

## NEWS

A Quarterly Newsletter of the Isotope Hydrology Section

#### **CONTENTS**

Isotope techniques in lake water studies	3
Lake Titicaca : history and current studies	6
The evaporation pan technique revisited	9
Groundwater renewal in water scarce areas	11
Isotope response to dynamic changes in groundwater systems due to long- term exploitation	11
Isotope Hydrology Calendar	11
Geothermal energy resources - Results and achievements of regional project RAS/8/075	13
Isotopes for improved drinking water resources management	13
Workshop on isotope data inter- pretation and integration in site- conceptual models	13
2 <sup>nd</sup> Interlaboratory comparison for deuterium and oxygen 18 analysis of water samples	14
Challenges and new techniques for light element stable isotopes	15

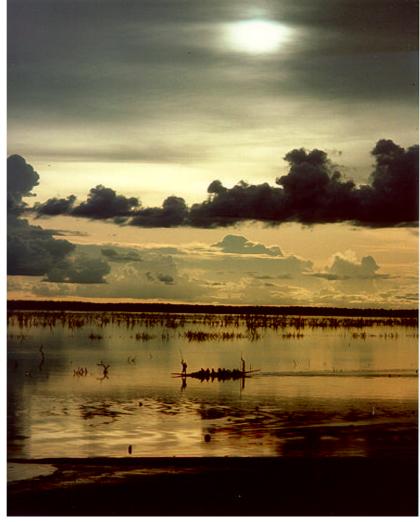


Photo credit: Laurence Gourcy/IAEA

Selingue lake, Mali



15

Issued by the

### **International Atomic Energy Agency**

Vienna, Austria



#### **EDITORIAL**



Since its inception in 1997, Water and Environment News has been well received by its readers and has improved the dissemination of current news and developments in Isotope Hydrology in our Member States. It also appears to capture a desirable readership, as there is an increased interest expressed for participation in upcoming coordinated research programmes and other activities.

We recognize that publication of the 3<sup>rd</sup> issue of 1999 of the News has been delayed. This delay resulted from key staff changes in this past year. Although periodic staff rotation is an essential component of the Agency's policies, there are occasions when some schedules are interrupted. We intend to minimize these interruptions as much as possible.

After a nearly 10 years tenure, the last five as Section Head, Dr. Klaus Froehlich retired from the Agency at the end of July. During Klaus' tenure, the Section's contributions to the Agency's technical cooperation programme were better recognized and Isotope Hydrology was recognized by the Member States as a significant priority programme of the Agency. We wish Klaus a very happy and productive retirement and look forward to benefiting from his advice from time to time.

I am privileged to have been selected to replace Klaus as the Section Head. Although it is a tough act to follow, I hope to successfully lead the Section in increasing the role of Isotope Hydrology in water resources management and in advancing the underlying science.

This issue of the News focuses on isotope studies related to lakes. Physical and bio-geochemical processes occurring at and below the surface of lake water influence lake - atmosphere interactions, surface and groundwater hydrology, and climatic archives in lake sediments. Dr. L. Gourcy has provided a review of some of the Agency's activities in the development and application of isotope techniques to study lake processes. Dr. J. Gibson and Dr. T. Edwards from the University of Waterloo describe an improved technique for measuring pan evaporation rates. Dr. M. A. Paredes Riveros from the Proyecto Especial del Lago Titicaca (PELT) Puno, Peru, and Dr. R. Gonfiantini from the Istituto di Geocronologia e Geochimica Isotopica del CNR, Pisa, Italy, describe the use of multiple isotope tracers to study the dynamics of Lake Titicaca. I would like to thank all our colleagues for giving so generously of their time to improve the quality of the News.

On behalf of myself and the Section, I wish you all a very happy New Year!

**Pradeep Aggarwal** Head, Isotope Hydrology Section

#### Contact Us

Isotope Hydrology Section
International Atomic Energy Agency
P.O. Box 100, Wagramer Strasse 5
A-1400, Vienna
AUSTRIA
Tel. +43-1-2600 + ext
Fax: +43-1-26007

Mr. Pradeep Aggarwal, Section Head, ext. 21735 e-mail: P.Aggarwal@iaea.org

Mr. Edmundo Garcia-Agudo, ext. 21739 e-mail: E.Garcia-Agudo@jaea.org

Mr. Cheikh B. Gaye, ext. 21733 e-mail: C.B.Gaye@iaea.org

Mrs. Jane Gerardo-Abaya, ext. 21742 e-mail: J.Gerardo-Abaya@iaea.org

Mrs. Laurence Gourcy, ext. 21734 e-mail: L.Gourcy@iaea.org

Mr. Manfred Groening, ext. 21740 e-mail: M.Groening@iaea.org

Mr. Yucel Yurtsever, ext. 21732 e-mail: Y.Yurtsever@iaea.org

Visit Us on the Internet

http://www.iaea.org/programmes/ripc/ih/index.html

#### ISOTOPE TECHNIQUES IN LAKE WATER STUDIES

#### Scientific Scope

Lakes in a variety of environments (tectonic including rift, glacial, coastal, volcanic and fluvial) cover a significant portion of the surface area of the continent. Freshwater lakes are among the most easily exploitable freshwater resources. Lakes are also recognized as major sedimentological features in which stored material can be used to study recent climate and pollution evolution. To adequately preserve these important landscape features, and to use them as climatic archives, an improved understanding of processes controlling their hydrologic and biogeochemical environments is necessary. The studies of lake processes can be separated in three categories, with specific isotope applications (Table 1):

## IAEA activities related to the study of lakes

#### **Research and Development**

The first Advisory Group Meeting (AGM) on the application of nuclear techniques to study lake dynamics was held in 1977 at the IAEA Headquarters in Vienna. Twenty-four specialists reviewed current research trends in order to obtain indications and quidelines for future activities in the field of isotope limnology. In 1992, a joint UNESCO/IAEA consultants' meeting assessed the new state of the art of isotope techniques in limnological studies and recommended a new Co-ordinated Research Programme. This Co-ordinated Research Programme 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. 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 to better understand the dynamics of these systems under growing anthropogenic influence. A compilation (TECDOC) of the results of this CRP is in press and is expected to be available in the year 2000.

Further improvement of the techniques used for lake studies is continuing in many laboratories. For water balance studies, sampling of water vapour to determine the evaporation factor is difficult to carry out in remote areas where no power supply is available. Development and testing of new techniques for water vapour sampling are on-going at the IAEA and in some other European laboratories. The tritium-helium isotopes and chlorofluorocarbon concentration meth-

ods have recently been used in many studies to determine the mixing processes and the apparent age of lake water. For the first time in 1999, such techniques were tried in Lake Titicaca where water balance parameters are difficult to obtain. These developments are expected to provide a better understanding of the lake processes.

