0,18	0,08	4,80	1,85	5,50
6	Vysne Wahlenbergovo pleso	2145	26 09 96	10,5	0,59	17,50	2,07	0,16	0,08	3,95	1,88	5,50
7	Vysne Wahlenbergovo pleso	2145	26 09 96	15,0	0,50	17,52	2,05	0,15	0,15	3,30	2,30	6,10
8	stream under VW pleso (VWs)	2075	05 06 96	0,0	0,08	9,13	1,67	0,06	0,40	1,90	0,65	3,05
9	stream under VW pleso (vWs)	2075	26 09 96	0,0	0,25	14,12	1,88	0,16	0,06	3,60	1,91	3,80
10	Nizne Wahlenbergovo pleso	2053	05 06 96	0,0	0,24	13,60	1,98	0,10	0,40	2,20	0,75	6,10
11	Nizne Wahlenbergovo pleso	2053	05 06 96	3,0	0,24	11,11	1,58	0,09	0,55	2,20	0,60	3,66
12	Nizne Wahlenbergovo pleso	2053	05 06 96	6,3	0,20	12,19	1,85	0,17	0,45	2,15	1,30	3,67
13	Nizne Wahlenbergovo pleso	2053	26 09 96	0,0	0,34	17,09	2,49	0,17	0,08	4,30	2,30	4,60
14	stream Furkota (nWs)	1800	06 06 96	0,0	0,41	15,20	2,27	0,17	0,45	3,15	1,30	3,66
15	stream Furkota (NWs)	1800	25 09 96	0,0	1,18	20,26	2,51	0,28	0,29	5,10	1,91	4,60
16	Vysne Furkotske pleso	1750	06 06 96	0,0	0,49	16,59	2,37	0,18	0,65	3,40	1,55	3,67
17	Vysne Furkotske pleso	1750	25 09 96	0,0	0,17	20,12	2,27	0,22	0,21	4,45	1,75	4,60
18	Strbske pleso	1350	06 06 96	0,0	1,55	23,64	3,34	0,98	1,00	4,85	0,08	10,98
19	Strbske pleso	1350	06 06 96	4,5	1,96	21,05	3,07	0,95	0,85	4,45	-0,05	9,76
20	Strbske pleso	1350	06 06 96	9,0	1,71	22,19	2,99	1,06	0,90	4,95	0,05	10,37
21	Strbske pleso	1350	06 06 96	13,5	1,39	22,86	3,40	1,01	0,90	5,40	0,05	9,76
22	Strbske pleso (bottom)	1350	06 09 96	17,9	1,80	25,49	3,34	1,07	1,05	4,95	-0,05	12,20
23	Strbske pleso	1350	25 09 96	0,0	1,85	25,18	3,27	0,94	0,78	7,25	0,19	9,90
24	Strbske pleso	1350	25 09 96	5,0	2,02	26,23	3,34	0,93	0,70	6,40	0,15	11,60
25	Strbske pleso	1350	25 09 96	10,0	2,77	25,14	3,27	0,90	0,70	4,30	0,06	12,80
26	Strbske pleso	1350	25 09 96	18,0	3,19	27,94	3,65	1,00	0,82	3,95	0,13	15,25
27	Lomnický štít	2632	07 03 96				0,08	0,2	0,036	0,65	3,75	0,55

Table V Results of waters chemical analyses - metals

No.	Locality	Altitude [m.a.s.l.]	Date	Depth [m]	Sr [mg/l]	Fe [mg/l]	Cu [mg/l]	Zn [mg/l]	Cd [mg/l]	Pb [mg/l]	Hg [mg/l]	Al [mg/l]
1	Vysne Wahlenbergovo pleso	2145	05 06 96	0,0	0,016	0,019	0,00055	0,0098	0,00012	0,00070	0,00006	0,1540
2	Vysne Wahlenbergovo pleso	2145	05 06 96	1 0	0,035	0,008	0,00083	0,0160	0,00010	0,00053	0,00003	0,0935
3	Vysne Wahlenbergovo pleso	2145	05 06 96	2 0	0,032	0,018	0,00160	0,0153	0,00003	0,00088	0,00009	0,0832
4	Vysne Wahlenbergovo pleso	2145	26 09 96	0,0	0,078	0,077	0,00074	0,0120	0,000072	0,00031	0,00026	0,0928
5	Vysne Wahlenbergovo pleso	2145	26 09 96	4,0	0,180	-0,001	0,00099	0,0090	0,000059	0,00047	0,00026	0,0246
6	Vysne Wahlenbergovo pleso	2145	26 09 96	10,5	0,070	0,009	0,00102	0,0070	0,000087	0,00041	0,00026	0,0333
7	Vysne Wahlenbergovo pleso	2145	26 09 96	15,0	0,078	-0,001	0,00040	0,0030	0,000059	0,00020	0,00026	0,0168
8	stream under VW pleso (VWs)	2075	05 06 96	0,0	0,037	0,008	0,00065	0,0097	0,00008	0,00070	0,00003	0,0938
9	stream under VW pleso (VWs)	2075	26 09 96	0,0	0,055	-0,001	0,00038	0,0040	0,000124	0,00033	0,00026	0,0343
10	Nizne Wahlenbergovo pleso	2053	05 06 96	0,0	0,045	0,010	0,00607	0,0225	0,00016	0,00153	0,00003	0,0887
11	Nizne Wahlenbergovo pleso	2053	05 06 96	3,0	0,041	0,015	0,00080	0,0101	0,00007	0,00055	0,00003	0,0727
12	Nizne Wahlenbergovo pleso	2053	05 06 96	6,3	0,034	0,170	0,00065	0,0337	0,00010	0,00056	0,00006	0,0530
13	Nizne Wahlenbergovo pleso	2053	26 09 96	0,0	0,073	0,005	0,00045	0,0070	0,000056	0,00007	0,00053	0,0696
14	stream Furkota (NWs)	1800	06 06 96	0,0	0,051	0,006	0,00032	0,0193	0,00003	0,00008	0,00006	0,0610
15	stream Furkota (NWs)	1800	25 09 96	0,0	0,052	0,002	0,00023	0,0020	0,000056	0,00021	0,00080	0,0227
16	Vysne Furkotske pleso	1750	06 06 96	0,0	0,053	0,006	0,00024	0,0090	0,00002	0,00018	0,00006	0,0313
17	Vysne Furkotske pleso	1750	25 09 96	0,0	0,053	-0,001	0,00040	0,0040	0,00001	0,00087	0,00053	0,0652
18	Strbske pleso	1350	06 06 96	0,0	0,130	0,024	0,00166	0,0117	0,00004	0,00030	0,00003	0,0111
19	Strbske pleso	1350	06 06 96	4,5	0,039	0,017	0,00282	0,0145	0,00002	0,00012	0,00006	0,0113
19	Strbske pleso	1350	06 06 96	9,0	0,039	0,023	0,00444	0,0174	0,00005	0,00041	0,00003	0,0155
21	Strbske pleso	1350	06 06 96	13,5	0,046	0,031	0,00390	0,0190	0,00001	0,00022	-0,00003	0,0120
22	Strbske pleso (bottom)	1350	06 09 96	17,9	0,089	0,070	0,00076	0,0273	0,00003	0,00011	0,00003	0,0171
24	Strbske pleso	1350	25 09 96	0,0	0,077	0,008	0,00064	0,0090	0,000020	0,00022	0,00053	0,0228
25	Strbske pleso	1350	25 09 96	5,0	0,078	0,044	0,00096	0,0050	0,000033	0,00024	0,00053	0,0765
26	Strbske pleso	1350	25 09 96	10,0	0,070	0,029	0,00115	0,0100	0,000020	0,00036	0,00053	0,0657
27	Strbske pleso	1350	25 09 96	18,0	0,060	0,260	0,00074	0,0140	0,000137	0,00077	0,00053	0,0544
28	Lomnický štít	2632	07 03 96		0,046	0,036	0,0001	0,0466	0,0003	0,0073	0,00056	0,066

built by granitoid rocks and their Quaternary derivatives Homogeneity of VW waters is visible from data as well It is important to notice that VW belongs to lakes with very long lasting reverse layering, inexpresiveness spring homothermy, very short normal

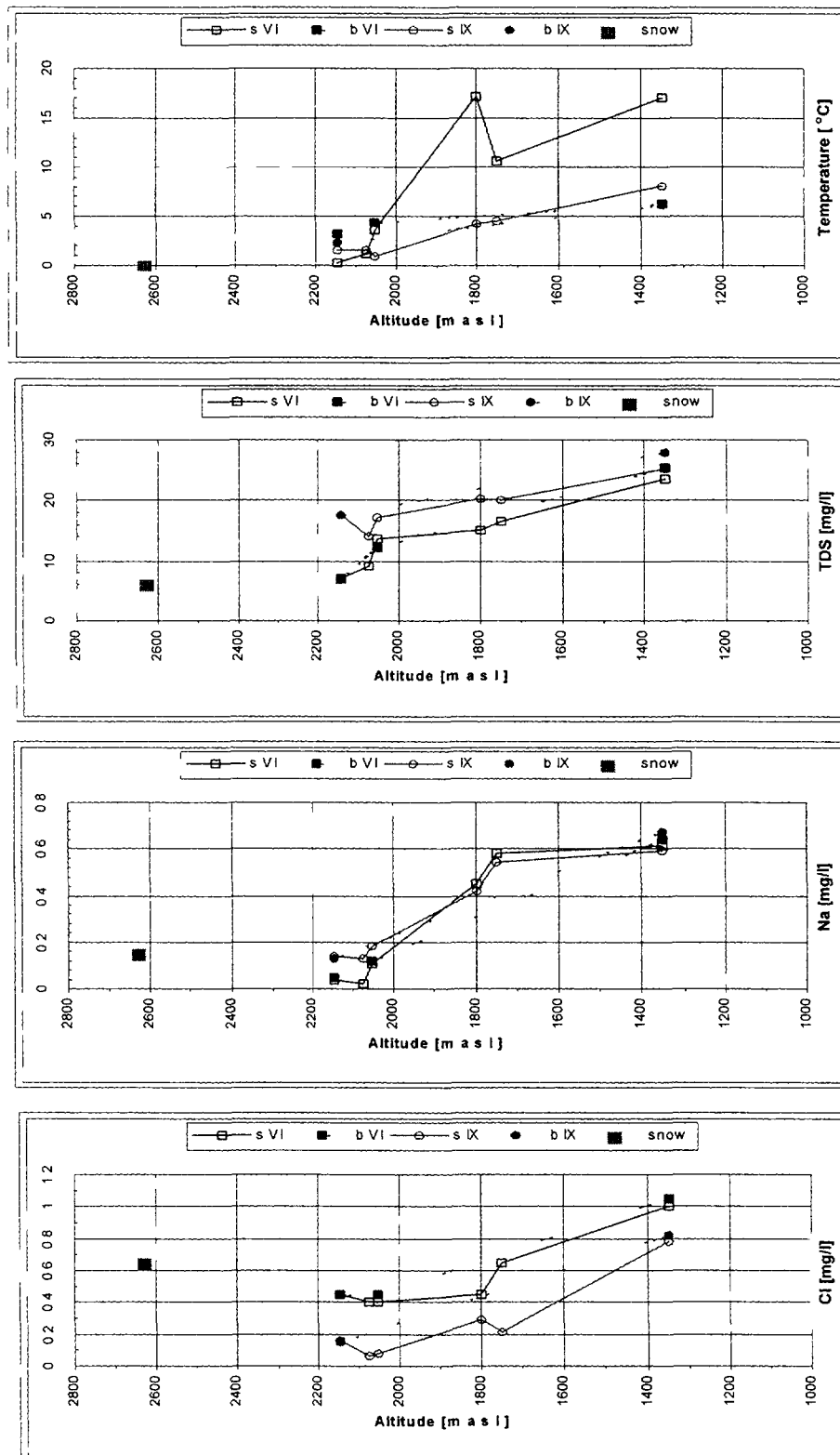


Fig 3 Selected parameters in altitudinal profile

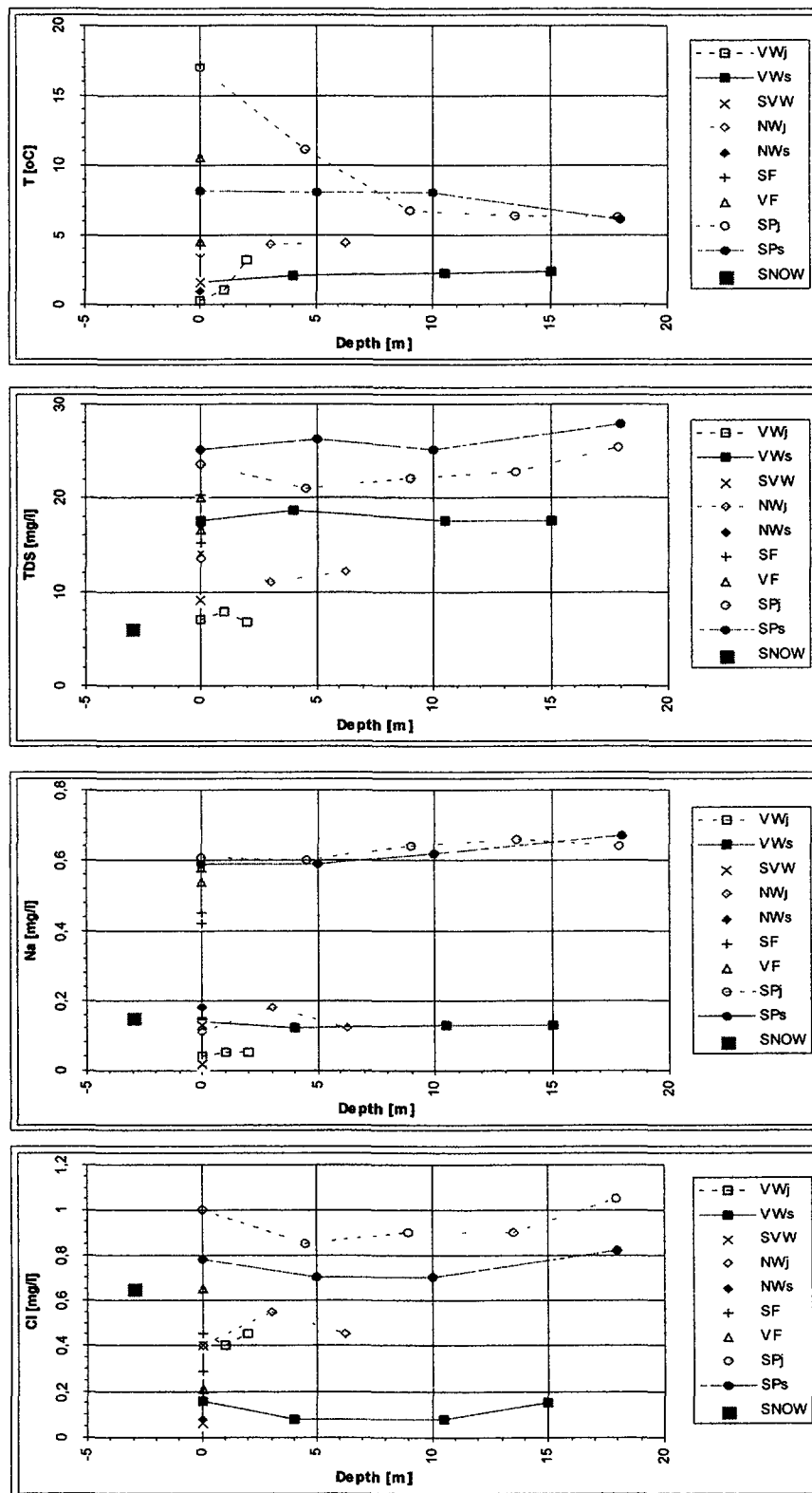


Fig. 4: Selected parameters in depth profiles for individual lakes

layering period and important fall homothermy. Period of ice cover lasts in mean 270 days per year. This is the reason for good water homogeneity in vertical profile of VW lake. Differences in chlorides content (typical conservative tracer, exclusively originating

in precipitation) in June and September are very probably due to variability chemical composition of precipitation (Fig. 4). Similar is behaviour of the other studied constituents (see Tabs. IV and V).

The hydrogeochemical characterisation of natural waters of Furkotska dolina valley can be documented on the profile where input is represented by chemical composition of snow pack (Lomnický štít altitude 2632 m a.s.l., average values from 20 years observations) and water chemistry is watched gradually with lowered altitude (Fig. 3). The TDS increase with the lowering altitude is in correspondence with the hydrologic and hydrogeologic natural water conduit. Values of pH in profile are rising up due to lowering of CO₂ content (stripping effect) in surface streams. Values of other compounds (Cl, SO₄, Mn) respond to their source - initial precipitation waters and water-rock interaction with influence of the biochemical processes.

The acidification is evaluated by empirical line dividing not acidified lakes (SP) from acidified lakes VW and VF. Calculated alkalinity values before beginning of acidification are shown in Tab II. In this table are used results from 1995 and November 1996 [7].

Acidification is due to inactive geological background (granites), high contribution of SO_x and NO_x from atmospheric deposition and low buffering ability of soil, which is practically not developed in the high altitudes. It is noticed that the acidification of lakes is lowered and state is slightly improving in comparison to the 1980 state and is coming back to the level before the acidification. This could be in response to the crisis of industry in Eastern Europe (and maybe even more environmental legislative measures) after 1989 changes, which led to drastic reduction of exhalates.

Based on relation of $\delta^{18}\text{O}$ and δD of studied waters and MWL said (Fig. 5) could be that all waters are meteoric in origin. For comparison snow pack values from localities Lomnický štít, Skalnaté pleso and Tatranská Lomnica [6] are shown. Water samples from Furkotska dolina valley follow MWL with natural trend of increasing content of heavy isotopes with lowering altitude.

In depth profiles of single lakes (Tab. III) isotope composition does not change - due to the natural conditions during sampling campaigns (spring and fall homothermy?). In the Furkotska dolina valley lakes (VW, NW, VF) are differences in isotope ratio of water at least between upper water layers. Similar is the isotope ratio in snow pack, differences could be understood as because there were whole year snow pack samples taken. Samples from Strbské pleso lake have specific position. They are enriched to the

heavy isotopes; we know only a few so “heavy” natural waters from Slovak territory – some mineral waters, some summer rains and some snow melt waters. Practically all samples fit an evaporation line – water in the sampled part of the lake is very homogeneous in the stable isotope composition. Evaporation could be explained by much longer residence time of water or by fact that the lake recharge is only from the last phases of snowmelt. Quite big differences between temperatures are excluding idea about homothermic state. It is necessary to keep in mind that Strbske pleso lake has no apparent surface inflow and outflow. Lake is fed and emptied due to hidden subsurface flows. It is true that only one of two known depressions (deep about 20 m and separated by 14 m shallow ridge) was sampled. In this way the Strbske pleso lake (SP) is not a typical terminal lake - seasonal oscillation of water level are very low. Sulphate sulphur isotope ratio of surface water from every lake was measured from September sampling period (Tab. III, Fig 6). Because of this, we could not observe seasonal differences. The $\delta^{34}\text{S}_{\text{SO}_4}$ are practically the same and they are identical with these of snow packs. From Fig. 6 it is

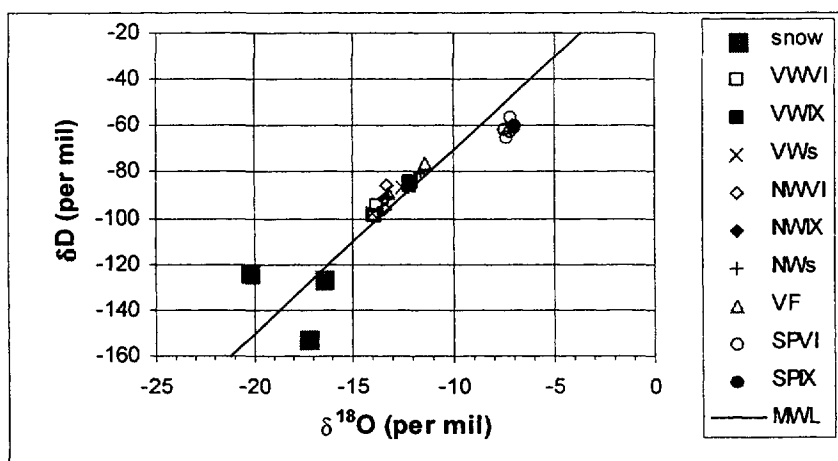


Fig. 5 Hydrogen and oxygen isotopes in snowpack and lakes

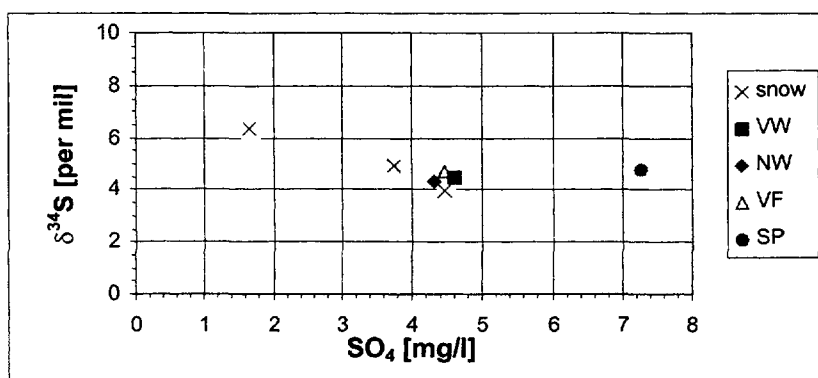


Fig. 6: Sulphur isotope composition in snowpack and lake water

clear that samples of water and snows are very near in the isotope composition of sulphur and sulphate content as well. Different $\delta^{34}\text{S}_{\text{SO}_4}$ in snow sample from Tatranska Lomnica could be explained by the influence of the local sources (maybe hotels in the neighbourhood). Higher concentration of sulphate in the Strbske pleso (SP) water is in good coincidence with idea of dominant evaporation influence on this lake water.

