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UNEDITED PROCEEDINGS

International Symposium
held in Vienna, 19–23 May 2003
organized by the International Atomic Energy Agency
and the International Association of Hydrogeologists
in cooperation with the International Association of
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FOREWORD

While great strides continue to be made in improving the availability of freshwater to rural and urban populations worldwide, more than one billion people today still lack access to safe drinking water. Global efforts to overcome the growing challenge of freshwater availability have been at the forefront of the world development agenda for nearly the last 30 years. A number of recent world events, including the UN Millenium Summit in December 1999, the World Water Forum in March 2000 (The Hague, Netherlands) and March 2003 (Kyoto, Japan), and the World Summit on Sustainable Development in September 2002 (Johannesburg, South Africa) have drawn attention to this growing challenge and to a variety of actions at all levels, technical, political, societal, etc., that are needed to meet it. The United Nations General Assembly proclaimed the year 2003 as the International Year of Freshwater in order to further focus world attention on the freshwater challenge.

Improved understanding of the Earth's water cycle has been widely recognized as one of the key elements of scientific information necessary for developing policies toward a sustainable management of freshwater resources. Over the last 50 years, environmental isotope techniques have provided insights into the processes governing the water cycle and its variability under past and present climatic conditions. Increasingly, isotope techniques are being integrated into water resources management practices. The International Atomic Energy Agency has played a pivotal role in promoting and expanding the field of isotope hydrology over the last four decades. Starting in 1963, the IAEA's quadrennial symposia on isotope hydrology have played a central role in developing this scientific discipline. Proceedings of these symposia published by the IAEA continue to be cited frequently in publications reporting current research and applications of isotope techniques in hydrology.

The 11th symposium in this series was convened by the IAEA from 19 to 23 May 2003 in Vienna.

Some 275 participants from 69 countries discussed the past, present and future of isotope applications in hydrology and climate research. A total of 55 oral and 120 poster presentations described many of the applications of isotopes. Extended synopses of these presentations are being published in these proceedings, together with a summary of the symposium results. Selected presentations are to be published in a special issue of the journal Hydrological Processes. It is hoped that these publications will be used as a basis for future research and field studies and that they will help to bring one of the remaining challenges in isotope hydrology, that is, to increase the general use and acceptance of isotope methodologies, into the mainstream hydrology and water resources management.

The IAEA officers responsible for the symposium and this publication were P. Aggarwal and J. Turner of the Division of Physical and Chemical Sciences.

EDITORIAL NOTE

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SUMMARY

The 11th International Symposium on Isotope Hydrology and Integrated Water Resources Management was held 19–23 May 2003 in Vienna, Austria. The symposium was divided into an opening session, eleven technical sessions, and a closing session. Summaries of presentations and discussions in these sessions are provided below.

Highlights from the opening session

In the opening session, introductory remarks were made by W. Burkart, IAEA Deputy Director General and Head of the Department of Nuclear Sciences and Applications, Honourable S. Prabhu, Member of Parliament in India and Chairman of the National Taskforce on Interlinking of Rivers, H.E. K.E. Brill, Ambassador of the United States of America to the IAEA, H.E. Y. Takasu, Ambassador of Japan to the IAEA, W. Schimon, Deputy Head of the Water Division, Federal Ministry of Agriculture, Forestry, Environment and Water Management of Austria (on behalf of the Federal Minister Honourable J. Pröll), and I. Kossina, Executive City Councillor for the Environment, Vienna Provincial Government.

In his opening address W. Burkart noted that substantial progress has been made in the application of isotope techniques over the past 40 years, as evidenced by the rapidly growing number of publications using these methods. He also noted that global demand for freshwater has been increasing much faster than the ability of most nations to meet these demands and that to sustain the current and future levels of human development, extensive hydrological information is necessary to protect available water resources from pollution and over-exploitation, as well as to prevent or resolve disputes among those who share the same resource. Integration of isotopes into mainstream hydrology still required a closer interaction between isotope hydrologists and the hydrological community and he expressed his hope that the symposium would help to bring this abaout.

One of the common themes highlighted by the distinguished panel in their opening remarks was how the issue of water resources is presently evolving from local scale problem to a global context because of the expanding world population and increasing demand for water. The importance of three measures that can be taken to tackle the problem was highlighted, including good governance and policy intervention, community participation and advancements in technology. In this context the role of isotope techniques and the topic of this conference fell squarely into the latter category.

Highlights from the technical sessions

The technical programme of the symposium comprised nearly 55 oral and 120 posters. The oral sessions were divided into nine technical sessions as follows: a keynote session, groundwater sustainability and dynamics (2 sessions), river system dynamics, unsaturated zone processes and artificial recharge, geothermal systems, climate and atmosphere, and biogeochemistry and water quality. Two poster sessions were conducted, one focused primarily on groundwater and the other one on surface hydrology and geothermal systems.

Session 1: Keynote papers

Speakers in the keynote session highlighted the vital need for water resources to be carefully used and protected in order to ensure the future of modern civilisation and the integrity of the natural environment. The outcomes from the 3rd World Water Forum held at Kyoto, Japan in March 2003 were reported upon by H. Oda, Secretary General of the Secretariat of the WWF. The main outputs of the forum — global water resource issues and world water actions and the portfolio of water actions, provided a very timely vision for global water in the future.

A provocative but relevant question was put to the symposium: "What have isotopes told us about groundwater systems that we didn't know before?" This is a question that is often heard, especially amongst the water management community and is a message well worth heeding when undertaking isotope studies. Indeed, it is a question well worth asking before an isotope study is undertaken, to ensure that new information is forthcoming from the efforts made. This message obviously struck a chord with conference participants because during the technical sessions presenters and audience alike often restated it. The answer was generally "a lot", but careful study design is necessary to ensure that effectiveness. Methods on how to facilitate adoption of isotope techniques to groundwater management were also presented.

An overview of methods for determining the age of young groundwaters was presented wherein natural tracers such as tritium, helium-3, chlorofluorocarbons, and sulphur hexafluoride were used for age-dating groundwaters recharged within the last approximately 50 years. Conclusions were that multiple tracers help to eliminate some data and models and identify the most reliable data. These tools are important because shallow, young groundwaters provide drinking water supply in many areas and also are most frequently subjected to contamination from anthropogenic activities. The statement made in 1983 by J.-Ch. Fontes, a leading isotope hydrologist and former staff member of the IAEA,: "the concept of groundwater age has little significance" was explored. It was concluded that investigation with multiple environmental tracers in groundwater systems can often help to refine the interpretation of groundwater age, hydrological concepts, and identify susceptibility of aquifers to contamination. Thus, while the quote is true, the "age" estimation must be translated into logical hydrological parameter. The IAEA's recent commissioning of a $^{3}H/^{3}He$ facility endorses the development of improved isotope techniques for dating of young groundwaters.

Sessions 2, 3 and 5: Groundwater sustainability and dynamics

More than 50% of oral and poster presentations at the Symposium were focused on one or more aspects of groundwater, demonstrating that groundwater sustainability issues continue to be a mainstay for applications of isotope techniques. In the two oral sessions on this issue, areas of application included groundwater dynamics, groundwater pollution and restoration, hydrological-isotopic modelling approaches, the origin and recharge of groundwater, palaeowaters, recharge estimation, and the assessment of low-renewable rate groundwater resources. An overview of the ^{14}C method as a gropundwater age-dating tool concluded that groundwater dating by means of environmental isotopes is a vital, effective and frequently indispensable tool for hydrological studies, numerical hydrological modelling, and groundwater budget estimations. The remainder of the presentations were case studies demonstrating methods and how they are used in determining groundwater reserouce sustainability and dynamics.

Session 4: River system dynamics

In this session, several papers were presented on the application of isotopes to continental-scale river systems. Isotopes have significant advantages in integration of hydrological processes at large scales. Advances in this field were indicated by the development of models using isotopic tracers and water balance in river systems at the continental scale. These efforts are at an early stage of development and indicate that future trends in the field will focus on isotope applications to regional water balance and climate change responses integrated over large river basins. Nutrient source identification in large rivers has received a boost from new analytical developments that permit rapid and accurate measurement of $\delta^{18}O$ and $\delta^{15}N$ in nitrate, a major river and groundwater pollutant.

Session 6: Unsaturated zone processes and artificial recharge

A broad range of topics in unsaturated zone processes and artificial recharge were presented. The principal subject of this session is related to the use of isotopes in understanding the migration/pathways of solutes (pollutants) and water in the unsaturated zone. Issues such as the rate of contaminant migration (very slow/very fast), pathways of migration (vertical simple piston flow/preferential flow along lenses of permeable soil zones, micropore flow or fractures), mechanism of degradation of solutes/contaminant by biogeochemical reactions along flow paths, and impacts of solutes/pollutants on aquifer property were presented. The papers on artificial recharge which is being increasingly used water resource management tool showed novel applications of isotopes to assess the effectiveness and water quality processes in artificial recharge.

Session 7: Geothermal systems

Papers in this session demonstrated how isotope techniques are used to understand the potential of geothermal resources and how they can be used in in management and environmental decision making in geothermal systems.

Session 8: Climate and atmosphere

Understanding and predicting climatic processes is a significant challenge. Such predictions are based on complex modelling, whose accuracy depends on the quality of the data on which they are based. The symposium session on climate and atmosphere included papers that presented recent advances on coupling of atmospheric circulation models with data on isotope variations in the water cycle, where isotopes are proving particularly useful in validating the physical processes simulated in the models. Several papers considered the issue of moisture sources in the Asian monsoon region that showed the potential for employing isotopes to understand the source and transport of moisture and rainfall pattern variability. The isotopic links between two key global cycles of water and carbon were highlighted as well as the application of isotope in the study of ocean climates. The IAEA’s role in developing and co-ordinating the GNIP database emerged again as a key resource enabling many aspects of these papers. Environmental isotopes are one of the most powerful tools to investigate climate change and the associated enviornmental responses. This important role of isotopes in understanding past climate changes also holds the key to predicting future changes — changes that may not only influence global temperatures, but also energy needs, availability of drinking water, and food security. This role was well demonstrated by papers in this session and the critical role that isotopes will continue to play in this field.

Session 9: Biogeochemistry and water quality

Application of isotopes in understanding the biogeochemical processes is one of the recent developing areas. It is particularly important for understanding the transformations of nitrogen, sulphur, and carbon in the hydrological cycle and hence plays a key role in monitoring of contaminant impacts on water quality and the remediation of poor water quality.

Session 10 and 11: Poster sessions

In the groundwater poster session (Session I), the main themes were pollution, modelling approaches, the origin and recharge of groundwater, and palaeowaters. Session II covered various aspects of precipitation, surface waters, watershed, large river, lakes, wetlands, estuaries, geothermal systems, and recent analytical developments. This last section included new developments in the area of compound-specific isotope analysis relevant to biodegradation of pollutants in groundwater.

Closing session

From the groundwater perspective, arid zone hydrology is still considered as an important area of application for isotope techniques, and the interface zones are still relatively poorly understood for example the interface zones processes between the unsaturated and saturated zones and groundwater and surface water. Fractured rock aquifers are increasingly being used for groundwater supply, however natural tracer techniques and isotopes are not yet fully utilized in their study. The area of ecohydrology and the dependence of ecosystems on groundwater is an important area for isotope applications, especially as decisions concerning water demand management and water allocation affect them. Isotopes have application in identifying water sources for groundwater dependent ecosystem. Water management strategies such as artificial recharge is a field where there are emerging isotope aopplications and methods for analyzing and interpreting sparse data sets and upscaling are also becoming topical. Isotope applications were seen to need expansion in some other areas of direct water resource management such as the areas fo irrigation systems and irrigation management, articifical recharge and the sustainable use on management of groundwaters of different "age". Some other water management arteas where isotope applications were seen to have greater opportunities in the future were in the area of desalination technologies, alinity management, water re-use and reclamation of saline to brackish water.

In large scale river basin hydrology, the application of isotope techniques has a substantial amount to offer and progress is under way in the IAEA CRP on this topic. This CRP is providing a global focal point for data collection on large river systems and is attracting significant attention. In addition further potential applications exist in the IAHS Predicition in Ungauged Basins (PUB) programme and the upcoming 2nd International Hydrological Decade.

One of the most useful areas of isotope application highlightred once again was in terms of the calibation and validation of global climate models, and especially the validation of physical processes on which these models are abased. The data demands for such applications are high however and data sets on isotope composition of rainfall and atmospheric water vapour are sparse, even recognising that databases such as GNIP are vailable. From the climate perspective there is a need to integrate climate records more fully with records from isotope hydrology, and to use isotopes to monitor climate changes. In this context there is a need to expand and re-double efforts in global database collection, and the GCM's should provide guidance on the spatial and temporatl frequency that the data is needed. The application of isotope techniques in tropical humid areas should not be neglected in favour of arid and semi-arid zones only.

In the area of water quality and pollutant source identification, isotope techniques have developed significantly in recent years and new tools and techniques for measuring ^{18}O, ^{17}O, ^{15}N in nitrate and dissolved oxygen and ^{18}O and ^{34}S in SO_4 have become available. In summary more effective isotopic tools are becoming available and the understanding with which to interpret data is advancing steadily.

It was recognized that ocean systems had been largely under-represented at the symposium and that there was a need to improve cross-fertilization and integration between the ocean and hydrological sciences, especially in tracer oceanography where lessons can be learned. For example, a new method for measuring ^{18}O in microgram quantities of aqueous nitrate was developed for oceanographic purposes. As a community of scientists we should try to be more ambitious and do more to integrate process studies that apply multi-isotope systems that employ models of greater numerical complixity for analysis and interpretation.

Finally, the symposium concluded that greater efforts are required to increase the acceptance of isotope methodologies in mainstream water resources management and decision-making. In this context there is a need to expand efforts in global data collection in all environments. A lack of substantial efforts in field data collection during the 1970s and 1980s were considered to be partly responsible for a perceived stagnation in the field of isotope hydrology, retarding its integration in hydrological sciences.

OPENING STATEMENT
W. Burkart

Deputy Director General
Department of Nuclear Sciences and Applications
International Atomic Energy Agency, Vienna

On behalf of the Director-General and on my own behalf, I welcome you to the headquarters of the International Atomic Energy Agency and to this International Symposium on Isotope Hydrology and Integrated Water Resources Management. This event marks the 40th anniversary of the first symposium in this series, which was held in 1963. More than 250 participants from 69 countries are present here today, which is clear evidence of the keen interest in the science, and the relevance and role of the IAEA's water resources programme.

As many of us here today are aware, the global demands for freshwater have been increasing much faster than the ability of many nations to meet these demands. Presently, more than a billion people lack access to safe drinking water. In the Millennium Declaration, in Agenda 21, at Johannesburg/Rio+10 last year, the world leaders committed themselves to reduce by the year 2015 the proportion of people without access to potable water. At present levels, this means that more than 250 thousand additional people should be provided access to safe water every single day from now to 2015! That is the city of Vienna every week! Clearly, a lot of resources will be required, both human and financial, and perhaps with new and innovative approaches. The World Bank estimates that up to 20 billion dollars per year may be required to meet the stated goal of access to safe water.

But besides financial requirements, there is another, vitally important, consideration. We need to have the additional water resources actually available for meeting the goals that we have set for ourselves. Currently, surface waters in rivers and lakes are being exploited to the maximum, and ground water resources are getting depleted or contaminated in many parts of the world. Extensive hydrological information is necessary to sustain the current and future levels of human development, to protect available water resources from pollution and over-exploitation, and additionally to prevent or resolve disputes among those who share the same limited resource.

Isotope techniques help to provide rapidly hydrological information for large areas and will undoubtedly be a key component of global efforts in water resource assessment and management. The field of isotope hydrology, started nearly 50 years ago with a limited number of research centres in developed countries, is practiced today in most countries, 69 of which are represented here in this Symposium. Isotope hydrology now is a fully recognized discipline of hydrologic sciences in its own right. To illustrate this, between 1965 and 1970, less than 100 papers in hydrology published in major scientific journals included the use of isotopes. This number rose to more than 7000 between 1995 and 2000.

As you are aware, the history of development of isotope hydrology over the last four decades is inter-twined with that of the IAEA's water resources programme. IAEA activities continue to facilitate development and integration of isotope techniques in hydrology. Much progress has been made, shown by the degree of integration of isotope techniques into other fields of hydrology. In addition to scientific efforts, integration of isotopes into mainstream hydrology requires a closer interaction between isotope hydrologists and the hydrological community at large. Our programme increasingly aims to bridge this gap. I am pleased to note that two of the major scientific associations in hydrology, the International Association of Hydrologic Sciences and the International Association of Hydrologists have co-sponsored this symposium.

In this the International Year of Freshwater, your contributions to and discussions in this Symposium will focus attention on the key role of isotope techniques in hydrology and integrated water resources management. The Symposium programme comprises some 55 oral papers and 120 posters. Additionally, I hope that the airy corridors and many coffee bars here in the Vienna International Centre, and the pleasant environment of the City of Vienna, would provide more and ample opportunities for serious discussions on the science and its applications. The Vienna region itself is a place blessed with abundant and high quality water. The city has a long record of using it in a sustainable way, as you will see later in the week.

The challenges are significant, but I am confident that you will succeed in your objectives. I wish you a very pleasant stay here in the IAEA and in Vienna, and a productive and successful meeting. I declare this Symposium open.

Oral Sessions

KEYNOTE PAPERS

(Session 1)

Chairpersons

B.K. Kim
IAEA

D.D. Sood
IAEA

IAEA-CN-104/186

WATER RESOURCES PROSPECTS FROM A HYDROLOGICAL SCIENCES PERSPECTIVE

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The 21st Century has started with a rapidly rising demand for water, an increasing toll of death and destruction from floods and droughts and a mounting burden of water pollution. These and a host of other problems provide overwhelming evidence that the world's water resources are subject to intensifying pressures and growing constraints. They highlight the vital need for water resources to be carefully husbanded and protected in order to ensure the future of modern civilisation and the integrity of the natural environment.

Distributed unevenly in both space and time across the globe by the hydrological cycle, the world's water resources are stored and moved as a gas, a liquid and as a solid, above, on and below the ground surface. The quantity of these resources is usually the attribute of prime concern, however in many situations their quality, both chemical and biological, is even more important or as equally important. The river basin and the aquifer define the spatial limits of water resources, while their dimensions in time can range from seconds to the century and far longer.

Hydrology is the science which deals with the water resources of planet earth and, most recently with those of other bodies in the solar system. In particular it provides the scientific basis for their assessment, development and management. Indeed over the last 300 years or so, the application of the principles of hydrology has been essential to socio-economic development. These same principles must be used now to promote sustainable development and to avoid the world water crisis which a number of authorities consider will arise later this Century.

While attempts to assess water resources may have started in ancient Egypt and in early China, little progress seems to have been made until Perrault carried out a hydrological study in the basin of the Seine in the 17th Century. His results and those of Marriote showed conclusively from observations that the rainfall over the basin was more than sufficient to produce river flow. Their findings overturned the long-held theory that rivers rise from subterranean springs fed from an internal hydrological cycle.

With the series of advances in the last century and this, the present day practice of water resources assessment has progressed far from those rudimentary techniques employed in the Seine. But in the last 10 to 15 years they have also needed to account for possible climate change, as well as a host of other complications stemming from factors such as land use change and the volume and variety of pollutants being introduced into the aquatic environment. Ideally they would always be employed as a lead into the development and management of water resources, but this is often not the case. The planning, design and construction of water supply schemes, those for the generation of power, irrigation projects, flood mitigation works and the like need such assessments. The same methodology employed in real time is important to forecasting systems for floods and droughts.

The initial components of a water resources assessment programme: namely the design of hydrological networks, the performance of instruments and methods of observation of hydrological processes, together with the assimilation and management of data, demand a sound scientific base. This applies equally to the subsequent stages; such as the development and application of water resources models, including areal and regional techniques, archiving and disseminating water resources information and to the forecasts and predictions which may be made.

While the scientific problems of these different components are taxing and demand dedicated research effort, they cannot be divorced entirely from problems of governance, funding and like considerations. And although research may offer scientific solutions, putting these solutions into practice may come up against insurmountable difficulties, particularly those of an institutional or an administrative nature. However until a substitute for the tasteless, colourless, odourless liquid known as water can be found, hydrologists and scientists and engineers in allied areas of endeavour face a continuing challenge.

HYDROLOGICAL PROCESS STUDIES USING COSMIC RAY PRODUCED RADIONUCLIDES

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The field of hydrology is presently assuming new dimensions in response to dramatic advances made in our understanding of the evolution of past climates. It is now apparent that even changes in the solar flux alone do not regulate climates. To understand mechanisms of climate regulation, it is essential to fully understand the role played by the water and carbon cycles, and therefore also, the characteristics of the principal reservoirs where water and carbon are stored; the atmosphere, biosphere and the hydrosphere. How water is transported through these reservoirs and what factors regulate the transport of water, are the central questions which must be answered to understand the global hydrological cycle, which are a prerequisite to understand climatic changes.

The global hydrological cycle is the vastly complex dynamic of transfers of all phases of 'water' molecules, gas, liquid and solid, through the atmosphere, land and the oceans. Its complexity ultimately owes itself to the properties of the phase diagram of water in part, and in part to the appreciable latent heat involved in the change from one phase to the other. Transport of water is therefore closely linked with the transport of energy. The operation of the hydrological cycle is therefore closely related to the climate; climate controls the hydrological cycle, and as the cycle evolves with climate, it produces strong feedbacks which regulate the climate in an important manner. An example of extreme coupling between the hydrological cycle and climate is the concept of 'Snowball Earth', which could have happened in climates different from what we are used to thinking about!

Tracers provide a convenient way of obtaining space-time integrals of motion of 'water' molecules over both large and small range of space and time. It is now well recognized that a large number of cosmic ray produced isotopes are used for dating and tracing components of geological/geophysical/geochemical systems. Some of the tracers are well suited to study the time scales involved in the transport/mixing of water molecules since they follow the motion of water molecules. Others, which do not follow the motion of the water molecules (as a result of their removal from the fluid by biogeochemical processes), serve as useful tracers to characterize properties of the reservoir.

Both natural and artificial, stable and radioactive nuclides are employed as tracers. Their usefulness in hydrology has been demonstrated since the emergence of the field of isotope geochemistry in the fifties. The earliest applications of isotopes as tracers was the identification of a clear-cut isotopic relationships between ^{18}O and ^{2}H in worldwide fresh surface waters, arising due to isotopic fractionations occurring in the operation of the hydrologic cycles (Craig, 1961). The relationship, called the " global meteoric water line" is only global in application; it is the average of several regional meteoric water lines, and emphasizes the central point that meteoric waters evolve in a predictable fashion, and that therefore one can model the water trajectories. Subsequently both *naturally and artificially produced radionuclides*, have been extensively applied to study processes and time scales in hydrological cycles. The former are produced by (i) nuclear interactions of cosmic rays on the Earth, and (ii) radiogenic and nucleogenic processes associated with the ^{238,235}U and ^{232}Th. Artificially produced radionuclides are released from testing of nuclear weapons and operation of nuclear reactors.

Each class of isotopic tracer has its own niche, providing detailed information on specific processes, and time scales. For obtaining information about the hydrological cycle in its operation through different scales of space and time, it becomes necessary to simultaneously study two or more tracers. In fact any model(s) used to treat a tracer data has to be consistent with the information based on all the tracers. Thus whilst it may not be apparent in some cases, multiple tracers are indeed often being deployed to study hydrological cycles.

In this presentation, we will consider the applications of the cosmic ray produced (cosmogenic) isotopes in hydrology, with a brief discussion of the history of their applications, current applications, and finally the promise of cosmogenic isotopes in hydrology.