#### Technical assistance on isotopic lake studies

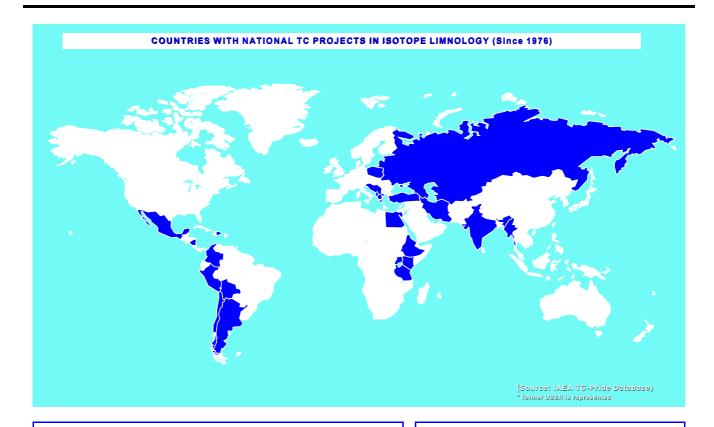
The support of the IAEA to its Member States in lake studies, through the Technical Cooperation Programme, is often related to the protection of the water reservoirs and to understanding the water dynamics and contamination problems (Table 2). Lakes representing local or regional interests have been studied, like lakes Mogan and Eymir in Turkey, Beseka in Ethiopia, Manzala in Egypt, Titicaca in Bolivia and Peru, Prespa in the Republic of Macedonia, Greece and Albania, and Chapala in Mexico.

Project NIC/8/010 on the study of the water balance of Lake Xolotlan was of particular interest for the possibility of determining underground components (groundwater inflow and outflow rates). The water stable isotopes were used successfully together with pollen, <sup>137</sup>Cs and <sup>210</sup>Pb of the bottom sediment. Artificial tracers have been used in various countries (Chile, Turkey) to study seepage flow, to determine the turnover time in lakes, and to identify the possible pollution path.

Another important problem encountered in lake system is the water level variations. The Caspian Sea is the world's largest closed basin. The fact that the drainage basins of its major tributaries (Volga, Ural..) are located in humid climatic regions, whereas the Sea is in the semi-arid zone, makes the Caspian Sea sensitive to hydroclimatic changes. This climatic sensitivity is evidenced above all, in the continuous fluctuations of the sea level. Its rapid rise (about 2.25 metres since 1978) is causing great concern to all five riparian countries: Azerbaijan, Iran, Kazakhstan, Russia and Turkmenistan. Despite many years of study, knowledge of the causes of the Sea's water-level rise and fall is still limited, although it has been demonstrated that the water budget fluctuations are likely climatically induced. A regional West Asian project (RAW/8/004) provided support for the use of isotopic techniques in tackling sea level rise and its negative consequences on the economies of the riparian countries.

On the other hand, Lake Beseka in Ethiopia presents the particularity of having extended at an astounding rate for three decades. The continuous rise of the lake level creates problem for highways,





#### Table 1: Role and application areas of isotopes in limnology

Lake Budget

\* evaporation rate estimation

- <sup>18</sup>O, <sup>2</sup>H, <sup>3</sup>H, <sup>36</sup>Cl

\* precipitation - <sup>18</sup>O, <sup>2</sup>H, <sup>3</sup>H

underground and subsurface inflow and outflow, origin of water - <sup>18</sup>O, <sup>2</sup>H, <sup>3</sup>H, <sup>37</sup>CI, <sup>87</sup>Sr/<sup>86</sup>Sr

Lake Dynamics

\* horizontal and vertical mixing rates, transit time and water veloc-

ity

- artificial tracers; <sup>3</sup>H - rare gases; <sup>3</sup>He/<sup>4</sup>He, <sup>20</sup>Ne, <sup>222</sup>Rn - <sup>226</sup>Ra/<sup>222</sup>Rn

- <sup>18</sup>O, <sup>2</sup>H, <sup>3</sup>H

\* apparent age/time of segregation of deep water from the atmo

sphere

- <sup>3</sup>H/<sup>3</sup>He, <sup>36</sup>Cl - freons (CCl<sub>2</sub>F<sub>2</sub> and CCl<sub>3</sub>F)

\* redox processes and recycling carbon and lake ventilation - <sup>13</sup>C, <sup>14</sup>C in DOC and DIC, <sup>3</sup>H \* sedimentation rate and migration of sediments on the lake floor

(sediment dating)  $-^{210}$ Pb,  $^{137}$ Cs,  $^{14}$ C,  $^{32}$ Si,  $^{10}$ Be, U/Th series

- <sup>13</sup>C and <sup>18</sup>O of carbonates and dissolved water

\* migration of chemical species in sediments and the exchange of different substances between sediments and overlying water

- artificial tracers <sup>3</sup>H

- anthropogenic radionuclides;  $^{90}\rm{Sr},\ ^{137}\rm{Cs},\ ^{144}\rm{Ce},\ ^{239}\rm{Pu}$  - natural radionuclides;  $^{7}\rm{Be},\ ^{40}\rm{K},\ ^{210}\rm{Pb}$ 

Contamination

<sup>34</sup>S

- <sup>15</sup>N, <sup>18</sup>O

Paleolimnological investigation

reconstructing hydrological conditions; <sup>18</sup>O, <sup>13</sup>C
 ice formation; <sup>18</sup>O, <sup>2</sup>H

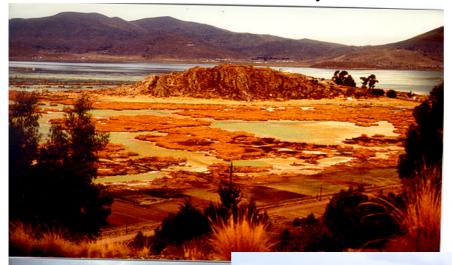
#### Table 2: IAEA-ongoing TC projects related to lake studies

Country	Title	started
Turkey	Study of lakes using isotope techniques	1993
Nicaragua	Evaluation of anthropogenic impact on Lake Xolotlan	1995
Peru and Bolivia	Isotopic and hydro- chemical study of the Lake Titicaca	1997
Turkey	Nuclear techniques for lake and marine pollution studies	1997
Ethiopia	Use of isotopes in the study of Lake Beseka	1997
Colombia	Hydrodynamics of Lake Tota and their effect on pollution	1999
Macedonia Greece Albania	Study of the Prespa lake using nuclear and related techniques	1999



railways and farm lands. Due to high salinity and fluoride concentration, waters of this lake are not considered potable. Stable water isotopes, tritium and carbon-14 of dissolved inorganic carbon were used to provide conclusive evidence that the lake level rise occurred due to a decrease in the lake outflow. This outflow decrease resulted from an increase in the groundwater elevation to the south and east of the lake, most probably due to increased irrigation return over the last three decades.