5. CONCLUSIONS

In the framework of International Atomic Energy Agency No. 8675/RB project "Stable isotopes in lakes of High Tatra mountains, Western Carpathians, Slovakia" were sampled water of selected lakes in this region. Under this project were collected data of the oxygen, hydrogen and sulphate sulphur stable isotopes from the water of lakes Furkotska dolina valley (Vysne Wahlebergovo pleso, Nizne Wahlenbergovo pleso and Vysne Furkotske pleso) and stream between them and "dead ice lake" Strbske pleso in the Vysoke Tatry Mts., Slovakia. This data set represents the first set of this kind of information on the territory of Slovakia. Moreover a complete set of chemical composition of waters was taken and compared to preceding results and contemporary state of acidification was evaluated.

Values of studied chemical compounds respond to their source - initial precipitation waters and bedrock character with influence of biochemical processes. Acidification is due to inactive geological background (granites), high contribution of SO_x and NO_x from atmospheric deposition and low buffering ability of soil. Acidification of lakes is lowered from 1980 and is approaching to level before acidification, probably as consequence of industry crisis in Eastern Europe after 1989.

Water samples from the Furkotska dolina valley water system follow the MWL with natural trend of increasing content of heavy isotopes with lowering altitude. In depth profiles of single lakes isotope composition does not change - due to natural conditions during sampling campaigns (probably lakes were reached in the state of the spring and fall homothermy), all waters are meteoric in origin. The water of the Strbske pleso lake is enriched to heavy isotopes, all samples fit an evaporation line. This could be explained by longer residence time of water or by recharging mainly from last phases of snowmelt, or by combination of both factors. Sulphate sulphur isotope ratio from lakes is the same and they is identical with this of the snow packs.

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Abstract

The ^3H - ^3He age of a water mass is a measure of the time that has passed since the water mass was last in contact with the atmosphere. Between 1992 and 1995 a detailed study of ^3H - ^3He ages was conducted in Lake Baikal, the deepest and largest lake by volume on Earth, to investigate deep water renewal in its three major basins. Maximum ^3H - ^3He ages found were 14–17 years in the Southern Basin, 16–18 years in the Central Basin, and 10–11 years in the Northern Basin. Rates of renewal of deep water with surface water, deduced from volume-weighted mean ^3H - ^3He ages below 250 m depth, are about 10% yr^{-1} in the Southern and Central Basins and 15% yr^{-1} in the Northern Basin. In the Southern Basin the mean ^3H - ^3He age below 250 m depth increased steadily from 9.6 years in 1992 to 11 years in 1995, indicating a slight diminution in deep water renewal during this time. Correlating oxygen and dissolved helium-4 concentrations with ^3H - ^3He age allowed us to determine the mean hypolimnetic oxygen depletion rate in the water column ($4.5 \mu\text{mol L}^{-1} \text{yr}^{-1}$), as well as mean helium fluxes from the lake bottom ($2.8 \cdot 10^{11} \text{ atoms m}^{-2} \text{s}^{-1}$ in the Northern Basin, and $1.3 \cdot 10^{11} \text{ atoms m}^{-2} \text{s}^{-1}$ in the Central and Southern Basins).

1. INTRODUCTION

Lake Baikal (Fig. 1), located in east Siberia, is the deepest (1632 m) and largest (23015 km^3) lake by volume on Earth. It holds about one fifth of the global fresh surface water. The lake is divided by underwater sills into three main basins: the Southern Basin (max. depth: 1432 m), the Central Basin (1632 m), and the Northern Basin (897 m). The three major rivers entering the lake, the Selenga, the Upper Angara and the Barguzin, account for more than 70% of the total annual river inflow. The only outflow is the Lower Angara at the south-western end of the lake.

Despite the lake's great depth, dissolved oxygen concentrations exceed 80% relative saturation throughout the entire water column. CFC-12 ages determined from the vertical distribution of chlorofluorocarbons (CFCs) are less than 16 yr in the entire lake [1]. Both observations indicate that deep-water renewal is surprisingly rapid and raise the question of how it occurs in such a deep lake.

A thorough theoretical analysis of stability and neutrally buoyant transport in deep, cold lakes was developed in Ref. [2]. Based on these concepts, a general analysis of processes of deep-water renewal in Lake Baikal was presented in Ref. [3]. Helium and tritium concentrations measured in Lake Baikal from 1992 to 1995 were discussed in Ref. [4]. A six box model of Lake Baikal which bases on these data and on CFC-11 and CFC-12 concentrations was presented by Ref. [5].

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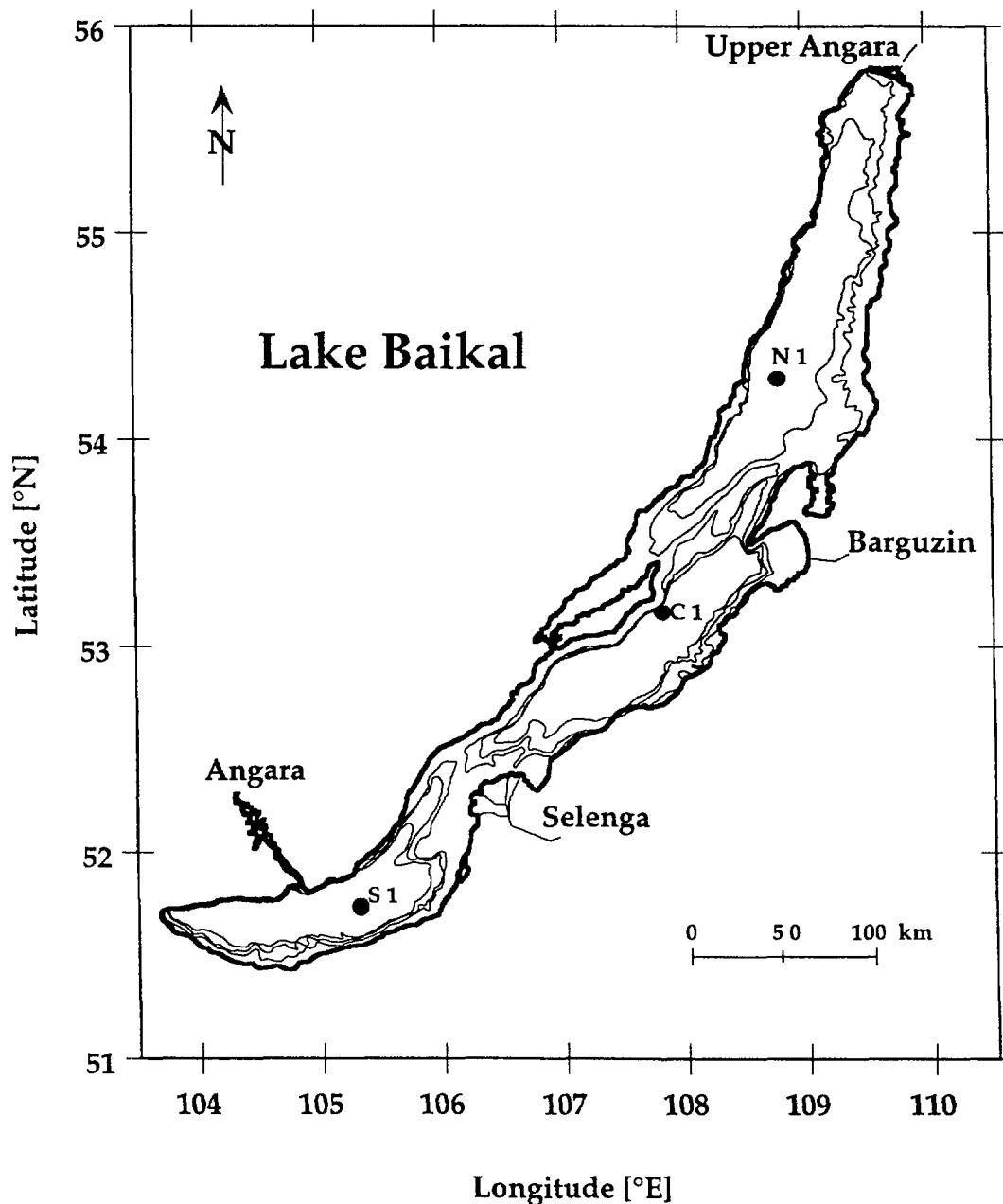


Figure 1. Map of lake Baikal with isobaths at 400, 700 and 1000 m depth. The lake is divided into three basins: S1, C1 and N1 mark the deepest points (●) of the southern, central and northern basins, respectively.

2. FIELD DATA AND DISCUSSION

2.1. Potential temperature, ionic salinity and oxygen concentration

Profiles of potential temperature q , ionic salinity S_c , and oxygen concentration $[O_2]$ measured at the deepest station of each basin (marked by ● in Fig. 1) in May 1995 are shown in Fig. 2. All temperature profiles (Fig. 2a) show inverse stratification with respect to temperature in the top 200 m of the water column. At about 200 m depth, the temperature reaches its maximum, the so-called mesothermal temperature maximum (MTM), where it is equal to the temperature of maximum density (thin dotted line in Fig. 2a). Below the MTM, temperature decreases steadily. In the deepest 20 to 50 m of the Central Basin temperature decreases by $0.05 - 0.1^\circ\text{C}$. Similar bottom layers were also found in the other basins [3].

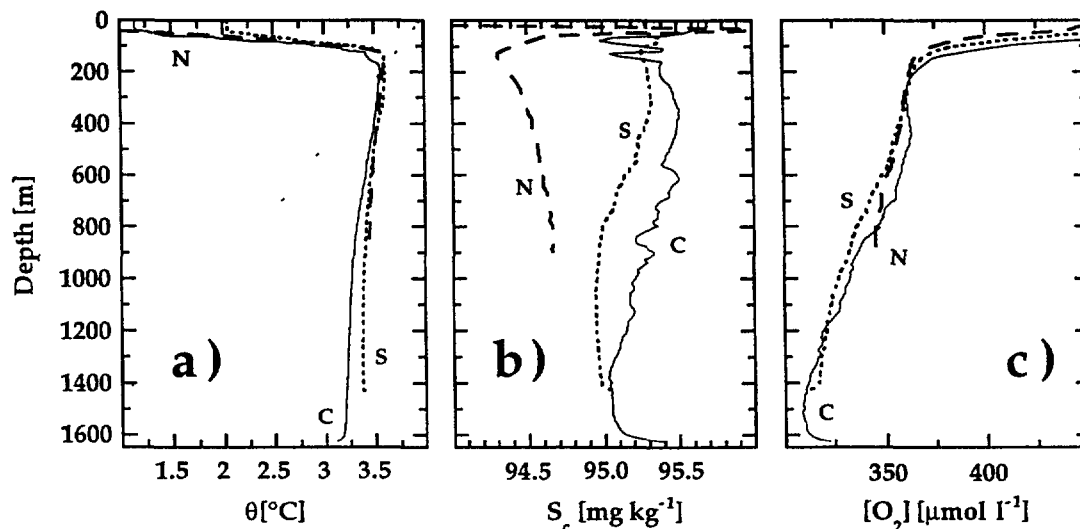


Figure 2. (a) Potential temperature q , (b) ionic salinity s_c , and (c) dissolved oxygen concentration $[O_2]$ at stations S1 (dotted line), C1 (solid line), and N1 (dashed line) measured from May 18–24, 1995. The straight line in (a) is the temperature of maximum density, t_{md} .

Ionic salinity (S_c) is low and varies by less than $1 \text{ mg} \cdot \text{kg}^{-1}$ within the water column and between the basins (Fig. 2b). The vertical salinity distribution in the Southern and Central Basins is similar. The destabilising effect of the slight decrease in S_c with depth in the interior of these basins is small and compensated for by the gradient of q (Fig. 2a). In the Northern Basin, salinity is significantly lower than in the other basins. Here, it increases steadily with depth and thus contributes to the vertical stability of the water column.

Oxygen concentrations are high throughout the entire water column (Fig. 2c). Even at the bottom of the lake, the relative oxygen saturation generally exceeds 80 %.

2.2. ^3H - ^3He ages

The ^3H - ^3He age (t) was calculated from the concentrations of tritium (^3H) and tritiogenic helium ($^3\text{He}_{tri}$), i.e. the helium produced by the decay of tritium, using the following equation [6]:

$$\tau = \frac{1}{\lambda} \ln \left(1 + \frac{^3\text{He}_{tri}}{^3\text{H}} \right), \quad (1)$$

where $\lambda = 0.05576 \text{ yr}^{-1}$ is the decay constant of tritium [7]. The ^3H - ^3He age of a water mass is a measure of the time that has passed since the water mass was last in contact with the atmosphere. Since it is a non-linear function of ^3H and $^3\text{He}_{tri}$, mixing may result in a discrepancy between it and the true age [4].

^3H - ^3He ages in the three basins from 1992 to 1995 are shown in Fig. 3. The similarity of the curves in all three basins is remarkable: the ^3H - ^3He ages increase steadily with depth from values close to zero at the lake surface to their maxima at about 100–300 m above the lake bottom. The greatest ^3H - ^3He ages found were 13–17 yr in the Southern Basin (Fig. 3a), 16–18 yr in the Central Basin (Fig. 3b) and 10–11 yr in the Northern Basin (Fig. 3c). In the bottom waters of all basins, the increase in ^3H - ^3He age with depth is halted (Southern and Central Basins) or even reversed (Northern Basin, sometimes in the Central Basin) implying that the bottom layer is renewed more efficiently than the water masses found directly above the bottom layer.

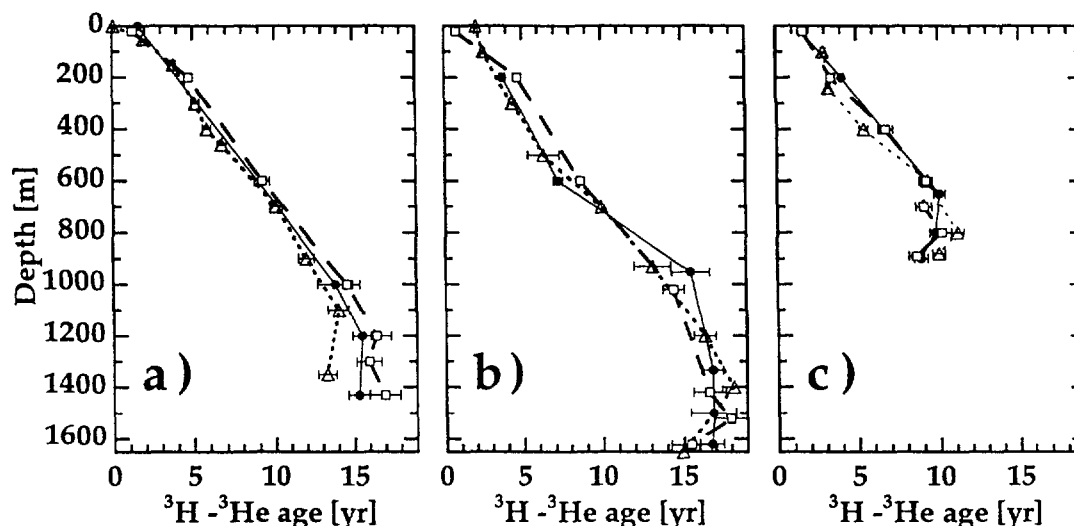


Figure 3. ^3H - ^3He ages calculated from eq. (1) at stations S1, C1, and N1 in 1992 (Δ), 1993 (\bullet), and 1995 (\square).

Between 1992 and 1995, the ^3H - ^3He age in the surface and intermediate layers of all basins remained approximately constant, i.e., the increase in ^3He concentration due to the radioactive decay of tritium was balanced out by the decrease due to the flux of excess ^3He to the atmosphere by vertical mixing and gas exchange. A different picture was found in the bottom layers (lowermost 200 m). In the Southern Basin, the ^3H - ^3He age increased steadily during the observation period, indicating that the renewal of the bottom layer was proceeding less efficiently than in previous years. In the Central and Northern Basins, renewal of the bottom layer varied from year to year, but on average the ^3H - ^3He age was practically constant.

2.3. Deep-water renewal rates

The volume-weighted mean ^3H - ^3He ages below 250 m depth (Table 1) provide reasonable estimates of the mean residence time of the waters in this layer. Deep-water renewal rates derived from these values are about 10 % yr^{-1} in the Southern and Central Basins, and about 15 % yr^{-1} in the Northern Basin. Corresponding mean vertical exchange velocities across the 250 m isobath are 71 - 81 m yr^{-1} in the Southern Basin, 73 - 77 m yr^{-1} in the Central Basin and about 58 - 61 m yr^{-1} in the Northern Basin. These values are in good agreement with the mean value of 75 m yr^{-1} reported by Ref. [1].

In the Southern Basin, the mean ^3H - ^3He age of the deep water increased steadily from 9.6 yr in 1992 to 11 yr in 1995, which caused the vertical exchange velocity to drop from 81 m yr^{-1} to 71 m yr^{-1} . This is consistent with the observation made above that the renewal of the deepest 200 m of the basin was slight during the observation period.

2.4. Oxygen consumption rate and ^4He flux from the lake bottom

The ^3H - ^3He age provides a natural time scale for the determination of oxygen consumption rates in aquatic systems. Fig. 4a shows the oxygen saturation anomaly calculated at the in situ temperature plotted against ^3H - ^3He age below 200 m in all three basins for the years 1993 and 1995. The average oxygen consumption rate *per unit volume*, given by the slope of the regression line, seems to be constant in space and time: $J_{\text{O}_2} = (4.5 \pm 0.3) \mu\text{mol l}^{-1} \text{yr}^{-1}$. Oxygen is consumed both in the water column and at the sediment surface. Thus, J_{O_2} combines both the volume

Table 1: Mean ^3H - ^3He age below 250 m depth and mean vertical velocity v_z of water across the 250 m isobath. \bar{h} is the mean depth of the basin below 250 m.

Basin	\bar{h} [m]	year	^3H - ^3He age [yr]	v_z [m yr^{-1}]
South	781	1992	9.64 ± 0.47	81.1
		1993	9.86 ± 0.82	79.2
		1995	11.01 ± 0.51	70.9
Central	807	1992	10.54 ± 0.38	76.5
		1993	11.10 ± 0.52	72.7
		1995	10.47 ± 0.55	77.0
North	438	1992	7.19 ± 0.85	61.0
		1993	7.62 ± 0.73	57.6
		1995	7.52 ± 0.80	58.3

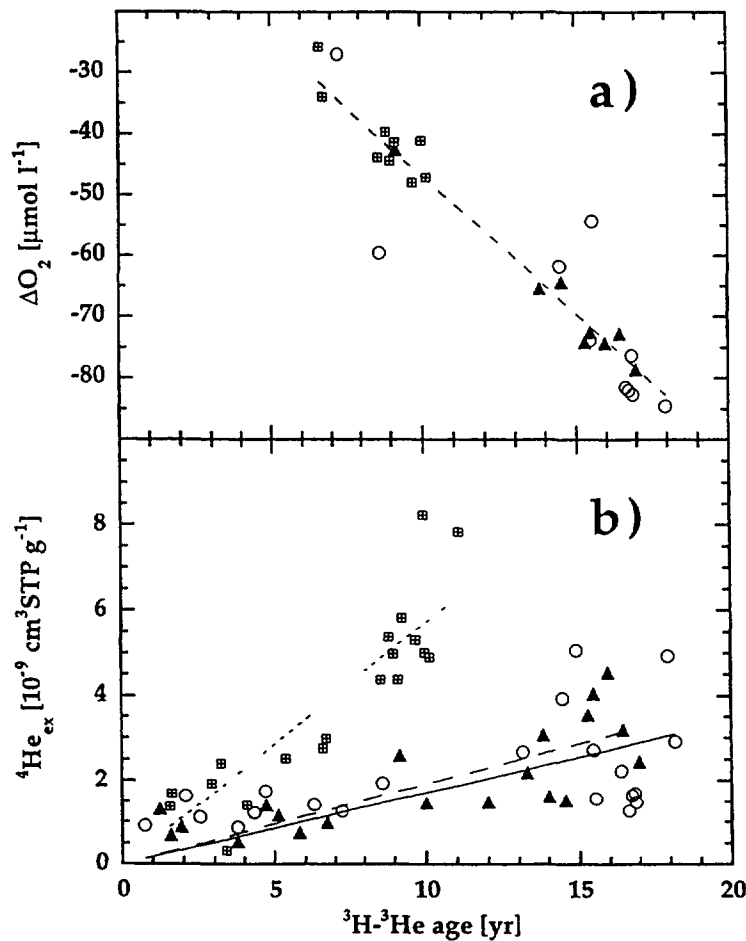


Figure 4. (a) Correlation between oxygen deficit and ^3H - ^3He age, and (b) between ^4He excess and ^3H - ^3He age in the southern (\blacktriangle), central (\circ) and northern (\boxplus) basins in 1993 and 1995. The regression lines in (b) have been forced through the origin.