Cosmic rays produce nine radionuclides of half-lives ranging between 10 years and 1.5 my, and five, between 2 weeks and 1 year (Lal and Peters, 1967). Useful radionuclides are also produced directly in the oceans by cosmic ray interactions Lal et al. (1988). In Table 1, we present a broad overview of the applications which the cosmogenic nuclides have found to date. With increase in sensitivity of measuring small amounts of isotopes, the field of cosmogenic tracers in hydrology is expanding, finding new applications in hydrology, including studies of ground water infiltration rates and soil dynamics (Lal, 2001). It should be realized that the cosmic ray source function is a very weak one! The global average flux of cosmic ray nuclei at the top of the atmosphere is ~ 1/cm^2.sec. The incident energy flux is ~ 5 x 10^{-3} cal/cm^2/yr, which is ~ 4 orders of magnitude smaller than global heat flow, and more than 8 orders of magnitude smaller than the solar flux. However, the mean energy per cosmic ray particle is much larger, and sufficient to induce nuclear reactions in matter, causing significant changes in the composition of matter, and thereby injecting tracers in the geospheres. And it is this reason that even the weak cosmic ray source is able to make a significant contribution to earth sciences (cf. Lal, 1991).

Finally, in closing it must be pointed out that tracers, stable or radioactive are not a “panacea’’; their proper utilization requires a very good understanding of the characteristics of the system under study. This information has to be obtained through studies of conventional hydrological methods and that based on distribution of stable isotopes. Tracer radionuclides modeled appropriately provide information on time scales and rate constants. Naturally produced radionuclides have an important attribute in that their source functions are well known. However note that in some cases, very useful information can be obtained by pulsed injections of tracers, as in the case of radionuclides injected in the atmosphere by nuclear weapons’ testing. Overall, since one employs tracers using “black box” models, representing the mixing and exchange properties of atmosphere and the hydrosphere, it is necessary to employ multiple tracer types to validate the results of tracer models (cf. Phillips 1994). And it is indeed gratifying to see that generally we have available a great variety of tracers available in hydrological studies.

TABLE 1. Important characteristics and principal applications of selected cosmogenic tracers.

1.1. Isotope	**Half-life**	**2. Principal applications**
i) Isotopes which label constituent molecules in the atmosphere and the hydrosphere		
^{3}H (H_20)	12.3 y	Characterizing water molecules in the atmosphere, hydrosphere and cryosphere
^{14}C (CO_2, CO_3, HCO_3)	5730 y	Characterization of the carbon cycle reservoirs
^{32}Si ($HSiO_3$, SiO_2)	~150 y	Biogeochemical cycle of silicon, ground water infiltration rates
^{33}P, ^{32}P (DIP, DOP)	14.3, 25.3 d	Biogeochemical cycle of phosphorous
(ii) Isotopes which do not form compounds		
^{3}He	Stable	Air-sea exchange; escape of helium from the atmosphere
^{37}Ar	35 d	Air-sea exchange; tropospheric circulation
^{39}Ar	268 y	Air-sea exchange; vertical mixing in oceans
^{81}Kr	2.3×10^{5} y	Ground water ages, and constancy of cosmic radiation
iii) Isotopes which attach to aerosols/particles		
^{7}Be	53 d	Atmospheric circulation, vertical mixing in surface ocean waters
^{10}Be	1.5×10^{6} y	Role of particle scavenging in the coastal and open oceans; dating of sediments and accretions
^{26}Al	7.1×10^{5} y	Role of particle scavenging in the coastal and open oceans; dating of marine sediments and accretions
^{32}Si ($HSiO_3$, SiO_2)	~150 y	Labeling the dissolved oceanic silicon pool; atmospheric circulation
^{33}P, ^{32}P	14.3, 25.3 d	Labeling the dissolved oceanic phosphorus pool; tropospheric circulation

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ENVIRONMENTAL ISOTOPES AS GROUNDWATER MANAGEMENT TOOLS: INDISPENSABLE OR SUPERFLUOUS?

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The widespread application of isotopic techniques over the past four decades to determine palaeo-recharge, groundwater residence times, recharge mechanisms, recharge areas etc., have proved valuable to improve our understanding of the behaviour of groundwater systems. It is fitting to reflect, at this 40th Anniversary of “The IAEA”, on the achievements in facilitating global applications of the isotope methods. But water resource management is complex. It requires specific information to make allocations that may be unpopulay amongst users or other stakeholders. Those decisions need to be made through a transparent process of assessment criteria, and one founded on sound scientific and cognisant of cultural, political, social context. It is not self evident that the success of the science and application of isotope hydrology has been transalated water resource management. Such techniques are rarely, either directly or indirectly, incorporated into information from which decisions are made by water policy makers. Similarly water managers have trouble in knowing how environmental isotopic information can be taken into consideration when allocating groundwater to users. One might be tempted to think that it is a matter of educating managers into the intricacies of isotope hydrology, however such ‘soft’ information may not be of much value where precise solutions to specific issues are needed.

The limited uptake of the method may be due to a number of factors. Until relatively recently, isotope hydrology has remained a largely academic pursuit, or measurements were the domain of national atomic energy agencies. A large fraction of the information lies buried in the grey literature or in arcane technical journals. Interaction with local or regional water resource agencies has been the exception rather than the rule. The need for precise and quantitative information, and the tendency for equivocation given the (real) limitations of the isotopic data are frustrating for people who need reasonably precise data to use in say water balance models. Furthermore, the proliferation of easy to use nemerical computer models that generate colourful maps, which tend to disguise the large natural variability of hydrogeological parameters, are more intuitive and flexible for classically trained water engineers.

Resource agencies often take an adaptive management approach that relies on observation of impacts for a given pumping regime. This has some dangers in that deletrious effects may take a very long time to manifest themselves, and the ‘signal’ related to anthropogenic impacts may be lost in the ‘noise’ of natural climate variability, or long term climate change. The most compelling case for including isotopic information into groundwater management is by providing an integrated view of groundwater systems (in space and time) that are not afforded by conventional methods. Only by seeking quantitative and rigorously obtained data can the following issues such as the following be addressed: a) the resilience of the groundwater system, (sometimes labelled sustainability) which is the ratio of total storage to net annual recharge, b) effects of exploitation that are not directly associated with extraction amounts such as salinisation, and c) impacts on dependent ecosystems, including pollution. Isotopes can help at the very least in deciding on the most appropriate management strategy. These range from incremental stressing and monitoring of response (water level decline) to detailed water balance estimates from which water allocations can be decided (usually some fraction of natural recharge). Several case studies which cover a range of possible scenarios (ranging from high volume low recharge systems to low volume high recharge system) are discussed to suggest ways that isotopes can be used dircetly to facilitate effective management strategies and policies (Table 1).

TABLE 1. List of different groundwater systems in Australia where isotope data are used in groundwater management. The usefulness of isotopic data depend on the problem to be addressed and are of greater value to management where quantitative estimates of some hydrogeologically relevant parameter is obtained.

Type of system	**Name**	**Volume**	**Recharge rate**	**Use of isotopic information for management**
Very large sedimentary basin	Great Artesian Basin	Very large	Very low	Flow rates; recharge rates incorporated into groundwater models
Karstic lenses	Eyre peninsula	Very small	Moderate Episodic	Replenishment rate; monitoring of pumping
Fractured Rock Aquifers	Clare Valley	Very small	moderate	Recharge rates; sustainable use Monitoring of ASR
Urban aquifers	Various	Varies	Moderate to high	Monitoring of pollution and artificial recharge
Basalt aquifers	Atherton Tableand	High	High	Recharge rate; discharge to streams
Multiple sedimentary aquifers	Otway Basin	Medium-high	Moderate	Incorporation into model (CCM) Estimates and mechanisms of recharge to karst system
Fractured Rock Aquifers	Clare Valley	Very small	moderate	Recharge rates; sustainable use Monitoring of ASR
Urban aquifers	Various	Varies	Moderate to high	Monitoring of pollution and artificial recharge
Basalt aquifers	Atherton Tableand	High	High	Recharge rate; discharge to streams
Multiple sedimentary aquifers	Otway Basin	Medium-high	Moderate	Incorporation into model (CCM) Estimates and mechanisms of recharge to karst system

DATING OF YOUNG GROUNDWATER

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During the past 40 years, a variety of methods have been developed that can provide information on the age of young groundwater (0-50 year timescale) [1]. Groundwater age refers to the time elapsed since recharge, but is model dependent, being based on an interpretation of measured concentrations of environmental tracers in groundwater samples. As a reference point, an "apparent age", which assumes unmixed samples (piston flow) is often reported, although a number of mathematical models have been developed that can be used to interpret mean age (residence time) of water that discharges from a groundwater reservoir. Other applications incorporate environmental tracer data in the calibration of numerical models of groundwater flow.

Environmental tracers that have proven most useful in providing groundwater age information have an atmospheric source and can be grouped according to (1) those based on measurement of the concentrations of both parent and daughter isotopes, such as in applications of $^{3}H/^{3}He$ in groundwater, (2) those based on the measurement of the activity of a single radionuclide in groundwater, such as in applications of ^{3}H and ^{85}Kr in groundwater dating, and (3) those based on measurement of the concentration of anthropogenic gases in groundwater, such as in applications of chlorofluorocarbons (CFCs) and sulfur hexafluoride (SF_6). In the first case, the initial concentration of the radionuclide is reconstructed from the measured concentrations of the parent and daughter isotopes and age is then determined from the decay equation. The second case requires *a priori* definition of the initial concentration of the radionuclide recharged to the aquifer, and then age is estimated from the measured concentration and the decay equation. In the third case, age information is derived from *a prior* knowledge of the atmospheric input function of an anthropogenic gas, its solubility in water, and the measured concentration in the water sample. Each method has advantages and limitations, and therefore, a multi-tracer approach is recommended.

The $^{3}H/^{3}He$ age is based on an isotope mass-balance calculation that determines the amount of tritiogenic ^{3}He in the water sample, and has been applied to dating waters from the late 1960s to modern. Several conditions are necessary to calculate and interpret the age, including detectable ^{3}H (greater than approximately 0.5 TU), and relatively low concentrations of terrigenic helium.

The source for atmospheric ^{85}Kr is primarily from reprocessing of fuel rods from nuclear reactors. Because of difficulties in collection and analysis, ^{85}Kr has not yet been widely used in groundwater studies, though it has considerable potential for dating on the 0-30 year timescale. In CFC-contaminated environments, or in anoxic environments, noble-gas dating techniques such as those based on $^{3}H/^{3}He$ and ^{85}Kr measurements are usually more reliable than those based on CFCs. However, because of their low detection limit, CFCs can be detected in water from the late 1940s.

Sulfur hexafluoride (SF_6) is primarily of anthropogenic origin but also occurs naturally in some aquifers that contact crystalline rocks. The troposphere mixing ratio of SF_6 has increased from a steady-state value of 0.054 ± 0.009 to about 5 parts per trillion during the past 40 years. The history of SF_6 mixing ratios in the atmosphere is now well established, with values currently increasing at about 6 percent per year; whereas mixing ratios of CFCs are nearly constant or decreasing, resulting in ambiguity in ages based on CFCs in waters recharged since the mid-1990s. CFCs have a useful dating range of about 1950 to the early 1990s. The potential dating range of water with SF_6 is from about 1970 to the present, and the SF_6 method is particularly useful in dating very young (post-1993) groundwater, if there are no terrigenic sources of SF_6.

In bimodal (binary) mixtures of young and old (pre-tracer) water, the first case (such as for $^3H/^3He$ dating) yields directly the age of the young fraction in the mixture, but with the second (^3H, ^{85}Kr) and third cases (CFCs SF_6, etc.), the measured concentrations must be corrected for dilution before the age of the young fraction can be estimated. Ratios of CFCs or SF_6/CFC ratios have proved useful in dating young fractions in some groundwater mixtures. Other models with other age distribution functions have been applied to interpret groundwater residence times in aquifers.

Knowledge about the age of groundwater can be used to define recharge rates, refine hydrologic models of groundwater systems, reconstruct historical loadings of contaminants to aquifers, predict contamination potential, and estimate the time needed to flush contaminates from groundwater systems. Detection of environmental tracers in groundwater can be used to trace seepage from rivers into groundwater systems, provide diagnostic tools for detection and early warning of leakage from landfills and septic tanks, and can be used to assess susceptibility of water-supply wells to contamination from near-surface sources.

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GROUNDWATER SUSTAINABILITY AND DYNAMICS I

(Session 2)

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IAEA-CN-104/148

RADIOCARBON DATING OF OLD GROUNDWATER — HISTORY, POTENTIAL, LIMITS AND FUTURE

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The principles of groundwater dating up to about 40 000 yr by means of ^{14}C were elaborated about fifty years ago. Prior this time hydrologic estimates of the recharge rate and flow velocities of groundwater were poor. Already the first ^{14}C dates proved that any elderly water budget or geohydraulic concept had to be substantially revised especially in arid zones. Groundwater is usually considerably older than expected before the introduction of the ^{14}C method. During one decade of gathering experience with groundwater dating it was recognized that absolute dates of groundwater require a so-called reservoir correction either based on the carbon isotope or hydrochemical compositions of the inorganic carbon species or both. A variety of simple to complex correction models for conventional ^{14}C dates was elaborated besides more easily applicable empirical correction methods. Attempts to date groundwater with ^{14}C in the dissolved organic constituents elucidated other kinds of hydrological problems.

The requirement of absolute dates is primarily restricted, however, to scientific-relevant paleohydrological studies. In applied hydrology geohydraulic estimates of the budget of fresh groundwater directly profit from easily determinable relative groundwater ages. Such ^{14}C dates allow estimates of regional geohydraulic parameters of the aquifer and its over and underlain aquitards, monitoring of the groundwater movement and detection of overexploitation.

In any case the interpretation of groundwater ages requires a good understanding of the hydrodynamics of the system to be dated beside that of the hydrochemical composition. In arid and semi-arid zones, these dates allow to differentiate between renewable and non-renewable groundwater resources. This information is indispensable for numerical modelling as neglecting of non-stationary recharge conditions results in overestimated recharge rates.

The difficulty to determine absolute ^{14}C dates of groundwater has supported manifold efforts to search for other environmental isotopes applicable for water age determination. ^{36}Cl has been a promising isotope to date fresh water resources with ages between 100 000 and more than 1.5 million years. However, there are several severe problems in the interpretation of ^{36}Cl dates. One is underground production during groundwater aging and the other is the usually high mineralisation and chloride concentration of old groundwater which lower drastically the detection limit. Similar problems obstruct groundwater dating by ^{129}I theoretically within 3 to 90 million years. Isotope hydrologists hope to simplify the detection of ^{81}Kr. This method namely dates also mineralized groundwater with ages between 50 000 up to 1 million years. At present the analytic and detection requirements are, however, still too complicated for its wide use in applied hydrology.

The uranium isotope compositions allow dating within the oxygenated zone of fresh groundwater resources as successfully proved for limestone and sandstone aquifers. The situation in the reduction zone is theoretically well evaluated but the complexity of processes as absorption and formation of chemical complex compounds has still prevented any successful application.

Theoretically, the continuos formation of ^3He and ^4He as well as ^{40}Ar in aquifers allows groundwater dating between 10 000 and 10 million years. Diffusion loss, complex exhaustion of such gases from both the earth mantle and crust prevents, however, reliable datings of groundwater.

Age determination of old groundwater challenges modelers and isotope hydrologists to find a linkage between the results of finite element modeling and isotope hydrological studies. Even the basic principles are not yet elaborated. On one side a groundwater sample to be dated represents a relatively large compartment of unknown in size of the groundwater resource. On the other side, this compartment contains an unknown number of finite elements of the model. Therefore, the modeled ages of single elements cannot be simply linked to isotope dates. Success is wanted as isotope dates are most suited to calibrate and validate numerical models.

IAEA conferences have been an ideal forum for the sometimes explosive and enthusiastic development and improvement of the various dating methods of groundwater. Controversial discussions sharpened and opened the understanding for a reliable hydrology-related interpretation of groundwater dates. These conferences set benchmarks for the various methods. Moreover, it was the IAEA support in training and application of these methods, in setting up laboratories round the world which formed the solid platform for the world-wide successful introduction of these methods in the management of fresh groundwater resources and the protection measures against pollution.

ESTIMATING AMOUNT AND SPATIAL DISTRIBUTION OF GROUNDWATER RECHARGE IN THE JULLEMEDEN BASIN (NIGER) BASED ON ^{3}H, ^{3}HE AND CFC-11 MEASUREMENTS

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The Continental Terminal (CT) formation of the Jullemeden Basin is located in southwest Niger (Africa) between 12.5-14.5°E and 2.5-4.5°N. The formation comprises three vertically structured aquifer compartments, which are mostly well separated by impermeable silt and clay layers. In this study only the uppermost aquifer (CT3) was investigated. The CT3 aquifer is unconfined and has a thickness of maximally 180 m and it is well sealed against the underlying CT2 aquifer. The average depth to the water table at the selected bore holes is 37.6m.

The regional climate is dominated by semi-arid conditions where average annual rainfall is about 500-600 mm/y. Precipitation has found to be mainly convective. Rainfall events are usually short, intensive and very variable over short distances [1]. About 90% of the precipitation occurs from June to September whereas from December to February virtually none occurs.

Groundwater recharge was only detected in the top aquifer of the Continental Terminal 3 (CT3). Today's estimations of recharge amounts range from 10 to 100 mm/y [2,3,4]. Leduc (1997) proposed that the primary infiltration process occurs through temporary pools and flow channels, and that spatial recharge is very small or negligible. However, stable isotope ratios of CT3 groundwater samples mostly coincide well with the local meteoric water line indicating that the water did not remain at the surface longer than a few days because the high evaporation rates lead to rapid isotope fractionation. All together, the today's picture of amount and spatial distribution of groundwater recharge is rather vague even though this information is essential to provide a reasonable management of the available groundwater resources.

^{3}H, ^{3}He and CFC-11 results from 23 bore holes of the CT3 aquifer were analysed to determine the recharge rates more accurately and to get more information about the spatial distribution of infiltration. The model used to simulate the transport of the three transient tracers is composed of a model for the unsaturated zone followed by a dispersion box model to determine the age distribution of the sampled groundwater volume. For the unsaturated zone transport the model approach of Cook & Solomon (1995) was used and extended for the transport of ^{3}H in the water and the gas phase. A similar approach was used by Brennwald*, et al.* (2002) to estimate the average recharge rate into the CT3 aquifer. The transport equation was numerically solved with an implicit Crank Nicholson scheme assuming known atmospheric tracer concentrations at the top of the soil column and zero diffusion at the groundwater table. The tracer concentrations at the groundwater table are then used as input functions for the dispersion box model. When we fix the soil parameters (porosity, tortuosity and dispersion) three unknown parameters are remaining, namely the recharge rate, the mean residence time and the dispersion parameter.

Since a high dispersion coefficient tends to an exponential age distribution it can be seen as an indicator for spatially distributed recharge. A small dispersion coefficient, on the other hand, tends to a piston-flow distribution and can be seen as local recharge at a distant location and subsequent transport to the sampling site. Therefore, it is possible to outline regions where recharge preferably occurs. Since the soil parameters are highly variable in space they have to be estimated within a certain range. Additionally, the tracers are measured with a different accuracy. To include these uncertainties a Monte Carlo simulation was applied considering the uncertainties of the soil parameters and the measurement errors.

The results show that estimated recharge rates of 50-200 mm/y are still quite rough because the soil parameters were set in a wide range. Particularly a better estimation of the average soil wetness would lead to more accurate results. Since some samples fit well for small dispersion parameters and some do for large ones indicates that it is possible to determine regions where groundwater recharge preferably occurs. In our project area recharge seems to occur at the rim of the ancient river beds where surface runoff is gathered and leads to spatially limited high recharge events and possibly to the observed pools, when the soil is not permeable enough.

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USE OF ENVIRONMENTAL ISOTOPES (^{18}O, ^{2}H, ^{3}H, ^{13}C, ^{14}C) AND HYDRODYNAMIC MODELLING TO HIGHLIGHT GROUNDWATER MIXING IN THE SOUTHWESTERN PART OF THE IULLEMMEDEN BASIN (NIGER)

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The study area, located in the south-western part of the Iullemmeden Basin (03°10’ - 04° 10’ East, 11°30’ – 13°40’ North), is characterized by a semi-arid climate (560-809 mm.year^{-1}), a lack of surface water and a very low aquifer recharge. Geologic setting consists mainly of sandy and silty continental sediments of Cretaceous (Continental Hamadien/Intercalaire) and Tertiary (Continental Terminal: CT) age separated by marly and chalky marine deposits of Paleocen/Eocen age. Four aquifers are identified in these formations.They are: i) one unconfined sandy and silty aquifer in the Continental Terminal (CT3) and alluvial deposits of dry valleys, ii) two sandy and/or oolithic confined aquifers of the Continental Terminal (CT2 and CT1) and iii) a confined aquifer in the Cretaceous sandy deposits of the Continental Hamadien/Intercalaire. Changes in lithology of the clayey layers between the different Continental Terminal units make leakage possible. Because of the difficulty in differentiating the CT3 unconfined aquifer and the confined CT2 in the southern and the northern parts of the area, previous studies assumed that they constitute a single unit. A more precise definition of their relationship is now essential for their sound management.

Our study, carried out as a PhD thesis prolonging the RAF/8/022-NER Project, uses isotopic methods (^{18}O, ^{2}H, ^{3}H, ^{13}C and ^{14}C) to locate the zones of possible mixing between the aquifers. A numerical modelling with the USGS MODFLOW program (McDonald M.G. and Harbaugh A.W., 1988) is used to check the consistency of the conceptual flow model of the unconfined aquifer inferred from the isotopic results.

The isotopic composition of groundwaters discriminate two main groups of samples (fig.1).The first group from the unconfined aquifer (CT3 and alluvial) is characterized by a mean isotopic content of -4.6 ‰ versus V-SMOW for δ^{18}O and -28.4 ‰ vs V-SMOW for δ^{18}O. Its tritium content vary widely from 2 to more than 26 TU where’as the ^{14}C activity shows values between 90.85 ± 0.94 and 182 ± 0.71 pmC suggesting a high spatial variability of the modern recharge process throughout the area. The second group from the confined aquifers (CT2, CT1 and CH) is characterized by more depleted and homogeneous values of stable isotope contents (mean δ^{18}O = -7.41‰ vs V-SMOW, mean δ^{2}H = -53‰ vs V-SMOW), suggesting cooler and/or more humid conditions than the present day climate. These groundwaters are free of tritium and their ^{14}C activity is less than 5 pmC showing a mean residence time older than 15 000 years B.P. Between these two groups lies a group of samples from unconfined (CT3 and alluvial) and confined (CT2) aquifers. Their intermediate isotopic characteristics indicate a mixture between groundwaters from unconfined and upper confined aquifers. Two samples of this group are from the unconfined aquifer (Patchinga and Kawara Ndébé). They are tritium-free and have a particularly low $A^{14}C$ (16.6 ± 0.9 and 66.6± 0.6 pmC respectively) in comparison with the whole upper aquifer, indicating a mixture of 54 to 38 % of old groundwatwers and 46 to 62 % of modern recharge. In these parts of the basin, the three aquifers of the CT system constitute a single unit, the clayey layers becoming more sandy and silty by the western side of the area (Patchinga) where'as in the lower part of the Maouri dry valley (Kawara NDebe) lake water formed by the discharge of the confined aquifers (CT1, CT2) *via* a spring line diffuses in the alluvial aquifer. At the opposite, two samples from the CT2 (Gagila and Garanga) are enriched in ^{14}C (29 and 34.4 pmC) with respect to the other points of this aquifer ($A^{14}C$ less than 5 pmC) indicating a recharge from the upper unconfined aquifer. Similar observations were suggested by previous isotopic data (INC, 1986 ; Beyerle et al., 2003). However, ages up to 4.5 kyr estimated for these mixed groundwaters by Beyerle et al. are not representative of the confined aquifer of CT2. The downward or upward leakage from aquifers, when existing, seems to be restricted to some locations where changes in lithology of the upper aquitard or defective equipment of boreholes favour connection between the unconfined and confined aquifers. These results are consistent with piezometric observations which show a rise of water table in the confined aquifer in these parts of the basin.