#### Laurence Gourcy



The highly contaminated Puno Bay (photo credit : L. Gourcy/ IAEA)

Serma dam, Yogyakarta, Indonesia View of the artificial lake. (Photo credit: E. Garcia-Agudo/IAEA)



Serma dam, Yogyakarta, Indonesia Discharge gauging with artificial tracers. (Photo credit: E. Garcia-Agudo/ IAEA)



#### LAKE TITICACA: HISTORY AND CURRENT STUDIES

From the early Quaternary, the Altiplano, the flat region at about 4000 m a.s.l. in Peru and Bolivia between the eastern and western Andean Cordilleras, was occupied by lakes, in shape and extent different from the present ones. The history of these lakes is documented by lacustrine sediments.

After the end of the last glaciation, during the Holocene, the Lake Titicaca attained its present shape, at a mean altitude of 3810 m a.s.l., a total surface of 8400 km<sup>2</sup>, and a volume of 930 km<sup>3</sup>. It consists of three main water bodies, the largest (approx. 6500 km²) and deepest (288 m) of which is by far the Lago Mayor in the North, mainly in Peruvian territory. The Lago Menor (approx. 1400 km<sup>2</sup>) in the South, with a depth of 20-30 m, is mostly located in Bolivia and connected to the Lago Mayor through the Tiquina Strait which is 850 m wide. The third lake region is the Bahia de Puno, a large (approx. 500 km<sup>2</sup>), shallow, highly contaminated bay in front of the town of Puno on the western coast of Lago Mayor.

Lake Titicaca is the major water source for about 1,000,000 people living in the lake region. In the native tradition the lake is consi-dered a gift of god, and is invoked by riparians as father of life.

#### Water balance of Lake Titicaca

As in all closed lakes, the water balance of Lake Titicaca is unstable, as indicated by the lake level oscillations of up to 5 m recorded in the current century. The minimum level (3807 m a.s.l.) was attained during the long drought of 1940-1945, and the maximum level (3812 m a.s.l.) was reached in 1987 after some rainy years. It is therefore of interest to briefly discuss here the water balance of Lake Titicaca. In fact, a good assessment of water inflow and outflow is of paramount importance for the lake water management.

Direct precipitation over the lake

provides about 55 % of the water inflow. On the Altiplano, precipitation mainly occurs from December to March, in correspondence with the astronomic summer and the southern shift of the ITCZ (Intertropical convergence zone). The yearly precipitation amounts to about 700 mm around the Lake Titicaca, and decreases to about 400 mm in the South at the latitude of the town of Oruro, and to 200 mm in the salares (salt plains) region. Rains are more abundant on the lake where they range from 800 to 1400 mm/a: this is possibly an indication that part of the water removed by evaporation returns to the lake as rain.

Rivers and streams provide about 45 % of the water inflow to Lake Titicaca, i.e. about 20 % less than direct precipitation, and almost the whole salt inflow. The major rivers are Rio Ramis (mean discharge 74 m<sup>3</sup>/s), Rio Coata (47 m<sup>3</sup>/s), Rio llave (38 m<sup>3</sup>/s), Rio Huancané (19 m<sup>3</sup>/s), Rio Suches (11 m<sup>3</sup>/s), Rio Keka, all flowing into the Lago Mayor; and Rio Tiwanacu which flows in the Lago Menor. The discharge varies largely in the course of the year, from practically zero during the dry season up to 10 times the average discharge in the rainy season.

Diffuse groundwater leakage into the lake from coastal aquifers is believed to represent a negligible term of water balance.

Evaporation from the lake is strong and accounts for more than 95 % of the water losses. Data provided by Class A evaporation pans range from about 2000 mm/a at Suana Island and Puno, to 1300 mm/a at Conima and Copacabana and 1200 mm/a at Isla del Sol. However, these evaporation data are affected by the pan conditions and temperature variations, which may differ considerably among stations. Therefore, it is difficult to assess the lake evaporation rate with sufficient accuracy from these data.

Water is removed by Rio Desaguadero (literally: river which removes water) from the Lago Menor, which accounts for the missing 5 % of water losses. Rio Desaguadero works as an overflow for the lake and helps to reduce the lake level changes. It flows towards the South across the Bolivian Altiplano and after 400 km reaches the Lake Poopó (3686 m a.s.l.), south of Oruro; the excess water ends up in the south-western salar de Coipasa (3657 m a.s.l.). With its limited discharge (mean value 30 m<sup>3</sup>/s after collecting water from small tributaries all the way from Lake Titicaca to Lake Poopó), the Rio Desaguadero is the most important water resource for the arid Bolivian Altiplano.

Evaporation is therefore the largest water balance term and possibly the one which shows the least interannual variability. Unfortunately, evaporation is also the most difficult parameter to measure with good accuracy.

# The Autoridad Autónoma Binacional del Lago Titicaca (ALT) [Binational Autonomous Authority for Lake Titicaca]

After the strong drought which struck the Altiplano in summer 1982-1983 - the rains were less than the half of the average amount, in a possibly fortuitous coincidence with a strong El Niño event – the Peruvian Government established the Proyecto Especial del Lago Titicaca (PELT), with Headquarters in Puno, with the general task of fostering studies and activities leading to a better assessment, exploitation and management of the resources of the region, including farming, cattle breeding, fishery, water resources, etc.

About the same time the preparation of a Binational Master Plan for water resources management and protection-prevention of floods, started with the support of the European Community. In the following year the Governments of Peru and Bolivia established the Autoridad Autónoma Binacional del Lago Titicaca (ALT) with Headquarters in La Paz, Bolivia. PELT became the executive arm of ALT and was converted into a binational body. The zone of activity was extended to the whole Lake Titicaca basin which has a surface of 144,000 km2 including the Bolivian Altiplano. Among the PELT undertakings, worthy of mention is the creation of the lake research centre in Chucuito, about 20 km South-east of Puno.

## The IAEA Technical Cooperation Project RLA/08/022

In December 1997, the International Atomic Energy Agency launched the Technical Cooperation Project RLA/08/022 for the application of isotope techniques to the investigation of Lake Titicaca, for which ALT and PELT were the major counterparts. Other important counterparts were the Instituto Peruano de Energia Nuclear (IPEN) in Lima and the Instituto de Investigaciones Químicas (IIQ) of the Universidad Mayor de San Andrés in La Paz. The major objective of the project was to improve the lake chemical and isotopic balances in order to better assess the water resources available from the lake. This objective implied the organization of an extensive network of stations for sampling the lake and its major tributaries, precipitation, groundwater, and the execution of experiments to improve the evaporation estimate. The sampling network and frequency were established in 1997, it includes 18 lake sites to be sampled biannually at various depths, 9 rivers and 11 precipitation stations for monthly sampling, and a number of wells and springs for groundwater sampling.