($J_{O_2,V}$) and the areal ($J_{O_2,A}$) oxygen sinks [8]. A rough estimate of the volume oxygen sink, $J_{O_2,V} = (4.2 \pm 0.5) \mu\text{mol l}^{-1} \text{yr}^{-1}$, is yielded by neglecting the data from the 200 m thick bottom layer of each basin where the ratio of sediment area to water volume is particularly large and the areal sink therefore expected to be dominant.

A similar approach can be adopted to determine the helium flux from the lake bottom. Excess ^4He plotted against the ^3H - ^3He age is shown in Fig. 4b. As a first approximation, the ^3H -

^3He age is assumed to be independent of the flux of terrigenous helium from the lake bottom, and thus the ^4He -flux *per unit volume* from the sediment (J_{He}) can be estimated as the slope of the regression curve. Multiplying by the mean basin depth \bar{h} yields the He flux *per unit area*, F_{He} . Helium fluxes in the Southern and Central Basins are similar ($F_{\text{He}} \approx 1.3 \cdot 10^{11} \text{ atoms m}^{-2} \text{ s}^{-1}$). In the tectonically most active Northern Basin, where the largest ^4He excess is observed [4], the flux is significantly larger ($F_{\text{He}} \approx 2.8 \cdot 10^{11} \text{ atoms m}^{-2} \text{ s}^{-1}$). The ^4He flux in Lake Baikal is about one order of magnitude larger than the average flux from the continental crust ($\approx 3 \cdot 10^{10} \text{ atoms m}^{-2} \text{ s}^{-1}$ [9]), but smaller than the fluxes related to the injection of mantle helium into lakes in active tectonic or volcanic regions (e.g. Refs. [10, 11]).

The helium isotope ratio of the terrigenous helium component injected from the lake bottom, determined from measurements of water from hydrothermal springs in the vicinity of the lake, was reported to be $\sim 2.2 \cdot 10^{-7}$ [4].

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DYNAMICS OF LAKE KÖYCEĞİZ, SW TURKEY: AN ENVIRONMENTAL ISOTOPIC AND HYDROCHEMICAL STUDY

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Abstract

Lake Köyceğiz, located in southwestern Turkey, is a meromictic lake with a surface area of 55 km². Impermeable ophiolitic rocks, and groundwater bearing alluvium and karstified limestone are the major geologic units around the lake. Köyceğiz lake, fed mainly by rainfall and stream flow, discharges into the Mediterranean Sea via a 14 km long natural channel. The average water level is estimated to be slightly above the sea level and the estimated lake volume is 826 million m³. Lake level fluctuations are well correlated with rainfall intensity. Lake Köyceğiz comprises two major basins; Sultaniye basin (-32m) at the south and Köyceğiz Basin (-24m) at the north which are connected by a 12m deep strait. Environmental isotopic and chemical data reveals that the Lake Köyceğiz has complicated mixing dynamics which are controlled mainly by density-driven flow of waters from different origins. The lake is fed mainly by rainfall and stream flow as low density waters and by high density thermal groundwater inflow at the southern coast. Complete annual mixing can not be achieved, because of the density difference between mixolimnion and recharge. Continuous high-density thermal water input into the Sultaniye basin is the major factor controlling the lake dynamics. The high density thermal groundwater discharging into the lake sinks to the bottom of Sultaniye basin and overflows toward the north along the bottom surface. During its travel, dense bottom water is mixed with mixolimnion water and as the distance from the thermal water inflow increases, the density tends to decrease throughout the lake. Calculations based on long-term average electrical conductivity data reveal that about 60% of mixolimnion in both basins is replenished annually, whereas the annual mixing with mixolimnion for Sultaniye and Köyceğiz Basins is 20% and 30%, respectively. Turn-over times for mixolimnion and monimolimnions of Sultaniye and Köyceğiz Basins are estimated to be 2 years, 5 years and 3.5 years, respectively.

1. INTRODUCTION

Lake Köyceğiz, located in southwestern Turkey, is among the "Specially Protected" areas because of its natural beauty and ecological and archeological importance. The lake is connected to the Mediterranean Sea coast, Iztuzu, where endangered sea turtle species, *Caretta caretta*, nest and breed (Figure 1). Studies for the protection of this environment which is also among the promising touristic development sites, from anthropogenic activities have been initiated in the 1980's Biological inventory of the area has been prepared, and some preliminary information regarding the hydrochemical structure has also been produced in these studies [1, 2].

However, since the proper design and management of the activities directed to develop the touristic potential of the region need more accurate and reliable information on the hydrologic system, a detailed study has been initiated by the International Research and Application Center

for Karst Water Resources (UKAM) of the Hacettepe University, Ankara, Turkey. International Atomic Energy Agency (IAEA) supported these activities under the scope of Coordinated Research Program entitled "Isotope Techniques in Lake Dynamics Investigations". National institutes such as, Electrical Power Resources Research Authority (EİE) which is in

charge with the operation of national hydrometric observation network, and the Technical and Scientific Research Council of Turkey (TUBİTAK) has also participated to/contributed in the project.

Because of the complicated geologic, hydrologic and hydrogeologic nature of the area, wide variety of investigation techniques such as, hydrometric measurements, in-site hydrochemical measurements/analyses, spatial depth-specific physical and chemical observations, environmental isotopic evaluations etc. have been employed to produce most reliable data that characterize the hydrologic system [2].

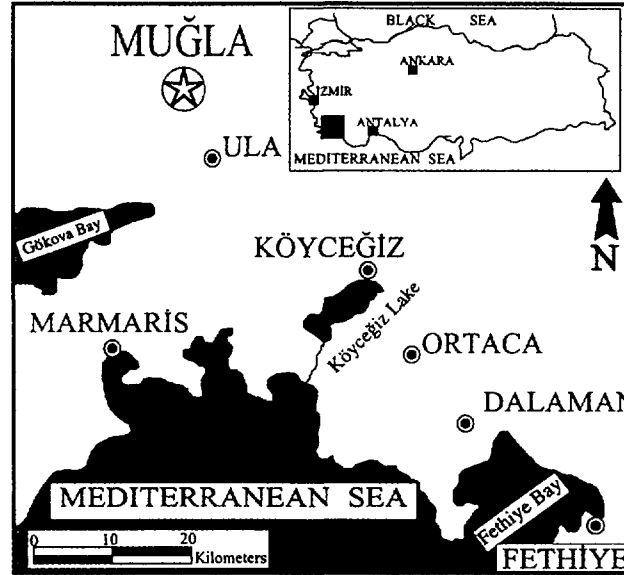


Figure 1: Location map of the Lake Köyceğiz.

2. MORPHOLOGIC CHARACTERISTICS OF LAKE KÖYCEĞİZ

Lake Köyceğiz has a shape of slightly distorted rectangle extending in NNE-SSW direction (Figure 2). Maximum length and width of the lake are 12km and 6.5km, respectively. The average surface area is 55 km². The lake is permanently stratified in terms of distinct chemical and isotopic composition and thus, it is classified as meromictic. Lake level does not fluctuate to a great extend and usually is at its equilibrium level which is ca. 2 m asl. During episodic winter rainfalls and streamflow fed by these events, the lake level rises temporarily about 1m above its normal, but the excess water is rapidly discharge into the Mediterranean Sea via a 14km long naturally formed channel which is a part of estuary located between the lake and the sea.

The area where Lake Köyceğiz is located is a tectonically active horst-graben region. The Asia Minor "or the Anatolian Plate" has been pushed northward by the Arabian plate toward "Russian Plate" located to the north. Since the "Russian Platform" forms a resistant barrier, the Anatolian Plate moves westerly against "European Plate" which is another relatively stable crustal component. The Anatolian and European plates meet along the Aegean Sea where, the weaker Anatolian Plate spreads in north-south direction to form horst and graben structures along the coastal zone. Horst-graben tectonics in the western Anatolia is characterized by ridges and plains extending perpendicular to the sea. Deep faults and hydrothermal activity associated with these faults are common in this area. Two of these graben structures form the Köyceğiz and, to the east, Dalaman Plains. The Lake Köyceğiz extend in the Köyceğiz plain between the mountains in the northeast and the Mediterranean Sea in the southwest.

Current geomorphologic features suggest that the formation of Lake Köyceğiz is a result of interplay of tectonic and fluvial processes. Whereas, the plain is being filled by alluvium brought from mountainous part via large rivers, such as, Namnamçay and Yuvarlakçay, horst-graben faulting causes the plain surface to subside continuously. Echo-sounding profiles indicate active fault lines along the lake bottom.

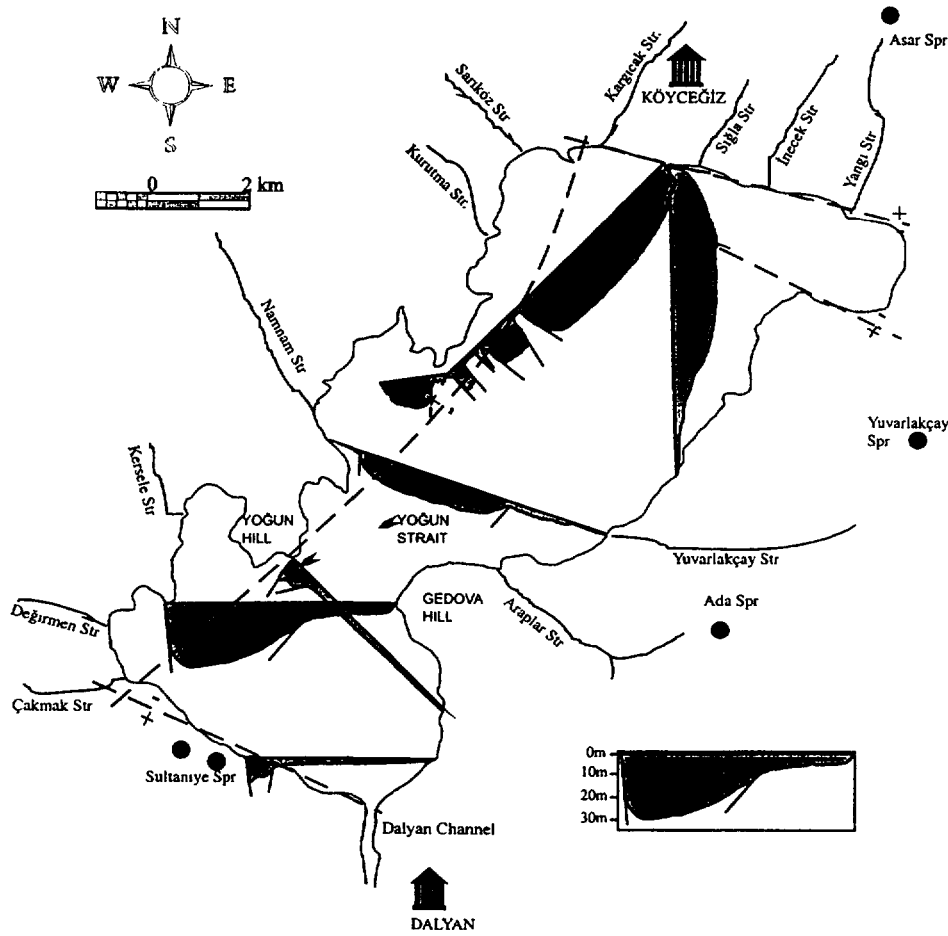


Figure 2: Bathymetric profiles and the site names mentioned in the text.

The lake comprises of two basins; first located at the northern part named as “Köyceğiz Basin” and, secondly located at south, named as “Sultaniye Basin”. These names have been attributed from the settlements situated nearby the respective basins. The maximum depths in the Köyceğiz and Sultaniye basins are 24m and 32m from the mean lake surface, respectively. The basins are connected by the Yoğun Strait that extends between Cape Yoğun and Gedova Hill where the distance between the facing coasts of lake reduces to 1,750m. The lake depth becomes shallow (max. 6 m) in most parts of the Yoğun Strait, but suddenly deepens at the western end (Cape Yoğun) where a normal fault extending in NNE-SSW direction passes through. Here, the lake bottom comprises the down-thrown block of the fault, and the maximum depth is 12m. Three years’ observation carried out in this study indicated that the depth of Cape Yoğun has a drastic control over the permanent stratification of lake water, especially in the Sultaniye basin. The boundary between mixolimnion (top water zone) and monimolimnion (bottom water zone) passes along 12m depth in both basins of the lake during most of the year. However, the thickness of mixolimnion in Köyceğiz Basin deepens up to 16m in high water season, whereas it is absolutely constant at 12m in the Sultaniye Basin.

3. DATA COLLECTION AND QUALITY

A vast amount of hydrologic, chemical and environmental isotopic data has been collected in this investigation. Since the volume of data is well beyond the limits of this paper, only a brief summary is given here. Readers willing to access all the data should refer to progress reports prepared under IAEA Research Contract RB/7997 [2, 3]. However, in order to provide an insight for the quality of data which have been evaluated in this paper, detailed explanations regarding the data collection, field measurements and analyses are given in the following paragraphs.

Stream flow-rate measurements based on the velocity-area method were carried out once a month in all streams discharging into the lake. In the wet season, when episodic floods occur, the sampling frequency was increased up to four measurements per site per month. The quality of measurement is $\pm 10\%$ of the measured value. Meteorological observation data have been collected from the records of nearby stations operated by the State Meteorological Affairs (DMI). Locations of hydrometric measurement and meteorological observation stations are shown in Figure 3.

Water samples for in-situ measurements and laboratory analyses of hydrochemical and isotopic parameters have been collected from thermal and cool karstic springs, streams, sea, rainfall and the lake. Seasonal (four times a year) samples have been collected from thermal and cool karstic springs located around the lake. Sampling procedures suggested by APHA et al. [4] such as filtration through 0.45 micron filter, acidification of cation samples etc. have been followed in these studies. Depth-specific water samples from the lake have been collected in two ways. At

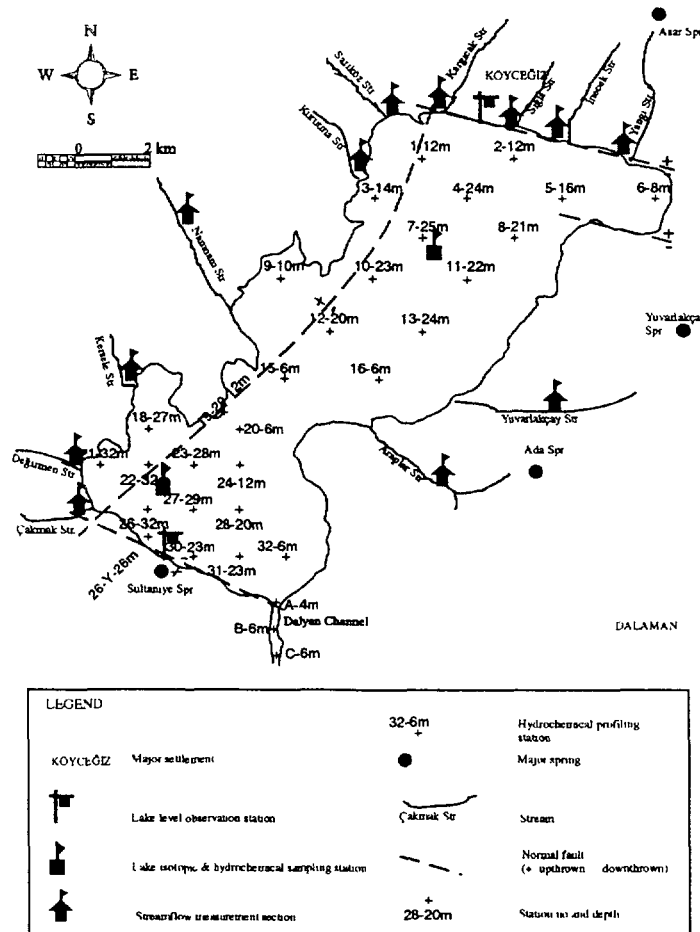


Figure 3: Map of hydrometric, meteorological and lake hydrochemical / isotopic sampling and profiling stations in and around Lake Köyceğiz.

the initial stage of research, a "Ruttrier type" sampler made of PVC (polyvinylchloride) has been used. In order to assure a better sampling quality, later on, a peristaltic pump with tygon tubing has been used. The inlet end of tubing has been fixed to Hydrolab Data Sonde 3 TM multiparameter water quality probe which is equipped with a depth gauge to determine the sampling depth within +/- 0.5m. Because of the permanent stratification in lake water, utmost care has been spent to collect water samples exactly from the pre-determined depths. Usually but not always, sampling works have been carried out when the lake water stands still in order to increase the sampling quality. Maximum error of sampling depth is estimated to have been +/- 1 meter. Lake water sampling locations have been pre-determined on a 1/25000 scale topographic map by considering the echo-sounding profiles obtained in a previous study by Bayari et al. [2]. A Global Positioning System (GPS) navigator has been used to locate the sampling sites within +/- 100m.

Physical and chemical parameters such as temperature, pH, specific electrical conductivity, dissolved oxygen, redox potential and turbidity have been measured in-situ. At the initial stage, these parameters were measured in water samples brought to the boat. However, after the fifth (inclusive) field campaign, they are measured in-situ, that is at the desired depth by means of a water quality probe equipped with relevant sensors. YSI (Yellow Springs Instruments™) Model 33 Salinity-Conductivity-Temperature (SCT) meter, YSI Model 54 Dissolved Oxygen Meter, ORION™ Model 290A digital pH meter have been used for the in-boat measurements. All instruments have been precisely calibrated according to manufacturers' instructions which conforms to APHA et al. Standards [4]. Alkalinity which is subject to rapid change upon CO₂ equilibration with atmosphere, has been measured in the field by means of Gran's potentiometric method [5].

Major cations (Ca²⁺, Mg²⁺, Na⁺, K⁺) and anions (Cl⁻, SO₄²⁻, CO₃²⁻/HCO₃⁻) have been analyzed from samples collected at each campaign, whereas trace metals (Fe, Mn, Cr, Cu, Pb, Zn) and nutrients (PO₄³⁻, NO₃⁻, NO₂⁻ and NH₃⁺) have analyzed when needed. Major cations and trace metals have been analyzed on a Perkin Elmer™ Model 280 Atomic Absorption Spectrometer according to the methods suggested in APHA et al. [4]. Nutrients and SO₄²⁻ have been analyzed on a Bausch Lomb™ Model Spectronic 21 UV-visible spectrometer following the methods given in APHA et al. [4]. Chloride analyses have been performed by means of Argentometric method [4]. Water samples collected for environmental isotope content (²H, ³H and ¹⁸O) have been analyzed IAEA's Vienna laboratories.

4. HYDROLOGY, GEOLOGY AND HYDROGEOLOGY

4.1. Hydrology

Most of the surface water into the Lake Köyceğiz is supplied by two perennial streams, which are Namnam Çay and Yuvarlakçay discharging into Köyceğiz Basin. Namnam Çay having the largest drainage area that lays over impermeable ophiolitic rocks supply most of the surface inflow, whereas Yuvarlakçay stream, fed mainly by a karstic spring, has a relatively small contribution. Mean annual discharges of Namnam Çay and Yuvarlakçay streams are 11 m³/sec and 4.5 m³/sec, respectively. Other streams distributed around the lake discharge intermittently only in wet season. The only outflow of Lake Köyceğiz is via Dalyan Channel, which is a 14km natural channel that connects the lake to the Mediterranean Sea. Simultaneous flow rate measurements carried out in flowing streams and the lake outlet indicates that the outflow exceeds the total inflow by streams and the difference is supplied by direct rainfall input over the lake surface.

Most of the annual inflow to the lake is provided between November and May. Accordingly, most of the discharge from the lake occurs in this period when the lake level reaches its maximum (Figure 4a and b). The response of lake level to the rainfall and streamflow input is rather fast, and the lake level reduces to its normal within several days. During summer

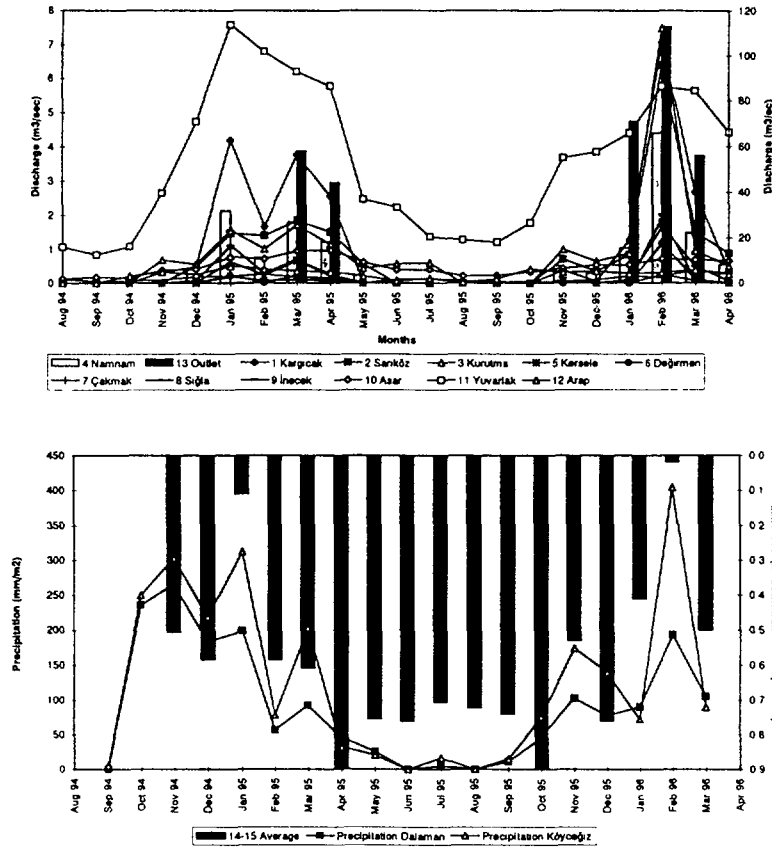


Figure 4: a. Variation of the rates of inflowing streams and the outlet (top). Discharge scale on the right is for Namnamçay and Outlet. b: Correlation of the outflow rate from the Lake Köyceğiz and the monthly precipitation of surrounding meteorological stations (bottom). Average lake level is given as "14-15 Average".

months, when the lake is fed only by small contributions from Namnam Çay and Yuvarlakçay streams, the lake level stands still slightly above the sea level. In Figure 4b, variation of mean lake level (average of northern and southern stations) is shown together with the monthly precipitation values of neighboring meteorological observation stations (i.e. Dalaman and Köyceğiz). Comparison of Figures 4a and 4b reveals that the lake level is more closely related to precipitation amount rather than flow rate of feeding streams.