Results of the numerical model, calibrated for steady state conditions in 1965, show values of net flux (balance between inflow and outflow in each cell) ranging from –9.0 to 6.3 $mm.year^{-1}$ (mean = 0.6 $mm.year^{-1}$), suggesting high heterogeneity in the recharge process. The negative values (-9.0 to –0.5 $mm.year^{-1}$) are located in region where downward leakage is highlihted by isotopic data and in the dry valleys where the depth of the water table is lower than 5 m. These values mean that outflow (pumping + evapotranspiration + leakage) exceed the inflow. Pumping rate was negligible in 1965 and cannot explain the negative flux balance. At depths of water table from 30 to 45 m, evaporation is lower than the modelled flux. In complement, transpiration cannot explain these highest values. The loss of water by downward leakage is then the most acceptable hypothesis.

Results from the two methods, isotopic and hydrodynamic, are consistent and show that in the study area, CT2 and CT3 aquifers are in contact at some locations. They also show the complexty of the relationships between the aquifers in this part of the Iullemmeden basin and the necessity to combine several methods for their investigation. A sound management of Water Resources in this area has to consider these relations:

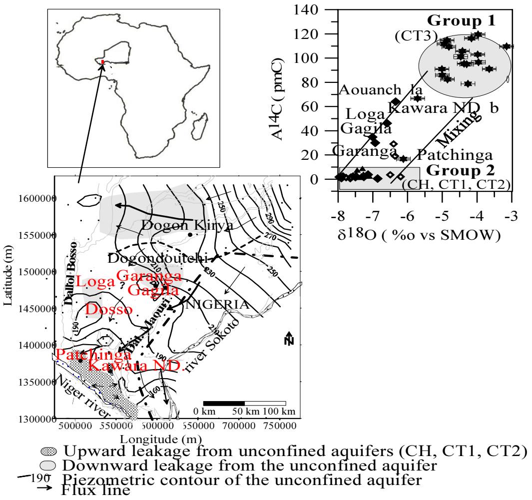

Fig.1- Geographical location of the study area, piezometric contours and Graph of $A^{14}C$ as a function of $\delta^{18}O$ for ground waters.

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CONTRIBUTION OF ENVIRONMENTAL ISOTOPES TO THE STUDY OF RECHARGE AND DYNAMICS OF THE MULTILAYERED AQUIFER SYSTEM OF ZEROUD BASIN (KAIROUAN PLAIN, CENTRAL TUNISIA)

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Most of the multilayered aquifer systems of central Tunisia, which represent considerable groundwater reserves, are characterised by the complexity of their hydrodynamics due to both natural (structure) and anthropic (management) features. In such contexts, investigations based on environmental tracers are particularly useful to better characterise the groundwater systems, to understand their hydrodynamic functioning and to discuss their recharge processes.

For the present study, undertaken with the support of IAEA (project TUN5/017), the aquifer system of the Zeroud wadi (Kairouan plain) was selected. Before crossing the plain, this wadi drains a basin that spreads on 8650 km^2 from the Tuniso-Algerian border. In order to protect the city of Kairouan against the violent floods of the wadi, the dam of "Sidi Saad" was constructed in 1983 at about twenty kilometres upstream the plain. The construction of the dam has obviously disturbed the natural flow regime and strongly influenced the relationships between the wadi and the groundwater system, which comprises a shallow and a deep aquifer contained in Plio-Quaternary (sands and clayey sands). Campaigns of artificial recharge, by water release from the dam, have been done regularly to maintain the recharge of the shallow aquifer.

Sampling and field parameters determinations (temperature, pH, total alkalinity$^-$) for groundwater (from wells and boreholes) and surface water (from reservoir lakes) have been carried out in two sampling campaigns (Fig.1): (i) during the humid season (November 1997) and (ii) at the end of the dry season (September 1998), when the water levels in reservoir lakes are relatively low. Rainwater samples were also collected in some stations located in the Zeroud basin, on an event basis.

Stable isotope analyses (^{18}O, ^{2}H, ^{13}C) have been performed in the laboratories of "OrsayTerre" in Orsay. Tritium concentrations were determined in the laboratories of IAEA. Carbone-14 dating and chemical analyses (Ca^{2+}, Mg^{2+}, Na^+, K^+, Cl^-, SO_4^{2-}) have been made respectively at the Laboratory of Radio-analyses and Environment and at the Laboratory of Geochemistry and Environment Sciences of ENIS

Rainfall isotope data, collected from late 1987 to late 2000 show that values range from -10 to -1.7‰ for ^{18}O and from -64.4 to +0.9‰ for ^{2}H. The mean is about –5 ‰ and -29‰ respectively in oxygène-18 and deuterium. Stable isotope values measured in lake water range from –4.47 to +7.41‰ for ^{18}O and from –40.5 to +27.9 ‰ for ^{2}H. In groundwater, values range from –6.36 to –4.5 ‰ for ^{18}O and from –41.2 to –24.8‰ for ^{2}H (Fig.2). The carbone-14 activities range from 0 to 73 pmC.

The evolution of the chemical facies, the spatial distribution of salinity, carbone-14 activities and stable isotope contents (^{18}O, ^{2}H) show that the recharge of the aquifer system comes from direct infiltration of rain, as well as from flood water of the Zeroud wadi. For the deep aquifer levels, the recharge is preferentially active in the bed of the wadi, in the upstream part of the basin. However, the shallow aquifer is recharged along the whole of the southern bank of the wadi. This recharge is particularly efficient in Menzel Mhiri and Argoub er Remth-Bled Ben Zina zones, due to a good permeability of sediments.

The similarity of isotopic signatures and chemical facies between shallow and deep groundwaters in some places, mainly upstream of the basin, confirm the vertical inter-aquifer leakage, already suggested by piezometry. This phenomenon may explain the low tritium contents (values range from 0 to 17 UT), sometimes measured in shallow water. However, old groundwaters with distinct chemical facies have been found in the deep level, downstream of the basin, and could be inherited from a palaeorecharge.

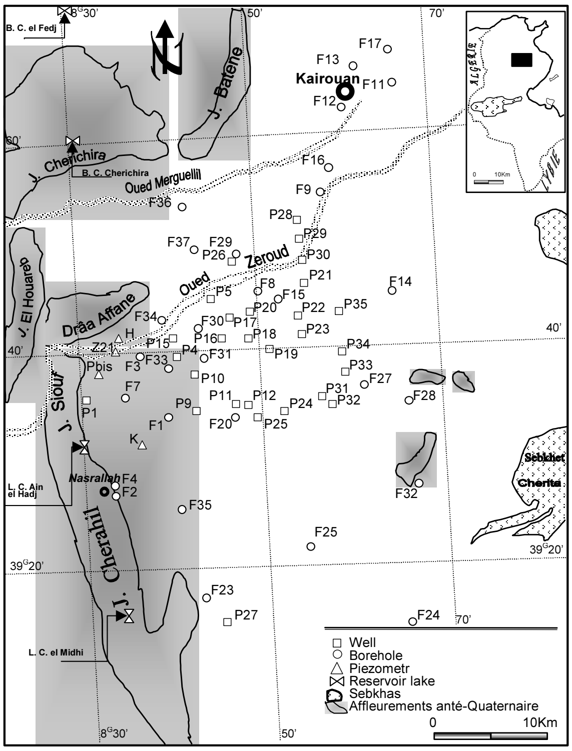

Fig. 1 : Location map of the study area and sampling points

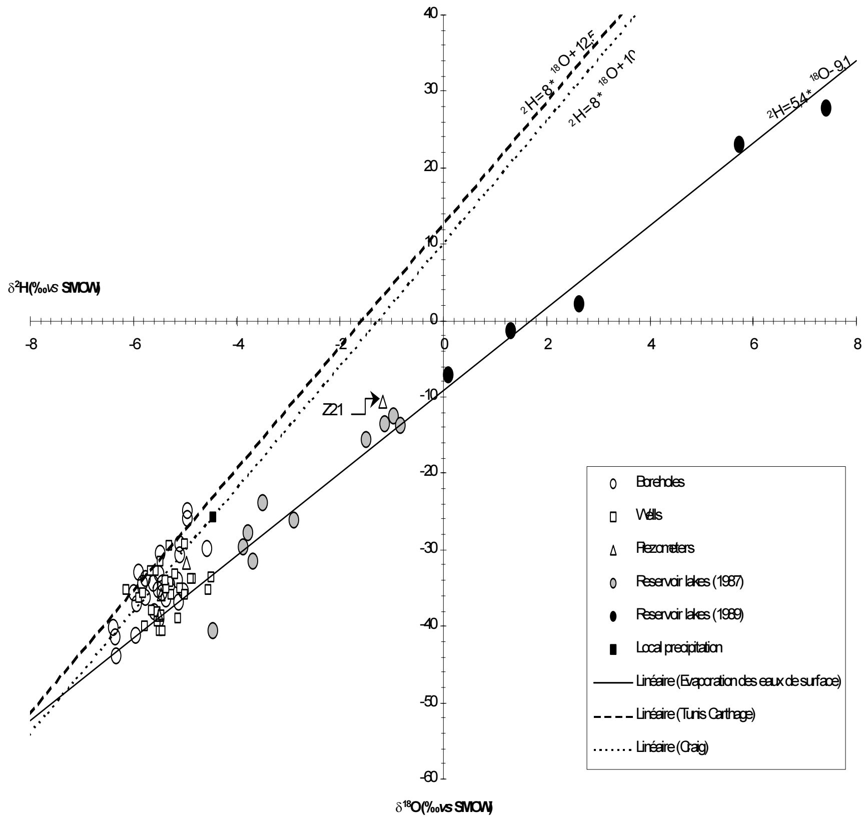

Fig. 2 : Oxygen-18/Deuterium diagram of Zeroud basin

GROUNDWATER SUSTAINABILITY AND DYNAMICS I
(Session 3)

Chairpersons

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France

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Tunisia

IAEA-CN-104/170

ORIGIN AND RESIDENCE TIMES OF THE GROUNDWATER IN THE MULTILAYERED AQUIFER OF TADLA (MOROCCO)

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Abstract

Ninety-four samples were collected from the multilayered aquifer (Mio-Plio-Quaternary, Eocene, Senonian and Turonian) of Tadla (Morocco) and have been analyzed for their major chemical elements and the stable and radioactive isotopes of the molecule of water (^{18}O, ^{2}H, ^{3}H) and of the Total Inorganic Dissolved Carbon TDIC (^{13}C and ^{14}C).

The multidimensional statistical study of these parameters by the Main Component Analysis (MCA) indicates the existence of two big groups of groundwater that are distinguished by their chemical and isotopic characteristics. These two groups correspond to the unconfined and the confined zones of the different aquifers.

The isotopes, and more particularly the $\delta^{18}O$, $\delta^{2}H$ and the ^{3}H contents indicate that the present recharge continues to function, notably in the North part of the basin, where all the aquifers outcrops. The present recharge continues also to function in the Turonian aquifer in its East and Southwest outcrop. The present recharge is done rapidly for the Turonian aquifer and after a certain time of retention in the unsaturated zone for the Senonian and Eocene aquifers, where the groundwater undergoes a kinetic evaporation.

Two other big periods of recharge could be distinguished. The first one corresponds to a cold climatic period. It would be produced toward 18000 B.P. years (Late Pleistocene). The groundwater of this paleo-recharge is found in the deep aquifers, but exclusively in their confined zones. Another important period of paleo-recharge, more recent, and relatively less cold, would be located toward 3500 B.P. years (Late Holocene). The groundwater of this paleo-recharge is found again in the whole aquifers, both in their unconfined and confined zones. It could correspond, on the other hand, to a mixing process between groundwater from the first paleo-recharge and groundwater from the present recharge.

All the chemical and isotopic parameters indicate indeed, the existence of a large intercommunications between the different aquifers “per descendum” in their unconfined parts and “per acsensum” in their confined parts.

All isotopes showed that the springs which are located in the South-West of the basin and supposed to be, by the previous studies, the natural outlet of the different aquifers, are very recent, with high ^{18}O and ^{2}H signatures due to the high altitude (Atlasic recharge type).

The integration of all isotopic results of this project will certainly permit the revision and the development of the resource management mathematical water model of the plain of Tadla.

CONCLUSION

The present recharge of the aquifers of Tadla basin continue to function principally to the level of the North outcrops. For the Turonian aquifer, it exists a contribution of Atlasic type to the level of the outcrops of southerly West and of the East. Two other periods of recharges could be considered. They took place under a cold climate, probably toward 18000 B.P years during last maximum corresponding glacier to the Late Pleistocene. The groundwater of this recharge is to found in the three deep aquifers (Eocene, Senonian and Turonian). The other period of recharge would be produced during the terminal Holocene, toward 3500 B.P years under a relatively hotter climate. The groundwater delivering “ages” of about 3500 years can also correspond in part to miscellanies between the present recharge and the Pleistocene recharge.

The present recharge to the level of the outcrops does quickly for the Turonian aquifer and after a certain time of retention in the unsaturated zone for the Senonian and Eocene aquifers. The Mio-Plio-Quaternary aquifer receives the local recharge by the precipitations and an Atlasic recharge via the surface network and superficial springs.

For the modes of discharge, no relation is made between the springs of the south West of the basin and the different aquifers, at least to the moment of sampling. If the relation exists, she would be surely of low ampleness. In all the cases, if any relation exists in the time, it is clear that the springs of the Tassaout aval don’t constitute the main outlet aquifers of the basin.

The integration of all isotopic results gotten during this project will certainly permit the revision and the development of the resource management mathematical water model of the plain of Tadla.

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EVALUATION OF MODERN RECHARGE IN THE LOS ARENALES DETRITIC AQUIFER, CENTRAL SPAIN

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A comprehensive study of the hydrogeological framework and groundwater resources using geochemical and isotope methods was recently carried out in the Los Arenales hydrogeologic unit. The aquifer extends over ~7.600 km^2 on the central part of the Iberian Peninsula, about 200 km north of Madrid. The stratigraphic sequence is composed of Upper Tertiary sediments (mostly Miocene) of continental origin that conform the Duero Basin. The sediments are mostly of terrigenous character, generally of low permeability, due to the presence of clay minerals. Lenses of sandy and silty materials, linked to palaeoriver-beds, constitute the main aquifers, extending to a maximum depth of 500 metres. However, most of these lenses are poorly interconnected due to the characteristics of the clayey matrix of the rock formation. This lithologic control is strongly limiting the existence of a regional groundwater flow from the mountainous regions towards the Duero river, as has been generally accepted till now in most of the previous hydrogeological studies. The aquifer is phreatic in certain areas, partly confined or confined in others.

Despite the abundant geological information available and the large number of boreholes and wells drilled and monitored in the area, the existing conceptual models were unable to explain the observed changes in the piezometric levels, the development of depressions as well as the variations in water quality. The lack of lateral groundwater flow, which is controlled by the existence of more permeable lenses, led to the development during the past 20 years of some serious piezometric depressions. The situation forced the local Water Authority to establish serious limitations to the exploitation of the aquifer.

The main characteristics of the most representative chemical components of groundwater, as well as its spatial distribution has been studied by sampling 141 pumping wells. Similarly, the same sampling points have been considered for stable isotopes (141 wells), while 50 wells were sampled for carbon-14 and carbon-13. The large spatial variability of all these parameters confirmed previous indications on the high heterogeneity of the flow pattern in the aquifer. In fact, the different hydrochemical maps produced suggest the existence of numerous aquifers poorly or not interconnected. Both carbon-14 and stable isotopes results have provided evidence of the presence of paleowaters, mainly, in the deepest wells. Similarly, the existence of sodium-bicarbonate facies, as result of cation exchange processes in the aquifer, pointed to a large residence time of most groundwaters in the system.

An estimation of the average recharge-rate R_a for the period 1953-1994 has been made on the basis of the tritium balance using the following equation:

$$(R_a)_{53-94} = (P_a)_{53-94} \frac{(I_T)_{aquifer}}{(I_T)_{precipitation}}$$

where P_a is the average precipitation and I_T the tritium inventory.

The value of $(I_T)_{precipitation}$ has been obtained from the tritium contents in precipitation measured in the Madrid station since 1970, and a general distribution model of tritium in precipitation valid for the Northern Hemisphere. A value of 45.000 Bq/m^2 was obtained. The tritium inventory in the aquifer (saturated zone) has been calculated individually for the 141 wells from the measured concentration values and the thickness of the water column deduced from the lithological columns. The contribution to the unsaturated zone has been considered null for those areas (Thyessen polygonal areas) where no or negligible tritium concentration was found and the carbon-14 "age" was higher than 1.000 years. The tritium balance has been corrected for tritium losses due to the water extraction made during the period 1953-1994.

An average recharge-rate for the indicated period of time equal to 32.2 mm/year was obtained, which represents a total annual recharge of 244.7x10^6 m^3/y. In spite of the uncertainty of some of the parameters used for the calculation, this recharge-rate is very similar to the estimations made by some authors using conventional hydrometeorological techniques. However, the most interesting result obtained by this investigation is the spatial distribution of the recharge (see Figure). It was concluded that about 96% of the recharge is concentrated in a surface of 3.530 km^2, that is to say, in ~46% of the aquifer surface. No modern recharge was obtained for the areas affected by the above-mentioned piezometric depressions.

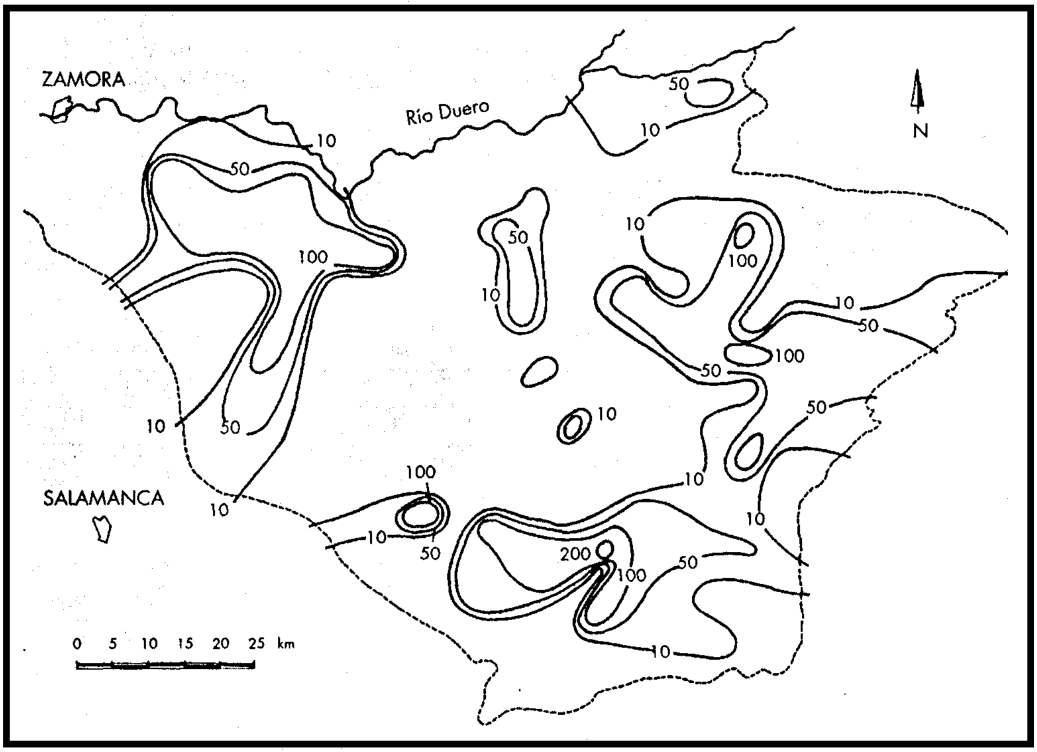

Fig. 1. Distribution of the modern recharge (in mm/a) in the LosArenales aquifer derived from the tritium balance method.

CHEMICAL AND ISOTOPIC TECHNIQUES FOR DEVELOPMENT OF GROUNDWATER MANAGEMENT STRATEGIES IN A COASTAL AQUIFER: KRISHNA RIVER DELTA, SOUTH INDIA

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The Krishna and Godavari districts of the Andhra Pradesh in India have a flourishing agricultural production and the farmers of these areas make use of the mineral rich alluvium of the Krishna river delta more effectively for the purpose. The delta comprises sediments of both fluvial and marine origin. The oscillating depositional environments, fluvial to marine, have led to a complex hydrogeological setting with heterogenous sediments. The river alluvium consists of clay, sand and gravel, whereas coastal alluvium comprises mainly beach sands. The paleo-channels with coarse sediments and flood plains with alternations of coarse and finer clastics form the repository of groundwater. Sand dunes and beach ridges also form aquifers of limited extent. The individual permeable sand beds and the thick confining impermeable clay zones are constituting a multi aquifer system in the Krishna delta. The laterally extensive as well as lens shaped bodies of granular zones and often inter connected layers comprising sand and gravel form the potential shallow, medium and deep aquifers.

Groundwater occurs under water table condition in shallow aquifers (upto 30 m bgl) and semi-confined to confined conditions in medium (30 to 60 m bgl) and deeper aquifers (>60 m bgl). The groundwater quality vary widely both laterally and vertically in the alluvial formations. By and large, the most potential fresh water aquifers occur as isolated pockets and their extent is more in upper deltaic plain, whereas in the coastal tracts the fresh water occurrence is limited to sand dunes and beach ridges at shallow depth up to 14 m. The quality of deeper aquifers down to about 200m is generally brackish to saline water in the deltaic region except in some pockets (Rao, 1999).

The irrigation demand is met through the extensive canal network that offtake from Prakasam Barrage located across the river Krishna in Vijayawada. In recent years it has been reported that groundwater is being extensively used in addition to the surface water supplied through the canal systems. The groundwater is also used to meet the domestic needs. Several tube wells have been installed in the northern part of the delta region. In the southern coastal region, due to the geological set up, wells have been drilled up to a depth of 120 m to meet the domestic needs as well as for the purpose of prawn culture activities. An earlier study by the state groundwater department indicated marginal advancement of the salinity front in the unconfined aquifers landwards in the period 1977 to 1996.

Identification of the origin of groundwater salinity and design of measures to control the salinisation process are the problems usually faced by a hydrogeologist. The conventional chemical data on groundwater allow formulation of hypothesis regarding chemical evolution and origin of salinity. Generally the ionic ratios such as Na^+/Cl^-, Ca^{2+}/Mg^{2+}, Cl^-/I^- are used for the purpose. However, in many cases the chemistry of water may undergo further secondary changes such as precipitation, ion exchange etc., which may make it difficult to identify the salinisation mechanism precisely. Environmental isotopes ^3H, ^{14}C, ^2H and ^{18}O could help in knowing the source of the salinity. Age evaluations using radio-isotopic techniques confirm the chemical differentiation arising from variations in groundwater residence time in aquifers (Cottechia, 1977). Measurements of stable isotopes, i.e., oxygen (^{18}O) and deuterium (^2H) may record the process by which the original isotopic composition of the freshwater component has been modified owing to mixing with seawater, evaporation or leaching. Modern seawater possesses increased ^{14}C (radiocarbon) and ^3H (tritium) activity owing to precipitation containing ^{14}C and ^3H from thermonuclear fallout. Therefore, modern seawater intrusion increases ^{14}C and ^3H concentration of the coastal groundwater, causing tritium easily detectable and the apparent ^{14}C ages to be younger. Further, in coastal tracts where there is a constant change in the sea level, seawater intrusion is the major cause for salinity in the groundwater apart from other sources. This salinity restricts the scope of groundwater utilization in the coastal area. It is thus important to differentiate between ancient and modern salinity to curb further salinisation. The best way to differentiate between modern and paleosalinity is to date the water by a suitable dating technique.

The present paper presents the details of a joint study undertaken by three Indian organisations namely, National Institute of Hydrology Roorkee, Bhabha ataomic Research Centre, Mumbai and Andhra Pradesh Ground Water Department under a World Bank aided project using isotopic and hydrochemical approaches to study the salinity conditions in the groundwater of the river Krishna delta region. The study also focussed on the identification of potential recharge zones to augment the groundwater resources by artificial recharge.