The activities carried out to present with the IAEA support are summarized below.

1. About 800 water samples were collected and their chemical and isotopic composition determined. A first assessment of chemical and

isotopic results is being made. It would be desirable, however, that sampling and measurements continue for some years in order to obtain statistically meaningful data.

- 2. The PELT boat was equipped with a new system for deep water sampling by Nansen bottles and with probes to measure water temperature and conductivity at depth.
- 3. A new evaporation pan was constructed, in which the water temperature is fixed by using the lake water as thermostatic fluid. The energy for the lake water circulation pump is provided by solar panels. The whole system is now installed and tested in the Taquile island.
- 4. The equipment of the Instituto de Investigaciones Químicas was upgraded and strengthened with a new ion chromatograph to cope with the high number of chemical analyses to be done. Intercalibration with the chemical laboratory of the Istituto di Geocronologia e Geochimica Isotopica (Pisa) is going on.
- 5. In April 1999, a Regional Course on Isotope Limnology was held in Chucuito on the Lake Titicaca, which was attended by scientists and technicians from Columbia, Cuba, Mexico, Nicaragua, and Venezuela, in addition of those from Peru and Bolivia.
- 6. Lake samples were taken for determining the freon concentration deriving from dissolution of anthropogenic freon present in the atmosphere. Freon concentration is determined by gas chromatography at the IAEA Isotope Hydrology laboratory.
- 7. Various fellowships have been awarded and the training for staff will continue in 2000.

## Preliminary short discussion of the Lake Titicaca data

Isotopic and chemical data on Lake Titicaca, obtained within the frame of the IAEA Technical Co-operation project RLA/08/022 are accumulating, and a preliminary, qualitative interpretation can be attempted. We summarize below the major observations and conclusions, and indicate activities to continue or initiate.

Closed lakes, where the major fraction of the inflowing water is removed by evaporation, exhibit a significant enrichment in heavy isotopes. This is due to the fact that the isotopically light water molecules (<sup>1</sup>H<sub>2</sub><sup>16</sup>O) evaporate from the liquid surface at higher rate than those containing heavy isotopes (<sup>2</sup>H or <sup>18</sup>O), the concentration of which increases in the residual liquid phase. Therefore, Lake Titicaca water, like all closed lakes, is enriched in heavy isotopes. In particular, the Lago Mayor is enriched by about 60 ‰ in <sup>2</sup>H and 12 ‰ in <sup>18</sup>O with respect to rivers and precipitation feeding the lake. Due to the large size and depth, and the relatively long residence time of water, the isotopic and chemical composition of the Lago Mayor is very uniform and constant in time.

A further enrichment of about 10-20 ‰ in <sup>2</sup>H and 2-3 ‰ in <sup>18</sup>O is observed in water of Lago Menor with respect to the Lago Mayor, accompanied by a salt concentration and conductivity increase of about 20-30 %. The isotopic and chemical composition of the Lake Menor is less stable and uniform than that of Lago Mayor, due to the shallow depth and short residence time of water. Isotopic and chemical values similar to those of Lago Mayor are found in the Tiquina Strait, while intermediate values are observed at the sampling site closest to the Strait in the Lake Menor. This indicates that the water movement is essentially unidirectional from the Lago Mayor to the Lago Menor, and there is no significant return of water from the Lago Menor.

On the contrary, the bulk of Puno Bay water is isotopically and chemically almost undistinguishable from the Lake Mayor, indicating that the water moves in both directions, i.e. from the lake into the bay and vice-versa. The identification of lake water major circulation patterns is important not

only for making water balances but also for predicting the contaminant dispersion and fate.

In all cases, the lake is isotopically quite different from groundwater in coastal aquifers (typical values vs. V-SMOW:  $\delta^{18}O$  –15 ‰ and  $\delta^2H$  –120 ‰), where in principle significant lake water contributions could be easily identified.

As already said, the isotopic and chemical composition values are quite uniform throughout the whole Lago Mayor indicating that the lake is vertically and horizontally well mixed. Thus, the application of models based on the isotopic and chemical material balances is quite straightforward.

More difficult is the estimate of mean values of input waters, and in particular the mean isotopic composition of rains and rivers and the chemical composition of rivers. Large variations occur for the rain isotopic composition as well as for the river, in spite of the fact that chemistry and isotopic composition of rivers are to some extent buffered by groundwater. This may require a long period of observation, in order to fully understand the processes governing the isotopic and chemical variations as a function of river discharge. To this aim, the sampling frequency may need to be increased during floods. Generally speaking, the design, installation and management of the sampling network may need to be revised on the basis of the acquired experience.

Evaporation rate is the major unknown in the Lake Titicaca balance. Evaporation experiments will be carried out in the special evaporation pans being built for the project (one is already installed in the Taquile Island). The scope is to establish the steady state isotopic composition of the evaporating water, and from this to contribute to assessing the characteristics of the evaporation pans for determin-

ing the evaporation rate. The new evaporation pans, when available in sufficient number, will hopefully contribute to reduce the current discrepancies between measurements carried out at different lake stations, thus improving the reliability of evaporation rate measurements.

## Marco A. Paredes Riveros<sup>1</sup> & Roberto Gonfiantini<sup>2</sup>

(1) PELT, Puno, Peru(2) Istituto di Geocronologia e Geochimica Isotopica del CNR, Pisa, Italia

For more information see C. Dejoux and A. Iltis (Editors): Lake Titicaca. A Synthesis of Limnological Knowledge, Kluwier Academic Publishers, Dordrecht, 1992.