4.2. Geology and Hydrogeology

The Köyceğiz Lake Basin is located at the western end of the Taurus mountain ridge which is a part of Alpine-Himalayan orogenic belt. As this tectonic belt has formed as a result of compression tectonics during the closure of Tethys ocean, the geologic structure comprises mainly of imbricated units. The geology of the Köyceğiz Lake basin has been studied by Graciansky [6]. Geologic structure comprises of three structurally different sequences of rock units, namely autochthonous carbonates and detritics, allochthonous Lycien Nappes, and ophiolite nappe (Figure 5). This tectono-stratigraphic sequence is overlain by the post-orogenic sediments of Plio-quaternary that expose in lowlands such as, riverbeds and Köyceğiz and Dalaman Plains.

The tectono-stratigraphic sequence starts with the metamorphic basement rocks belonging to Menderes metamorphic massive located to the northwest. Metamorphic rocks are covered by slightly metamorphosed carbonate rocks which in turn overlain by autochthonous Beydağları carbonates of Cenomanian-Early Miocene age. This formation is made up of thinly bedded

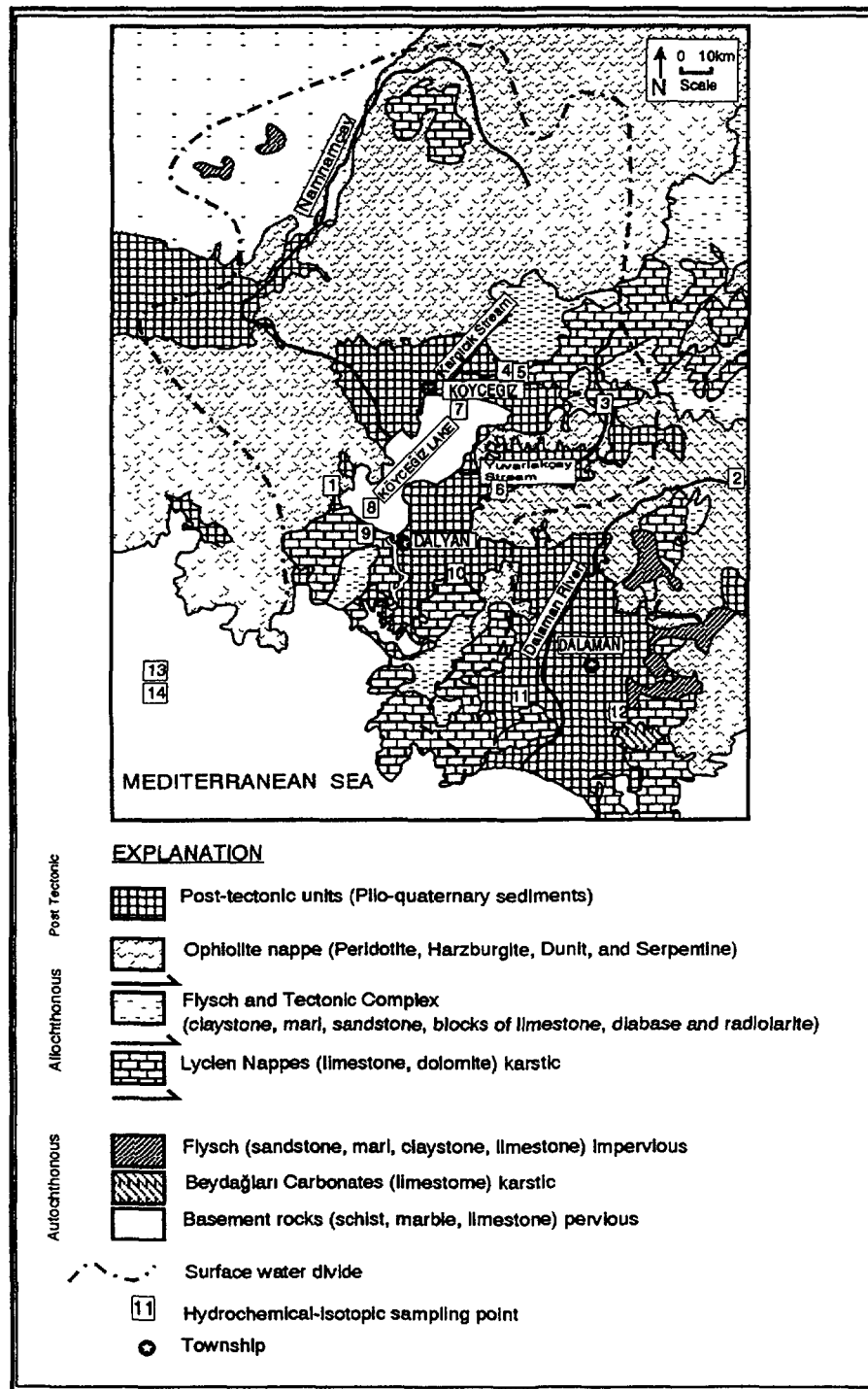


Figure 5: Geologic map of the Lake Köyceğiz Basin.

micritic limestone and thick bedded calcarenite. A Miocene flysch, comprising of alternating sequences of claystone, marl, sandstone and limestone, conformably overlies the Beydağları carbonates. Small outcrops of autochthonous sequence are observed in the northwestern part of the Köyceğiz Lake basin. The Lycien Nappes, which tectonically overlie the autochthonous sequence, are made up of limestone formations, each coming from a different paleogeographic origin and containing various stratigraphic units [6]. Another nappe unit, called the tectonic complex, lies tectonically in between the Lycien Nappes and the overlying ophiolite nappe. The tectonic complex is made up of limestone, radiolarite and diabase blocks. The ophiolite nappe,

containing peridotite, dunite, harzburgite and serpentine locally overlie the former geologic formations, where they form lowlands during the emplacement of the ophiolite nappe.

Two major tectonic phases that contributed the geologic evolution of the area is inferred [6]. At the initial stage, lateral tectonic movements were dominant and this phase were resulted in the settlement of allochthonous units over the basement rocks and autochthonous carbonates. After the Late Miocene period when the nappe settlement terminated, vertical (mostly normal) faulting leading to today's horst-graben morphology started to develop. As a result of the horst-graben tectonics, a number of normal faults trending NE-SW and forming horst-graben structures throughout the basin occurred. The present day thermal springs located in and around the basin are associated with recent faulting extending possibly down to the basement rocks. During the Pliocene, the lowlands (grabens), which form Köyceğiz and Dalaman Plains, were filled with terrigenous material comprised of marl, conglomerate and limestone. The Köyceğiz Lake started to form during the Plio-quadernary time as a result of the terrigenous material deposition between the lake and sea.

Allochthonous limestone formations (Lycien Nappes) and the Plio-quadernary alluvium are the major water-bearing units in the Köyceğiz Basin. Alluvium surrounding the lake is fed directly from rainfall and from the karstic limestone by means of seepage. The allochthonous

limestone exposing to the north of lake is also fed by underground drainage from the northern part of the Dalaman Basin located to the northeast [7, 8]. The ophiolite nappe, which crops out in many parts of the basin, is practically impermeable and, therefore is not significant from the hydrogeological point of view. The springs discharging from this unit are of local origin. The thermal and karstic springs discharge from allochthonous limestone where it is intersected by faults. The thermal springs are located in the southern part of the basin, whereas most of the karstic springs are located in the northeastern part. Hydrogeology of Köyceğiz Lake Basin has been studied in detail by Güner [9].

5. ENVIRONMENTAL ISOTOPIC EVALUATIONS

5.1. Data

Environmental isotopes (^3H , ^2H and ^{18}O) have been utilized in this study to identify the inter-relation among waters of different origin and to understand the interaction between monimolimnion and mixolimnion waters. Apart from the data produced from the samples collected in this study, those given by previous studies [2, 8] have also been used. All environmental isotope samples have been analyzed by the IAEA under various research projects.

5.2. End-Members and Lake Water

Variation of oxygen-18 and deuterium composition of all water samples imply that there exist four isotopically distinct water types in the study area (Figure 6). Starting from the one most isotopically depleted, these are 1: Sea water, 2: Thermal waters, 3: Lake waters (3a: monimolimnion, 3b: mixolimnion), 4: Local precipitation and fresh groundwater fed by this precipitation. Sea water (group 1) and fresh waters (group 4) represent the isotopic end-members in the area. Samples from group 4 scatter around a Local Meteoric Water Line (LMWL) with a deuterium excess value of +16 which is apparently higher than that of Global Meteoric Water Line (GMWL). Same deuterium excess value has also been reported by Yurtsever [10] for the precipitation observed in Antalya IAEA-WMO network station which is located 250 km to the east of study area.

Water samples other than fresh waters and precipitation deviate from the LMWL indicating a mixing between fresh waters (group 4) and sea water (group 1). Thermal waters (Kubbeli Hamam: Dommed Bath and Çamur Banyosu: Mud bath) are more closely located to

sea water samples. Position of thermal water samples on the $^{18}\text{O}/\text{D}$ graph implies that the thermal waters should have formed as a result of mixing of fresh water (group 4) and sea water (group 1) with dominant sea water component. This argument is supported by the chemical composition of water samples. Thermal waters have electrical conductivity values (35000 microS/cm) in between those of fresh water (max. 1000 microS/cm) and sea water (55000 microS/cm). Although, some of the ionic composition of thermal water should have been gained from the aquifer rock by dissolution, it is apparent that there is also substantial sea water contribution to the evolution of thermal waters. Considering the geologic structure in the area, it is concluded that the deep circulating fresh groundwater comes in contact with sea water (either connate or recent) and rises to the surface through the deep fault planes to form thermal springs in the area. Two of the thermal water samples (Kubbeli Hamam: Dommed Bath and Çamur Banyosu: Mud bath) deviate from the "mixing line" connecting fresh waters, lake waters,

thermal waters and sea water. Even if, these deviations may be explained by measurement errors, it is also possible that they may have undergone oxygen isotope shift because of exchange between thermal aquifer rock and water. However, degree of isotope shift observed in these samples is also much greater than those observed in waters in major geothermal fields of Turkey where reservoir and fluid temperatures as much as 130 °C and 250 °C have been observed, respectively.

Lake water samples which deviate from LMWL and cluster around the mixing line that connects these samples to thermal waters comprise of two groups each representing waters from mixolimnion (Group 3a) and monimolimnion (Group 3b). Monimolimnion (bottom) waters are more depleted isotopically and therefore, located more closely to thermal waters. The deviation of mixolimnion waters implies that they have subject to evaporation as expected from such an open water body. However, their shift from the original water located on the LMWL is also follows the mixing line between fresh water and thermal water. In other words, the mixing and evaporation effects upon isotopic composition of lake waters can not simply be separated on the $^{18}\text{O}/\text{D}$ graph.

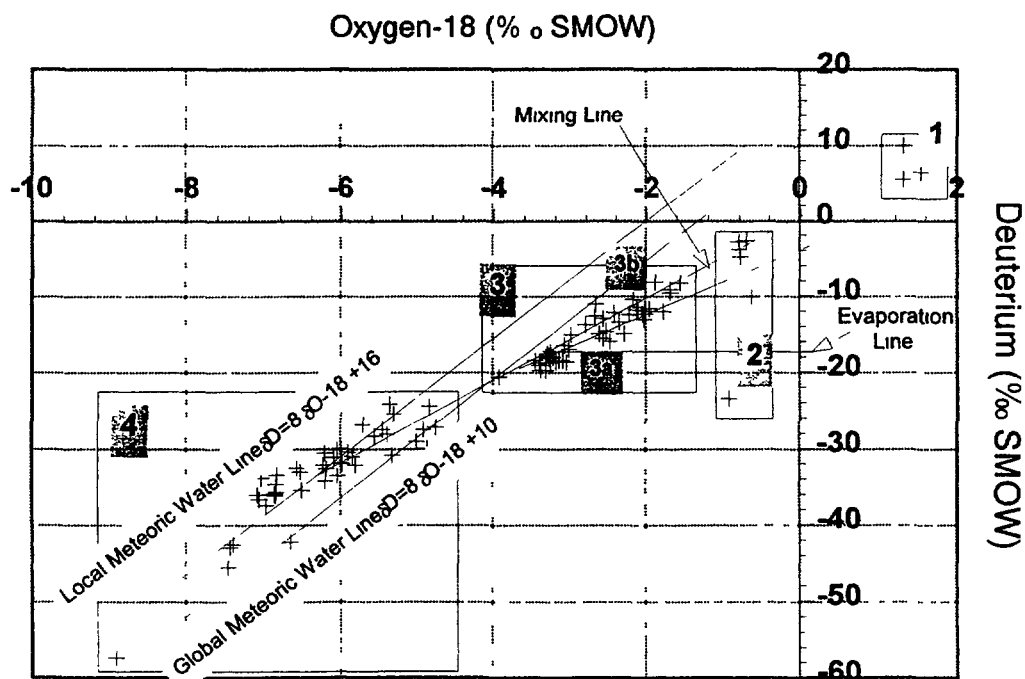


Figure 6: Meteoric water, evaporation and mixing lines fitting to waters samples collected from various points in and around the Lake Köyceğiz.

Closer inspection of $^{18}\text{O}/\text{D}$ indicates although, the samples from monimolimnion and mixolimnion are clustered roughly in separate groups, the monimolimnion samples from Sultaniye Basin are more depleted compared to those of from Köyceğiz Basin. It is clear that amount of stable isotopic depletion of monimolimnion samples increase with increasing depth. Similarly, isotopic depletion of mixolimnion waters from both basin also increases with increasing depth even if they are less depleted than those of monimolimnion waters. The difference between monimolimnion and mixolimnion waters in Sultaniye Basin is much more apparent than that of in Köyceğiz Basin. These observations imply that i) relatively good mixing occurs in Köyceğiz Basin, ii) most depleted waters are found in the deeper part of Sultaniye basin implying that the source of depleted water should be more closely located to this part of the lake. These arguments are also correlated well with the hydrochemical data as will be discussed in the following chapters.

5.3. Isotopic Profiles and Lake Water

Stable isotope profiles of lake waters from Sultaniye and Köyceğiz Basins are shown in Figure 7. These profiles indicate that the monimolimnion waters in both basins have more distinct isotopic compositions than those of respective mixolimnion waters which are less isotopically depleted. Relative isotopic enrichment observed in mixolimnion waters is attributed to the contribution from group-4 waters (i.e. precipitation, stream flow and rainfall). It appears that at least part of the monimolimnion waters mix with group-4 waters to form isotopic composition of the mixolimnion. The deuterium content in the mixolimnion in both basins is between -17 and -20 per mil SMOW, and does not show an appreciable variation along the depth. The isotopic homogeneity of mixolimnion water suggest that, after the formation of this water by mixing of group-4 and monimolimnion waters, the mixolimnion is well mixed.

The oxygen-18 composition of mixolimnion in both basins is between -3 and -3.5 per mil SMOW and like deuterium, the oxygen-18 content is also homogenous. The transition zone between monimolimnion and mixolimnion is rather sharp and extends along ca. 13m depth in this sampling period (December 1994). In succeeding field campaigns, it is well established that the transition zone is nearly constant at this depth in the Sultaniye Basin, whereas it fluctuates between 13m and 16m in the Köyceğiz Basin. The reason for this-fluctuation is believed to be the increasing inflow of Namnamçay and Yuvarlakçay streams discharging into the Köyceğiz Basin, and recent rainfall input. Both the deuterium and the oxygen-18 contents in the monimolimnion of Sultaniye Basin is nearly constant except the deepest sample (-32m from mean lake level). Deuterium and oxygen-18 contents range between -10.5 and -11.5 per mill SMOW and -2 and -2.5 per mill SMOW, respectively. However, in the Köyceğiz Basin, the monimolimnion is not isotopically homogenous as it is in Sultaniye Basin, and the stable isotope content is enriched linearly from the bottom water to transition zone. The stable isotope composition of bottom water (24m) in the Köyceğiz Basin is less depleted than that of bottom (32m) water of Sultaniye Basin but more or less the same as the sample collected from the same depth (24m) at the Sultaniye Basin.

The presence of most isotopically depleted samples at the deepest points of both basins may be accepted as an indication of the inflow of water that is isotopically most depleted. Except the sea water, the most isotopically depleted waters in the area are of thermal origin. Sea water intrusion via the Dalyan Channel toward the Lake Köyceğiz has not been observed during the observation period between 1993 and 1997; neither was such evidence presented in the studies carried out previously. Therefore, the most plausible source of isotopically depleted water in the monimolimnion of the Sultaniye Basin should be the thermal water contribution. Sultaniye spring, located just along the shoreline to the south of Sultaniye Basin, has an average temperature of 40°C and any such thermal water inflow that may discharge through the lake bottom is expected to have been influenced by this high temperature. However, no such evidence has

been obtained from extensive spatial temperature measurements carried out in various field campaigns, probably because of diffuse inflow of thermal water. It is inferred that some of the thermal water ascending to the Sultaniye Spring (which is more depleted than monimolimnion water) discharge into the lake through fractures/joints located on the southern bank of the lake. As will be demonstrated later in this paper, this water has higher density than that of any water in the Sultaniye Basin and sinks to the lake bottom to form monimolimnion water.

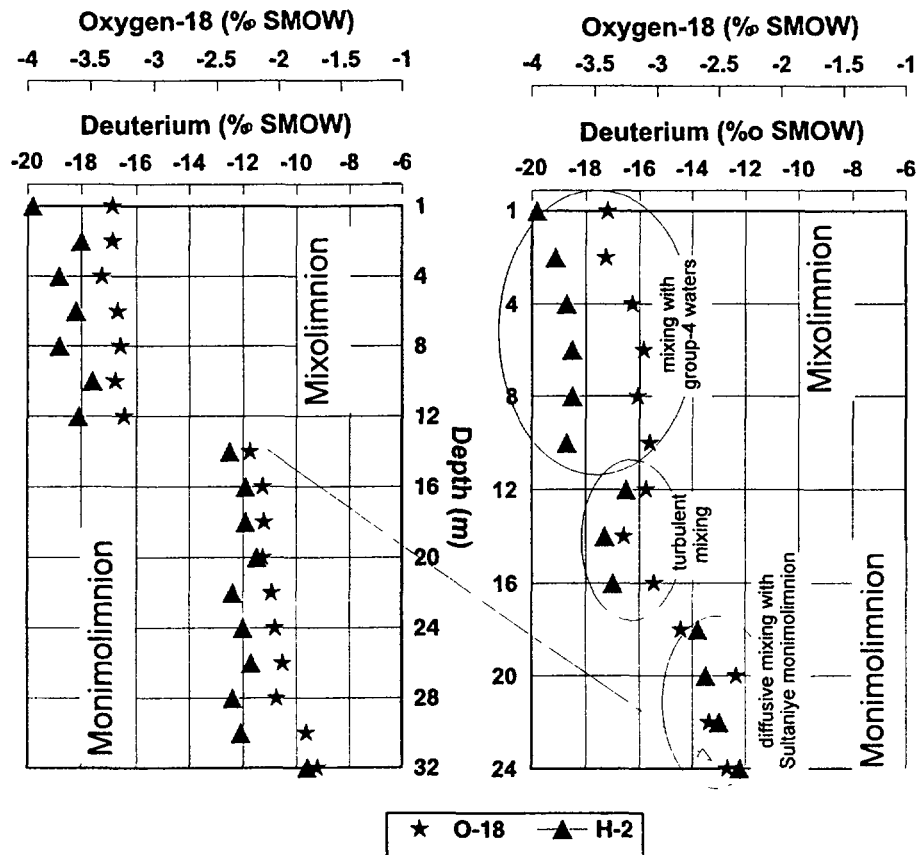


Figure 7: Deuterium vs. oxygen-18 profiles from two major station on the Lake Köyceğiz (Left: Köyceğiz Basin, Right: Sultaniye Basin).