The water samples that were collected from different locations in the river delta belonging to different aquifers, river, reservoir, canals , and sea etc were analysed for major cations viz. Ca^{2+}, Mg^{2+}, Na^+ and K^+ and major anions HCO_3^-, SO_4^{2-} and Cl^- along with Sr^{2+}, I^- and F^{-1} for few selected samples. The environmental tritium and cabon-14 measurements were carried out to date the waters. In addition, the water samples were also subjected to stable isotopic analyses (deuterium and oxygen –18 ratios) to understand the mixing and evaporation effect.

The results of the study that was conducted from October, 1999 to April, 2002 show that the salinity in the water bearing strata of the aquifer system is mostly due to palaeogeographic conditions and the modern sea water intrusion is limited to the intermediate aquifers (found between 30-60m below ground level) in the area adjoining to the coastal belt and shallow aquifers influenced by tidal inflow in the river Krishna or its distributaries only few kilometers from the sea coast (Figure 1). The analyses of hydrochemical data and the water type classification based on ionic concentrations shows that the groundwater is getting refreshened due to intense irrigation practices through canals. The direction of the refreshening front movement and the pattern of distribution of refreshening type or saline type are reflected clearly in the distribution of environmental tritium concentration in the study area (Figure 2). Combined use of hydrochemical and environmental tritium maps of the area for different aquifer systems clearly show the active zones of recharge to these aquifers. From these information, it is possible to develop a sustainable stratgey to enhance the groundwater recharge rate and to expedite the groundwater quality amelioration process.

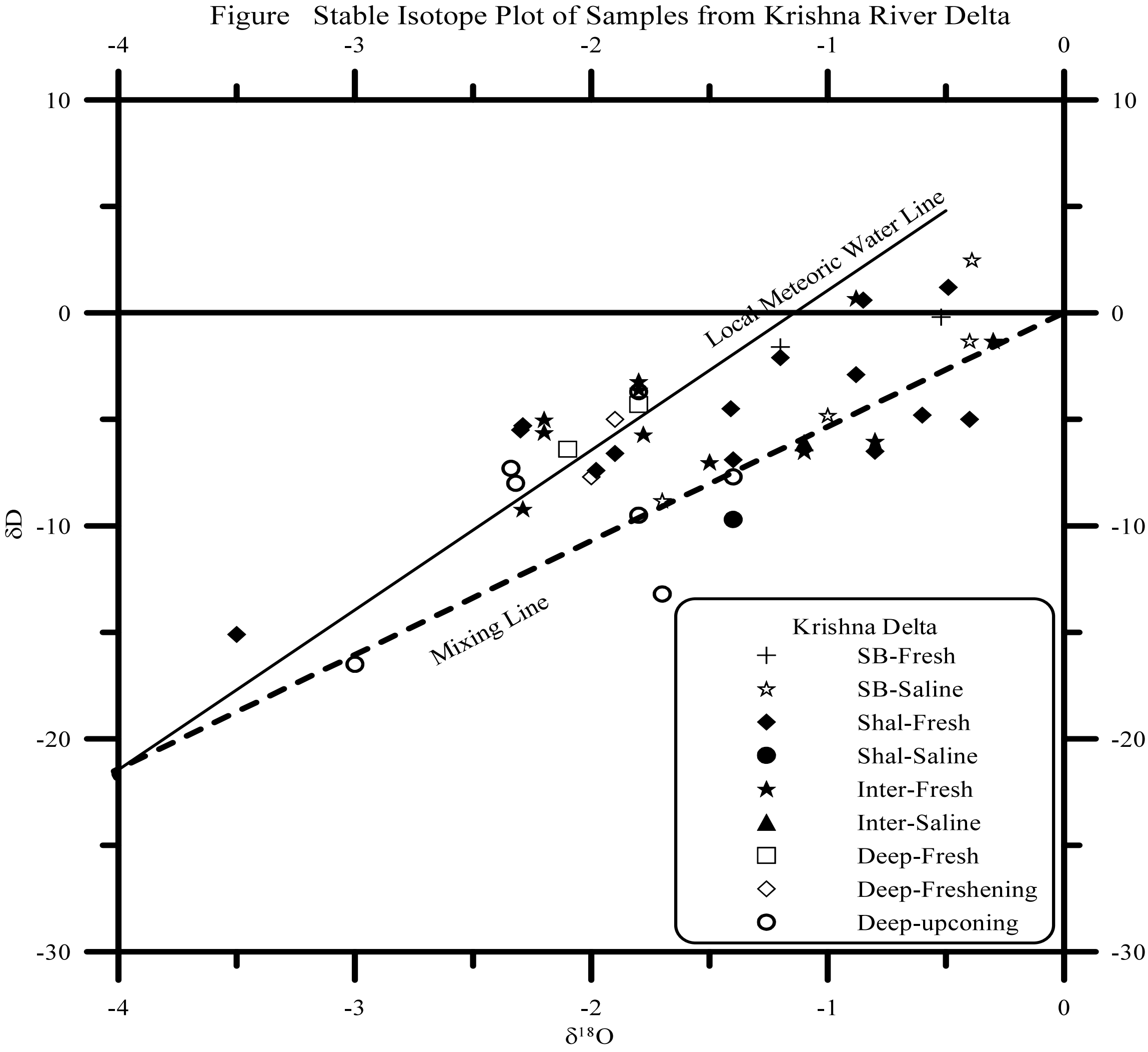

Fig. 1. δD-$\delta^{18}O$ plot of the data pertaining to the groundwater samples from the Krishna river delta region. The mixing trend as depicted by the mixing line is distinvt from the local meteoric water line.

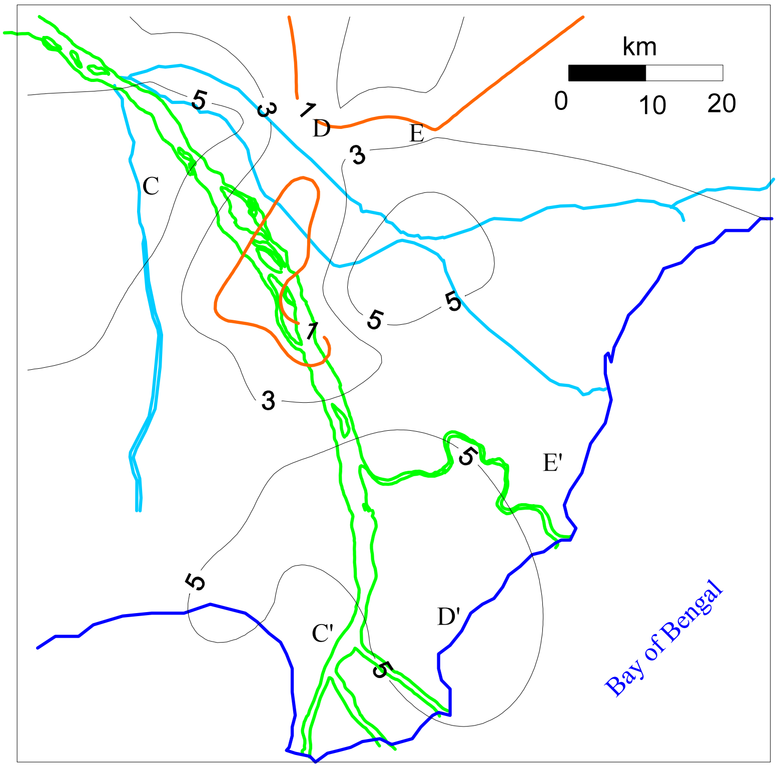

Fig. Environmental Tritium Contours in Shallow groundwaters (<30m).

Fig. 2. Distribution of Environmental tritium concentration in the shallow groundwater (<30m bgl) in the Krihna delta region (India).

IAEA-CN-104/132

ASSESSING AQUIFER CONTAMINATION VULNERABILITY USING TRITIUM-HELIUM AGES IN PUBLIC DRINKING WATER WELLS IN CALIFORNIA, UNITED STATES OF AMERICA

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We have sampled over 800 public drinking water wells as part of a study to assess relative contamination susceptibility of the major groundwater basins in California. This project is sponsored by the California State Water Resources Control Board, and is carried out in collaboration with the U.S. Geological Survey. The parameters used to rank wells according to vulnerability are groundwater age dates (using the tritium-^{3}helium method), stable isotopes of the water molecule (for water source determination), and occurrence of low level Volatile Organic Compounds (VOCs). The project, carried out in collaboration with the US Geological Survey, uses these observational data in a probabilistic approach to assess the vulnerability of public water supply wells to contamination by anthropogenic compounds. Sources of contamination to groundwater occur near the earth's surface, and have been present mostly since World War II. Therefore, wells that receive water that has recharged in the recent past (young groundwater ages) are more likely to intercept contaminants transported by advection.

Because of the large number of samples collected, the major basins used for drinking water supply can be compared and contrasted in terms of relative vulnerability. A large volume of both imported and locally captured water is artificially recharged in these urbanized, intensively managed basins. Imported recharge water from higher elevations is identified by lighter δ^{18}O signatures, while the downgradient flow pattern of recent recharge is outlined by increasing groundwater age. The presence of a continuous confining unit can be the key feature for protecting deep aquifers in areas with ubiquitous surface contamination. For example, an effective confining unit in the Santa Clara Valley basin (Silicon Valley) prevents widespread vertical transport of contaminants down to drinking water wells. In the Los Angeles County and Orange County basins of southern California, groundwater age and the frequency of occurrence of low-level VOCs are spatially correlated, with more recently recharged water likely to have VOC detections. In particular, the gasoline additive methyl tertiary butyl ether (MTBE), which has had widespread use only in the last decade or so, occurs only in the youngest groundwater. 'Pre-modern' water is nearly always free of VOCs, except when a suspected 'short circuit', (e.g., loss of integrity in well casing) allows near surface contamination to reach 'old' water.

Long-screened production wells used for public drinking water supply clean, high quality samples, and sample the resource that is being exploited. However, the groundwater age distribution from production wells may be quite broad, and comparisons to the predicted initial tritium value for the measured mean age, along with analysis of radiogenic ^{4}Helium are used to de-convolute the mixed age. The tritium that was present at the time of recharge is well defined from measurements of tritium in precipitation. A groundwater sample for which the measured age gives a decay-corrected tritium value that falls on or near the curve, does not have a significant component of water that dilutes the tritium measured. Samples that fall below the ‘initial tritium’ curve contain a fraction of water that recharged before 1955 (‘pre-modern’; Fig. 1).

The analysis of the age distribution of groundwater at production wells allows estimation of the dilution factor for a contaminant introduced in the young water fraction, and furthermore provides a predictive capability for the future trend to be expected for the contaminant. Water resource managers can use these vulnerability assessments to focus monitoring efforts, site new wells, plan land use, and evaluate remediation activities.

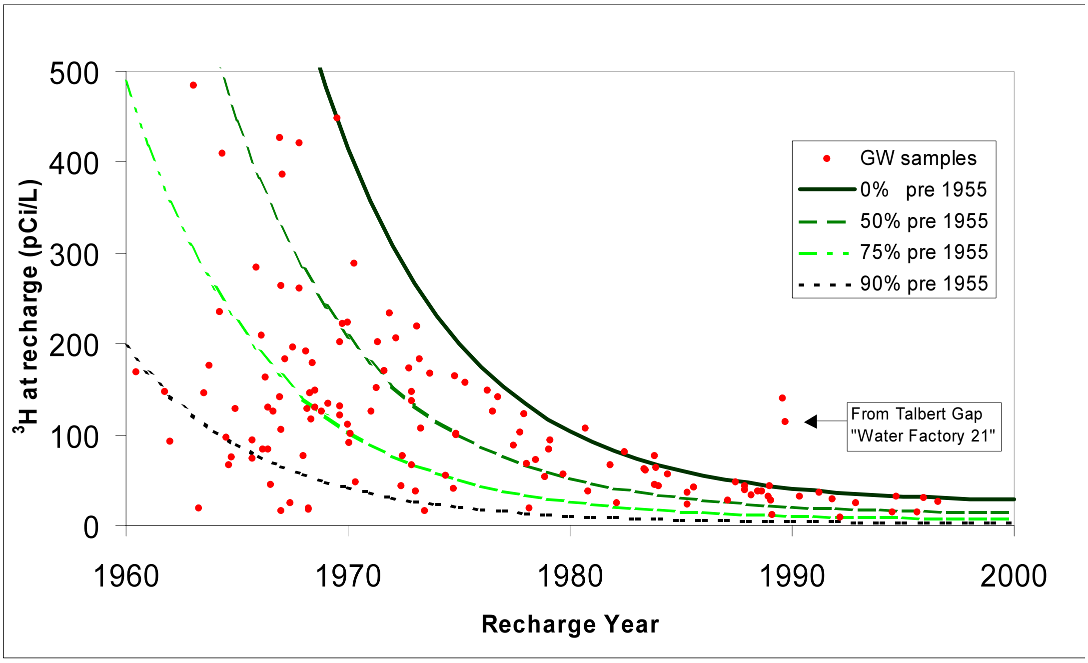

FIG. 1. The zero percent pre-modern curve shown represents tritium measured in precipitation over the last several decades. Curves for mixtures containing equal fractions pre-modern water are shown for reference. Well water samples from public supply wells in southern California, USA, are plotted according to the mean tritium-helium groundwater age measured, and the corresponding expected initial tritium value at the time of recharge. Many wells draw a large fraction of pre-modern groundwater. Two samples above the curves indicate the presence of a local industrial or medical tritium contribution.

This work was performed under the auspices of the U.S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under contract No. W-7405-ENG-48.

GROUNDWATER DATING WITH SULFUR HEXAFLUORIDE: METHODOLOGY AND FIELD COMPARISON WITH TRITIUM AND HYDRODYNAMIC METHODS

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The tritium method was regarded for several decades to be the simplest and most convenient tracer method for determining the ages of young groundwaters. However, with the tritium levels declining in the atmosphere, certain modifications of the tritium method were proposed, such as $^3He/^3H$ and $^3He+^3H$ methods [1]. Also some anthropogenic atmospheric trace gases have been adopted as dating tools for young groundwaters, for instance ^{85}Kr [2] and freons (F-11, F-12 and F-113) [3]. Another atmospheric trace gas of anthropogenic origin (SF_6) has recently been shown to a reliable tool for dating young groundwaters [4]. The SF_6 concentration in the atmosphere increases monotonically since about 1960 to the present concentration of about 5 pptv, which corresponds to about 2.2 fmol/l in water being in equilibrium with the atmosphere at the temperature of 10 °C. In the present study, performed partly under the BASELINE Project carried out within the EU Fifth Framework Programme, a simple methodology of SF_6 analyses in groundwater samples has been developed and interpretation procedures tested. The current detection limit of our analytical system is approximately 0.02 fmol/l. Samples are collected in glass bottles (ca. 2.4 l) without contact with the atmosphere and are transported to the laboratory where the dissolved gases are extracted using the headspace method. The extracted SF_6 is measured using gas chromatograph equipped with an electron capture detector [5].

Two confined Polish sandy aquifers of Tertiary age were investigated within the project. The hydrochemistry (major, minor and trace components) and environmental tracers (^3H, ^{14}C, ^{13}C, ^2H, ^{18}O, F-11, F-12, F-113 and SF_6) were measured. Tritium and SF_6 ages were estimated from time records of the tracers using the lumped-parameter approach [6]. The hydrodynamic modelling was performed with the Visual-MODFLOW, flow times estimated with the MODPATH, and the space distributions of tritium and SF_6 modelled with the MT3D. The presented work summarizes the results obtained so far in the Bogucice Sands aquifer, which belongs to the medium-size aquifers in Poland with the area of 176 km^2. It consists of sands and sandstones of a Badenian deltaic basin, with high carbonate material contents (3-10 % in sands and 25-29 % in sandstones). The recharge is mainly at the outcrops in the south, and by downward leakage near the outcrops and in some areas of extensive withdrawal. The general flow direction is towards the Vistula valley in the north, with discharge by upward leakage through the confining layers of clays and claystones. The hydraulic conductivity values found from pumping tests performed within the aquifer boundaries decrease in the direction of flow from approximately 8.8×10^{-5} to 2.3×10^{-6} m/s.

In general, tritium and SF_6 contents show similar space distributions, and their measurable concentrations roughly correspond to the position of the redox boundary. In some wells in spite of roughly constant tritium concentration of about 8 T.U. observed for three years, no measurable SF_6 was found. That discrepancy is easily explained by one of the fitted models (dispersion model with the mean age of 158 years and the dispersion parameter of 0.5). Similarly, in another well, the SF_6 data allowed to identify the most adequate model from those fitted to the tritium data. However, in general, the SF_6 data yield lower ages, which is qualitatively justified by shorter travel times of that tracer through the unsaturated zone [4].

The initial hydrodynamic and transport modelling yielded in some wells much lower and in other wells much higher SF_6 and tritium concentrations than those measured. This means that hydrodynamic and transport models do not yield unique solutions unless calibrated with the tracer data. Calibration of the numerical models with the tracer data in the area of young waters is under way, but the analysis of the data available to date shows that all the main discrepancies can be explained by known or probably existing complexities of the aquifer and confining layers. For the two most distant wells, where the stable isotope and ^{14}C data indicate a glacial age, the initial modelling with the MODPATH yielded 2 ka. However, glacial ages are easily obtainable in the model by adequate changes in the hydraulic conductivity of the permeable and semi-permeable layers.

Tracer data explain the existence of three different hydrochemical zones. Young waters with distinct tritium and SF_6 contents are aerobic, and of HCO_3-Ca-and HCO_3-SO_4-Ca types. In that zone slightly increased Na and Cl contents as well as the highest concentrations of SO_4 and nitrates are observed due to anthropogenic influences. Older waters are deeper, under the confining cover, in the zone of anaerobic conditions. Dissolved oxygen, nitrate and uranium contents are reduced, and Fe, Mn and NH_4 contents increase in that zone. In the third zone, waters are of glacial age and of HCO_3-Ca-Na or HCO_3-Na types with TDS values higher than 1 g/l and Na content higher than 200 mg/l, due to either admixtures of older waters, or still going on freshening of marine sediments.

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UNSTEADY STATE LUMPED PARAMETER MODELING OF ^{3}H AND CFCs TRANSPORT: ANALYSES OF GROUNDWATER RESIDENCE TIME DISTRIBUTION IN A MOUNTAINOUS KARSTIC AQUIFER

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Karstic aquifers with their potentially high infiltration capacity comprise of important groundwater reservoirs, which are also prone to rapid contamination due to relatively high flow velocities. These aquifers almost always posses an extremely heterogenous distribution of geohydrologic properties and usually have unmeasureable hydraulic head distribution. Additionally, the mountainous karstic aquifers are highly tectonized and have complex flow geometry as dictated by the intercalation of permeable and impermeable geologic units. In such systems, groundwater flow dynamics can not be determined with the present knowledge of analytical or numerical approaches of flow dynamics as used in distributed parameter models. Lumped parameter models present an alternative way by handling the whole aquifer as a system whose internal details are not known [1]. The "system analysis" approach allows the use of environmental tracer data to analyze the groundwater residence time distribution provided that tracer input series and observations on system's output is available. In this approach, all parameters and processes affecting the transport of water mass or tracer are lumped into one single equation, the system response function, which is user-selectable.

Developments in system analysis science and in associated mathematics enable the derivation of system response functions for more complicated conceptualizations under steady [2] or unsteady [3, 4] state conditions (i.e. variable in/out flux, variable volume of system components). A bundle of 15 different lumped parameter models (LUMPED UNSTEADY "LU", [5]), which are capable of using ^{3}H, ^{85}Kr, CFCs and SF_6, was developed to run under unsteady flow conditions. LU models are capable of simulating tracer transport in plug and exponential flow reservoirs, which may be connected in any combination of series or parallel fashion and may have by-pass flow and/or dead volume components.

The LU models have been applied to mountainous Aladag karstic aquifer in the Eastern Taurids Range of southern Turkey. The aquifer lays over an area of 750 km^2, extends between 400 m and over 3500 m elevations and comprises of 5 carbonate nappe slabs separated by impermeable covers. The whole system is drained by several springs, which are located in tectonic windows of overlying impermeable ophiolitic nappe. The minimum total groundwater discharge was estimated to be 31.5 m^3/sec. Our environmental tritium based lumped parameter modeling attempts in springs of shallow and deep groundwater circulation resulted in plausible residence time distributions and were in agreement with the hydrogeologic conceptualization of the flow systems (Figure 1). In general, the springs with shallow circulation conforms well to serially connected plug and exponential reservoirs with by-pass flow of varying degree while those of deep-circulation are in agreement with exponential (with some dead volume) and plug flow reservoirs. The same model runs with CFCs resulted in higher residence time values than those of tritium. The difference may be attributed to the presence of deep unsaturated zone, which might have caused by a time delay in transport of this tracer to water table. The results of unsteady and steady lumped parameter models [6] for the same field cases were also discussed in view of uncertainties in the model inputs.

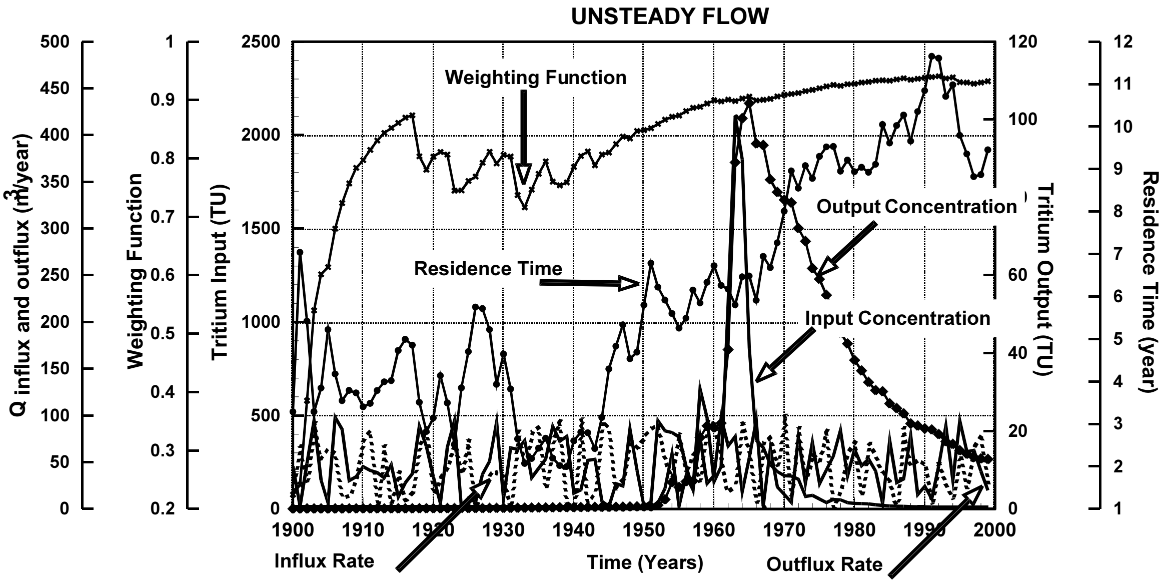

FIG.1. Unsteady state system response of a karstic spring in Aladag aquifer to environmental tritium input. The model comprises of an exponential flow reservoir. Weighting function shows the sum of weighting function series for each year.

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RIVER SYSTEM DYNAMICS

(Session 4)

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TRACING NUTRIENT SOURCES IN THE MISSISSIPPI RIVER BASIN, UNITED STATES OF AMERICA

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Periodic hypoxia in the Gulf of Mexico near the mouth of the Mississippi River is of increasing concern. The condition is thought to be primarily the result of nitrate delivered to the Gulf by the Mississippi River. However, as much as half of the nitrogen transported by large rivers to coastal areas is in dissolved or particulate organic form, with the remainder primarily as nitrate. Nitrate is thought to be conservatively transported in the Mississippi and other large rivers, but reduction can occur in marshy pools and backwater channels. Thus, it is important to examine all forms of nitrogen and their potential transformations, in both in groundwater and in iverine environments. To provide critically needed information for the development of management strategies to reduce N loads and enhance N attenuation mechanisms, we have been using isotopic techniques to investigate the sources and cycling of nutrients at a number of sites in the Mississippi Basin (which includes the Ohio and Missouri River Basins) since 1996, in collaboration with several national monitoring programs [1].