Meteorogical station in Taquile Island, Lake Titicaca (Photo credit: PELT)

ALT/IAEA joint Course on Isotope Limnology, Chucuito, Peru, 1999 Openning ceremony (Photo credit: PELT)



# THE EVAPORATION PAN TECHNIQUE REVISITED: OLD THEORY AND A NEW APPLICATION FOR TIME-WEIGHTED SYNOPTIC TRACING OF THE ISOTOPIC COMPOSITION OF ATMOSPHERIC VAPOUR

Reliable and consistent characterization of the stable isotope composition of atmospheric water vapour and its temporal variability are important prerequisites to the wider application of isotope mass balance methods in atmospheric and water balance studies, at scales ranging from the typical atmospheric general circulation model (GCM) gridsquare domain down to and including field-based studies conducted in small watersheds or at points near the ground surface. Precipitation sampling conducted within the WMO/IAEA Global Network for Isotopes in Precipitation (GNIP) and affiliated national networks has made significant contributions to our understanding of temporal and spatial variations in the isotopic composition of atmospheric moisture using the equilibrium assumption, i.e., that the isotope distribution in precipitation is an "equilibrium proxy" for that in vapour, based on assumed temperature-dependent equilibrium isotope exchange effects. However, because precipitation predominantly occurs as discrete events separated in time, especially in arid or seasonally-arid climates, liquid-phase sampling may not provide a good time-weighted estimate of vapour-phase isotopic composition, nor does it provide information on changes occurring between precipitation events. This is further complicated by uncertainty in the relation between cloud temperature and climatological temperature, which is difficult to ascertain without specific knowledge of the atmospheric boundary layer structure. Conversely, improved understanding of the isotopic relations between precipitation and vapour could potentially provide important hydroclimatological insight, for example yielding clues about the nature and causes of variations in the slope of local evaporation lines in  $\delta^{18}O - \delta^2H$ space, or providing information for evaluation of atmospheric feedback or throughput in coupled evaporative systems (e.g. Gat and Bowser 1991).

Routine sampling of atmospheric water vapour using cryogenic traps has not been widely adopted in field studies, primarily due to logistical constraints, and it has rarely been integrated within precipitation sampling networks. Moreover, field-based sampling campaigns are commonly of rather limited duration, yielding short-term data sets that may have limited applicability at water balance timescales or may be poorly suited for meaningful comparison with records of precipitation isotope composition. Challenges also exist to design efficient trapping systems, because of the potential for fractionation arising from incomplete vapour recovery.

Field work in remote areas of continental northern

Canada, an arid region that is typically characterized by 15-20% wetland area because of underlying permafrost, has prompted development of a new approach for characterizing the isotopic composition of vapour-phase atmospheric moisture and its variability. The method employs conventional evaporation pans and is especially suitable for use in water balance studies of lakes at local to regional scales. Due to the pronounced seasonality of precipitation, proportionately large snowmelt input and short thaw season, lakes in the region rarely attain isotopic steady state, but instead often display systematic seasonal enrichments and spatial trends that are strongly dependent on the shifting isotopic composition of local atmospheric vapour.

Intensive experiments (Gibson *et al.* 1999) have demonstrated that five- to ten-day flux-weighted records of the stable isotope content of ambient atmospheric vapour can be obtained through careful monitoring of the isotope and mass budgets of evaporation pans, coupled with the well-known layered resistance model of Craig and Gordon (1965). This conclusion is reinforced by successful use of pan-derived vapour  $\delta^{18}{\rm O}$  and  $\delta^2{\rm H}$  values in a detailed isotope-mass balance analysis of a small lake at Lupin, Nunavut, which yielded evaporation rates in close agreement (±10%) with results based on Bowen ratio energy balance and aerodynamic profile calculations (Gibson *et al.* 1996a,b).

Previous evaporation pan experiments mainly focused on investigation of isotope exchange parameters using relatively small pans sensitive to rapid changes in ambient conditions (e.g. Gat 1970; Welhan and Fritz 1977; Allison et al. 1979; Allison and Leaney 1982). In contrast, the new approach utilizes standard class-A pans, which have sufficient volume (220 I) to buffer short-term transient variations in atmospheric conditions, justifying the assumption of constant kinetic isotopic fractionation effects in concert with precisely measured temperature and relative humidity to derive vapour isotopic composition.

A major strength of the method is that pan-derived vapour isotopic compositions are naturally flux-weighted, as represented in the Craig and Gordon (1965) model, and can thus be applied directly to isotope mass-balance analysis of nearby lakes. Fortunately, although the use of kinetic isotope effects that are inherently dependent on the turbulence regime of the boundary layer is a potential weakness,



this factor seems to be remarkably uniform on synoptic time scales or, alternatively, it can be indexed on the basis of other routinely measured climatological data.

As an example, Figure 1 shows a comparison of pan-derived atmospheric vapour  $\delta^{18}O$  and  $\delta^2H$  at the Lupin study site with data obtained from cyrogenically trapped vapour during the daytime and calculated vapour  $\delta^{18}O$  and  $\delta^2H$  assuming isotopic equilibrium with discrete occurrences of precipitation. The pan-derived values clearly provide comparable records of temporal changes in atmospheric moisture  $\delta^{18}O$  and  $\delta^2H$ . Note that the daytime vapour-trap estimates are biased relative to the daily pan-derived estimates because of the influence of vapour from local lakes and tundra bryophytes.

The results suggest that isotopic sampling of existing, conventionally operated class-A evaporation pans could offer a straightforward and cost-effective solution to the problem of documenting the shifting isotopic distribution in atmospheric moisture. The method could provide continuously-weighted records of vapour  $\delta^{18}O$  and  $\delta^2H$  for use in isotope-climate research, which would be of partic-

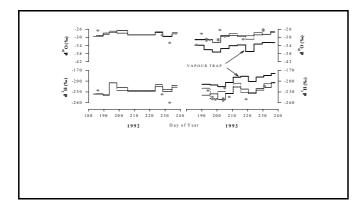


Figure 1. Time-series of step-wise atmospheric vapour  $\delta^{18}$ O and  $\delta^2$ H values derived from class-A pans (solid lines), average of moisture collected daily in vapour trap at height of 6-m over tundra (bold lines), and estimates of vapour  $\delta^{18}$ O and  $\delta^2$ H based on the assumption of isotopic equilibrium with discrete occurrences of precipitation (diamonds). (See Gibson *et al.* 1999.)

ular value for stations receiving little or highly variable precipitation. As studies in Canada have shown, such data are applicable in hydrometeorological studies at various spatial and temporal scales. Significant potential also exists for incorporation into major international hydroscience initiatives, like the ongoing continental-scale regional hydrologic studies within the Global Energy and Water Cycle Experiment (GEWEX), as well as being a resource for validation of the global isotope field as depicted by atmospheric GCMs field as depicted by atmospheric GCMs.

#### References

Allison, G.B. and Leaney, F.W. 1982. *Journal of Hydrology* **55**, 151-161.

Allison, G.B., Brown, R.M. and Fritz, P. 1979. *Journal of Hydrology* **42**, 109-127.

Craig, H. and Gordon, L.I. 1965. In: E. Tongiorgi (Editor), Stable Isotopes in Oceanographic Studies and Paleotemperatures, Lab. Geologia Nucleare, Pisa, 9-130.

Gat, J.R. 1970. In: *Isotopes in Hydrology*, 1970. IAEA, Vienna, 151-162.

Gat, J.R. and Bowser, C.J. 1991. In: H.P. Taylor, J.R., O'Neil, and I.R. Kaplan (Editors), Stable Isotope Geochemistry: A Tribute to Samuel Epstein, Special Publication No. 3, The Geochemical Society, San Antonio, Texas, 159-168.