The rate of isotopic depletion in the Sultaniye monimolimnion decreases upward with a sudden shift at -12m from the average lake surface where the transition zone between mixolimnion and monimolimnion in this basin is located. Bathymetric profiles of Sultaniye Basin indicates that the isotopically depleted monimolimnion water can outflow only toward the Köyceğiz Basin via Yoğun Strait where the lake bottom rises to -12m below mean lake level (m.l.l.) because the bottom elevation of the lake outlet to the Dalyan Channel is at 6 to 7m below m.l.l. It appears that the high density thermal water sinking into the bottom of Sultaniye Basin is subject to diffusive mixing as the infilling dense water rises to transition zone. At the top of monimolimnion of Sultaniye basin, the stable isotopic composition is enriched with respect to deeper parts. The outflowing Sultaniye monimolimnion water is still denser than the mixolimnion waters of both basins. Therefore, the outflowing water tend to sink into the bottom of monimolimnion of Köyceğiz Basin. The similarity between the isotopic compositions of outflowing water (that is, Sultaniye monimolimnion water with $\text{O-18} = -2.23\text{‰}$ and deuterium $= -12.5\text{‰}$ at $12\text{m}/13\text{m}$ depth) and the bottom water of Köyceğiz Basin (with $\text{O-18} = -2.43\text{‰}$ and deuterium $= -12.2\text{‰}$ at 24m depth) is quite striking. This similarity implies that the dense water outflowing from Sultaniye monimolimnion keeps its isotopic composition during its travel to the bottom of Köyceğiz basin. This is somewhat surprising, because the mixolimnion water

from Köyceğiz basin flows in opposite direction and is expected to cause turbulent mixing along the transition surface. Absence of such a turbulent mixing can be accepted as a sound evidence of very low flow velocities along the mixolimnion and monimolimnion surface at the Yoğun Strait or the presence of a connection between two basins that is located below the transition surface.

The depth of transition zone at 12m in the Sultaniye Basin is a dominant characteristic as revealed by the hydrochemical data obtained in all field campaigns. The endurance of transition zone at 12m in the Sultaniye Basin is believed to be due to the physical (bathymetric) barrier created by the depth of Yoğun Strait connecting both basins (see Figure 2). It seems, even though the surface water inflow into the Köyceğiz Basin causes a mixing of monimolimnion and mixolimnion to some extent, the resultant water is still less dense than the monimolimnion of Sultaniye Basin and most of the this water leaves the lake via Dalyan Channel by flowing over the monimolimnion of Sultaniye Basin.

Three distinct regions are observed in the stable isotopic composition of the Köyceğiz Basin. The bottom water which expose isotopic similarity to the upper most monimolimnion water of Sultaniye Basin, becomes increasingly enriched as the transition zone located at 16m depth is approached. Between the bottom of monimolimnion and the transition zone the isotopic enrichment is linear and correlated well with the depth. Between 12m and 16 m depths, the isotopic composition is almost homogenous implying that turbulent mixing is effective. Above 12m depth up to the surface, the isotopic composition becomes increasingly enriched probably because of the recent surface and rainwater input in to the lake. The isotopic composition of mixolimnion in both basins are very similar especially in the surface (-1m) samples.

5.4. Tritium profiles

Tritium composition of lake water has been determined in dry (August 1994) and wet (February 1994) seasons (Figure 8). Although, the variation of tritium content with depth in both basins suggests a small decrease, systematic variation observed in stable isotope profiles is not clearly demonstrated here. Even though, this irregular variation can be attributed to measurement error which is roughly around ± 0.5 TU, it is apparent that there is no large difference between the tritium composition of monimo and mixolimnion waters. In both periods the relatively low tritium contents are observed in the bottom waters confirming the deductions made on the basis of stable isotope content. The Sultaniye thermal spring's water which is believed to sink to the lake bottom in this sector has also low tritium content (0.4 ± 0.3 TU in August 1994 and 0.5 ± 0.3 TU in February 1994).

Because the degree of measurement error does not allow to make deductions on the evolution of Sultaniye monimolimnion water, a rough mixing calculation was made based on the average stable isotope, electrical conductivity values of assumed end-members. Table x shows that when Sultaniye thermal spring and Sultaniye mixolimnion are mixed at 40% and 60%, respectively, the electrical conductivity and stable isotope composition of hypothetical mixing water resembles well enough to monimolimnion water in this basin. To maintain the obtained mixing ratio, the tritium content of the mixolimnion is calculated to be 10.4 TU. It may be assumed that the error associated with this figure is, like real measurements, ± 0.5 TU. Although, the calculated tritium content is above the measured values in the lake, it can still be accepted as a plausible value. Previously measured mixolimnion tritium contents (Köyceğiz basin = 13.2 ± 0.6 TU, Sultaniye basin = 12.5 ± 0.5 TU; [8]) and those measured in local springs which are fed from annual rainfall (Marmarlı spring, 9.1 ± 0.5 TU in August 1994 and 15.0 ± 0.3) suggest that the calculated tritium content for mixolimnion is within acceptable limits.

Table 1: Major components contributing to monimolimnion of Sultaniye Basin.

End-member	Conductivity	Oxygen-18	Deuterium	Tritium
	microS/cm	‰ SMOW	‰ SMOW	TU
Thermal water (A)	30000	-0.8	-3.9	0.5
Sultaniye mixolimnion (B)	4900	-3.33	-18	10.4*
Sultaniye monimolimnion	14750	-1.78	-12.1	6.4
Mixing (%40 A + %60 B)	14940	-2.318	-12.36	6.4

Note: * Calculated mixolimnion tritium content.

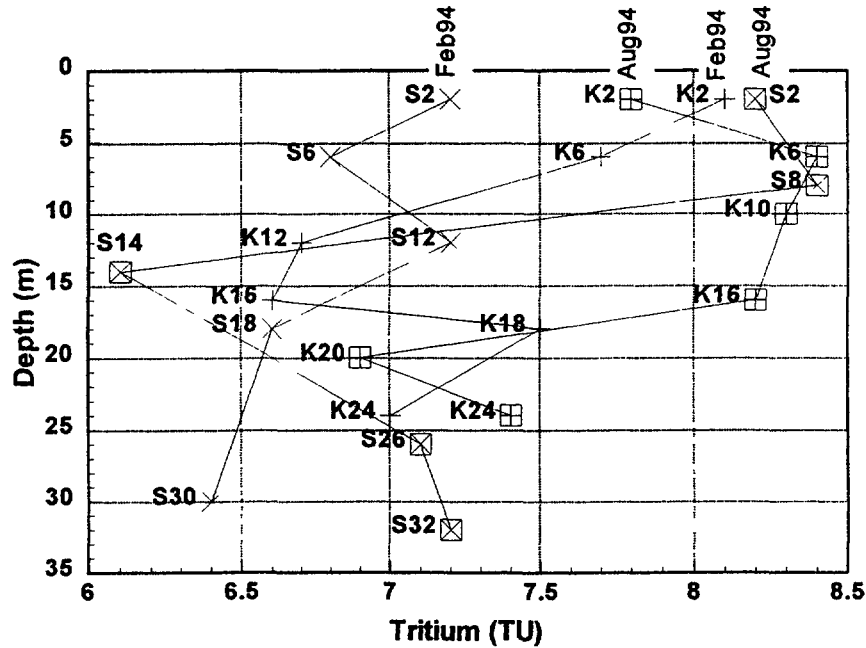


Figure 8: Tritium profiles from Köyceğiz and Sultaniye Basins.

6. HYDROCHEMICAL EVALUATIONS

6.1. Data

In order to have a complete picture of the dynamics of Lake Köyceğiz, and to provide supporting evidence for evaluations made on isotopic data, 6 hydrochemical field campaigns have been carried out. Evaluation of field data is given in the following paragraphs. At this point, method of data collection should be mentioned to explain the reliability of field data. In the first 5 sampling campaign the field parameters have been measured on the boat just after the depth specific sample has brought to the boat via "Ruttner" sampler. Although, the time between the closure of Ruttner sampler at the desired depth and the measurement on the boat has been tried to be minimum, it has been between 5 and 10 minutes depending on the sampling depth. During this time interval, it is possible that properties of sample could have been changed because of the temperature equilibration with the upper levels of the lake. Furthermore, those properties, evidently, changes during measurements made on the boat, because the water sample tends to equilibrate with atmosphere. In spite of the fact that utmost care has been spent in these measurements, the measured parameters should have had slightly different values from those at the sampling depth. However, these problems have been minimized to instrument's accuracy

level in the last field campaign by the use of “Hydrolab Datasonde 3” multiparameter water quality probe with which measurements have been made at the desired depth. As will be shown in the following paragraphs, the field data provide good evidences on the dynamics of interaction between the monimolimnion and mixolimnion waters.

6.2. End-Members and Lake Water

Like the isotopic data, hydrochemical data suggest also the same end-members as shown in trilinear diagram which is based on data from second field campaign (August 1995) (Figure 9). Figure 9 implies that the typical regional groundwater is represented by Yuvarlakçay karstic spring. Other groundwater samples (such as, Marmarlı, Asar and Ada springs) which are more closely located to the Lake Köyceğiz exhibit local chemical variations such as sulfate reduction and cation exchange, but stay within the region of fresh (group-4) waters. Thermal waters are located closely the Sea Water region which is located to the right-hand end of central diamond, and the lake waters are located in between sea water and thermal waters. A general view of the hydrochemical composition of water samples from Lake Köyceğiz and surrounding sampling points is given in Figure 10.

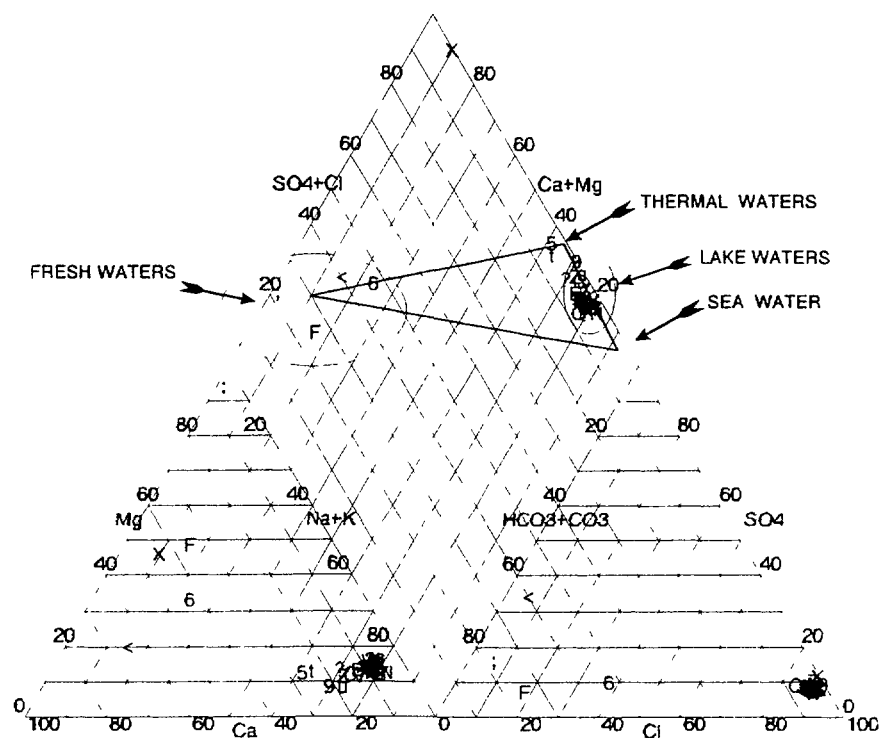


Figure 9: Trilinear diagram of water samples collected in and around Lake Köyceğiz (data from August 1994 field campaign).

6.3. Temporal Hydrochemistry of Lake Water

Temporal variations in the physical and chemical characteristics of lake water have been investigated with a number of field measurements carried out in typical wet and dry months. Apart from the parameters that have been measured in the field, water samples have also been collected for the determination of major ion, trace element and nutrient composition. The variation of both the field and laboratory parameters are in good agreement with those inferred from isotopic evaluations. The following evaluations are based on field measured parameters

carried out two lake stations that represent the hydrochemistry of Köyceğiz and Sultaniye Basins. The locations of temporal measurement stations were chosen to reflect deepest profiles in both basins.

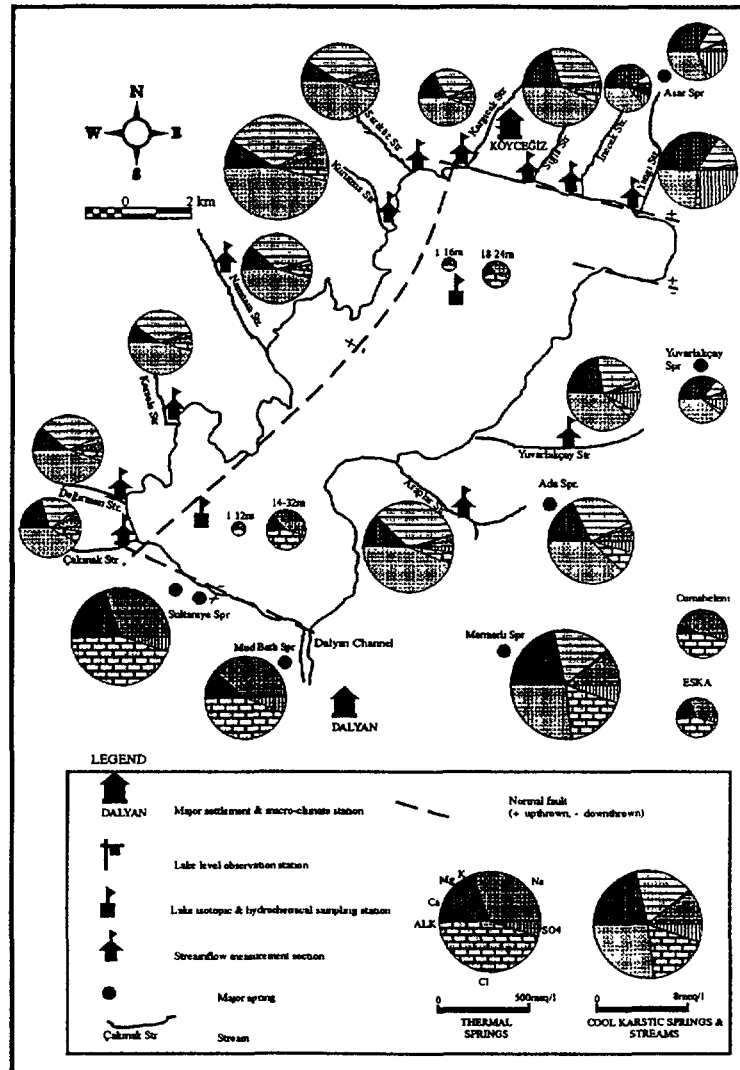


Figure 10: Circular diagrams showing hydrochemical character of sampling points (data from August 1994 field campaign).

6.3.1. Temperature :

Mixolimnion temperature in the Lake Köyceğiz varies depending on the equilibration with atmospheric temperature (Figure 11). As indicated earlier the depth to transition zone between monimolimnion and mixolimnion in both basins is controlled by the depth of Yoğun Strait that connects both basins. Temperature measurements from all campaigns indicate that the monimolimnion temperature in the Sultaniye Basin is rather stable and show only slight variations which may partially be attributed to measurement and calibration errors. However, the mixolimnion temperature of Sultaniye basin fluctuates all year round apparently because of temperature equilibration with air. High and low mixolimnion temperatures are observed in summer and winter months. According to temperature profiles, the mixolimnion extends to -12m whereas, the transition zone is located between -12m and -14m. Stability of monimolimnion profile indicates clearly that the permanent stratification is dominant in the Sultaniye Basin.

However, temperature profiles observed in Köyceğiz Basin is less stable in the monimolimnion region. Mixolimnion temperatures fluctuates annually as observed in Sultaniye Sector. Interestingly, temperature values observed in the bottom water of Köyceğiz Basin's monimolimnion and the monimolimnion of Sultaniye Basin. This supports the idea that the monimolimnion water from Sultaniye Basin flow toward the bottom of Köyceğiz Basin due to its higher density which is maintained by continuous thermal water sink and overflow

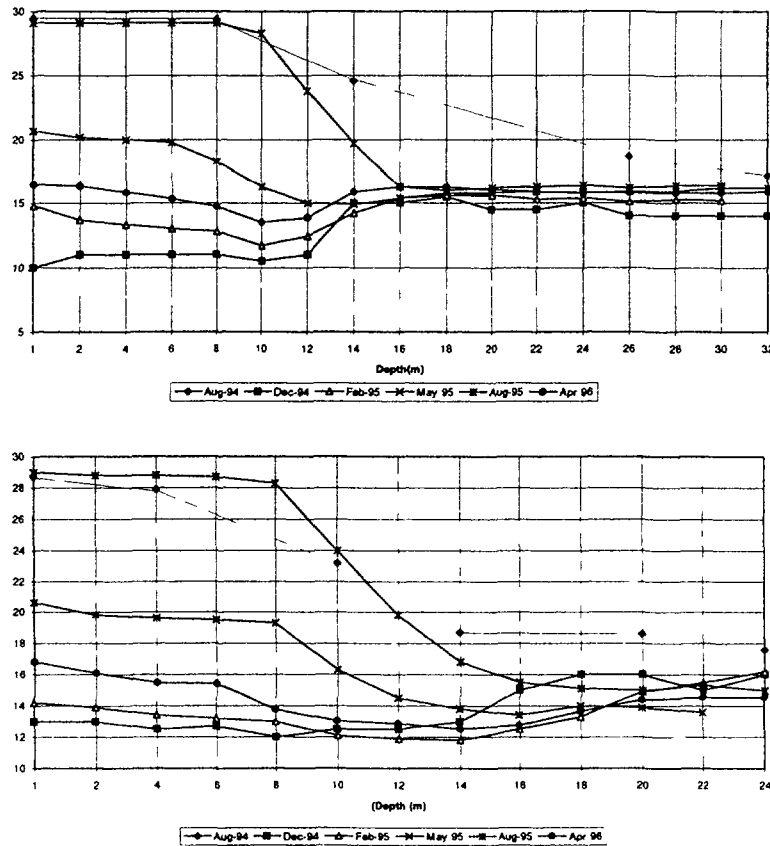


Figure 11: Temperature profiles in Lake Köyceğiz (Values are in °C Top. Sultaniye Basin, Bottom: Köyceğiz Basin; August 1994 data is based on measurements made in samples brought to the boat).

6.3.2. Specific Conductivity:

Specific conductivity as a measure of total ion content is one of the best indicators of the interaction between monimolimnion and mixolimnion. In the Sultaniye Basin, alike temperature profiles, the specific conductivity profiles of monimolimnion and mixolimnion are separated sharply. Here the mixolimnion extends between surface and 8/12m. Depth to transition zone changes as a result of fresh water input from surface flow and rainfall, and the thickness of mixolimnion increases as expected when this input occurs (e.g. in December 1994 and April 1996). Contrary to the variations in Köyceğiz Basin, the top of monimolimnion in Sultaniye Basin is fixed at 14m depth regardless of the time of the year. The specific conductivity profiles in the mixolimnion of Köyceğiz Basin are nearly the same except that of December 1994 (Figure 12). This suggest that the mixolimnion water is chemically stabilized (or gets homogenized) within a very short period. In contrast to mixolimnion, specific conductivity profiles in the monimolimnion vary in a wider range suggesting that, although mixolimnion gets homogenized rapidly, mixing of mixolimnion with monimolimnion occurs gradually. As a result of this gradual mixing, the depth of monimolimnion reduces to 20m and the transition zone is thicker (i.e. between 8m/12m and 20m).

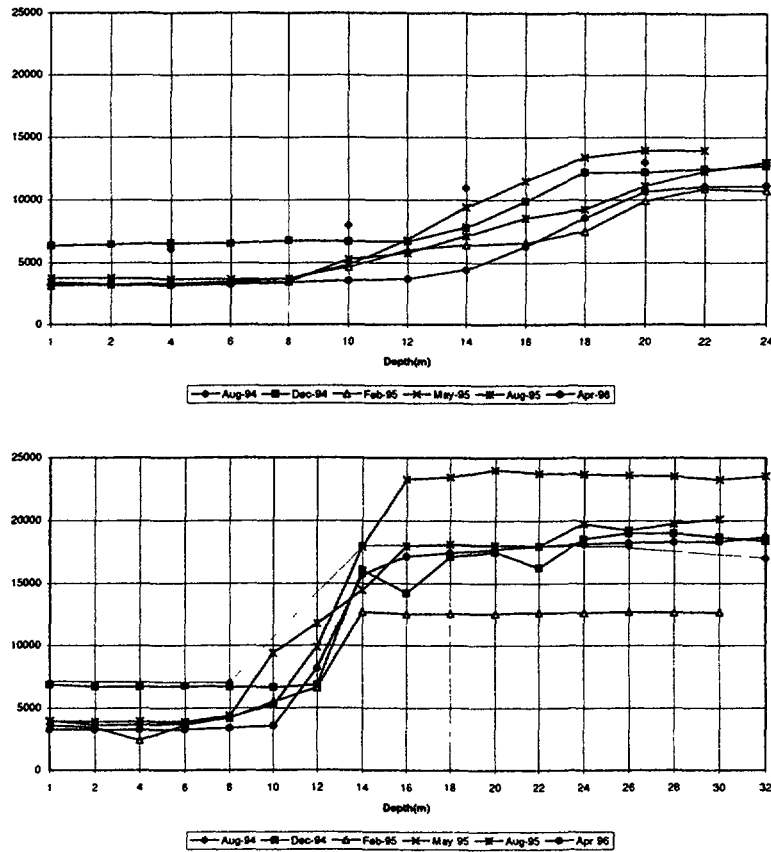


Figure 12: Specific conductivity profiles in Lake Köyceğiz (Values are in microSiemens/cm.. Top: Köyceğiz Basin, Bottom: Sultaniye Basin).