One of our most noteworthy finding was that about half of the POM in the Mississippi (and other big rivers in the USA) is composed of plankton and/or heterotrophic bacteria. This suggests that in-situ productivity may be a significant source of bioavailable organic matter contributing to the hypoxia in the Gulf of Mexico [1]. Monthly samples from 19 river sites in the Basin sampled over 5 years showed that δ^{15}N and δ^{13}C were quite useful in discriminating among four major categories of POM: terrestrial soil, fresh terrestrial vegetation, aquatic macrophytes, and plankton/bacteria. The δ^{13}C values for the sites ranged from about -35 to -20‰, and the δ^{15}N values ranged from about -15 to +15‰. The isotopic data, along with ancillary chemical and hydrologic measurements, were also useful for documenting seasonal changes in in-situ processes.

A pilot study in 2000-2001, designed to investigate the usefulness of isotopic techniques for determining nutrient sources in 24 medium and large watersheds in the Basin, found that nitrate and POM from basins with different land uses (e.g., row crops, animal farming, urban development, and undeveloped) had moderately distinctive isotopic compositions [2]. The nitrate $\delta^{18}O$ and $\delta^{15}N$ values of the large rivers sites resembled the compositions seen in sites dominated by row crops. Sites with livestock tended to have high $\delta^{15}N$ values characteristic of manure, and urban and undeveloped sites tended to have higher $\delta^{18}O$ values characteristic of a significant fraction of atmospheric nitrate. The $\delta^{18}O$ data were critical in showing abrupt changes in nitrate sources with discharge [3].

Because of the success of the pilot studies, a more thorough study of nutrient sources in the Ohio River Basin was initiated in 2002. For this study, nitrate, POM, and water were collected 15-20 times each year at 6 small NAWQA-program watersheds in the White River-Miami River basins, and at the 7 large river NASQAN-program sites in the Ohio River Basin. Nitrate samples were analyzed for $\delta^{15}N$ and $\delta^{18}O$, POM for $\delta^{15}N$ and $\delta^{13}C$, and water for $\delta^{18}O$ and $\delta^{2}H$. We have also attempted to use the $\delta^{15}N$ and $\delta^{13}C$ of fish as indicators of nutrient sources. Other studies have also indicated that POM consists primarily of phytoplankton [4,5]. Additionally, these studies indicated that POM transported in the water column, particularly size fractions < 1-mm diameter, were the primary food source for food webs in the Ohio and Upper Mississippi Rivers.

The sites being sampled are part of ongoing USGS studies to investigate a) transport and fate of agricultural contaminants and b) nutrient enrichment effects on aquatic biota in the Ohio River Basin. Questions we hope to answer in this pilot study are: (1) Are there event-related shifts in isotopic values and hence nitrate and POM sources? (2) Are there significant differences in isotopic compositions between agricultural and urban impacted sites? (3) To what extent are these differences related to land-use practices and/or to seasonally-related microbial transformations? (4) Do the isotopic compositions in small watersheds show more storm-related variability than in larger basins? (5) At what scale does a particular land use lose its characteristic isotopic signature? (6) Are nitrate microbial transformations more easily seen at sites draining small areas? (7) What are consumer responses to agricultural and urban impacts, and does the level of impact to the food web change seasonally?

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ISOTOPE TRACING OF WATER BALANCE AND CLIMATIC VARIABILITY ALONG THE MACKENZIE RIVER

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The Mackenzie River, draining an area of 1.7 million km^2, incorporates a diverse range of geographic source regions, including 8 of the 15 distinct ecoclimatic regions identified in Canada [1]. The basin is mountainous in the west and relatively flat-lying in the east with strong north-south climatic gradients, and generally cold, dry climate conditions compared to other large river basins in the world. As a major contributor of freshwater discharge to the Arctic Ocean, the river is also distinct due to the occurrence of several large lakes (Lesser Slave, Athabasca, Great Slave, Great Bear) which naturally act as flow, sedimentation, and biogeochemical regulators along its main drainage network.

Evolution of the isotopic composition of river discharge from the headwaters of the Mackenzie River to the mouth also reflects many of these complexities, particularly the mixing of tributary inflows and the buffering effect of large lakes. A map of the oxygen-18 composition of summer runoff in tributaries (Fig. 1) reveals distinct spatial patterns across the basin. Notably, the most depleted isotope signatures (<-20‰ in $\delta^{18}O$) are observed for tributaries of the Western Cordillera, especially the Mackenzie Mountains (min. of -22.9‰ in $\delta^{18}O$), which are characterized by higher altitude precipitation, greater snowfall, and higher runoff/precipitation ratios than other parts of the basin [2]. In shield-dominated areas to the east of Great Slave Lake and Lake Athabasca, and to a lesser extent in the central boreal-taiga plains, tributary runoff is typically enriched by lake and wetland evaporation in low-relief areas where rivers traverse extensive string-of-lakes and bog-fen drainage networks. Oxygen-18 values in major tributaries typically range between –16 to –14 ‰ in shield areas with peak enrichment observed in wetland dominated drainage of the south-central Boreal Plain (Wabasca R. ~-13.9‰).

A synoptic survey along the main stem of the Mackenzie-Athabasca River (Fig. 2) reveals the periodic fluctuation of oxygen-18 from headwaters to mouth due to interaction of tributaries draining both western alpine regions (with depleted isotope signatures) and eastern lowlands (with enriched isotope signatures), overprinted by lake storage effects. In general, lakes serve a regulatory role in the runoff regime by reducing seasonality of discharge and amplitude of isotope variations. The 2-3 ‰ overall enrichment of oxygen-18 from headwaters to mouth, despite the north-flowing drainage network and northeastward decrease in oxygen-18 in precipitation across the region (see [3]) emphasizes the cumulative importance of open-water evaporation losses in the basin water budget (~15%).

Seasonality in the isotope composition of discharge, as measured near the river mouth upstream from the Mackenzie Delta is pronounced (Fig. 3). Peak flow produced by snowmelt typically occurs in April (~Day 150) at the basin outlet, and conincided with roughly a 2‰ depletion in $\delta^{18}O$ during the early 1980s. Significantly higher depletions during freshet are often observed in smaller tributaries, with similar recessions to higher $\delta^{18}O$ values in summer and late fall. Reduced isotope variability is generally observed during extended winter periods with thick ice cover, and reflect the predominance of groundwater sources (~19.0‰ in $\delta^{18}O$) although the signature of water derived from lake storage is also evident during some years (max of –17.5‰ in $\delta^{18}O$).

This paper presents an overview of isotope datasets collected within the Mackenzie Basin since 1969 (Figs. 1-3) as well as more recent hydrograph separation, water balance and evaporation-transpiration partitioning studies conducted under the auspices of the Global Energy and Water Cycle Experiment, Mackenzie Study (GEWEX-MAGS) and the IAEA Coordinated Research Project "Isotope tracing of hydrological processes in large river basins". One long-term objective of the research is to incorporate tracers in the suite of models currently being implemented and tested with the MAGS study. Coupled simulation of isotopic and hydrologic fluxes and storages, particularly on the land surface and in streamflow will be used to evaluate and refine these models so that they more realistically depict processes, and so that they evolve to become more relevant for evaluating and predicting both water quantity and quality impacts, especially in vast ungauged regions of the basin and other parts of northern Canada.

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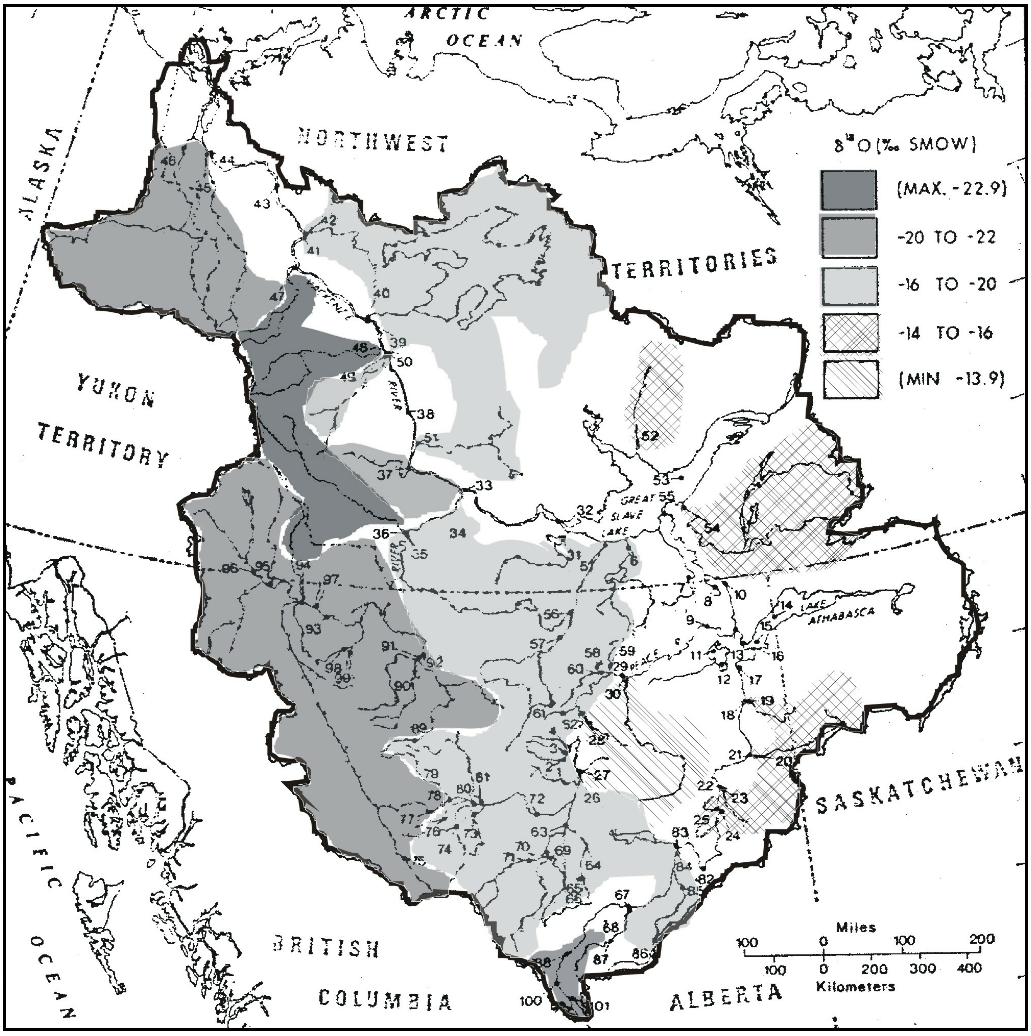

Fig. 1 Map of the Mackenzie Basin showing spatial distribution of $\delta^{18}O$ in summer runoff during 1969 (modified after [2]).

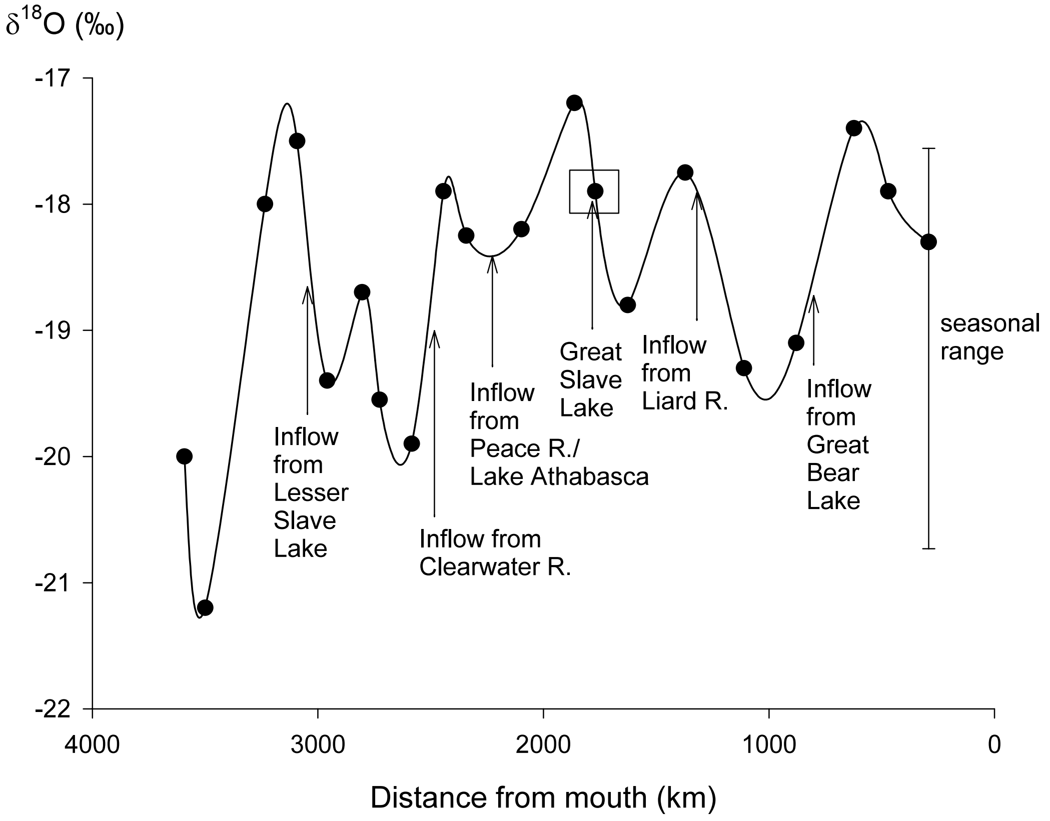

Fig. 2 Synoptic $\delta^{18}O$ survey along the main stem of the Mackenzie-Athabasca River system. Data are generated from the above survey. Approximate seasonal range is from Fig. 3.

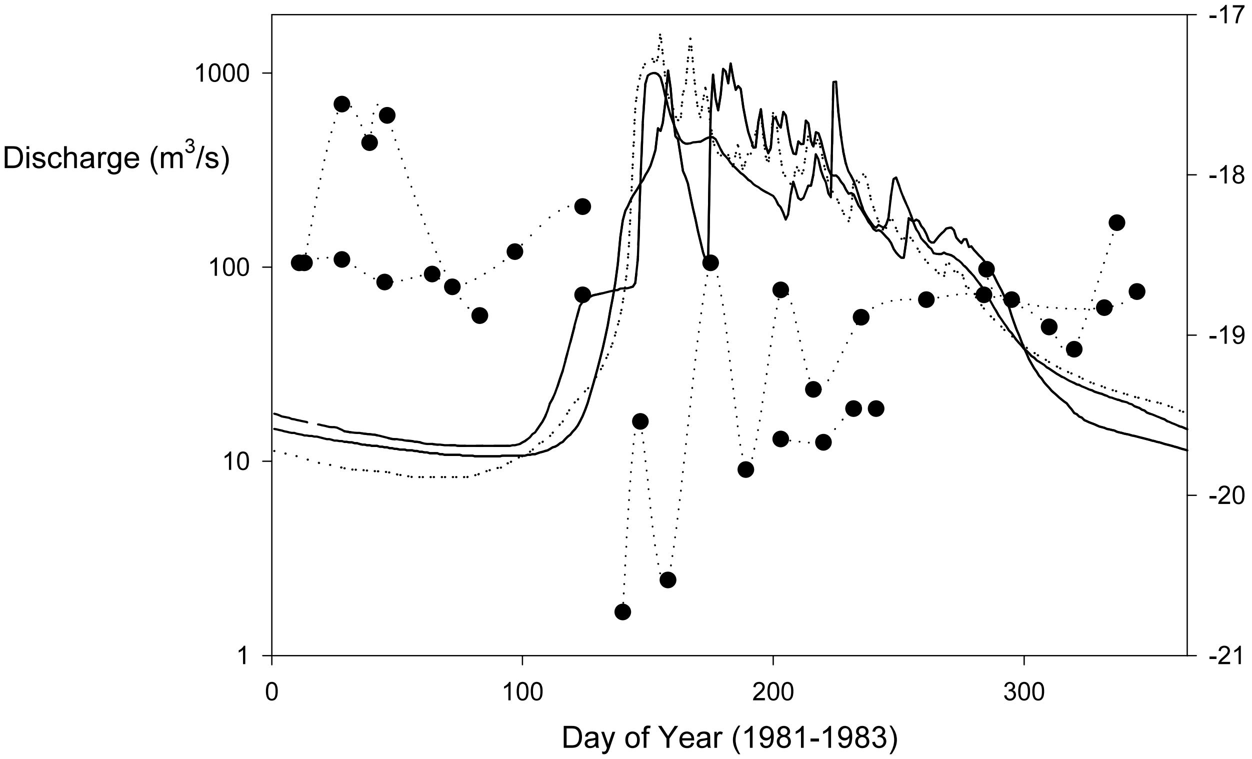

Fig. 3 Composite time-series of river discharge and $\delta^{18}O$ content (solid circles) sampled near the mouth of the Mackenzie River, 1981-1983. Isotope data are from W.G Mook (pers. comm.)

THE ISOTOPIC RIVER CONTINUUM MODEL — IRCM

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The enrichment of the stable isotopes of water in a water body exposed to evaporative water loss, in particular the change of the d-excess value [1], is used to quantify the water balance of such a water body. When the rain-fed inflow waters are in isotopic equilibrium with the ambient moisture, this is a straight-forward procedure. In a river system, the interplay of varying inputs, water extraction and evaporative water loss under a non-equilibrium situation along the river pathway, results in a more complex situation where the local character of the hydrological processes act on an isotopic composition inherited from the upstream part of the river system. In analogy to the “River Continuum Concept” of the Ecologists [2,3] we propose the IRCM, with the aim of identifying the isotopic parameters which can be employed to characterize the water balance and river/environment interactions along the river course. In a way, this is an extension of the “string of lakes effect” [4] to include the interaction between the river and its terrestrial environment.

The isotope composition of an undisturbed flowing river is the amount-weighted summation of the composition of its tributaries [5]. This usually has a pronounced seasonal pattern and is a sensitive monitor of changes in the structure of the watershed. Bank storage, i.e the infiltration into the adjacent aquifers at high water stage and its release during the low water stage, manifests itself as a phase shift of the seasonal pattern. The water loss by direct evaporation from the watercourse or from lakes or reservoirs manifests itself by a decrease of the d-excess value, especially under arid conditions [6]; however the slope of the evaporation line in the delta plane differs from the classical line obtained under equilibrium conditions between the water and the ambient humidity. The non-evaporative water loss by pumping or other extraction of water from the river is not directly recorded in the isotopic makeup, but manifests itself through a larger shift in the isotope composition along the evaporation line for a given amount of evaporation. For a total water balance of the system, therefore both discharge rates and the isotope composition have to be monitored along the watercourse.

The IRCM gives both the conceptual and mathematical tool for quantifying the situation along the river. It takes into account the accumulative stage, the effect of holdup in lakes and reservoirs as well of bank storage and flood plains, the processes of water extraction and subsequent releases from agricultural backflow or urban activities. In all cases the data are evaluated vis-a-vis the isotopic composition of the precipitation and the watershed processes.

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ISOTOPE CHARACTERIZATION OF MAJOR RIVERS OF INDUS BASIN, PAKISTAN

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Abstract

ISOTOPE CHARACTERIZATION OF MAJOR RIVERS OF INDUS BASIN, PAKISTAN

Pakistan lies between latitudes 24° and 37° North and longitudes 61° to 76° east. It possesses quite complicated and attractive physiographical features. There are very often a series of mountain ranges possessing deep broad valleys in-between. It includes the famous valley of the Indus having Indus River, which is one of the longest rivers in the World. It has five major tributaries viz. Bias, Satlej, Ravi, Chenab and Jhelum joining from eastern side, while a number of small rivers join the Indus on the right side. All these main rivers are perennial. They originate from the mountains. Physiography and climate of the catchments of these rivers vary widely. Going from the catchment of the River Satlej to the catchment of Indus River, altitude increases and temperature decreases. In Northern Areas, mountains are covered with glaciers and some of the peaks are higher than 8000m, which get snowfall even in summer season. The basic sources of these rivers are snowmelt, rainfall and under certain conditions seepage from the formations. From the middle of March to the breaking of monsoon, in mid July, river water is drawn from the melting of snow. During monsoon, rainfall run-off is added to the rivers over and above of snowmelt, so their discharge increases manifold. During 1980-84, samples were collected on monthly basis from the river Satlej at Sulimanki, the river Ravi at Baloki (upstream including Qadirabad-Baloki Link Canal originating from the river Chenab) and Sidnai including two link canals originating from Trimu Headworks (just after the confluence of the rivers Chenab and Jhelum), Panjnad (combination of five eastern tributaries) and the river Indus at Tarbela and Taunsa. The samples were analyzed for ^{18}O, ^{2}H and ^{3}H isotopes. The isotopic data (ranges, mean values) and δ^{18}O-δ^{2}H correlations are tabulated below.

Station	δ^{18}O (‰)			δ^{2}H (‰)			Tritium (TU)			d-excess (‰)			δ^{18}O-δ^{2}H
	Min	Max	Avg.	Min	Max	Avg.	Min	Max	Avg.	Min	Max	Avg.	
Tarbela	-14.2	-10.3	-12.6	-102	-71	-88				7.2	19.0	13.1	$\delta^{2}H = 6.9\ \delta^{18}O - 1.5$
Taunsa	-13.5	-8.6	-11.8	-88	-55	-74	36.8	75.3	60.0	13.4	25.6	19.3	$\delta^{2}H = 6.1\ \delta^{18}O - 2.7$
Marala	-12.8	-6.4	-9.7	-79	-35	-59	23.0	88.0	50.1	9.0	20.7	15.1	$\delta^{2}H = 6.2\ \delta^{18}O + 1.2$
Trimu	-13.0	-6.8	-9.6	-80	-38	-59	23.9	70.0	44.9	13.2	24.1	18.4	$\delta^{2}H = 7.1\ \delta^{18}O + 9.1$
Baloki	-11.7	-6.9	-8.8	-71	-36	-53	24. 8	68.0	41.4	10.8	22.4	17.0	$\delta^{2}H = 6.8\ \delta^{18}O + 6.3$
Sidnai	-11.1	-6.3	-8.6	-54	-74	-37	25.0	78.0	45.3	10.3	19.7	14.8	$\delta^{2}H = 7.6\ \delta^{18}O + 11.4$
Sulimanki	-11.3	-7.4	-9.1	-73	-43	-57	25.3	58.0	41.9	12.1	20.9	16.2	$\delta^{2}H = 7.4\ \delta^{18}O + 10.4$
Paninad	-10.8	-8.6	-9.8	-68	-52	-61	43.0	64.0	52.0	15.8	21.7	17.6	$\delta^{2}H = 7.0\ \delta^{18}O + 7.5$

ALTITUDE EFFECT

All the rivers have vide ranges of stable isotopes and tritium. The river Indus coming from highest altitude has relatively the most depleted values of $\delta^{18}O$ and $\delta^{2}H$ at Tarbela and Taunsa because of major contribution of snowmelt coming from glaciated peaks in Northern Areas. Tritium is also higher due to some contribution of old snow fallen during high tritium period in 1960s. The rivers Sutlej and Ravi have the most enriched values of $\delta^{18}O$ and $\delta^{2}H$ because their catchments have relatively low altitude and contribution of snowmelt is also less. The river Chenab at Marala has the widest ranges of $\delta^{18}O$ and $\delta^{2}H$ because of mixing of snowmelt originating from higher altitudes and rainfall of piedmont areas. Data of Trimu, which show the combined discharge from the rivers Chenab and Jhelum is almost similar to that of Marala.