Gibson, J.J., Prowse, T.D. and Edwards, T.W.D. 1996a. *Hydrological Processes* **10**, 1369-1382.

Gibson, J.J., Prowse, T.D. and Edwards, T.W.D. 1996b. *Nordic Hydrology* **27**, 1-24.

Gibson, J.J., T.W.D. Edwards and Prowse, T.D. 1999. *Journal of Hydrology* **217**, 55-74.

Welhan, J.A. and Fritz, P. 1977. *Geochimica et Cosmochimica Acta* 41, 682-686.

J.J. Gibson and T.W.D. Edwards
Department of Earth Sciences
and Environmental Isotope Laboratory
University of Waterloo,
Waterloo ON N2L 3G1 CANADA





## GROUNDWATER RENEWAL IN WATER SCARCE AREAS

The final coordination meeting of the CRP entitled "Isotope based assessment of groundwater renewal rate in water scarce areas" was held in Vienna, from 18 to 21 October 1999. Fourteen Institutes were involved in this project which is now closed. Detailed information on physiography, lithology, rainfall, unsaturated zone moisture content and a variety of chemical and isotopic constituents was collected at a total of 44 benchmark sites located mainly in arid regions. The purpose was to evaluate the use of chemical and isotopic tools to understand history of recharge and to estimate recharge rates. Evaluation of chloride and tritium concentrations from unsaturated zone profiles (up to a depth of 45 m) provided recharge rate estimates ranging from fractions of a millimetre to tens of millimetres per annum. The methodology adopted and verified through applied field research has proved the applicability of unsaturated zone isotopic/hydrochemical profiles for estimation of natural renewal rate of aquifers in such arid regions, and has provided a unique approach for this purpose. The results and findings of the CRP will be published as a TECDOC by the Agency in 2000.

Y. Yurtsever

## ISOTOPE RESPONSE TO DYNAMIC CHANGES IN GROUNDWATER SYSTEMS DUE TO LONG-TERM EXPLOITATION

The first Research Co-ordination Meeting of the recently initiated CRP entitled "Isotope response to dynamic changes in groundwater systems due to long-term exploitation" was held in Vienna, from 8 to 12 November 1999. The main motivation for the initiation of this CRP was the fact that during the last few decades major sources of freshwater have been exploited to meet the ever increasing demand for water supply to different sectors (domestic, agricultural and industrial). The stresses imposed on the available water resources due to man's impact (exploitation, release of pollutants through domestic/ industrial waste waters, and agricultural practices) have resulted in many parts of the world in depletion of the available reserves as well as the deterioration of water quality. This impact is more pronounced in arid and semi-arid regions. Therefore, the CRP is directed mainly towards making an assessment of the potential utility of isotopes in the quantitative understanding of the long-term changes induced by exploitation. Furthermore, applied field research in selected bench-mark systems with different hydrogeological settings and spatial scales will enable methodological developments for more reliable predictions of future behaviour of the systems under different exploitation scenarios.

Y. Yurtsever

#### ISOTOPE HYDROLOGY CALENDAR



#### 2000

#### IAEA MEETINGS AND TRAINING

#### **February**

Advanced course on numerical modelling - RAS8084 - Bangkok, Thailand, 14 - 25

#### March

**RCM** on The use of tracers and stable isotopes in surface water pollution, RC-701.2 - Vienna, 13 - 17

#### **April**

Executive Meeting for Water Resources Managers, RAS/8/084 - Taejon, ROK

#### IAEA Meeting Categories

AGM: Advisory Group Meeting;

RCM: Research Co-ordination Meeting;

CS: Consultants Service; CM: Consultants Meeting; SYM: International Symposium

#### GNIP-SCIENTIFIC STEERING COMMITTEE MEETING

n 1 and 2 July 1999, the first meeting of the Global Network for Isotopes in Precipitation - Scientific Steering Committee (GNIP-SSC) was held at the IAEA Headquarters in Vienna. The scope of the GNIP-SSC, as defined in the Memorandum of Understanding relating to GNIP signed by the IAEA and the WMO, is to "provide advice to the IAEA and WMO on matters related to the GNIP and to the GNIP Data Base".

## The main recommendations made by the Steering Committee are:

- WMO/IAEA should consider approaching meteorological/hydrological services to help in the management of national networks.
- A list of national networks on isotopes in precipitation should be completed.
- IAEA should compile all the publications using the GNIP data, and this list should complete the information given to the national networks and GNIP stations.
- The SSC recommended including scientists from other continents (Asia, Australia, South America) in the SSC.
- The SSC asked that a task group

be formed to consider the gaps and needs for more stations.

- Some regions have already been identified and should be contacted in order to start/continue sampling (Brazil, tropical Andes, West Africa, India, Central Asia).
- The SSC recommended that the networks of Global Atmosphere Watch (GAW) of WMO be used as much as possible for the GNIP networks.

#### Composition of the first GNIP-Scientific Steering Committee

The first committee members have been selected in order to present a good equilibrium between scientifics from the United Nations agencies and scientifics from research institutes. Both climatologists and hydrologists are represented. The SSC expressed interest in having additional members of the hydrological/hydrogeological communities in the GNIP committee.

#### \* IAEA

- Head of the Isotope Hydrology Section
- Isotope Hydrology Section staff in charge of the GNIP

#### \* WMO

- Director of the WCRP
- to be suggested by WMO
- \* IGBP / PAGES
- to be suggested by PAGES
- \* Experts representing the scientific community
- Environmental Physics:
   U.Schotterer, ISOHYC, Switzerland
- Meteorology:
- S. Hastenrath, University of Wisconsin-Madison, USA
- Climatology:

M. Latif, Max Planck Institute for Meteorology, Germany

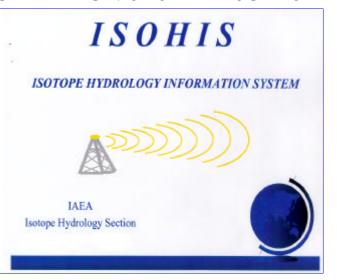
The full report of the first GNIP-SSC and more information about the Global Network for Isotopes in Precipitation can be requested from Laurence Gourcy

L.Gourcy@iaea.org

#### ISOTOPE HYDROLOGY INFORMATION SYSTEM ISOHIS

The ISOHIS database allow gathering, storage and dissemination of isotope, chemical, hydrogeological and geographical data from water studies around the world. The software for entering and verifying records, and for managing local/regional databases called Data Entry Module is available since May 1999.

You can download directly the software and User Manual in *ftp://ftp.iaea.org/dist/isohis/* or request the CD-ROM from Laurence Gourcy.