Comparison of specific conductivity profiles of Köyceğiz and Sultaniye Basins reveals that, even if the specific conductivity of mixolimnion in both basins are nearly the same, there is an apparent difference between the specific conductivity's of monimolimnions. The higher monimolimnion specific conductivity in the Sultaniye Basin should be due to continuous thermal water sink into this basin. Alike the stable isotope and temperature data, the specific conductivities of the waters of monimolimnion of Sultaniye Basin and that of Köyceğiz Basin's bottom water have similar values suggesting that monimolimnion water at 13m depth in the Sultaniye basin flows toward the bottom of Köyceğiz Basin.

6.3.3. Dissolved Oxygen:

Dissolved oxygen is among the primary field parameters that helps to identify the stratification variations in Lake Köyceğiz. Dissolved oxygen in the mixolimnion of both Basins varies between 5 mg/l and 10 mg/l (Figure 13). Dissolved oxygen content of monimolimnion is less than 2 mg/l. Lowest dissolved oxygen values in the of monimolimnion have been recorded in April 1996 campaign during which the measurements were made "in-site" by using multiparameter water quality probe. In these measurements it is believed that the maximum accuracy has been obtained since a magnetic stirrer fitted to the end of dissolved oxygen probe has also been used. It appears that dissolved oxygen content of mixolimnion is controlled both by water temperature and the intensity of biologic activity. Higher values are observed in colder periods when the oxygen solubility is increased but the biologic and chemical activities consuming oxygen is depressed. Dissolved oxygen profiles reveal that monimolimnion in Sultaniye and Köyceğiz Basins start at depths 12m/14m and 14m/16m, respectively. Accordingly, mixolimnion extends down to 6m/8m in Köyceğiz Basin, and to 10m in Sultaniye

Basin. Previous observations suggesting inflow from Sultaniye Basin's monimolimnion towards the bottom of Köyceğiz Basin are also supported by the dissolved oxygen data.

6.3.4. pH:

The pH provides also a robust portrait of the interaction between monimolimnion and mixolimnion in both basins. In the mixolimnion of both basins, the pH range between 8.4 and 8.8 as expected from an open water body which is abound with nutrients and photosynthetic organisms (Figure 14). Although seasonally changes, the pH does not show any drastic variation along the depth of mixolimnion, indicating that mixolimnion water is homogenized well. This is also the case for monimolimnion in both basins even if lower pH values observed there. The major factor controlling the value of pH in the mixolimnion is the biologic activity of floral species such as, alga. During higher biogenic activity periods, because of the photosynthetic use of dissolved carbon-dioxide, higher pH values are observed. According to pH values, the mixolimnion extends down to 8m in the Köyceğiz Basin, whereas it continues to 8m/10m in the Sultaniye Basin. The monimolimnion starts in the Köyceğiz and Sultaniye Basins at 20m and 16m, respectively. The decrease of pH in the monimolimnion of both basins may be attributed to several reasons: i) thermal water input (which virtually has no oxygen) into the monimolimnion and, ii) chemical reduction processes occurring due to depletion of oxygen by inorganic/organic reactions. Normally, the depletion of oxygen in aquatic systems leads to reducing conditions which result in proton (H^+) release into the water. Here, again the similarity between the pH values of the monimolimnion water of Sultaniye Basin and that of bottom water in Köyceğiz

Basin is noteworthy. This may be accepted another evidence for the outflow of Sultaniye Basin's monimolimnion toward the bottom of Köyceğiz Basin.

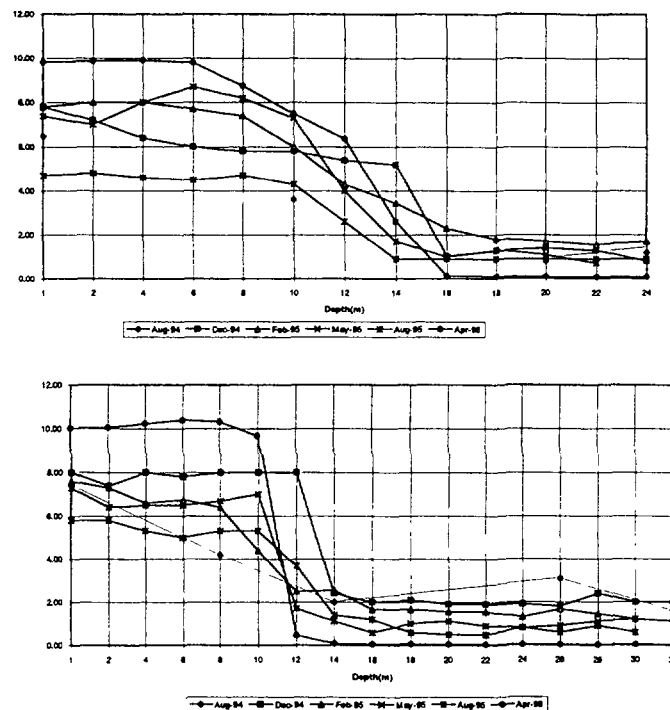


Figure 13: Dissolved oxygen profiles in Lake Köyceğiz (Values are in mg/l. Top: Köyceğiz Basin, Bottom: Sultaniye Basin).

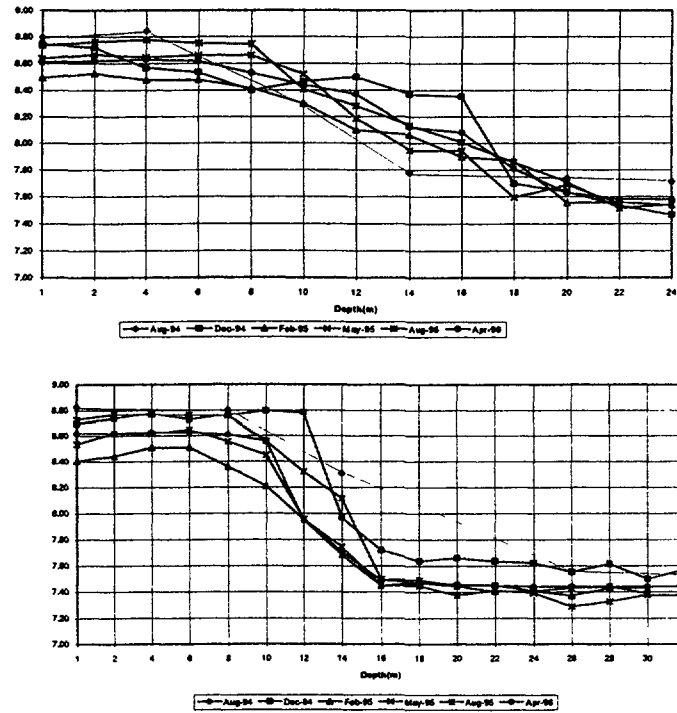


Figure 14: pH profiles in Lake Köyceğiz (Values are in standard units. Top: Köyceğiz Basin, Bottom: Sultaniye Basin).

6.3.5. Major Ion Composition

Major ion, trace element and nutrient data produced in all field campaigns expose a portrait that is in accordance with the deductions made on field measured data (i.e., electrical conductivity, dissolved oxygen and pH). Detailed evaluation of laboratory data will be given elsewhere and only the temporal variation of chloride ion, as a conservative species, is discussed here.

Variation of chloride composition in the Lake Köyceğiz suggest that the chemical composition of lake water do not show any substantial variation in the long run (Figure 15). The highest chloride content is observed in the monimolimnion of Sultaniye Basin where there is thermal water sink chemically resembling to Sultaniye thermal spring of which average chloride content varies around 400 mg/l. The chloride content of the Sultaniye Basin's monimolimnion is rather stable around 200 mg/l and reduces to 150 mg/l at the top of this zone at 14m depth. As expected, the chloride content of the bottom water in Köyceğiz Basin is similar to this value.

6.4. Spatial Variation of Chemical and Physical Parameters in Lake Köyceğiz

Spatial variation of some physical and chemical parameters have been measured “in-situ” by using a “Hydrolab Data Sonde 3 TM” multiparameter probe. Use of this instrument not only helped to increase the number of profiling stations (from 2 to 31, see Figure 3 for station locations and their depths), but also enhanced the quality of data because the measurements have been made at the desired depth without bringing water samples to the surface. Although, 7 parameters including temperature, pH, dissolved oxygen, specific electrical conductivity, redox potential and turbidity have been measured, because of the scarcity of space, only the variation of temperature and specific electrical conductivity are evaluated briefly here. More detailed evaluations including other parameters will be given elsewhere (see also [3]).

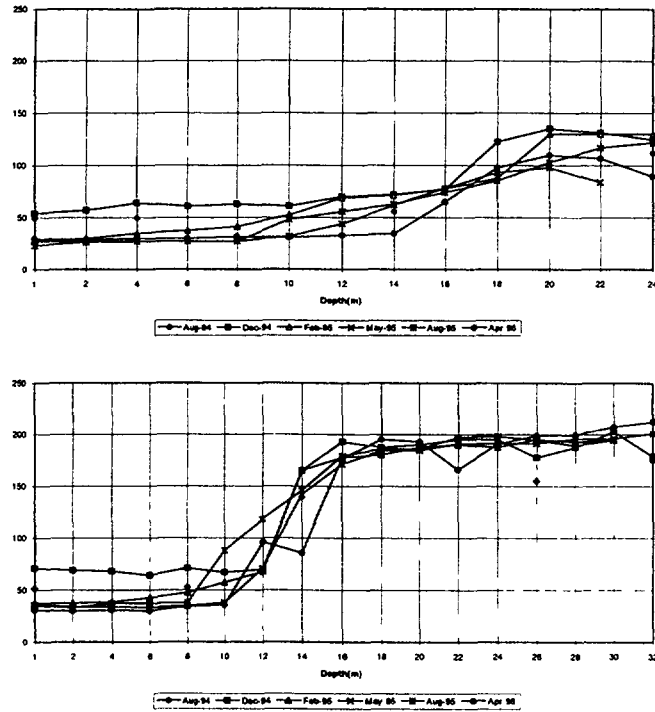


Figure 15: Cl profiles in Lake Köyceğiz (Values are in meq/l Top: Köyceğiz Basin, Bottom: Sultaniye Basin,).

6.4.1. Temperature:

Three main features in the temperature profiles are noteworthy (Figure 16). First, the monimolimnion temperatures in the Sultaniye Basin is apparently higher than those of Köyceğiz Basin, second temperature profiles in both monimolimnion have different shapes, third the mixolimnion temperature profiles vary in a wider range compared to those of monimolimnion. The difference between the shapes of temperature profiles in the monimolimnion of both basins suggests that, the monimolimnion in Sultaniye Basin is more stable in terms of heat balance. In both basins, the monimolimnion temperature becomes stable below 20m depth. Moreover, the monimolimnion temperature profiles of Sultaniye Basin also reveals that only the top 6m (between 14m and 20m) is influenced by the mixolimnion temperature variations.

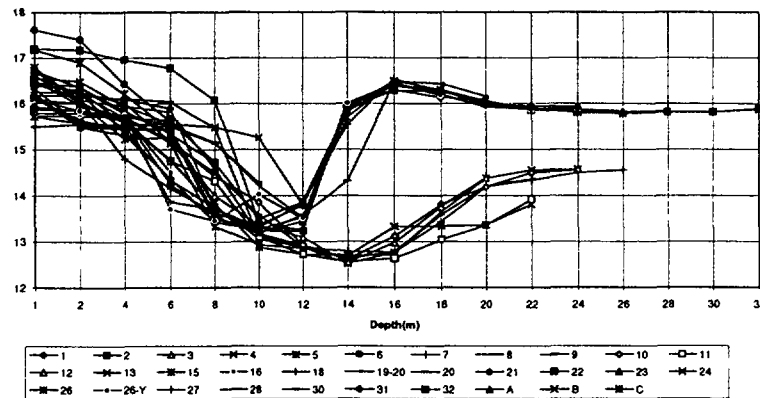


Figure 16: Variation of temperature at 31 stations in the Lake Köyceğiz (Values are in °C, Data from April 1996 campaign).

6.4.2. Specific electrical conductivity:

Alike temperature profiles, specific conductivity profiles as well suggest the same depiction. That is, the specific conductivity of mixolimnion is nearly the same all over the lake and the specific conductivities in the monimolimnion of either basins are apparently different, with higher values belonging to the Sultaniye Basin (Figure 17). According to specific conductivity profiles, the transition zone extends between 10m and 20m in both basins. Below 20m, the specific conductivity apparently does not change to a great extent. On the other hand, specific conductivities observed in the monimolimnion of Sultaniye Basin is more homogenous than those of Köyceğiz Basin, implying that mixing of mixolimnion and monimolimnion is more important in the Köyceğiz Basin.

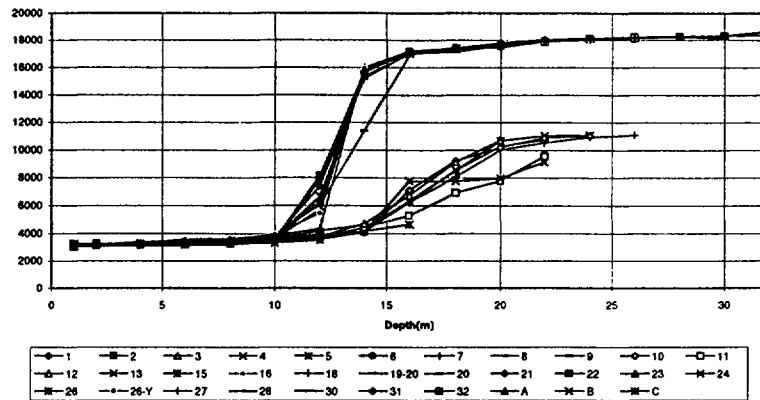


Figure 17: Variation of specific electrical conductivity at 31 stations in the Lake Köyceğiz (Values are in microSiemens/cm, Data from April 1996 campaign).

7. DENSITY VARIATIONS

In order to have a better understanding of the mixing dynamics, density variation in the Lake Köyceğiz has been investigated by means of “sigmatee” data for selected profiling stations. The “sigmatee (τ_i)” is the difference between the density of a water sample and that of pure water. Since, the density variations are small numerically, by convention, the sigmatee values are multiplied by 1000 to have a better expression. The pure water has a sigmatee value of zero and the higher the density of water the higher the sigmatee values. The “international equation of state for sea water” that accounts for the effects of salinity, temperature and hydrostatic pressure upon density has been used for the calculation of sigmatee values. Variation of lake waters’ density in vertical direction for all stations is shown in Figure 18 which is based on the data collected in April 1996 field campaign. Data from other field studies reveals similar portraits in terms of density variations. Variation of sigmatee values in April 1996 indicates that the waters with highest density are found in the monimolimnion of Sultaniye Basin where dense thermal water sink is suggested by chemical and isotopic data. Slightly lower sigmatee values are observed in the monimolimnion of Köyceğiz Basin. Densities observed in the bottom of Köyceğiz Basin are similar to those of 12m depth of Sultaniye Basin. This observation is accepted as another supporting evidence for the fact that the monimolimnion water in Sultaniye Basin flows through 12m deep Yoğun Strait toward the bottom of Köyceğiz Basin.

A simplified view of sigmatee variation in Lake Köyceğiz is given in Figure 19 for stations located between station no.2 (offshore of Köyceğiz town at the north) and station “a” (lake outlet at the south). Figure 19 reveals that the lowest density in the Lake Köyceğiz is observed in station 2 whereas, the highest density is observed at the bottom of station 31 that penetrates into the monimolimnion of Sultaniye Basin. Lake water density in the mixolimnion increases progressively from station 2 toward station ‘a’ which is most closely located to the sea.

However, it appears that the density of Sultaniye monimolimnion originates from thermal water sink rather than sea water intrusion because the density observed in this station is substantially lower than those observed in Sultaniye monimolimnion.

The argument that suggests monimolimnion overflow toward the bottom of Köyceğiz Basin from the Sultaniye monimolimnion is also supported by Figure 19. Densities observed in the transition zone between monimolimnion and mixolimnion of Sultaniye Basin at the depth of 13 m (i.e. in between 12m and 14m depths) correspond to density of bottommost water of profile 12 in the Köyceğiz Basin. From this profile toward those located to the north, density of lake water in the top and bottom waters reduces progressively indicating that the main source of dense water in the Köyceğiz Basin is the monimolimnion of Sultaniye Basin.

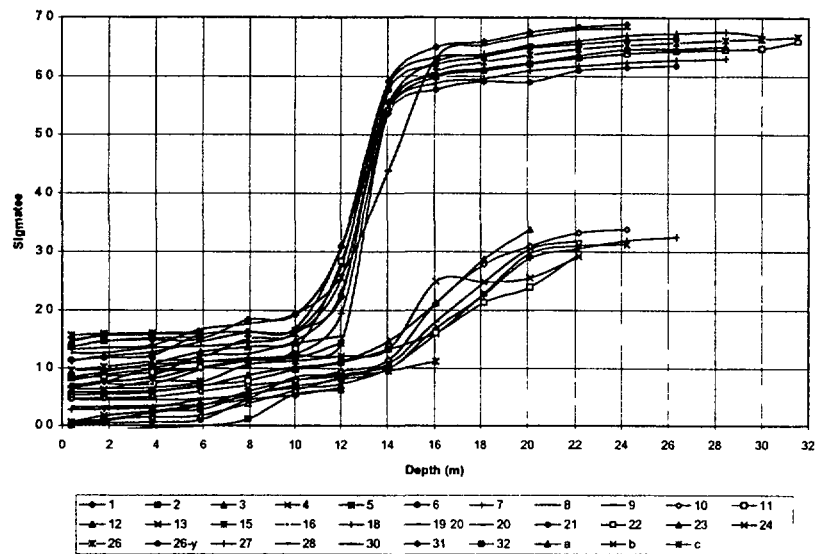


Figure 18: Variation of sigma-tee values among profiling stations in the Lake Köyceğiz (data based on April 1996 field campaign).

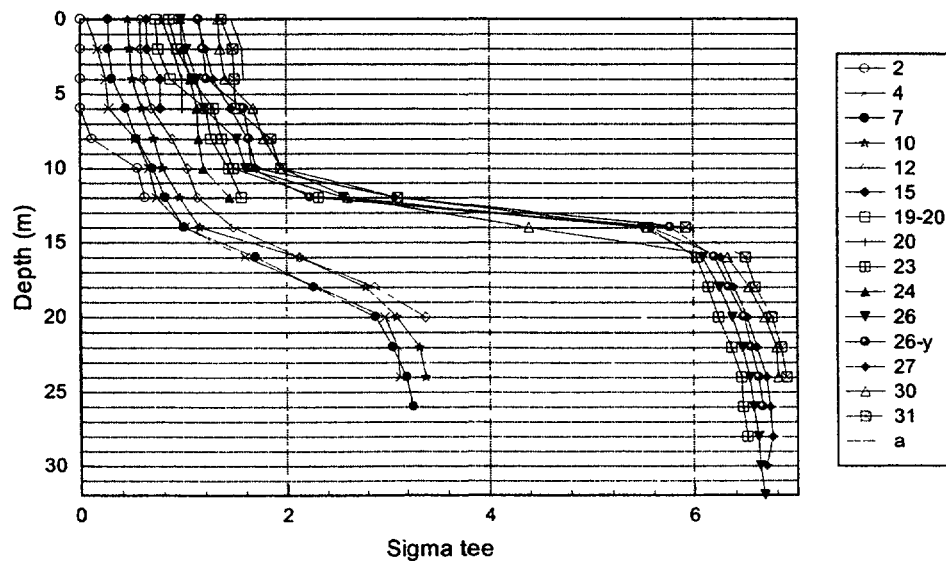


Figure 19: Variation of sigma-tee values along profiling stations located between station no.2 (Köyceğiz town offshore at the north) and station "a" (lake outlet at the south).

8. EPILOGUE: LAKE DYNAMICS MODEL

Overall evaluation of isotopic, chemical and density data collected in this study reveals that the Lake Köyceğiz has a complicated mixing dynamics which is controlled mainly by density-driven flow of waters from different origins (Figure 20). The lake is fed mainly by rainfall and streamflow as low density waters and by high density thermal groundwater. Apart from the streamflow brought by two major streams Namnamçay and Yuvarlakçay which discharge into the northern part, the main source of low density water input is the rainfall. However, because of the density difference between mixolimnion and recharge, it appears that complete annual mixing in the lake can not be achieved.

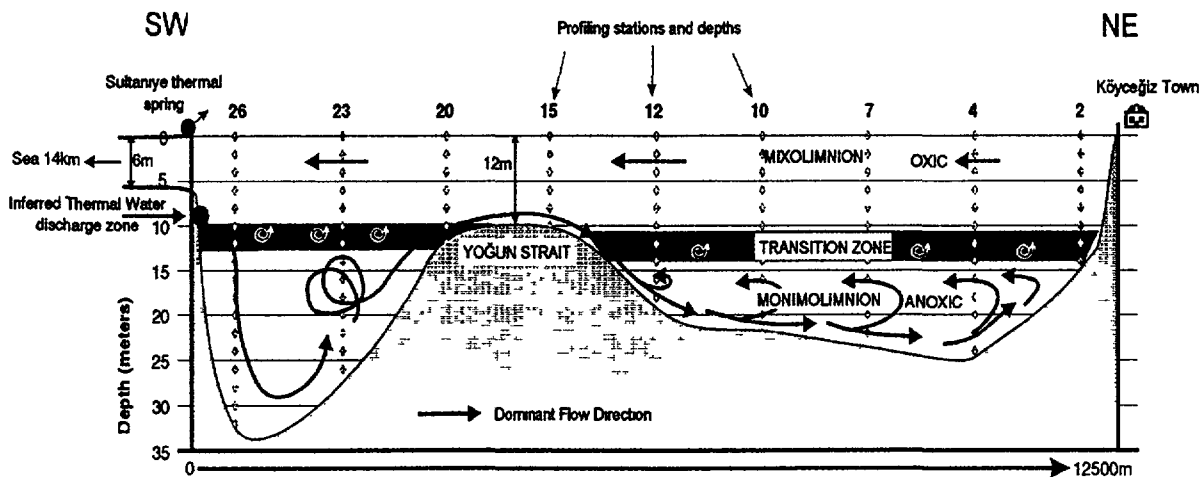


Figure 20: Conceptual lake dynamic model.