SEASONAL VARIATION OF ISOTOPES

Temporal variations of $\delta^{18}O$ and the reservoir level of the river Indus at the outlet of Tarbela Dam Reservoir are shown in Fig. 1. Both the parameters show year wise cyclic behavior. The most depleted values of $\delta^{18}O$ are in August-September when the reservoir level is generally highest and the most enriched values are found during April-May when the reservoir is at its minimum level. The d-excess ($= \delta^{2}H - 8\ \delta^{18}O$) of all the samples does not have any significant correlation with $\delta^{18}O$ and reservoir level. Therefore, this cyclic enrichment is not dominantly due to evaporation effect. The snow/glacier melt coming from high mountains of Himalayas is very depleted in heavy isotopes and due its major contribution, the $\delta^{18}O$ is the most depleted during full/highest level of the reservoir. When the reservoir level is low during April-May, groundwater of nearby areas recharged at low altitude having enriched isotopes ($\delta^{18}O$: -7 to –6‰) drains into the reservoir and input of local rains increase the $\delta^{18}O$ of the reservoir. Seasonal variations of $\delta^{18}O$ of water samples collected from the rivers Chenab at Marala and Jhelum at Rasool Barrage during 1983-1988 show that the most depleted values are encountered during monsoon when the discharge is high and the enriched values appear in winter/dry period when the discharge is low.

THE $\delta^{18}O$ - $\delta^{2}H$ RELATIONSHIP

Regression equations $\delta^{18}O$ and $\delta^{2}H$ for different stations are given in the above Table. The slopes of regression lines are significantly less than that of GMWL. Fig. 2 represents $\delta^{18}O$-$\delta^{2}H$ plot for the river Chenab at Marala. Most of the data points lie above the GMWL. The departures of the points having highly depleted values of $\delta^{18}O$ and $\delta^{2}H$ are more than those corresponding to the enriched samples. Generally the highly depleted values are during the major contribution of snowmelt which have high d-excess due to some climatic effects or having source of winter precipitation from western air masses/Mediterranean Sea. The data points with enriched $\delta^{18}O$ and $\delta^{2}H$ have relatively less d-excess because of contribution from monsoon rains originating from Bay of Bengal. Therefore the slopes of $\delta^{2}H$-$\delta^{18}O$ regression lines for all the cases are less than that of GMWL.

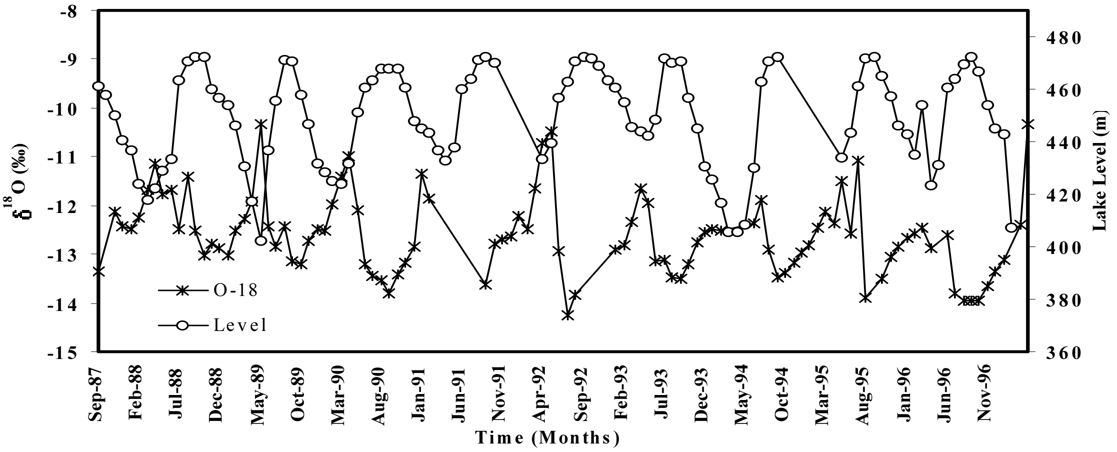

Fig.1. Temporal variations of $\delta^{18}O$ and reservoir level of Tarbela Lake

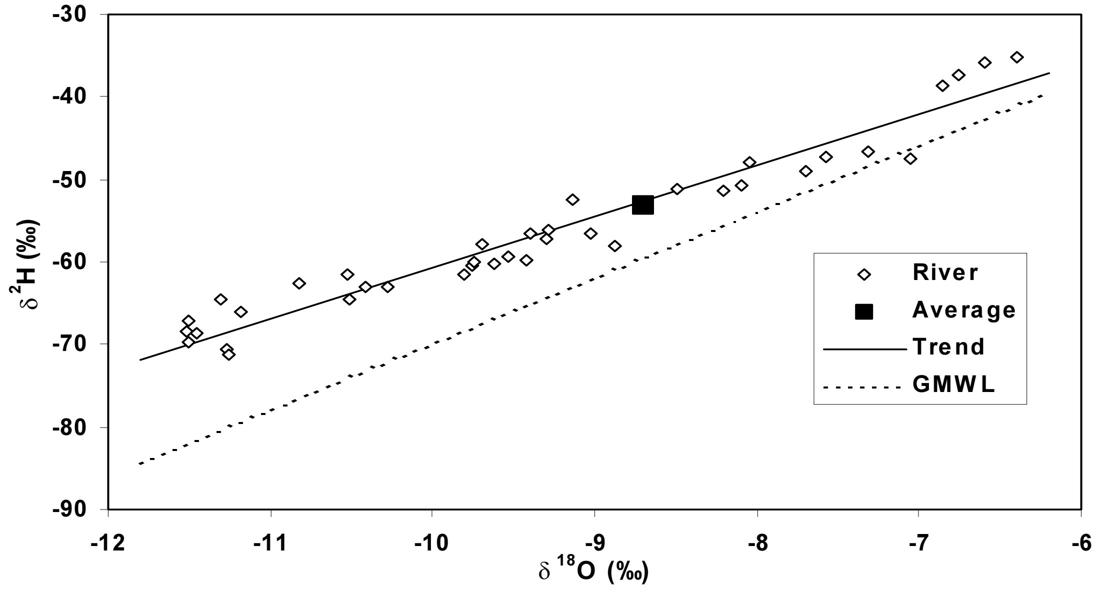

Fig. 2. $\delta^{18}O$ Vs $\delta^{2}H$ of River Chenab at Marala Barrage

DYNAMICS OF WATER TRANSPORT THROUGH CATCHMENT OF THE DANUBE RIVER TRACED BY ENVIRONMENTAL ^{3}H AND ^{18}O — THE NEURAL NETWORKS APPROACH

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River systems constitute an important part of the hydrological cycle. On one hand, they remain the basic source of potable water for human population. On the other hand, they are subject of dramatic impact of man's activities in a form of massive and widespread pollution. In many instances natural cleaning capabilities of those systems were surpassed with the resulting conversion of numerous rivers into biologically dead sewage channels. In this context, better understanding of the dynamics of river systems on a catchment scale and their interaction with groundwater becomes an urgent task.

Environmental isotopes such as tritium, deuterium and oxygen-18 are well recognized tools for studying dynamics of hydrological cycle on different spatial and temporal scales. In river systems, ^{18}O and ^{2}H have been used mostly in small-scale investigations for separating different flow components [1]. Time series of tritium content in rivers were used to derive information on the mean transit time of water on a catchment scale [2,3]. Long-term, systematic observations of isotopic composition of rivers exist for several large rivers in the United States (^{3}H) and for the Danube river in Europe (^{3}H, ^{18}O).

The neural networks approach has been widely used over the past decade to study dynamics of complex systems [4,5]. Here, an attempt was made to apply the neural networks to describe the transport of environmental isotope tracers (^{3}H, ^{18}O,) through catchment of a large river system with the principal aim to gain a better insight into the dynamics of water flow within such system. The available long term time series of tritium and oxygen-18 content in the Danube river were used for this purpose. In paralell with the neural networks modelling of the Danube data, also the lump-parameter models were used to derive information on the mean transit time of water in the studied catchment. Transport of both tracers (^{3}H and ^{18}O) was investigated. In the case of tritium, the input function was constructed from the observed ^{3}H levels in monthly precipitation in Vienna and in the stations located on the catchment area upstream of Vienna. In the case of oxygen-18, long-term changes of the content of this isotope in precipitation were used as a tracer signal signal transported through the catchment.

Comparison of the modelling results obtained by these two completely different approaches suggest that neural networks represent a potentially attractive alternative for the modelling of water flow in such complex systems as catchments of large rivers. The tritium content in the Danube river measured in Vienna over the past thirty five years could be much better reproduced with the aid of neural networks modelling then is was the case of the lump-parameter models (Fig.1.). The neural networks modelling yields the transit time distribution function for the studied system, whereas the box-model approach is capable to deliver only the mean value of the transit time. The apparent transit time distribution function derived from neural networks modelling can be far more complex than usually assumed in the lump-parameter approach, better reflecting the actual dynamics of water flow through the catchment.

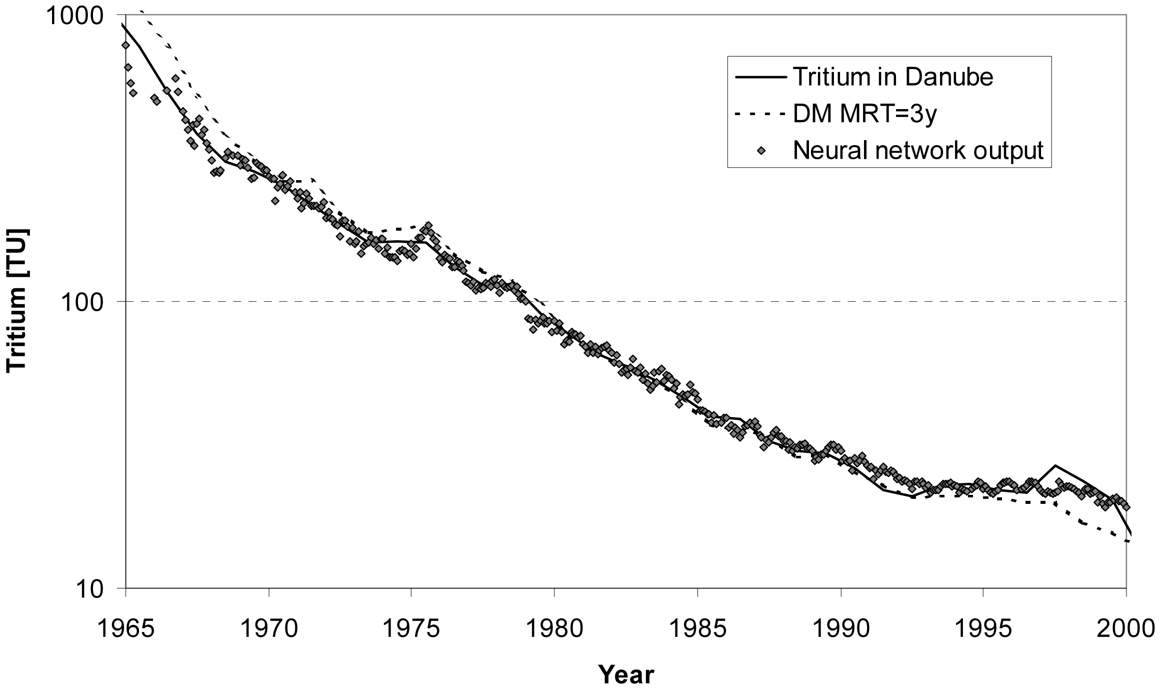

Fig.1. The tritium content in the Danube river over the past 35 years simulated with the aid of the lump-parameter modelling (dispersion model, MRT = 6 years) and the neural networks modelling. The measured tritium content in the river Danube over this time interval is also shown (heavy line).

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ORGANIC CARBON SOURCES AND CYCLING IN THE ST. LAWRENCE RIVER: STABLE ISOTOPES AND ELEMENTAL APPROACHES

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The St. Lawrence River ranks 16th in the world for its mean annual discharge and 13th for its watershed area [1]. One of its major particularities lies in the in the size of the Great Lakes, at its head (245 700 km^2). The mean residence time of water in the Great Lakes exceeds 100 years, resulting in relatively buffered physico-chemical properties of the water flowing through the river. The St. Lawrence River carries very low suspended particulate matter to its estuary compared to other major rivers [2]. As a result, low concentrations of particulate organic carbon (POC) are observed downstream in opposition to relatively high concentrations of dissolved organic carbon (DOC).

The general aim of the present study is to establish a comprehensive carbon budget in the St. Lawrence River, with special attention to seasonal and interannual variations. In an earlier study, we examined inorganic carbon fluxes and budgets [3]. Here, we provide complementary information on organic carbon fluxes and cycling. Added to concentration measurements, isotopic approaches combined with C/N analyses were used to document sources and cycling of DOC and POC in the river. Four sampling sites have been monitored since 1997. The first one is located in the Montreal area. It illustrates inputs from the Great Lakes. The second one is located in the Quebec City area. It illustrates outputs from the St. Lawrence River into its estuary. In addition, two tributaries were sampled to put constraints on two chemically distinct rivers that feed the St. Lawrence River. The first one, the Ottawa River, is the largest tributary of the St. Lawrence River. It was sampled near its outlet. It drains mainly Precambrian rocks of the Canadian Shield, which are generally overlain by thin soils. The other one is a very small tributary (the Mascouche River) that drains exclusively Paleozoic carbonate rocks of the St. Lawrence Lowlands. There, thick and rich soils are present and are intensively cultivated. All sampling locations were visited on a two-weekly basis since mid-1997 and the sampling program is still underway. Here we use data spanning June 1998 to November 2001. In situ measurements included water temperature, pH, redox potential, conductivity, alkalinity and dissolved oxygen concentration. Samples were then analyzed for δ^{13}C-values in DOC, POC and in dissolved inorganic carbon (DIC), δ^{18}O-values of dissolved oxygen, as well as for the C/N ratios and concentrations of dissolved and particulate organic matter (respectively DOM and POM). The limit between DOM and POM was set using pre-combusted 0,3 μm glass fiber filters. Mean annual isotopic compositions of DOC, POC and DIC as well as their concentration and C/N ratios are summarized in table 1. Elemental analysis of POC revealed low C/N ratios suggesting a prominent planktonic and/or bacterial origin for POM. C/N ratios of DOM are also relatively low, except in the Ottawa River which yielded higher values suggesting a more important contribution of terrestrial organic matter. Moreover, δ^{13}C-values in POC from the St. Lawrence River show a strong seasonal pattern not unlike that depicted by δ^{13}C-values in dissolved CO_2 (fig.1). This suggests that organic matter in the St. Lawrence River is mainly produced within the river or the Great Lakes, at its head. Based on our monitoring program, total annual discharge rates could be calculated for DOC, POC and DIC. They were respectively $1.38*10^{12}$, $0.10*10^{12}$ and $5.25*10^{12}$ gC in year 2000.

	St. Lawrence River		**Tributaries**	
	Montreal	Quebec City	Ottawa R.	Mascouche R.
δ^{13}C-POC (‰ vs VPDB)	**-24.84**	**-24.88**	**-29.15**	**-28.81**
[POC] (mg/l)	0.064	0.224	0.185	0.593
C/N (POC)	4.67	4.37	5.19	5.88
δ^{13}C-DOC (‰ vs VPDB)	**-26.31**	**-26.38**	**-26.82**	**-27.46**
[DOC] (mg/l)	3.22	4.05	6.04	8.68
C/N (DOC)	6.47	7.86	13.84	6.95
δ^{13}C-DIC (‰ vs VPDB)	**-1.41**	**-3.18**	**-10.9**	**-13.04**

Table 1. Mean annual concentrations, C/N ratios and isotopic composition of DOC, POC and DIC, at the monitoring stations.

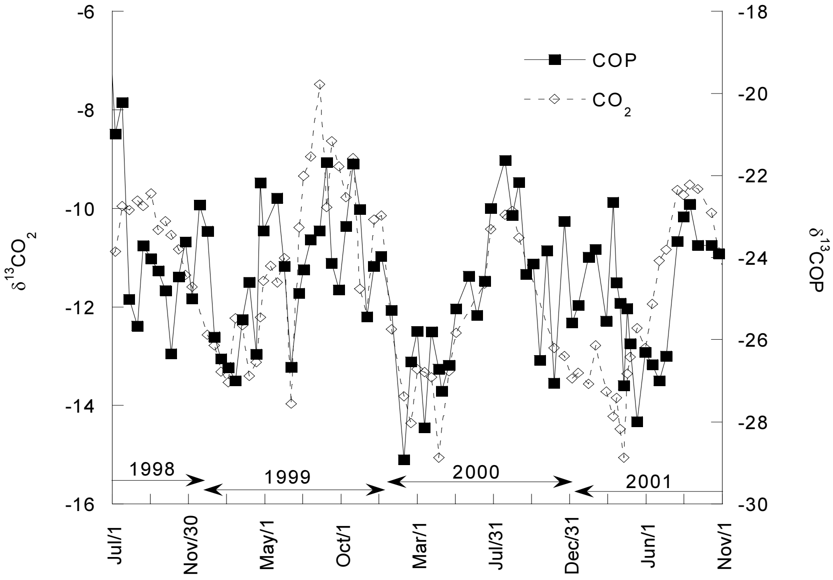

FIG.1. Seasonal variationss of δ^{13}C-POC and $\delta^{13}CO_2$ in the St. Lawrence River at Montreal.

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RUNOFF PROCESSES AND SMALL WATERSHEDS

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Small watersheds are a fundamental landscape unit for quantifying inputs and outputs of water, sediment and nutrients. Small watersheds have been used historically for defining runoff processes and flood response to storm precipitation. Early conceptualizations of runoff production during the International Hydrological Decade in the 1960s focused on the importance and movement of event water as overland flow to the stream channel. Use of mass balance mixing models using stable isotope tracers in the 1970s and 1980s directly challenged early ideas of where water goes when it rains, residence time of catchment waters and flow paths of subsurface runoff towards the stream. These data showed that the majority of water in the stream during a precipitation event was water that existed in the watershed prior to the event. While credible physical mechanisms of old water mobilization have only been defined in the past decade, stable isotope tracer approaches are now mature enough to offer new potential for informing new model structures of how small watersheds work. Isotope tracer data in small watersheds and mass balance separations also represent new ways of validating and calibrating watershed models. This presentation will chronicle the use of isotope tracers in small watersheds and provide examples of how these data can be used in models of runoff processes and for providing valuable input for water resource management at larger basin scales.

TRITIUM BALANCE MODELING IN A MACROSCALE CATCHMENT

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The Institute of Hydrology at the Freiburg University (IHF) is working in cooperation with the German Federal Institute of Hydrology (BfG) on a project implementing tritium data into modeling concepts of large river systems [1,2]. Tritium concentrations that are measured in precipitation (Global Network of Isotopes in Precipitation - GNIP) and discharge (BfG - HYDABA data base) are combined with information on water balance components on monthly basis over a period of 50 years. In a first step the Fulda, Werra and Weser-1 catchments (6.890 km², 5.410 km² and 15.320 km²) in Germany were used to test the model approach, to study residence times, groundwater storage behaviour and water balance components. Environmental tritium in precipitation that was mainly introduced into the water cycle by nuclear weapon tests in the 60s is the source of tritium input in this catchments. Precipitation and potential evapotranspiration were calculated from the German Weather Authority (DWD).

The TRIBIL software was developed to process a large amount of data sets. It allows to consider tritium input from precipitation, nuclear power plants and channel systems. Evapotranspiration from land and water surface as well as snow cover are considered for calculations of infiltrating water. Beneath a direct runoff component the amount of infiltrating water is distinguished into fast and slow groundwater reservoirs were each consists of a mobile and immobile fraction. The amount of tritium stored in these groundwater fractions is calculated using discharge recession curve analyses.

An outline of the model structure as well as results for the river systems Fulda, Werra and Weser-1 will be presented. A comparison of measured and modeled tritium concentrations in discharge showed considerable fits (Fig.1). Modeling efficiencies are around 0.8. The results allow an interpretation of storage volumes and residence times of the supposed groundwater reservoirs. Because there is no influence through nuclear power plants, tritium processing industries and channels the Fulda and Werra catchments serve as a reference for continuing studies in the Weser catchment (48.300 km²). An implementation of tritium emission by nuclear power plants will be considered with extending catchment site. Including the conservative tracer tritium into large scale modeling is a rather new approach. Feasibilities and possibilities will be discussed within this contribution. Balancing of solutes in catchment studies can be improved and this approach can serve as an additional validation tool for water balance models.

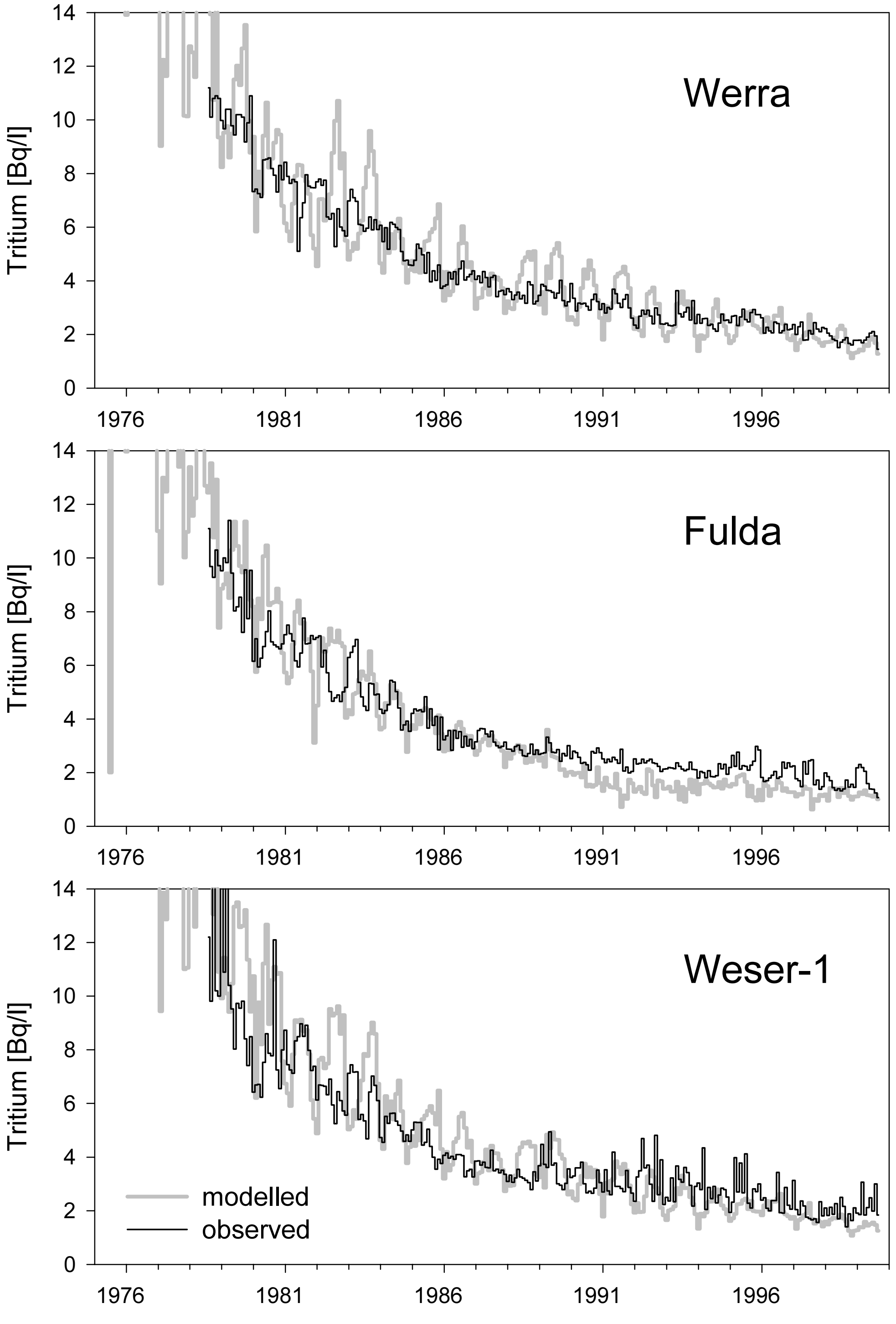

Fig.1 Comparison of measured and modelled tritium concentrations in the Fulda, Werra & Weser-1 basin.