GEOTHERMAL ENERGY RESOURCES - RESULTS AND ACHIEVEMENTS

workshop to assess this regional project was held in November 1999 in Indonesia. The workshop was attended by representatives from China, Indonesia, Philippines and Thailand, who collaborated in the project, as well as by counterparts of on-going IAEA Technical Cooperation projects on geothermal energy in El Salvador, Costa Rica, Ecuador, Peru and Guatemala.

Regional Project RAS/8/075 was implemented with the general objective to support the utilization of isotope and geochemical techniques for geothermal

reservoir management.

The project included three sets of activities:

- Field investigations using isotope and geochemical techniques for the exploration of low-medium temperature geothermal systems, commonly occurring hydrological problems associated with exploitation and reinjection in high temperature systems, as well as environmental impacts due to waste water reinjection on the shallow groundwater.
- Interlaboratory comparison which assessed the quality of chemical and isotope analyses in the participating laboratories.
- Development of a regional database on geothermal waters as a pre-requisite to planning and ma-

nagement of the geothermal resources.

The regional programme recognized the availability of scientific expertise in the countries of the region. Manpower resources have been developed, information exchanged and disseminated, and the applications of isotope techniques to practical hydrological and geochemical problems associated with exploration and management of geothermal reservoirs accelerated. The regional collaboration has harnessed and optimized the available expertise in participating countries consistent with the intentions of TCDC.

J. Gerardo-Abaya

#### ISOTOPE FOR IMPROVED DRINKING WATER REOURCES MANAGEMENT

The first assessment workshop of the UNDP/IAEA/RCA Project RAS/8/084 was held in Vietnam from 27 September to 8 October 1999.

A workshop reviewed the results of Interlaboratory comparison for chemistry. The role, strategy, design and concepts in isotope investigations, formulations of conceptual models for quantitative interpretation of isotope data in hydrology, and general modelling

concepts for isotope data interpretation in groundwater hydrology were discussed. The various approaches to data processing and interpretation were exposed during the presentations and will be useful for participants to consider in their continuing investigations.

The participating countries are encouraged to facilitate transfer of technology through regular communication. Countries with established expertise in the fields of isotope hydrology and modelling reiterated their willingness to impart information to less experienced Member States.

The initial training and hands-on exercises on numerical modelling were provided on MODFLOW and MT3D which will be used in the project for development of site-specific dynamic simulation models for groundwater flow and transport for the study sites included into the project. The lectures and computer exercises provided the capabilities for use of the software, including data input, simulation, calibration and post-processing of the simulation results.

#### Y. Yurtsever/J. Gerardo-Abaya

#### WORKSHOP ON ISOTOPE DATA INTERPRETATION -PROJECT RAF/8/029

regional workshop on Isotope Data Interpretation and Integration in site conceptual models was held from 27 September to 8 October at the Schonland Research Centre, University of Witwatersrand, Johannesburg, South Africa. The Course was organised within the framework of the ongo-

ing regional Technical Co-operation Model Project RAF/8/029 and was attended by 14 participants from the 7 countries involved in the regional project, namely Kenya, Madagascar, Namibia, South Africa, Tanzania, Uganda and Zimbabwe. In addition to provision of training, the workshop was also aimed at reviewing the status of the Model Project and updating the workplan.

The workshop provided a detailed

overview of the principles and applications of isotope hydrology. Lumped parameter models to interpret groundwater isotopic data as well as hydrologic models were introduced with emphasis on the hands-on use of MULTIS and VISUAL MODFLOW. The Isotope Hydrology Data base (ISOHIS) developed by the Isotope Hydro-logy Section of the IAEA was also introduced.

C. B. Gaye

## LABORATORY ACTIVITIES

#### 2<sup>nd</sup> INTERLABORATORY COMPARISON FOR DEUTERIUM AND OXYGEN-18 ANALYSIS OF WATER SAMPLES

The IAEA Isotope Hydrology Laboratory organised in 1998/99 the 2<sup>nd</sup> interlaboratory comparison test for the analyses of hydrogen and oxygen isotope composition of water. The test was open to all laboratories engaged in isotope analyses of water samples world-wide.

The main objective of this exercise was to help the laboratories to assess their precision and accuracy for the range of  $\delta^{18}O$  and  $\delta^2H$  values normally observed in meteoric waters. More than 115 laboratories from 43 countries indicated their willingness to participate in the exercise and received four water samples (OH-1 to OH-4) for analysis.

#### STATISTICAL EVALUATION OF THE RESULTS

During this intercomparison exercise all participants remained anonymous. Their full addresses are listed in the Annex of the Report, but no link to their identifying lab number used in the data presentation is given (except the IAEA laboratory, ID no. 10). Only the participants were able to identify themselves. By the end of April 1999, 87 of the participating laboratories had reported their data.

Results of seven laboratories, selected by the IAEA for their high analytical quality, were used to assign a "consensus" value for the analyses with the lowest attainable uncertainty.

Figure 1 is an example of the way the evaluated data set was presented in the IAEA report. The  $\delta^{18}$ O-values of the sample OH-1 are sorted in ascending order and plotted versus the laboratory ID numbers. Vertical bars indicate the standard uncertainty (1  $\sigma$ ) quoted by each laboratory. The solid line represents the adopted consensus value. The dotted line represents the weighted mean value as calculated from the whole set of laboratories with the standard uncertainty indicated by the two dotted lines. The data presentation in such an S-shaped plot shows the large number of laboratories participating in the intercomparison exercise and the range of values reported by these laboratories. Full circles indicate the accepted values, open circles indicate the rejected outliers. Visually, one might notice the importance of the reported standard uncertainty of each laboratory in respect to the rejection of values: Deviating values might still be accepted as long as the laboratories state a reasonable uncertainty and vice versa.

Finally, one should realise the shift between the consensus value (solid line) and the weighted

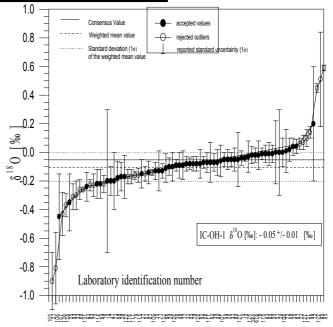


Figure 1: S-shape plot of  $\delta$  Deuterium values sample OH-1 in ascending order versus the Laboratory Identification numbers. For explanations see text.

mean of the whole group (dashed line). This shift towards more depleted values is systematically found for all four water samples and might be explained by evaporation of improperly stored internal standards.

#### **CONCLUSIONS**

The participating laboratories are a representative portion of the entire analytical community engaged in this type of measurements. Therefore, it is believed that the results of this test properly reflect the current situation with respect to accuracy and precision of stable isotope analyses of water samples.