It appears that there is continuous high-density thermal water input into the southern (Sultaniye) basin of the lake where along thermal springs are located along the coast. Some of the thermal groundwater discharge into the lake from a depth of 8m to 10m along this coast line. Because of the high density, the thermal groundwater discharging into the lake sinks into the bottom of Sultaniye basin where the highest density among all lake waters is observed. The infilling of southern basin is controlled by the bottom topography. Since, this basin has two outlets, one located at 12m depth toward the northern basin, and another located at 6m depth toward the sea, the bottom (monimolimnion) water tends to overflow toward the northern basin. It appears that this overflowing water follows the bottom surface in the northern basin and is accumulated at the deepest point. During the travel of dense bottom water current, it is mixed with top (mixolimnion) water and as the distance from the high density water increases, the density tends to decrease. Consequently, highest and lowest density waters in the top water are found in the most southern and northern ends of the basin, respectively. These conclusions are in good agreement with those drawn from isotopic and chemical data. Isotopically most depleted waters in the area are represented by thermal groundwater discharges located on the southern shore of the lake. The variation of the stable isotopic composition of the lake water is also in good agreement with density-driven flow scenario. Most isotopically depleted lake water are found in the bottom water of southern basin and the bottom water becomes progressively less depleted toward the north of the lake. Due to mixing with recent recharge, the top water is isotopically more enriched. The same conclusions are also valid for the variation of other physical and chemical parameters of the lake water. It is difficult to arrive at firm conclusions on the turn-over rates of bottom and top waters in both basins. However, rough calculations based

on long-term average electrical conductivity data reveal that about 60% of mixolimnion in both basins is replenished by annual recharge where as the annual mixing of monimolimnion with mixolimnions in Sultaniye and Köyceğiz Basins are 20% and 30%, respectively. Therefore, the turn-over times for mixolimnion and monimolimnions of Sultaniye and Köyceğiz Basins are estimated to be 2 years, 5 years and 3.5 years, respectively.

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STABLE ISOTOPE STUDY OF LAKE TURKANA, EAST AFRICA

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Abstract

The water level of Lake Turkana, East Africa, has fluctuated widely since measurements began in the late 1880s. Lake level has ranged from 15 meters above to 5 meters below the 1968 datum over the last 105 years. This study was initiated to compare the historic record of lake level for Lake Turkana to several records of the isotopic composition of carbonates found in the lake sediments. The ubiquitous presence of inorganic carbonates in Lake Turkana sediments, both spatially and temporally, allows for an evaluation of the use of the isotopic composition of carbonates as a proxy for paleo-lake level.

1. INTRODUCTION

The isotopic composition of carbonates has been used in numerous lacustrine studies to determine paleoclimatic information. Fluctuations in the isotopic record preserved in carbonates are created mainly by variations in the temperature and composition of the water in which the carbonate formed. In turn, these variations can be caused by climatic changes in the lake basin. Therefore carbonates are potentially an archive of the paleoenvironment of a lake basin.

In tropical or closed-basin settings, shifts in the oxygen stable isotopic composition of carbonates are often attributed to shifts in the evaporation to input (E:I) ratio of a lake. Previous workers have used the relationship between changes in the $\delta^{18}\text{O}$ value of carbonates and the E:I ratio of a lake basin to discuss qualitative changes in paleo-lake levels. Although the relationship between the $\delta^{18}\text{O}$ composition of lake water and the various inputs and outputs to a basin has been described quantitatively (e.g. see Refs [1-2]), only one quantitative comparison between a historical lake level record and lake level determined from the $\delta^{18}\text{O}$ composition of carbonates has been attempted [3].

Here a comparison is made between the historical record of the level of Lake Turkana and the isotopic composition of authigenic calcite preserved in its bottom sediment. Lake Turkana presents advantages and disadvantages in this type of study. Recent lake level variations at Lake Turkana are climatically induced variations, therefore avoiding complications due to human impact. Lake Turkana is a large and old lake. It has good potential for a long and continuous climate record. However, the size of the lake also introduces the possibility of significant spatial variability in lake conditions, thereby complicating the interpretation of $\delta^{18}\text{O}$ records.

Lake Turkana (Figure 1) is a large closed-basin lake in northern Kenya. It is in an arid setting and has one major inflow, the Omo River, which drains the Ethiopian Highlands to the north. The other major rivers in the basin, the ephemeral Turkwell and Kerio Rivers, supply only 10% of the total input to the lake [4]. The lake has been closed for the last 4000 years [5] and has been described extensively [6-7].

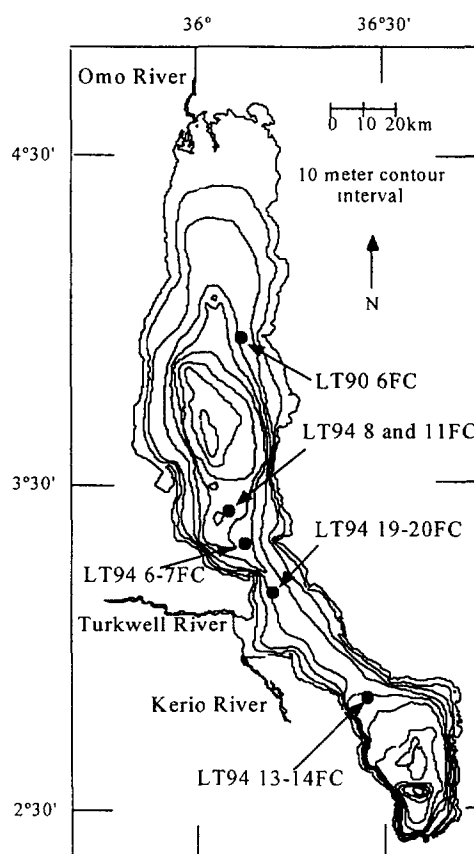


Figure 1: Chart of Lake Turkana showing the bathymetry of the lake and major rivers. The Omo River is the main source of fresh water to the lake while the Turkwell and Kerio Rivers are ephemeral. Open circles are the locations of the freeze cores discussed in the text (figure from Ref. [8])

2. MATERIALS AND METHODS

The nine freeze cores analyzed in this study were collected from Lake Turkana in 1990 and 1994 (Figure 1). Core LT90-6FC was divided into 5-cm sections in the field [9]. All of the cores collected in 1994 were transported back to Nairobi, Kenya, as frozen slabs. Cores LT94-7FC, 11FC, 14FC and 20FC were divided into 2 to 4-cm sections at the National Museum of Kenya, Nairobi, while cores LT94-6FC, 8FC, 13FC and 19FC were air freighted back to the United States as frozen slabs, where they were photographed, x-rayed, and subsampled for ^{210}Pb analyses at the Lamont-Doherty Earth Observatory.

Stable isotopic analyses were done on micrite from the cores subsampled in Kenya. Samples were sieved at $44\mu\text{m}$ to remove ostracodes, the only other carbonate of any significant abundance [10]. The residue finer than $44\mu\text{m}$ was vacuum roasted at 350°C to remove organic carbon. Carbonate samples were analyzed on a Finnigan MAT 251 with a Kiel device at North Carolina State University. Water samples were also collected from the

lake in 1994 (Figure 2), and analyzed for oxygen and deuterium isotopic composition at the International Atomic Energy Agency Laboratories in Vienna, Austria.

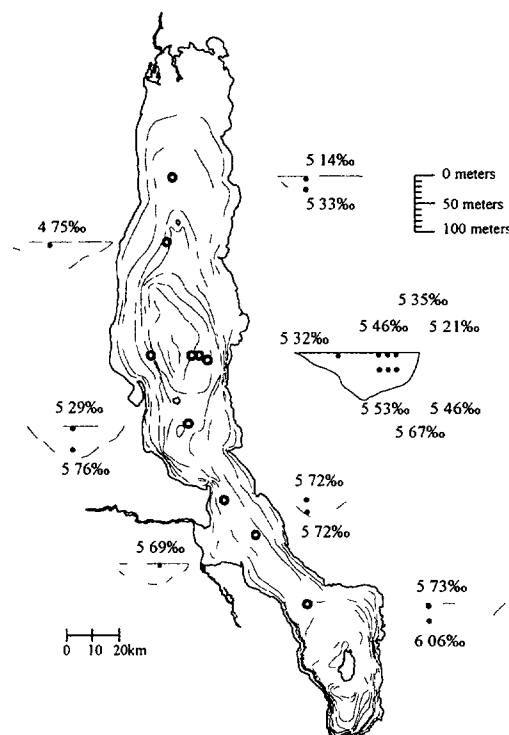


Figure 2: Isotopic composition of water ($\delta^{18}\text{O}$, SMOW) collected from Lake Turkana in 1994. (figure from Ref. [11])

3. DISCUSSION

There are strong differences in the stable isotopic composition of carbonates between freeze cores (Figure 3). Carbonates from cores taken from the central part of the lake have consistently lower $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values. Spatial variability in the isotopic composition of the carbonates (in the case of $\delta^{18}\text{O}$ values) is due either to gradients in lake water temperature or isotopic composition. The range of water temperatures implied by the $\delta^{18}\text{O}$ values of the carbonates from several of the cores, assuming equilibrium precipitation from modern Lake Turkana water (Figure 2), is 5 to 25°C warmer than modern conditions. Spatial temperature gradients of this magnitude are not observed in Lake Turkana, so the spatial variability observed in the carbonates must reflect heterogeneity in lake water composition. Although we measured some heterogeneity in water composition (Figure 2), the limited temporal extent of our sampling probably failed to capture the complete range of $\delta^{18}\text{O}$ values found in the lake.

There is a strong covariance between $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values when the data from all the freeze cores are combined ($r = 0.85$; Figure 4). The cores closest to the Turkwell and Kerio River deltas (7FC and 20FC) have the lowest $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values while cores farther from the deltas (11FC, 14FC, and LT90 6FC) have progressively higher values. The likely explanation for this observation is that relatively fresh waters, with lower $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values, is flowing out of the Turkwell and Kerio Rivers and strongly impacting the core sites which are closest to the river deltas. Unfortunately, the isotopic composition of water from these two rivers has not been measured during the peak of the flood season, therefore the full impact of water from these rivers is not known.

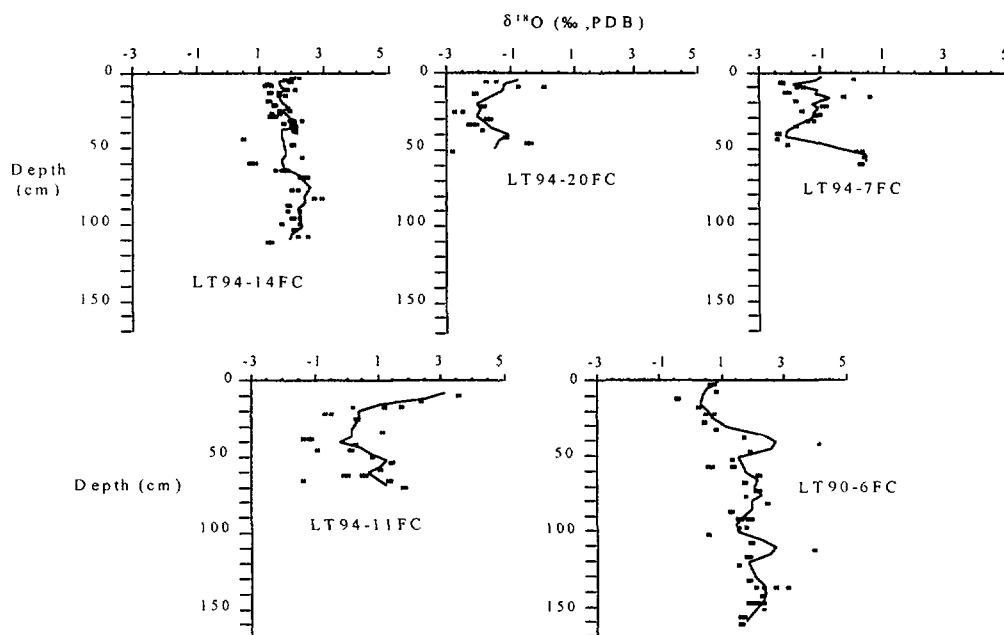


Figure 3: $\delta^{18}\text{O}$ vs. depth profiles for 5 of the freeze cores. The solid line is a 3-point running mean of the data. Cores are displayed from south to north. (figure from Ref. [8])

Changes in the isotopic composition of lake water will affect the composition of carbonate, whether it forms in equilibrium with the water or is offset from equilibrium by a fixed amount. A mass balance equation for oxygen isotopes in Lake Turkana was used to calculate lake level from calcite oxygen isotope compositions:

$$d(V\delta_{\text{lake}})/dt = Q_{\text{input}}\delta_{\text{input}} - Q_{\text{evaporation}}\delta_{\text{evaporation}}$$

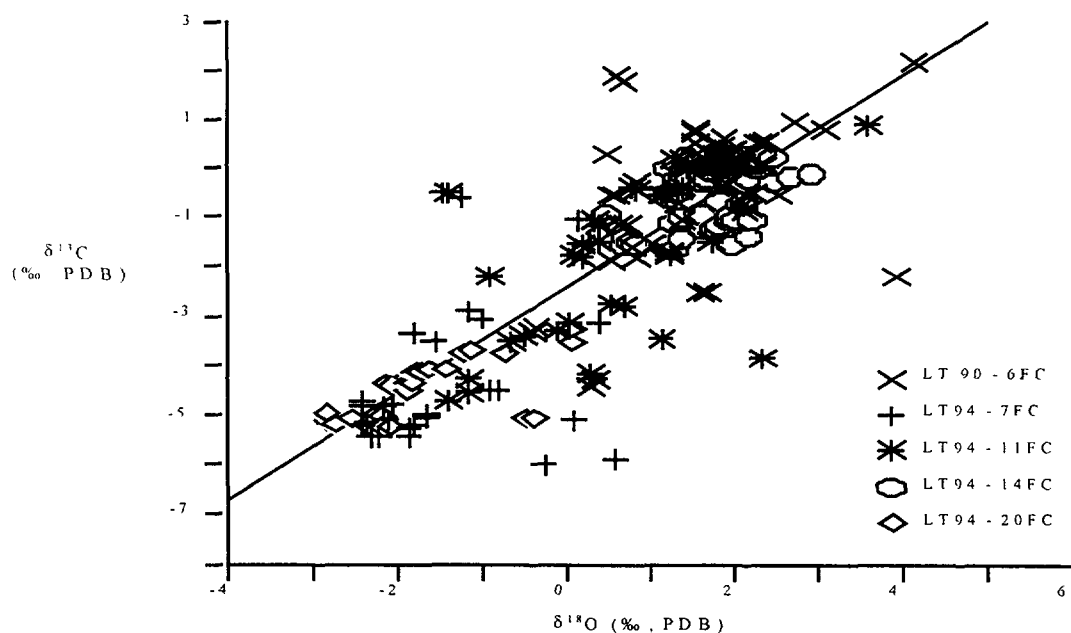


Figure 4: $\delta^{13}\text{C}$ vs. $\delta^{18}\text{O}$ for the freeze core data. Individually the freeze cores have coefficients of correlation (r values) below 0.7. Considered together the freeze core data have the relatively high r value of 0.85. R values above 0.7 have been hypothesized to be indicative of closed basin lakes [12] (figure from Ref. [8]).

V is the volume of the lake, t is time, Q is the amount of the flux, and δ is the isotopic composition of the respective flux. Using a derivation of δ evaporation [2] and climatic parameters for the Lake Turkana basin [13-14], a lake level curve for Lake Turkana was generated. Since the $\delta^{18}\text{O}$ values from the freeze cores has a large amount of spatial variability, the $\delta^{18}\text{O}$ values from the cores with viable chronologies (7FC, 11FC, and 14FC) were normalized and stacked. This stacked and normalized data set was transformed into paleo- $\delta^{18}\text{O}$ values for the lake water and substituted into a form of the mass balance equation. The lake level curve generated using this method is similar to the historical lake level curve (figure 5). Both data sets have a trend towards falling lake level and the records are, at most, 7 meters apart.

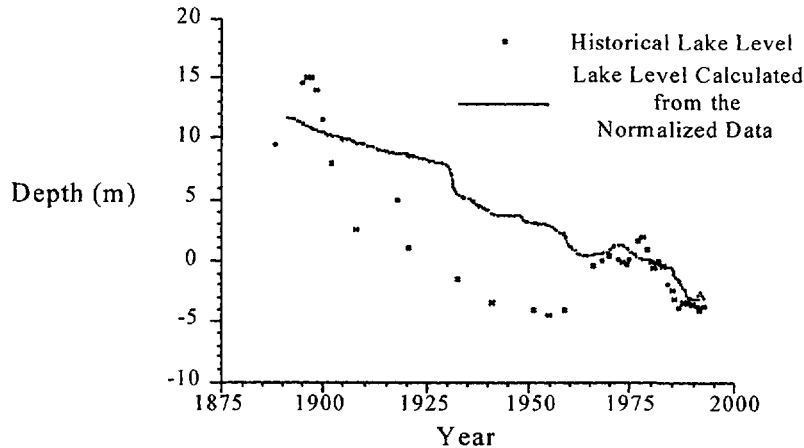


Figure 5: Depth vs. Year for the modeling results, using the normalized and stacked freeze core data compared to the historical record of lake level [15-16]. The fit between the modeled data and the historical record is remarkably high considering the spatial and temporal variability of the freeze core data. (figure from Ref. [8])

The match between the historic lake level curve and the curve generated using the normalized and stacked data is not exact, but it is much better than any lake level curve generated using non-normalized data. The poorest portrayal of the historic record, although still relatively accurate, is generated by the calculations during the earliest part of the record. This is at least partially due to the spotty data available from core LT94-14FC, the only core with carbonate of this age, and the spotty historic data during this period. The normalized data gives a surprisingly accurate portrayal of lake level from 1965 on, when all three cores are included in the stacked data set.

Part of the reason for the poor portrayal of the historical lake level record using the oldest $\delta^{18}\text{O}$ values is caused by the assumption that changes in lake level (proxied by the $Q_{\text{evaporation}}$ to Q_{input} ratio) are the only cause of variations in the $\delta^{18}\text{O}$ record. It appears that a large amount of the variation in the $\delta^{18}\text{O}$ records from the freeze cores is due to variations in $Q_{\text{e}}/Q_{\text{i}}$, but variations in other climatic parameters will also affect the $\delta^{18}\text{O}$ values of the calcite.

The cores that have been strongly affected by their proximity to sources of fresh water contribute significantly to the calculations. In addition, isotope profiles that do not explicitly track lake level still contain quantitative information about lake level. As expected large closed-basin lakes are more complex, and therefore the sediment records from them are more difficult to interpret, than those from small, closed-basin lakes. The data illustrate that a reasonably accurate record of high frequency lake level fluctuations (on the order of 100 years) can be obtained from data with a large amount of spatial and temporal variability.

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THE LAKES OF THE JORDAN RIFT VALLEY

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Abstract

This paper presents a summary of the proceedings of a workshop on the Lakes of the Jordan Rift Valley that was held in conjunction with the CRP on The Use of Isotope Techniques in Lake Dynamics Investigations. The paper presents a review of the geological, hydrogeological and physical limnological setting of the lakes in the Jordan Rift Valley, Lake Hula, Lake Kinneret and the Dead Sea. This is complemented by a description of the isotope hydrology of the system that includes the use of a wide range of isotopes: oxygen-18, deuterium, tritium, carbon-14, carbon-13, chlorine isotopes, boron-11 and helium-3/4. Environmental isotope aspects of the salt balances of the lakes, their palaeolimnology and biogeochemical tracers are also presented. The scope of application of isotopic tracers is very broad and provides a clear insight into many aspects of the physical, chemical and biological limnology of the Rift Valley Lakes.

1. GEOLOGY AND HYDROLOGY OF THE VALLEY

The Jordan Rift Valley which hosts three lakes of very different character is situated in the northern part of the East African-Syrian rift system. It developed on an active transfer fault which opened up during the late Miocene and Pliocene and has continually widened since. It was evidently connected to the ocean system for a long period, during which massive sedimentary sequences were deposited. These sediments are composed mostly of evaporites which form large diapirs, one in the southern part of the Dead Sea basin, the other in the divide between the two parts of the basin and another just south of Lake Kinneret. The evaporites are mainly rock salt. Pleistocene sediments reflect the acceleration of basin subsidence; they comprise several kilometers of lacustrine sediments. The structure of the Dead Sea basin is that of a fault bounded depression, divided internally into a number of segments by transverse faults. In the southern basin accumulation of Neogene and Pleistocene sediments probably exceeds 10 km; in the northern basin a relatively thinner cover overlies the Cretaceous sequence. The depth to basement was estimated from magnetic and gravity calculations at 8-10 km in the north and at probably 14 km in the south.