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APPLICATION OF ISOTOPE TRACERS IN CONTINENTAL SCALE HYDROLOGICAL MODELING

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Tracing isotopes in hydrological systems is becoming an important tool for hydrologist to study hydrological processes. Stable isotopes such as ^{2}H and ^{18}O are particularly usefull since these elements are building blocks of the water molecules and behave slightly differently in phase changes and diffusion than regular water molecules. Hydrologists working on small and regional scales have demonstrated the value of stable isotope traces in various application such as distinguishing the source of surface whater (old water from the ground-water pool and new water surface runoff), differentiating evaporation (from open water) from transpiration (from plants), snow and smelt glacier mixing, etc.

Application of isotope tracers at large scale is far behind the regional application mostly due to the lack of isotopic data for large regions. The International Atomic Energy Agency has started a major effort inviting experts and instutions from all over the world to change this situation and promote the collection and distribution of isotopic data about various component of the hydrological cycle. IAEA and WMO (World Meteorological Organization) already established a Global Network for Isotopes in Precipitation (GNIP) and IAEA recently initiated a new effort the Global Network for Isotopes in Rivers (GNIR).

The present paper attempts to utilize these emerging isotopic datasets by incorporating isotope tracing in large scale hydrological simulation. The available precipitation and river isotopic composition data are analysed in simple GIS context to demonstarte the consitency of the isotopic data with other Earth system data such as various climate forcings (air temperature, precipitation, vapor pressure, etc.) land characterisation data (land-use, soil types, river networks, etc.) and river discharge data.. After the initial GIS-based analysis, the isotopic data are tested in a modified version of a well established large scale water balance/water transport modeling system (WBM/WTM). The modified WBM allows the simulation of the fractionation of isotopic composition during the evapotransporation processes, while the WTM is used to simulate the mixing of spatially varying runoff during horizontal water transport and estimate the isotopic composition of the river water in a simulated river network.

The paper demonstrates the use of the isotope tracer enabled WBM/WTM by applying in continental scale study. It highlights the power and the challenges of tracking isotopes in a WBM/WTM context and evaluates the performance of the model. The paper provides recommendation for future efforts to make such simulations more realistic and improve their performance.

INTERLINKING OF RIVERS IN INDIA IN THE CONTEXT OF AVAILABLE HYDROLOGICAL INFORMATION

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Perspective:

India is in a unique position with regard to fresh water resources and their management. With roughly 2.5% of the world's land area, it has about 4% of the world's water resources. It ranks first with regard to total irrigated area[1] and has utilised the ground water resource to the extent of 60%. However, it ranks 133rd with regard to water - availability per person per year[2]. The distribution of water resources in the country is highly uneven over space and time. Over 80 to 90% of the runoff in Indian rivers occurs in four months of the year and there are regions of abundance which is rather harmful and vast populations live in areas of acute scarcity. The country has to grapple with several critical issues in dealing with water resource development and management. Major attitudinal and organisational changes would be necessary to deal adequately with all the issues and concerns. In this context, the polarisation of views on large projects and local watershed and water resource conservation and development is unfortunate. The two issues are complementary to each other and there is need for the whole range of structures and plans in trying to meet people's requirements. The initiatives that the Government of India has taken and proposes to take in this International year of Freshwater (2003), is very much in keeping with the Millennium Declarations adopted by the General Assembly of the United Nations in 2000, in which the world leaders resolved 'to halve, by the year 2015, the proportion of the world's people who are unable to reach, or to afford, safe drinking water', and 'to stop the unsustainable exploitation of water resources'. I am tempted to quote Kofi Annan (Secretary General, United Nations) in this connection who in his foreword to the 'World Water Development Report, Water for People, Water for Life (2003)' said, 'If the water problems facing our world are sometimes a cause of tension and concern, they can also be a catalyst for co-operation'.

1. WATER AVAILABILITY IN INDIA

Precipitation, in the form of rain and snowfall, is a crucial component of the hydrological cycle which makes fresh water available on a renewable basis. The geographical area of the country is 329 million hectares (Mha). The mean annual rainfall, taking the country as a whole, is 1,170 mm. This gives an annual precipitation of about 4,000 Km^3. A significant part of this precipitation returns back to the atmosphere as evaporation. A large part of the remaining precipitation seeps into the ground and the balance flows through streams and rivers and collects in water bodies adding to the surface flow. Thus the surface and the ground water sources are inter-linked and are continuously inter-active. It is, therefore, extremely difficult, if not impossible, to quantify them separately over a period of time in given locations. In accordace with the present estimates prepared by the Central Water

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[1] Table in a subsequent chapter
[2] Table 4.2, The UN World Water Development Report, 2003

Commission, the total water resource in the country available from the river basins is 1953 BCM (Billion Cubic Metre) and that from the ground water is 432 BCM, putting the total to 2385 BCM.

River basin is the basic hydrologic unit for planning and development of water resources. It is, therefore, useful and convenient to make the assessment of water resources basin wise. A system of rivers normally flowing into a common terminus constitute a single drainage basin as per the definition given in the Convention on the non-navigational Uses of International Water Courses adopted by the United Nations.

Based on the physiography, the river systems of India can be classified into four groups, viz. (i) Himalayan rivers, (ii) Deccan rivers, (iii) Coastal rivers, and (iv) Rivers of the inland drainage basin. The main Himalayan River Systems are those of Indus and Ganga-Brahmaputra-Meghna systems. The Himalayan rivers receive very heavy rainfall in monsoon months and the rivers swell, causing frequent floods. The flows in the summer months are due to melting of snow and glaciers and, therefore, these rivers have continuous flow throughout the year. The important river systems in the Deccan are the west flowing rivers of Narmada and Tapi and the east flowing rivers of Brahmani, Baitarni, Mahanadi, Godavari, Krishna, Pennar and Cauvery. The Deccan rivers are rainfed and some of them are non-perennial. There are numerous coastal rivers which are comparatively small. Most of them are non-perennial. While only a handful of such rivers drain into the sea near the deltas of the east coast, there are as many as 600 such rivers on the west coast. The west coast rivers are short in length and have limited catchment areas. A few rivers in Rajasthan do not drain into the sea. They drain into salt lakes or get lost in sands with no outlet to sea.

Earlier, the entire country was suitably divided into 20 river basins by the Central Water Commission. These comprised 12 major basins (having a drainage area exceeding 20,000 sq.km.) and eight other river basins each combining a number of medium and minor rivers. However, it was seen that some areas such as the area north of Ladakh not draining into Indus and areas of Andaman, Nicobar and Lakshadweep islands are not covered in the 20 rivers basins. The drainage area of the country has now been divided into 24 basins, which includes the two basins, namely areas of North Ladakh not draining into Indus and Drainage area of Andaman, Nicobar and Lakshadweep Islands. The group of minor rivers of East Coast, South of Mahanadi have been divided into five basins in place of the earlier two basins and the rivers draining into Myanmar and Bangladesh have been grouped under two separate basins, in place of the earlier one basin. The rivers of West Coast South of Tapi are grouped into one basin in place of the earlier two basins. Area of inland drainage of Rajasthan which was one of the twenty basins is deleted. The list of basins so proposed along with their catchment areas is given in Table.

TABLE
Catchment Area of Basins

S. No	**River Basin**	**Catchment Area Km^3**	**States Covered in the Basin**
1	**2**	**3**	**4**
1.	Indus	321289	J&K,Punjab,Himachal Pradesh,Rajasthan and Chandigarh
2.	Ganga-Brahmaputra-Meghna Basin		
2a	Ganga Sub-basin	862769	Uttar Pradesh, Himachal Pradesh, Haryana, Rajasthan, Madhya Pradesh, Bihar, west Bengal and Delhi UT
2b	Brahmaputra Sub-basin	197316	Arunachal, Assam, Meghalaya, Nagaland, Sikkim and West Bengal
2c	Meghna(Barak)Sub-basin	41157	Assam, Meghalaya, Nagaland, Manipur, Mizoram and Tripura
3.	Subernarakha	29196	Bihar, West Bengal and Orissa
4.	Brahmani-Baitarani	51822	M.P., Bihar and Orissa
5.	Mahanadi	141589	M.P., Maharashtra, Bihar and Orissa
6.	Godavari	312812	Maharashtra, A.P., M.P., Orissa and Pondicherry
7.	Krishna	258948	Maharashtra, A.P. and Karnataka
8.	Pennar	55213	A.P. and Karnataka
9.	Cauvery	87900	Tamilnadu, Karnataka, Kerala and Pondicherry
10.	Tapi	65145	M.P., Maharashtra and Gujarat
11.	Narmada	98796	M.P., Maharashtra and Gujarat
12.	Mahi	34842	Rajasthan, Gujarat and M.P.
13.	Sabarmati	21674	Rajasthan and Gujarat
14.	West Flowing Rivers of Kachchh, Saurashtra and Luni	334390	Rajasthan, Gujarat and Daman and Diu
15.	West Flowing Rivers south of Tapi	113057	Karnataka, Kerala, Goa, Tamil Nadu, Maharashtra, Gujarat, Daman and Diu and Nagar Haveli
16.	East Flowing Riverss Between Mahanadi and Godavari	49570	A.P. and Orissa
17.	East Flowing Rivers Between Godavari and Krishna	12289	Anadhra Pradesh
18.	East Flowing Rivers Between Krishna and Pennar	24649	Andhra Pradesh
19.	East Flowing Rivers Between Pennar and Cauvery	64751	A.P., Karnataka and Tamilnadu

20.	East Flowing Rivers south of Cauvery	35026	Tamilnadu and Pondicherry UT.
21.	Area of North Ladakh not draining into Indus	28478	Jammu and Kashmir
22.	Rivers draining into Bangladesh	10031	Mizoram and Tripura
23.	Rivers draining into Myanmar	26271	Manipur, Mizoram and Nagaland
24.	Drainage areas of Andaman, Nicobar and Lakshadweep Islands	8280	Andaman, Nicobar and Lakshadweep
	Total	3287260	

Source : National Commission for Integrated Water Resources Development Vol-I (1999)

Annual mean flow in a river basin is reckoned as water resource of the basin. After reviewing the estimates of average flows made by several agencies, the CWC's estimates are adopted with some modification. The total water resource of the country is estimated now at 1952.87 km^3 or 1953 km^3. The water resource of Ganga-Brahmaputra-Meghna basin is estimated as 1200 km^3 which is 60 percent of the total water resource flows while the basin occupies 33 percent of the geographical area. Water resource of west flowing rivers south of Tapi is estimated as 200 km^3, which is 11 percent of the total water resource, whereas the basin occupies only three percent of the geographical area of the country. The remaining 64 percent of the area has a water resource of only 553 km^3.

The utilisable flow from a basin can be taken as the quantum of water that can be withdrawn from its place of natural occurrence. After considering the storages, barrages and diversions that have been constructed, those that are under construction and the identified future projects, the CWC has estimated that about 690 km^3 can be utilised from conventional schemes of water resources.

Ground water is an important source of water in many places. For use and development, only annual replenishable component of ground water is considered. The total replenishable ground water is estimated as 432 km^3. Out of this, 396 km^3 (90 percent of the balance) is used for irrigation. Nearly 50 percent of irrigation in the country is by ground water. Ground water also occurs in the aquifer zones below the zone of water level fluctuation, called static ground water. Central Ground Water Board has recently made preliminary estimates of static ground water available in the country.

Though considerable scope for exploitation of ground water still exists especially in surplus surface water areas, it would need substantial investments on energy and entail repetitive cost. Ground Water is available where surface water is also available. On the other hand the GW is in short supply where SW is also in short supply. There is therefore obvious reluctance to use GW to reduce cost of pumping energy. A large component of groundwater is derived from surface water and hence both need to be considered conjunctively. The efficacy of watershed development as an economic option to enable artificial recharge is however severely limited. A discrete mix of mega to micro-scale surface water storages in addition to in-situ conservation measures are called for to augment availability in a cost-effective manner.

2. ESTIMATES OF WATER REQUIREMENT

Water is required for agriculture production, for drinking purposes by human beings and animals, for municipal and commercial uses. Water is an essential input for all industries. Energy and navigation development also require water. When water is stored, a part of it is lost by evaporation. Release of fresh water into water courses and water bodies is also some times essential to ensure minimum flow and to restore quality to acceptable standard. Water requirement for agricultural production and domestic needs including drinking, cooking, sanitation, and municipal services and for trade, commerce and industries, together constitute the bulk of the total water consumption. The water need is closely related to population, demand for food, production of non-food agricultural and industrial items, production of energy, and for improvement in the quality of life and for preserving ecology of the nation.

According to available estimates, the total withdrawal / utilization for all uses in the year 1990 was 552 km^3 or 655 m^3 / person / year (MOWR, 1997). Out of the total water utilised in the country, irrigation accounted for nearly 83 percent; followed by drinking and municipal use (4.5 percent), energy development (3.5 percent) and industries (3 percent). Other activities claimed approximately 6 percent of the total use.

3. USES OF WATER (1990) IN INDIA

(Source : Ministry of Water Resources, 1997)

Item	Percentage
Irrigation	83%
Drinking & Municipal Uses	4.5%
Energy Development	3.5%
Industries	3%
Other activities	6%

Approaches to Estimating Water Requirement:

Water requirement is closely related to population, demand for food, production of non-food agricultural and industrial items, production of energy and improvement in the quality of life and preservation of ecology and environment.

The N.C.I.W.R.D Estimates of water requirements have been made for the years 2010, 2025 and 2050 at the national level. Several assumptions have been made to arrive at the figure of total water requirement for the country as a whole. While estimating demand by different sectors, aspects of management and technology are given due consideration. Also, international and Indian norms and standards have been taken into account. Requirement of food production would mainly depend upon country's population, per capita income and changes in dietary habits.

With the goal of food self-sufficiency at macro level, the demand estimates are converted into the domestic supplies, the latter being a factor of arable area and yield per hectare. Keeping in view the past trend and incremental changes in land use, cropping pattern, irrigation conditions, suitable assumptions are made for estimation of water requirement for irrigation. Water requirement for irrigation has been estimated between 628 km^3 (Low Demand Scenario) and 807 km^3 (High Demand Scenario) for the year 2050.

Keeping in view the existing national average of water supply and various suggested norms, the NCIWRD has suggested the final goal of providing 220 lpcd (litres per capita per day) for the urban areas and 150 lpcd for the rural areas in a phased manner. The total water requirement for domestic use for rural and urban areas is estimated at 111 km^3 and 90 km^3 in two population scenarios for the year 2050.

On account of serious dearth of information on the present use of water by industries and uncertainity about the future growth and composition of manufacturing activities, it is extremely difficult to estimate future water requirement of industries. The water requirement for industrial development estimated is 81 km^3 for the year 2050. Water requirement for energy / power sector has been estimated for high and low demand scenarios as 70 km^3 and 63 km^3 respectively for the year 2050.

The requirement of flow in navigation water channel needs are mostly expected to be met by seasonal flows in various river systems or canals. However, taking into account the actual releases downstream of Farakka Barrage, as an example, the requirement of water for the year 2050 has been projected as 15 km^3.

Requirement of water for abatement of pollution and managing quality of waters in rivers and other water bodies has been assumed as 20 km^3 for the year 2050 in the absence of reliable and adequate data. The evaporation losses from reservoirs have been estimated as 76 km^3.

The total water requirement of the country, thus, would be 694 to 710, 784 to 850 and 973 to 1180 km^3 by the years 2010, 2025 and 2050 respectively depending on the low demand and high demand scenarios. Irrigation would continue to have the highest water requirement, between 628-807 km^3 (or about 68 percent of total water requirement) followed by domestic water use, including drinking and bovine needs, at about 90-111 km^3 (or about ten percent of total water requirement) in the year 2050. The projected water use per capita per year in the year 2050 would be about 725-750 m^3 as compared to about 650 m^3 at present.

The country's total water requirement in the year 2050 barely matches the estimated utilisable water resources. It is of paramount importance that we should aim at reducing water requirement to the low demand scenario. While there appears to be no need to take an alarmist view, three major considerations have to be kept in the forefront while formulating an integrated water policy. First, that the balance between the requirement and availability at the national level does not imply that all basins are capable of meeting their full requirement from internal resources. Second, the issue of equity in the access to water, between regions and between sections of population assumes greater importance in what is foreseen as a fragile balance between the aggregate availability and aggregate requirement of water.

4. WATER RESOURCE DEVELOPMENT & MANAGEMENT

4.1 Irrigation

India has a long history of irrigation development. Grand Anicut across Cauvery river delta built in 2nd century was amongst the earliest irrigation systems. Development of irrigation continued at a slow pace until partition. Since Independence, the government gave highest priority to irrigation to tide over heavy food deficits and consequent imports of food grains. Countrywide programmes were taken up which included large river valley projects and medium and minor schemes including ground water structures. In the States ground water schemes received priority during the sixties leading to green revolution and it gathered momentum with increased availability of cheaper power with the spread of rural electrification. Since partition, irrigated area in India rose from 22.60 Mha to 80.76 Mha upto June, 1997, against the ultimate target of 140 Mha, of which ground water development has been nearly 50 percent. Such a large programme has been implemented almost entirely with indigenous technology and equipment.

During the course of implementation of projects, many lessons were learnt and measures for improvement and modernization were taken. On the development side, a large number of irrigation multipurposes projects were taken up by the States which were beyond their capacity of funding. As a result, there are inordinate delays in completion resulting in time and cost overruns. A few projects which were receiving external assistance were provided with relatively larger outlays. The establishment costs also mounted up. The available resources were applied on new projects and as a result, management issues were relegated to the background. There was disproportionately larger lag in irrigation utilization compared to potential created. Irrigation statistics also showed differences amongst figures collected by the Irrigation Departments and those by the Land Use Statistics.

Various remedial measures for prevention as well as reclamation of water logged areas have been recommended. Here also there is lack of appropriate data. The measures to prevent water logging and drainage system are best taken during the construction phase. Suggestions have been made to prevent and reclaim land affected by intrusion of salinity in the coastal areas and also the problems arising out of pollution of water from industrial and municipal effluents. Much greater efforts and attention needs to be given to management aspects of irrigated agriculture both from the technical point of view and the involvement of the users.

Important Projects taken up over last 50 years

(i) Hirakud Dam (1957): The project across the river Mahanadi is in the State of Orissa. It provides annual irrigation to 2.51 lakh hectares. The length of the dam (including Dykes) is 25.5 km.

(ii) Tungbhadra Dam (1958): Located across river Tungbhadra in the State of Karnataka, the project irrigates 37,500 ha. Annually. Its hydropower generation (installed capacity) is 59 MW.

(iii) Matatila Dam (1958): Located in the Ganga basin on the Betwa river, in the State of UP, the project irrigates 1.66 lakh ha. annually.

(iv) Kota barrage (1960): Located across Chambal river in the State of Rajasthan, its Hydropower generation(installed capacity) is 200 MW and the annual irrigation is of the order of 25 lakh ha. in MP and 21,300 ha. in Rajasthan.

(v) Gandhi Sagar Dam (1960): Located across river Chambal in the State of MP, this project has an installed capacity of 115 MW. It also provides regulated releases of water for hydel power generation as well as for irrigation through the projects located on its downstream.

(vi) Bhakra Dam (1963): Constructed across river Sutlej, irrigates 13.35 lakh ha. annually. Its hydropower genration (installed capacity) is 1204 MW and the height of the dam is 226 meter.

(vii) Jawahar Sagar Dam (1973): Located in the State of Rajasthan, completed in the year 1973, generates (installed capacity) 99 MW of power.

(viii) Farakka Barrage (1974): A terminal barrage on the river Ganga located in the State of West Bengal, it serves the purpose of augmenting water in the channels of Calcutta Port, as well as to augment water supply to Calcutta City.

(ix) Nagarjuna Sagar Dam (1974): A multipurpose project across Krishna river in the State of AP, it provides annual irrigation to 8.5 lakh ha. Its hydropower generation (installed capacity) is 202 MW and the storage capacity of the reservoir is 11,550 Million Cubic Meter.

(x) Paithan Dam (1976): Constructed on river Godavari in AP, this project provides irrigation of the orfer of 1.42 lakh ha.

(xi) Dehar Power House (1977): Located in the State of Himachal Pradesh on river Sutlej in Indus basin,the hydropower generation(installed capacity) of the project is 900 MW.

(xii) Ghataprabha Project (1979): Located in the State of Karnataka, across river Ghataprabha in Krishna basin, this project provides annual irrigation to 1.39 lakh ha. Its hydropower generation (installed capacity) is 41 MW.

(xiii) Mahi Bajaj Sagar Dam (1985): Located across the river Mahi in the State of Rajasthan, this project provides annual irrigation to 1.2 lakh ha. of land. Its hydropower generation (installed capacity) is 140 MW.

(xiv) Salal Project (1987): Located on the Chenab river in J&K, this project generates 690 MW (installed capacity).

(xv) Chamera Project (1994) (Stage-I): Located across river Ravi in the State of HP, this project generates 540 MW of hydropower (installed capacity).

(Source: Ministry of Water Resources)

4.2 Flood control and Flood Management

The Himalayan rivers bring considerable quantities of silt and their basins suffer from drainage congestion and flooding. Similarly, deltas and estuaries of the west and east flowing rivers also suffer from floods. On an average, area affected by floods annually is about 7.52 Mha of which the crop area affected is 3.521 Mha. The floods have claimed on an average 1,515 lives and 95,285 heads of cattle every year during a span of 44 years from 1953 to 1996. Inspite of flood protection works such as flood embankments and reservoir operations, the problems of floods remains. With the growing population and increased developmental activity, the flood plains are being increasingly occupied resulting in more and more damages Although it is feasible in most cases to provide certain degree of protection against flood in terms of reduced frequency and flood damages, there are no universal solutions which can provide complete protection against floods. The country has, therefore, to shift its strategy towards efficient management of flood plains, flood proofing including disaster preparedness and response planning and flood forecasting and warning and other nonstructural measures such as disaster relief, flood fighting including public health measures and flood insurance.

The need for flood management was felt in early fifties and the National Flood Management Programme was launched in 1954; the area provided with flood protection was then around 3 Mha. The total length of embankments was around 6,000 km. In the policy Statement made in1954, the objective set before the national was to rid the country from the menace of floods by containing and managing floods. However, it was realized afterwards that absolute imm certain proportion of hydro-power is essential in the regional power generation grid unity from flood damage was not physically possible even in the distant future because of the unpredictability of several events which occur along with worsening situation by manmade activities. Hence, it was decided to provide reasonable protection that was found to be technically and economically justifiable and lay greater stress on flood forecasting flood warning, flood fighting and flood management.

A number of National and State level committees was also set up from time to time upto 1976 when Rashtriya Barh Ayog (National Flood Commission) was constituted.The National Flood commission has estimated that the total area liable to floods in the country is around 40 Mha, that is, about one eighth the geographical area of the country. The major concentration of the flood prone areas is in the Ganga-Brahmaputra-Meghna rivers system and in the coastal deltas of the Peninsular Rivers.

4.3 Hydropower

Hydropower is one of the important uses of water and its advantages are well-known. A certain proportion of hydropower is essential in the regional power generation grid because of its inherent advantage in providing peak energy during peak hours. However, in spite of large hydro-power potential of nearly 84,000 MW at 60% load factor, the present development has been to the tune of only 13,000 MW.

Basin/Rivers	Potential MW at 60 percent Load Factor MW	Potential already developed up 31.8.98 MW	Potential under development from the on-going projects as on 31.81.98 MW
Indus	19988	2935.85	1332.83
Ganga	10715	1850.33	1147.55
Central Indian Rivers	2740	634.33	1528.00
West-flowing Rivers	6149	3445.33	756.13
East-flowing Rivers	9532	3661.42	701.32
Brahmaputra	34920	452.67	366.72
Total	84044	12979.93	5832.55

Source: Central Electricity Authority

River valley projects are an important element of optimum and integrated-water resource development planning. Large multipurpose storages provide benefits of irrigation,hydropower, flood control and water supply. The cost of dams is allocated amongst different uses, thus reducing the cost of each benefit. Hydropower, therefore, contributes not only to the larger availability of water but also to the reduction in the cost of benefits. In some cases hydropower competes with other uses such as irrigation or water supply, while in others it becomes a by-product of other priority uses. An overview of hydropower including the future scenario is, therefore, necessary in the context of long term and sustainable availability of water for meeting the future demand.