The apparent interlaboratory precision (one-sigma level), derived from the whole pool of the analysed results, is in the order of 0.11 % for  $\delta^{^{18}}\text{O}$  and 1.3 % for  $\delta^{^2}\text{H}$ . This is comparable with the typical standard precision reported by the majority of the laboratories.

- No major improvement of this performance indicator could be detected with respect to that in 1995 (1<sup>st</sup> interlaboratory comparison).
- At least 25% of the participating laboratories underestimate their overall standard uncertainty and/or suffer from systematic effects of varying nature and are therefore identified as outliers (fig. 1, open circles).
- No significant dependence of the obtained  $\delta$ -values on the type of the sample preparation procedure could be detected.

• The results for the entire population do not show normal distribution. A small but significant shift towards more negative  $\delta$ -values between the consensus value and the weighted mean value of the entire population is identified. Since an evaporative loss of only 0.1% of the initial mass of the used internal standard or of an improperly stored VS-MOW sample would be sufficient to explain the observed isotope shift in the observed order of 0.04 % for  $\delta^{^{18}}\text{O}$  and 0.3 % for  $\delta^{^{2}}\text{H}$ , such an evaporative enrichment with time after the calibration against VSMOW might be one possible explanation.

The final report "IAEA 2<sup>nd</sup> Interlaboratory Comparison for Deuterium and Oxygen-18 Analysis of Water Samples" will be made available as PDF document for download on the homepage of the IAEA Isotope Hydrology Laboratory under: <a href="http://www.iaea.or.at/programmes/rial/pci/isotopehydrology/hydrology\_main.htm">http://www.iaea.or.at/programmes/rial/pci/isotopehydrology/hydrology\_main.htm</a>

J. Lippmann / M. Gröning



## CHALLENGES AND NEW TECHNIQUES FOR LIGHT ELEMENT STABLE ISOTOPE MEASUREMENTS

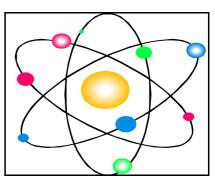
n Advisory Group Meeting on Stable Isotope Ratio Measurements by GC-IRMS and Laser Spectroscopy was held from 20-23 September 1999 in Vienna. The meeting aimed to review the current status of emerging techniques for the determination of stable isotope ratios of light elements. Besides isotope hydrology and isotope geochemistry, the range of disciplines using isotope signatures has broadened significantly during the last years, adapting and using isotopes to, for example, characterise physiochemical or biological pathways, fingerprint substances and trace material fluxes. As a consequence, the requirements of the instruments have changed significantly in some fields. Several new instrumental developments were discussed in the meeting with a focus on (1) Continuous Flow-Isotope Ratio Mass Spectrometers (CF-IRMS) and (2) optical techniques for stable isotope determinations.

Continuous Flow IRMS is a generic term for IRMS instruments coupled on-line to preparation or separation systems like Elementary Analysers, Gas Chromatographs, and Combustion or Reduction Interfaces. The key features of CF-IRMS include reduced sample size and analysis time and isotope measurements of individual compounds in complex mixtures.

Optical techniques use laser beams for measuring the absorbance of different spectral lines for the various isotope species, e.g.  $^{12}C^{16}O^{16}O$  vs.  $^{13}C^{16}O^{18}O$ , in the infrared region or for measuring the electrical response of gas discharge to optical perturbation. Various detection techniques are used, with significant improvements realised recently, offering some operational advantages such as simplified instrumentation, multiple simulta-

neous measurements, non-destructive determinations and reduced contamination risks, e.g. avoiding any isobaric interference. Even though tey are relatively young techniques, the analytical precision is not far from that achievable with mass spectrometry techniques. Further improvements are expected in the future, which will make these techniques widely competitive to mass spectrometry. Despite recent improvements, the measurement of stable isotopes is still reported as ratios relative to standards of known isotope ratio. The creation of reliable isotope standards or international reference materials for both techniques is critical not only to compare results between runs on a single machine, but also to relate them to other machines and laboratories. The requirements for isotope standards have increased dramatically with the new technologies, also due to the wider range of applications. As a result, there are new challenges for the isotope community to extend the availability of international reference materials. This meeting defined the most urgent needs for such materials and gave a starting point for a new field and direction for the Stable Isotope Reference Materials Program of the IAEA.

M. Gröning



#### STAFF CHANGES IN THE ISOTOPE HYDROLOGY SECTION



#### **Departures:**



Dr. Klaus Froehlich retired from the Agency at the end of July. Dr. Froehlich joined the Agency in 1988 as senior staff of the IHS and served as Section Head for the last five years. During his tenure as Section Head, he facilitated efficient collaboration with colleagues world-wide to foster further development and application of isotope techniques in hydrology and related environmental fields. Isotope Hydrology has increased its visibility among the Member States, and the programme was recognized by the General Conference as a significant achievement of the Agency. Among other initiatives, he was responsible for conceiving and launching Water and Environment News, establishing a Memorandum of Understanding on the Global Network for Isotopes in Precipitation (GNIP) between the IAEA and the WMO, and providing the GNIP database through Internet to the scientific community. He also initiated the setting up of the Isotope Hydrology Information System (ISOHIS). During the last two years he enhanced efforts towards launching a long-term Inter-Agency (UNESCO, WMO, WCRP etc.) collaborative programme called International Programme for Isotopes in the Hydrological Cycle.

He can be contacted at the following address : Viktor-Wittner-Gasse 63/7

A-1220, Vienna, Austria e-mail: K.Froehlich@aon.at

Mira Gattin left the IAEA at the end of December 1999 after working in the Isotope Hydrology Laboratory for more than 30 years. As a chemical engineer she started to work on tritium analysis and switched later to stable isotope mass spectrometry, where she was responsible mainly for sample analyses for  $\delta D, \, \delta^{13} C$  and  $\delta^{18} O.$  At the same time she was responsible for the training of many dozens of fellows in the field of stable isotope mass spectrometry. Her engagement, careful work attitude and friendly personality contributed considerably to the success of the laboratory. We wish her all the best for the new phase of life after her retirement.



Arrival:



**Michael van Duren** joined the Isotope Hydrology Laboratory in December 1999. By profession, he is a food chemist and previously worked in various branches of the Agency's Laboratories in Seibersdorf for the past 15 years. He will ensure the continuity in mass spectrometric measurements in the Isotope Hydrology Laboratory.

He can be contacted at : Telephone : +43-1-2600-21765 e-mail : M.Van-Duren@iaea.org

Water and Environment News, Isotope Hydrology Section, International Atomic Energy Agency, Wagramer Strasse 5, P.O.Box 100, A-1400, Vienna, Austria. Printed by IAEA in Vienna