Deformation takes place mainly along the transverse and longitudinal faults leaving the intervening sediments relatively undeformed. Significant changes occur with time in the nature of deformation along the main faults. The geometry of the Dead Sea basin is probably controlled by stretching of the entire crust along its long axis. The deformation occurred wholly within the crust without the participation of the upper mantle.

The present valley constitutes an internal drainage basin of about 40,000 km²; of which the Dead Sea is the ultimate terminus. The main water carrier is the Jordan River which runs from Mt. Hermon through Lake Hula and Lake Kinneret to the Dead Sea and drains an area of

about 18,000 km². Elevation difference between the headwater and the drainage basis is about 2000 m, the distance is about 200 km, and the mean precipitation depth decreases from north to south, from 1300 mm/y at Mt. Hermon to 80 mm/y at the Dead Sea. Three lakes lie along the course of the Jordan River: the Hula at an elevation of +70 m, the Kinneret at a mean elevation of -210 m, and the Dead Sea surface is situated at about 400 m below msl.

Additional waters drain periodically directly into the Dead Sea from an additional southern drainage basin, albeit an arid one.

In addition to the large changes in water balance over geologic times, most probably primarily controlled by climate changes during the Pleistocene and early Holocene, there have been major anthropogenic influences during this century. First the drainage and channeling of the Hula region, followed by the diversion of water both from Lake Kinneret and the Yarmoukh River for consumption and irrigation both in Israel and Jordan. This resulted in a marked decrease of the volume of flow in the lower Jordan River, as well as an increase in its salinity. The latter effect is due, in no small measure, to the diversion of a number of near-shore saline springs from Lake Kinneret to the lower Jordan.

Owing to the consumptive use of water and to fluctuations in precipitation depth, the discharge of the Jordan River into Lake Kinneret declined from 560 MCM/y (10⁶ m³/y) in the 1930s and 1940s to 460 MCM/y in the 1980s and early 1990s. The outflow from Lake Kinneret dropped during that time from 530 to 50 MCM/y, while the mean volume south of the confluence of the Yarmoukh and Jordan Rivers, dropped from 980 to 180 MCM/y. The latter is the amount of water delivered into the Dead Sea.

2. THE LAKES OF THE JORDAN RIVER VALLEY

2.1. Lake Hula

The most upstream lake of the system, Lake Hula, is a good example of a strongly manipulated system. Almost completely drained around the mid-century in order to reclaim agricultural lands, it is being reflooded in recent years to re-establish a natural wetland reserve and in order to mitigate the ill effects of the dried swamp lands on the downstream river system, namely mainly massive release of nitrates and other nutrients. Geochemical studies on the re-claimed Hula wetlands is illustrating the beneficial effects of the (controlled) wetlands on the nutrient and sedimentary balance in the downstream river.

2.2. Lake Kinneret

Lake Kinneret (also known as Lake Tiberias, Sea of Galilee or Lake Genezareth), the only sweet-water lake of the region is of major economic importance (fisheries, recreation and tourism) and a source of about 1/4 of the freshwater supply for agricultural and urban use in Israel, mainly by means of the NWC (National Water Carrier). It lies approximately 210 m below msl. It measures 22 kms from north to south and 14 kms from east to west, has a surface area of about 170 square kms, a mean depth of 24 meters and a maximum depth of 43 meters. When full, the lake has a total water volume of four billion cubic meters. The climate in this region is semi-tropical with long, hot summers and relatively cold, rainy winters.

From about mid-May to Late December or early January, the lake is strongly stratified into two distinct water masses, a warm (22-30°C), well-mixed upper layer (*epilimnion*), progressively deepening from about 16 to 26 meters, and a deeper, colder (13-16°C) stratum

(*hypolimnion*). During the winter, this two-layer structure breaks down and the water masses are completely mixed.

The NWC was inaugurated in 1964. The NWC links Lake Kinneret to Israel's other water sources and thus the lake became an integral and vital element in the national water economy. Presently 400-430 million cubic meters of water are pumped annually from Lake Kinneret and flow through the NWC. An additional 100 million cubic meters are supplied to local consumers round the lake, in the Jordan Valley and on the Golan Heights. Although a major portion of this water is still used for agriculture, increasing amounts are now supplied for drinking and domestic purposes, as well as for industrial and municipal requirements. Another extremely important function of the NWC is to supply good-quality water for recharging the major underground aquifer which runs along the coast of Israel. All this explains why maintaining and, if possible, improving water quality in the lake is a matter of prime national concern.

As water began to be pumped through the NWC, two major difficulties became apparent. First, it turned out that the salinity of the lake water was sufficiently high to damage sensitive crops such as citrus and avocado. Furthermore, using this relatively high-salinity water could drastically accelerate salinization of the irrigated soils and of the coastal aquifer lying beneath them. Secondly, there were incipient problems of taste and smell and general water quality which threatened to affect the utility of the NWC. The latter consideration was particularly serious because the NWC is a single-channel system and therefore all the supply must meet drinking water standards or, at most, require only slight treatment in order to do so.

The first of these problems, salinity, was minimized by diverting several major saline inputs at the northwest of the lake into a "salt water diversion canal" which discharges into the southern Jordan. The diversion removes about 60,000 tons of salt from the lake each year. An exceptionally rainy winter in 1968-1969 also served to lower salinity and thus the chloride concentrations in the lake have fallen to about one-half their level in the late 1950s. The salt-water canal is also used to remove secondary-treated sewage from Tiberias and other settlements along the western shoreline, and a pipe network has been built to collect and transport effluents from the villages on the eastern side so that none of this pollution enters the lake.

The overwhelming majority of the salinity in the lake is due to saline springs (both on the shore and underwater) and possibly also to seepage or diffusion of salt through the bottom sediments. A major geophysical and geochemical research effort was conducted in recent years to determine the source of the salinity as well as the driving mechanism of its introduction into the lake. As part of this effort a large array of isotopic parameters were engaged, including the ^{18}O , ^3H and ^2H content of the water, ^{14}C and ^{13}C in carbonates, S isotopes in sulfates and $^{37}\text{Cl}/^{35}\text{Cl}$ as well as $^{36}\text{C}/^{35}\text{Cl}$ ratios. Rare gases, especially the $^3\text{He}/^4\text{He}$ ratio, $^{87}\text{Sr}/^{86}\text{Sr}$ as well as the $^{11}\text{B}/^{10}\text{B}$ ratio were also measured. These and the general chemical composition of brines and brackish waters were discussed in a report by Bergelson, Nativ and Bein. Their conclusion, still somewhat debatable, is that the saline groundwater appears to be a mixture between a very saline end-member and meteoric fresh groundwater. The saline end member is an intensively evaporated marine brine which evolved in an inland basin within the Rift Valley. The intensive evaporation of this brine, beyond the onset of halite precipitation, is indicated by low values of the Na:Cl and Cl:Br ratios (0.5 and 150, respectively) and the high $\delta^{11}\text{B}$ (+44‰) documented in the most saline groundwater. Gypsum precipitation decreased the sulfate concentrations in the residual

solution. The dense evaporated brine intruded the Rift Valley formations where it further evolved into Ca-chlorine brine. Its high Mg concentrations enhanced dolomitization, resulting in high Ca:Cl and low Mg:Cl ion ratios (90.33 and 0.09, respectively). Sulfate concentrations were further decreased as a result of both additional gypsum precipitation following the increased Ca concentrations and by sulfate reduction.

The original brine was later diluted by fresher water to form the Tiberias Brine. Considering the relatively low (~seawater) salinity of the Tiberias Brine with respect to that of the original brine, the latter accounts for most of salts in the Tiberias Brine and controls its ion ratios and chloride isotopes, whereas the diluting freshwater component contributed most of the water. Because of its large water contribution and relatively large bicarbonate concentrations (with respect to the original brine), the diluting freshwater component controlled the oxygen, hydrogen and carbon isotopic compositions of the Tiberias Brine. The $\delta^{18}\text{O}$ and δD compositions is relatively light (-2.45 to -1.5‰ and -18.51 to -4.2‰) with respect to seawater, respectively, and the amount of radiocarbon (5.8 to 0.4 PMC) is also low.

A second dilution stage is believed to take place during the upwelling of the "Tiberias Brine" into shallow, freshwater aquifers to form the saline springs. Fresh groundwater, circulating in these aquifers mix with the Tiberias Brine, as evidenced by the measurable tritium (0-5.3 TU) and variable radiocarbon data of the saline springs. Although most of the upward migration must be rapid, as indicated by the high temperatures (up to 60°C) and radon fluxes, much slower transport, partly by diffusion, is proposed on the basis of the depleted ^{37}Cl values (-0.7 to -0.4‰) and the presence of radiogenic helium ($^4\text{He} = 3.97 \times 10^{-5} \text{ cm}^3/\text{liter}$, $^3\text{He}/^4\text{He} = 2.053 \times 10^{-6}$) and of radium.

The spatially variable chemical and isotopic features of the saline water found in the various spring clusters around Lake Kinneret suggest not only differential dilution by fresh meteoric water, but also different evaporation levels and dolomitization intensities in the original brine end-member. The preservation of these distinct features suggest that percolation of the ancient brine at different times along the evaporation event occurred into tectonically isolated blocks.

2.3. The Dead Sea

The Dead Sea represents the ultimate, highly mineralized, terminal lake whose water balance is under extreme anthropogenic stress. The resultant drop in water level, increase in salinity and exposure of new coastal land areas, have provided the major motivation for research.

The negative water balance of the Dead Sea since the beginning of the century has resulted in a decrease in its water level by about 20 meters. This has been accompanied by various changes in the chemical and physical characteristics of the lake and its brine.

In the beginning of the century the Dead Sea was a meromictic (stratified) lake with a relatively diluted epilimnion, down to a depth of 40 meters, and an anoxic, halite-saturated hypolimnion which formed the main water body of the lake. However, the negative water balance of the lake resulted in a continuous increase in the salinity of the epilimnion, and to the deepening of the transition layer between the two water bodies. Eventually, in 1979 the Dead Sea overturned and the water column homogenized. The present hydrographic behavior of the Dead Sea is that of a quasi-holomictic lake - annual stratification develops in spring,

and is maintained throughout the summer by a stabilizing thermocline which overcomes the destabilizing halocline. Overturn takes place in autumn due to the cooling of the surface waters. This annual holomictic cycle was interrupted twice since 1979, when a diluted surface layer developed following the massive freshwater inflow into the Dead Sea during the exceptionally rainy winters of 1979/80 and 1991/92. The stratifications that developed following these winters lasted three and four years, respectively, before overturn took place again.

In 1976, following the decline in the water level, the shallow southern basin was disconnected and dried out from the main water body. Massive halite precipitation began in 1983 which, apart from a short period, has continued to the present. The halite precipitation, and the industrial activities of the potash industries south of the Dead Sea which pump out Dead Sea brine and evaporate it in evaporation ponds, have resulted in a change in the composition of the brine. This is exhibited by decreasing Na/Cl and increasing Mg/K ratio over the last four decades. The annual weight of halite that precipitated in the lake since 1983 was estimated by various calculation methods to be $>100 \times 10^6$ tons. This does not include the salts that precipitate in the industrial evaporation ponds, estimated at about 35×10^6 tons/year.

A model based on results obtained from evaporation experiments indicates that under the present conditions the rate of evaporation will gradually decrease as the salinity of the brine increases. On the basis of a simplified relationship between salinity and evaporation, it is estimated by Gavrieli, Weinstein and Yechieli that a new equilibrium between evaporation and input will be reached within 400 years at a water level of about 500 meters below MSL. At the new equilibrium level, the Dead Sea volume would have decreased to 2/3 of its present volume while its salinity and density would be about 380 g/l and 1.27, respectively. This process will be accompanied by a more halite precipitation and a decrease in Na/Cl ratio from 0.25 to about 0.1. However, the lake will not attain saturation with respect to carnallite ($\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$) which is the mineral precipitating in the industrial evaporation ponds.

The inhibiting effect of the increasing salinity on the microbial population can be seen and the lake is approaching almost total sterility. However short-lived algal blooms follow the dilution of the surface brine by winter floods. Recently Luz and Barkan of the Hebrew University found evidence also of microbial oxidation in the abyssal waters, based on the isotopic composition of dissolved oxygen and carbon-dioxide as described below.

The dramatic lowering of the water level of the Dead Sea is exposing former saline lake floor on the coastline. Studies were concerned with the hydrological and ecological consequences of this process. Studies by Yehieli et al. on the restructuring of the saltwater/freshwater interface zone are worth mention. An interesting study on the renascent plants in the newly exposed coastal zone, by Yakir and Yehieli, utilize stable isotopes to indicate that growth occurred by virtue of the discriminatory utilization of freshwater lenses in the soil column. These resulted from either floods or in zones where upwelling of fresh groundwaters occur.

Some of the up-to-date research achievements were summarized in the book "The Dead Sea: - the Lake and its Setting" (T. Niemi, Z. Ben-Avraham and J.R. Gat, editors) recently published by Oxford Press.

3 THE SALT BALANCE OF THE LAKES OF THE JORDAN RIFT VALLEY

By virtue of its topographic situation at the deepest spot in the Jordan Rift Valley, the Dead Sea can be expected to conform to the model of a terminal lake. In such a lake, all of the water influx by means of precipitation and surface or groundwater runoff is lost by evaporation. The incoming salts, whether by aeolian input into the region or those originating from weathering of soils and rocks, then supposedly accumulate in the lake. Ideally the salt inventory of the lake (Q_s) would then be expressed as $Q_s = \sum F_s C_s dt$, where F_s and C_s are the water influx and the salt concentration in this stream, respectively. Under the assumption of steady state fluxes, the age of a lake can then be determined by comparing the salt inventory to the influx rates. This idea was already proposed in the 18th century, and applied to the case of the Dead Sea by Bentor [1].

In practice one often finds less than the expected salt load in a terminal lake. This discrepancy results from the burial of evaporites in the sediments (primarily gypsum, carbonates and halite) and because of the leakage of brines into and through the banks of the lake. Another possible factor is the aeolian export of seaspray. On the other hand, an excess of salt in the system may point to unaccounted submarine springs or salt seepages as well as the dissolution of minerals from the bottom layers, such as from salt diapirs.

Evidently then, one should add two terms (each either positive or negative) to the balance equation: one which accounts for the interaction of the lake with the sediments or its banks and another relating to the aeolian transport of salt. As discussed by Imboden and Lerman [2] these terms can reverse their sign on a variety of time scales, as a lake's condition changes.

In the case of the Dead Sea, three salient features dominate and determine the unique characteristics of the system:

- i) its position at the absolutely lowest elevation of the entire region;
- ii) the steep flanks bordering the Rift Valley, which limits the chance of aeolian export of salt from the region;
- iii) the varying water supply, which results in wide fluctuation of the water level of the lake and concurrently in changes of salinity and in the degree of saturation of halite in the Dead Sea brine. These were extreme when going back in time; the extent of the Pleistocene precursor to the lake, namely Lake Lisan, reached as far north as present-day Lake Kinneret (and its elevation about 200 m above the present level of the Dead Sea) and in the geological past there is evidence for a connection to the ocean, the area functioning as a lagoony system.

The obvious conclusion to be drawn from the first of these features is that an irreversible escape of brine from the lake and its coastal environment is not possible. However, due to the large fluctuations in lake level, a reversible salt flux associated with the bank storage, acting on a wide range of time scales, complicates the simple book-keeping for the system. For example, most of the salt springs near the Dead Sea shore are the result of flushing of the brines from the coastal area and saltwater - freshwater interface zone. The salinization of waters of Lake Kinneret (which is a major concern in the freshwater supply of Israel), is apparently due to such a reverse salt flux, bringing back brines from a pre Dead-Sea lake systems in the Rift Valley. The to-and-fro salt movement, which of course also modifies

the chemical character of the brine through rock-water interaction, appears to be the most dominant term of the salt balance.

As shown in the work of Shatkay et al. [3] the salinity on the Dead Sea shores (which derives both from coastal sea spray and newly exposed saline sediments) is, by and large, washed back into the sea unlike the situation for more open lakes, (such as Mono Lake [4]).

The conclusion to be drawn is that, in a way, the Dead Sea and its sedimentary sequence indeed functions as the ultimate terminal lake; this property is however realized on a very long (geological) time scale, with shorter term fluctuations of its salt content due to their temporary storage in adjoining formations.

In the final analysis, the major long term and irreversible losses of salinity for the Dead Sea system is of anthropogenic nature, resulting from the mineral exploitation of the Dead Sea works (in the form of potash, magnesium and bromine compounds), and the salinity pumped with the freshwaters diverted from the Jordan River watershed by the National Water Carrier and other irrigation schemes.

4 THE ISOTOPIC PALEOLIMNOLOGY OF THE THREE LAKES OF THE JORDAN RIFT VALLEY

The flow of the Jordan River connects three lakes: Lake Hula, Lake Kinneret and the terminal Dead Sea. These lakes differ in elevation, water residence time, salinity level and characteristic geochemical and biological features. The prevailing environmental climatic conditions are also different to some degree.

The stable carbon and oxygen isotopic compositions of the carbonate formed within the lake waters and stored in the sediments, bear the record of paleolimnological evolution and climatic variations, respectively. The isotopic variations of carbon-13 and oxygen-18 have been measured in the sediments of the three Jordan Rift lakes. The imprint of regional climatic variations has been found in coeval segments of the sedimentary column (dated by ^{14}C) of the three lakes. The ^{14}C dating also revealed that the ratio of the ^{14}C activities in coexisting carbonate and organic phases might be an indicator for the degree of aridity in the lake's environment. The ratio ^{14}C carbonate/ ^{14}C organic is much larger in the more humid conditions of Lake Hula and Lake Kinneret than in the arid environment of the Dead Sea. [5]

The carbonate- ^{13}C data indicate that productivity has increased gradually in Lake Hula from about 17000 years BP to present and in Lake Kinneret from 5100 years BP (the deepest available sediment section) to present [6]. In the Dead Sea, the ^{13}C data suggest a higher stand from about 6700 years BP to 4500 years BP; the highest lake level was about 5500 years BP.

There is a remarkable agreement between the evidence provided by the ^{18}O data of lakes Hula and Kinneret: warmer conditions prevailed from 5100 years to 2700 years BP, warmer than during the period 1200 years BP to 150 years BP [7,8]. In Lake Hula the track of the warmer period could be followed until about 8000 years ago (peaking at about 5300 years BP). The coolest period revealed by the ^{18}O data in Lake Hula was from 17000 to 11000 years BP.

Summarizing the isotopic evidence of the three lakes: warmer climatic conditions than nowadays prevailed from about 8000 years BP to about 3000 years BP. Between 6700 and 4500 years BP and peaking at about 5500 years BP, the climate was also more humid.

5 BIO-GEOCHEMICAL TRACING OF LIFE IN THE DEAD SEA

Bio-geochemical tracers suggest that bacterial life may exist in the deep water mass of the Dead Sea. These tracers are the concentration of total dissolved carbon dioxide (TCO_2), carbon isotopic composition of TCO_2 ($\delta^{13}\text{C}$), the ratio of dissolved oxygen to dissolved argon (O_2/Ar) and the isotopic composition of the dissolved oxygen ($\delta^{18}\text{O}$).

Unusual flooding during the winter of 1991/92 and freshening of the upper waters of the Dead Sea, resulted in a major algal bloom and in a very stable pycnocline that prevented ventilation of the hypolimnion. Following this flooding we have monitored TCO_2 , $\delta^{13}\text{C}$, O_2/Ar and $\delta^{18}\text{O}$ in a station located at the center of the lake. For several months after the formation of the stable pycnocline these parameters recorded changes in the deep water. In March 1992, TCO_2 was 852 $\mu\text{mol/kg}$, and in December 1992 it rose to 867 $\mu\text{mol/kg}$. During the same period $\delta^{13}\text{C}$ decreased from 1.6‰ to 1.2‰, and measurements of O_2/Ar ratio indicate lowering of the dissolved oxygen concentration. Thus the addition of TCO_2 seems to be due to oxidation of organic matter. From mass balance of carbon and its isotopes this change can be calculated to result from the addition of 15 $\mu\text{mol/kg}$ of TCO_2 with $\delta^{13}\text{C}$ of -21‰. Based on this isotopic composition the source of this added carbon is not likely to be oxidation of sinking plankton from the algal bloom, because the $\delta^{13}\text{C}$ of the latter is -13‰. The source of carbon may be detrital organic matter derived from the flood water or dissolved organic matter. The amount of labile organic matter was limited because after December 1992 the deep water did not show any significant change. This suggests that a limited amount of labile organic matter with $\delta^{13}\text{C}$ of -21‰ was introduced to the Dead Sea during the floods, and rapid oxidation consumed all the labile material over a period of several months.

The mechanism of this oxidation is uncertain, but our new measurements of $\delta^{18}\text{O}$ in the deep water is about 7‰ higher than at the surface. This enrichment in the heavy isotope is due to isotopic fractionation that took place during oxidation. The magnitude of this fractionation is calculated from the shift in $\delta^{18}\text{O}$ and from the change in the O_2/Ar ratio as -18‰. This isotopic discrimination is typical of bacterial oxygen consumption. Our preliminary results thus suggest that bacteria were present in the deep water of the Dead Sea following the floods of 1991/92. Whether such bacterial activity is more common in the Dead Sea and occurs in holomictic years after normal winter floods, is an open question. More research on oxygen concentration and its isotopic composition is necessary before we can solve this interesting problem.

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