The hydro-electric projects which have inherent ability for quick starting and stopping and almost instantaneous load acceptance and rejection, are ideally suited for meeting the peak hour demand and for enhancing system reliability in the most economic manner. The operation of hydro power projects is environment friendly and does not pose adverse impact unlike the thermal projects which have the associated problems of emissions and solid waste disposal. The hydro power projects have longer useful life spans. The hydro-electric projects are generally located in remote hilly and inaccessible areas and implementation of hydro power projets enables accrual of incidential benefits of development of road/rail communications, electrification, industrialization and improvement of the quality of life in the backward areas. Contrary-wise there are also adverse effects on forests and environment and on human beings in the form of displacement of people. Hydro power is the cheapest in the long run amongst the various sources of power supply. It has no fuel cost and is thus almost free from operating cost escalations. It is renewable in nature and promotes conservation of non-renewable fossil fuels. For an efficient and optimal operation of a power system, an optimal hydro/thermal mix (40:60) is considered necessary. However, of late the proportion of hydro power is going down. The present hydro/thermal mix of about 25:75 calls for increase in hydro power capacity. The operation of thermal plants at a very low load (during off-peak period) would adversely affect the efficiency of the system, the plant life and fuel consumption. Installation of hydro power plants will help in improving operational reliability, stability of the power system and also in optimizing the operational economy and meeting the peak load requirements.

Notwithstanding the availability of vast potential in India and many beneficial aspects, the pace of hydro power development has been slow due to a number of reasons such as delays in project formulation, need to preserve the pristine econlogy of certain regions in the interests of the larger environmental considerations, such as, biodiversity; rehabilitation and resettlement problems of affected people and the inherent delays in the construction of hydro power projects.

4.4 Inland Water Transport

Inland navigation is the cheapest mode of transport and should receive due priority in the regions where such movement is possible. Inherent advantages of inland navigation are lower operational costs, fuel conservation and better safety.

Inland Water Transport (IWT) cannot be left out of water resources planning, since for the rivers to be navigable, there has to be a water course of sufficient depth and width.

Inland Water Transport used to occupy a very important place in the transport system of yester years in India and had developed much earlier than other modes of transport. However, with the advent of railways and modern highways coupled with the poor organization and management of river services, navigation in the rivers gradually declined and inland water transport lost its importance with the passage of time. Heavy siltation in the lower reaches also rendered established facilities out of use. At present cargo transportation in an organized manner is confined to the States of Goa, West Bengal, Assam and Kerala.

The rivers like Ganga, Brahmaputra, Mahanadi, Narmada, Godavari, Krishna,Mandovi and Zuari, Tapi, the waterwaysof Sunderbans, the creeks in the east and west coasts, etc. provide facilities for inland water transport. Some of the important canals having navigation potential are the Cumbarjuna canal in Goa, Buckingham Canal in Andhra Pradesh and Tamil Nadu, West Coast Canal in Kerala, DVC and Krishtopur Canal in West Bengal and Orissa Coast Canal in Orissa. The total navigable length of canals is about 4,300 km. However, navigation by mechanized crafts is presently done only for short lengths.

In recent years, there has been a revival of interest in IWT. The existing transport corridors are saturated and the railways and roads which carry a major share of passenger and cargo traffic continue to fall short of demand. Even bulk commodities like coal are moved over long distances by road. As economic growth accelerates transport demand will grow at a faster pace and it will be wise to use IWT for movement of bulk commodities.

Economics of the Competing Modes

Rail and road modes face constraints because of land use and environmental factors, further complicated by the energy crisis. By the year 2000, India will be spending 74 percent of its export earnings on oil imports. The alternative mode of energy efficient, cost effective IWT, therefore, deserves reckoning. Water transportation is the most fuel efficient method of moving freight with the lowest level of emission as can be seen from below :

Mode	Fuel Consumption (Litres of H.S.d. per tonne-km	Fuel efficiency (Ton-mile per gallon)	Emissions (lbs.Per 100 ton-miles)		
			Hydro Carbon	Carbon monoxide	Nitrous Oxide
Rail	0.011	202	0.46	0.64	1.83
Road	0.04	59	0.63	1.90	10.17
IWT	0.0056	514	0.09	0.20	0.53

Source : Theme Paper 1999 IWRS-Vision 2050

According to recent studies carried out for the north east region, the investment cost for IWT works out to Rs. 1.37 per tonne-km. Against this, the road system costs approximately Rs. 2 per tonne-km and the railway system costs about Rs. 2.25 per tonne km.

Present Status of Development

In the development of water ways for IWT, there are many problems such as bank erosion, siltation, shallow depths, shifting channels, sand bars and lack of infrastructure. Conservancy measures such as bank protection works, revetments, river training, dredging and construction of modern terminal facilities are required in most of the waterways. Infrastructural facilities are essentially to be provided by the government. These facilities include assured fairway with navigational aids (including night navigation) and well equipped ports. For want of these facilities, private agencies are not keen to invest in the IWT. The Inland Waterways Authroity of India (IWAI), set up in 1986, has been charged with the responsibility of developing navigation on national waterways.

4.5 Domestic Requirements

The goal of the International Drinking Water and Sanitation Decade (1981-1990) was that, by the end of 1990, all people should possess an adequate water supply and satisfactory means of sanitation. This was followed by the New Delhi Statement after Global consultation on safe water and sanitation for the 1990s which stated that safe water and proper means of waste disposal must be at the centre of integrated water resources management.

Safe water is essential for sustenance of life and is needed in the households for drinking, cooking, washing and cleaning. The requirement is not very large overall compared to the requirements for all uses. The question is one of water availabilility, cost of development and efficiency of management.

Domestic water requirement is mostly of non-consumptive nature. Even assuming the higher rate of population growth, the total water requirement for domestic uses by the year 2050 has been estimated at 111 km^3. (Report of the NCIWRD, 1999).

The management issues are more critical. Widespread dissatisfaction among consumers is the result of improperly managed water supply systems, where people are forced to resort to alternate means or supplementary sources for collection of water in sumps and overhead tanks at considerable costs. It is so because 17-44 percent of total flow in distribution system is lost due to leakages in the mains, communication and service pipes and leaking valves as brought out by NEERI while conducting pilot studies on leaks in the distribution system of 13 cities in India. The need for according high priority to maintenance and leak detection and preventive measures is obvious. The utilities have to adopt a number of conservation measures. Demand management through pricing is an aspect which needs particular attention. Public awareness and participation especially of women has to be ensured through a massive campaign of communication through all available media. To arrest the fall in ground water table, measures like artificial recharge and rainwater harvesting have to be encouraged.

Potable water and adequate sanitation facilities undoubtedly reduce spread of diseases such as cholera, typhoid, infectious hepatitis, and dysentery. Chances of contamination in urban water supply system have to be reduced by adopting a variety of measures as indicated. Institutionalising the system of water quality monitoring and surveillance will prove a strong deterrent to over exploitation of ground water, which is the principal source of supply in rural areas and gets contaminated from point and non-point sources. Cheaper alternatives for human waste disposal, namely, oxidation ponds or water stabilisation ponds need to be examined and experimented upon with a view to evolving affordable systems that can provide universal sanitation coverage in the near future.

Water requirement for industries in India although insignificant when compared to the demand for other uses like agriculture creates problems by creation of point loads on available resources. Water use in industries is mostly of non-consumptive nature and with suitable treatment can be recycled and re-used by process industries for their requirements of processing, cooling, boiler feed and other miscellaneous uses. Cost effective strategies have been demonstrated and should be adopted by industry. Tariffs have to be prescribed such that industry is compelled to look into technological interventions leading to reduced use per unit production of waste water, which will further reduce generation of pollution load and consequent cost of treatment.

Hazardous waste management is another important aspect of industrial waste management. Preliminary data gathered by MOEF, CPCB and institutions like NEERI suggest that the disposal methods currently practised are not environmentally compatible. Sites for disposal of hazardous wastes are not also readily available. Industrial zoning should be done in such a manner that water intensive industries are located in arid and semi-arid areas. In the latter areas, Green category of industries have to be promoted.

5. LEGAL AND INSTITUTIONAL FRAMEWORK WITH REGARD TO WATER RESOURCE MANAGEMENT IN INDIA

5.1 Constitutional Provisions and Existing Laws

The Constitution of India lays down the legislative and functional jurisdiction of the Union, State and local Governments regarding ‘Water’. Under the scheme of the Constitution, ‘Water’ is basically a State subject and the Union comes in only in the case of inter-state river waters.

List II of the Seventh Schedule, dealing with subjects regarding which states have jurisdiction has following as Entry 17 :

"Water", that is to say, water supplies, irrigation and canals, drainage and embankments, water storage and water power subject to the provisions of Entry 56 of List I

Entry 56 of List I (Union list), reads as follows :

"Regulation and development of inter-state rivers and river valleys to the extent to which such regulation and development under the control of the Union, is declared by Parliament by law to be expedient in the public interest".

The Constitution has a specific article (Article 262), dealing with adjudication of disputes relating to matters of inter-state rivers or river valleys, which reads as follows :

Article 262 (1): Parliament may by law provide for the adjudication on any dispute or complaint with respect to the use, distribution or control of the waters of, or in, any inter-state river or river valley.

(2) Notwithstanding anything in this Constitution, Parliament may by law provide that neither the Supreme Court nor any other Court shall exercise jurisdiction in respect of any such dispute or complaint as is referred to in clause (1).

The recent 1992 amendments to the Constitution regarding Panchayats and Municipalities introduced the following entries in the schedules listing the subject-areas in which he State Governments and Legislatures may devolve functions to such bodies, so as to make them evolve as local self-governing institutions :

In the Eighth Schedule (Part IX) dealing with Panchayats, the subjects, "minor irrigation, Water management and Watershed development", "drinking water" and "maintenance of community assets" are listed.

In the Twelfth Schedule (Part IX A) dealing with municipalities, the subjects "water supply of domestic, industrial and commercial purposes" is listed.

Functional responsibilities are, thus, visualised for local Governments in respect of several aspect of water use.

The two laws enacted by the Union under Article 262 and Entry 56 of List I are the Inter-State Water disputes Act, 1956 (as amended up to 1980) and the River Boards Act, 1956. In recent years since the Constitutional does not have an entry relating to 'Environment', using the residual powers, the Union has enacted laws on environment and control of pollution, which have effect on water use, including ground water and its exploitation.

A large number of Acts dealing with irrigation, canals and their maintenance, water rates and cess, command area development and maintenance of tanks are in force in each state. Some of the Acts are as old as the 1860s and 70s.

There are a number of complex legal issues when matters regarding integrated development of inter-state rivers, allocation of river waters, inter basin transfers, utilisation of ground water, water rights and people's participation are considered. There is a suggestion that since water is a national resource and asset, a national perspective is needed for equitable development, “Water”, which is now a state subject, should be included in the Union or concurrent list. It is not practicable to think of this suggestion.

What is needed is that the union should fully exploit its powers regarding interstate rivers in the Constitution and pass laws to more effectively deal with interstate rivers.

Parliament enacted the River Boards Act, 1956, under Entry 56 of List I, to promote integrated and optimum development of waters of interstate rivers and river valleys. The Act provides only for Advisory Boards and not for river Basin Organisations vested with powers of management. In fact, no river board, even of the advisory kind has been set up under this Act. The enactment of a law on interstate rivers, in the place of River Boards Act, called the Inter-State Rivers and River Valley (Integrated and Participatory Management) Act is strongly urged. The Act would provide for the constitution of a River Basin Organisation (RBO) for each major basin.

Parliament enacted the Inter-State River Water Disputes Act in 1956. The Act provides for setting up tribunals for the adjudication of water disputes. Experience shows that a long time is taken both in constituting the Tribunals and in giving the awards and this has been the cause for some interstate tensions for years. Also, though the jurisdiction of courts is barred by the Act, matters are taken to the higher courts on issues other than water sharing, especially in the case of specific subjects. The Sarkaria Commission, which examined the issues in great depth, made five recommendations, which were considered by the Interstate Council. The Council recommended that (i) once an application is received from a state, the Union government should constitute the Tribunal within one year (ii) the Tribunal should give the award within a period of three years, extendable by two years (iii) the award should be given effect to in two years (iv) there should be Data Bank and Information System and (v) the Award of a Tribunal should have the same force as an order or decree of the Supreme Court.

The Constitutional provisions do no specifically permit or prohibit the transfer of surplus flows from one basin to a deficit basin. No state is willing to accept that it has surplus flows over and above its requirements. It is felt that through the River Basin Organisations, the States may come together for holding serious discussions on sharing of waters including diversion to non basin States, ultimately paving way for reaching an agreement on the basis of mutual needs. The proposed Inter-State River (Integrated and Participatory Management) Act, may provide necessary legal backup to the RBOs.

5.2 Institutional Framework

Presently the Ministry of Water Resources assisted by its attached office, Central Water Commission, carries out the work of policy formulation and supervision for the programmes of water resource development and management in the country.

The Ministry of Water Resources was concerned, from its earlier days as Ministry of Irrigation and Power, mainly with 'irrigation' aspect of water resources. Its current mandate, as per the 'Allocation of Business Rules' is "Development, conservation and management of water as a natural resource; overall national perspective of water planning and co-ordination in relation to diverse use of water".

Water supply - urban and rural, soil conservation and watershed development, environment, water quality, etc. are dealt with by other ministries / departments. Since water has diverse uses, the entire subject cannot be brought under one ministry. What is essential is, to ensure co-ordination. Therefore, the Ministry (of Water Resources) and the CWC needs to have multi disciplinary capacity.

Capacity building of the institutions has been recognised by the Government and efforts are under way to reorganise and restructure the organisational framework. The Government of India constituted the National Water Board in September, 1990 with the Secretary, Ministry of Water Resources, Government of India as its Chairman, Secretaries of concerned Union Ministries, Chairman, CWC, and Chief Secretaries of States / UTs as members. The Board has served as a useful forum for Centre State discussions at the senior officers' level and on a number of complex issues, agreement could be reached at the level of officers.

6. INITIATIVES OF GOVERNMENT OF INDIA ON WATER RESOURCES MANAGEMENT AND DEVELOPMENT OVER THE YEARS

Apart from the implementation of a large number of irrigation, hydro-power and water supply projects as has been listed earlier, the Government of India, through its six ministries and departments (i.e. the Ministry of Water Resources, Ministry of Agriculture, Ministry of Environment and Forests, Department of Land Resources, Department of Drinking Water supply and Ministry of Urban Development) undertakes plans and programs on watershed development, soil & water conservation, River conservation, Desert development, Integrated wasteland development, Drought prone area programme, and Rural and urban water supply and sanitation programmes on a continuing basis. Apart from these, the initiatives that the Government of India has taken on water resources development over the years are listed below:

6.1 National Perspective for Water Development (1980)

A National Perspective for Water Development was framed in August,1980 by the Ministry of Water Resources. It was discussed at various governmental levels and a National water Development Agency was set up in1982 to carry out detailed studies in the context of the National Perspective. Considerable work has been done and the National Perspective has been developed in fair detail.

The basic aim is to utilize all the possible utilizable waters. For this purpose, creation of storages and interbasin transfer from the surmised surplus rivers basins to deficit basins has been the guiding objective. An argument of integrating the rivers contributing to national integration has also been advanced. It has been considered that population would be stablised by 2050 AD and that self sufficiency in food can be achieved only by utilsing the water otherwise going to waste in the surplus river basins. On this basis, it is considered imperative that all the rivers in the country be linked by a national grid to met the shortages in the various parts of the country(IWRS, 1996).

The broad approach adopted in the National Perspective is as follows (NWDA, 1998):

- Existing uses have to be kept undisturbed.
- Normally water development under the existing legal and constitutional framework is assumed to take place fully by the turn of the century.

- The development envisaged is within the framework of all the existing agreements between the states.
- While planning inter-basin and inter-state transfer of water, reasonable needs of the basin states for the foreseeable future have to be kept in view and provided for.
- Most efficient use of land and water in the existing irrigation and hydro power stations should be a principal objective to be achieved.

The National Perspective brought out by the Ministry of Water Reosurces has two main components, (a) Himalayan Rivers Development and(b) Peninsular Rivers Development. The Himalayan Rivers Development envisages construction of storage reservoirs on the principal tributaries of Ganga and the Brahmaputra in India and Nepal along with interlinking canals systems to transfer surplus flows of the eastern tributaries of the Ganga to the west, apart from linking of the main Brahmaputra and its tributaries with Ganga and Ganga with Mahanadi . Peninsular component is divided into four major parts :

(i) Interlinking of Mahanadi-Godavari-Kirishna-Cauvery rivers,
(ii) Interlinking of west flowing rivers north of Bombay and south of Tapi.
(iii) Interlinking of Ken-Chambal and
(iv) Diversion of other west flowing rivers.

6.2 National Water Policy, 1987

A National Water Policy delineating the intent of the Government of India with regard to issues like water allocation priorities, Ground water development, Drinking water, irrigation, Water rates, Participation of Farmers and Voluntary Agencies, Water Quality, Conservation of water, Water zoning, Drought Management, Flood control and Management and Research and training in the Water sector, was adopted by the Government in 1987. The aim was to get all the States to subscribe in broad terms to a minimal set of propositions of a general nature, which could then form an agreed basis for a more detailed policy-making and action-plans. However, the operationalisation of the policy has not made much headway and the Government is planning a review and re-look of the policy.

6.3 High Powered Commission for Integrated Water Resources Development Plan, 1996

With a view to ensure an integrated development of water resources in the country, a high powered commission for Integrated Water Resources Development Plan was set up by the Government in 1996 under the Chairmanship of Sh. G.V.K. Rao (succeeded subsequently by Dr. S.R. Hashim, Member, Planning commission) with the following terms of reference:

(i) To prepare an Integrated Water Plan for development of water resources for Drinking Irrigation, Industrial, Flood Control and Other Uses ;
(ii) To suggest modalities for transfer of surplus water to water-deficit basins by inter-linking of rivers for achieving the above objectives;
(iii) To identify important On-going Projects as well as new Projects which should be completed on priority basis together with phasing;
(iv) Identify a technological and interdisciplinary research plan for the water sector with a view to maximize the benefits;
(v) To suggest physical and financial resources generation strategies for the water sector;
(vi) Any other related issue.

The Commission submitted its recommendation to the Government in September,1999. The recommendations have shaped the follow up action of the Government in a major way.

6.4 Task Force on Interlinking of Rivers, 2002

With the objective to provide guidance on norms of appraisal of individual projects and modalities for project funding etc. and to bring about a consensus among the concerned states, the Central Government on 13th December, 2002, set up a Task Force under the Chairmanship of Shri Suresh Prabhu, Member of Parliament (Lok Sabha). The members of the Task Force consist of technical experts (including legal,environmental, sociological and economic experts) and distinguished persons from water deficit and water surplus states. The terms of reference of the Task Force are to:

i. provide guidance on norms of appraisal of individual projects in respect of economic viability, socio-economic impacts, environmental impacts and preparation of resettlement plans ;
ii. Devise suitable mechanism for bringing about speedy consensus amongst the States;
iii. Prioritize the different project components for preparation of Detailed Project Reports and implementation;
iv. Proposes suitable organizational structure for implementing the project;
v. Consider various modalities for project funding; and
vi. Consider international dimensions that may be involved in some project components.

It is envisaged that the Task Force would ensure completion of feasibility studies by 2005, completion of Detailed project Reports by 2006 and implementation of the Project by 2016.

It may be observed that the terms of reference of the Task Force are focused toward inter-basin and intra-basin transfer and the time-frame has also been earmarked signifying the definite intention of the Government.

7. INTER-LINKING OF MAJOR RIVERS OF INDIA

The concept of inter-linking was given effect in India as early as in1839 when Lt. Gen. Sir Arthur Cotton pioneered interlinking of peninsular rivers for inland navigation. The plan was abandoned later as railways got priority.

Two main studies conducted much before the National Perspective Plan include a note on the National Water Grid prepared by the then Central Water & Power Commissioner (in 1972), elaborated further by Dr. K.L. Rao and a proposal for Garland Canal put forward by Captain Dastur. Dr. K.L. Rao had advocated one of the alignments (of the three possible alignments proposed by the then Water and Power Commission for the Ganga-Cauvery link) along with a few other links including the Brahmaputra and Ganga link. The proposal was not found feasibile by the Central Water Commission and was not pursued further. The fate of the proposal of Captain Dastur, who had recommended mainly two canals of which one was proposed to be aligned along the southern slopes of the Himalayas and the other was proposed to be in the form of a central and southern garland canal with about 200 integrated lakes, was similar. The proposal was found to be technically unsound and economically prohibitive.

The inter-linking of rivers is a continental scale programme being undertaken in India for inter-basin transfer of waters. Transfers between sub-basins also are included in the programme. The title ILR is considered more appropriate for India's size of the country as it connotes interdependence of different regions of the country aiming at promotion of integration through sharing and caring for each other's needs.

Often, some parts of a river basin are surplus in availability when compared with needs/demands, depending on orography and direction of moisture laden winds, while some others face deficit. It may be that a surplus region of a basin may be just adjoining or physically contiguous to a deficit region of an adjoining basin. Transfer of water between such regions, within and outside a river basin across high ground between such regions, has been practiced by mankind for a long time, to remedy such imbalances. It mostly involves construction of storages for holding/impounding waters and raising their elevation to enable transfer. Diversion structures involving little or no storage are also constructed for withdrawals through canals and by pumping, where the river flow quantum is adequate and where high ground is not encountered. Incidentally storages wherever constructed invariably absorb and reduce flood peaks downstream in the basin, enabling better flood management. The concept of inter-basin transfer in reality is practiced within basin also. For example, when a canal crosses several tributaries for in-basin development, the transfer occurs between sub-basins. Many times inter-basin transfer through a canal negotiating a ridge is less expensive if the deficit area of an adjoining basin is close to the ridge, than a longer canal serving deficit area quite distant from the serving reservoir. Adoption of ILR to transfer flood water is one of the most effective ways to augment the available potential through traditional or conventional means.

ILR IN INDIA IN PAST

Inter-linking of rivers has been in vogue in India even prior to 20th century. A spectacular and successful example is the South India's transfer of water of the west flowing Periyar to the Vaigai system in east. Another example is the successful Perambikulam - Aliyar Project in South India. Koyna and Sharawati diversions from east flowing rivers to westwards are the other two special examples, which have helped Maharashtra and Karnataka States fulfill their energy needs and enable rapid economic development. Indus Basin has several large scale sub-basin transfers, which have brought prosperity not only to the States of Punjab, Haryana and Rajasthan, but have proven a boom for the whole country. The recently commissioned Sardar Sarovar Canal has linked more than 8 rivers in the North of River Narmada and is on the threshold of transforming the scarcity regions of Gujarat and Rajasthan dramatically. The transfer of surplus water of Ravi – Beas to Rajasthan right upto Jaisalmer, Barmer through Indira Gandhi Nahar Pariyojna is one of the impressive examples of recent times. This project eliminated virtually the drought conditions in western Rajasthan transforming the desert wasteland into an agricultural productive area. Over one Mha of sand dune area has been brought under irrigated agriculture through this link, which contributes annually to agricultural products worth Rs. 1750 crores. The canal water has also been a boon for meeting drinking and domestic needs. The defence personnel protecting western frontiers receive valuable life support from this canal. The project has miraculously transformed the lives and the socio-economic conditions of the people in the area. There are several such examples within the country where the concept has been successfully adopted.

ILR programme as presently envisaged

The NWDA has identified in all 30 links as technically feasible and economically viable on the basis of pre-feasibility studies. All these links are under feasibility appraisal. In fact for 8 links, feasibility studies are completed but they are under discussion with the concerned States for evolving consensus about their acceptability and for firming them up before the process for preparation of detailed project reports (DPR) is undertaken. It is expected that the process will soon be launched for paving the way for undertaking implementation of at least some of the schemes as soon as the DPRs are ready.

ILR would significantly reduce the regional imbalance in the availability of water in the different river basins. Surplus flood-waters which are flowing waste to sea would be fruitfully utilised. It is assessed that it will provide additional irrigation benefit to 35 million hectare (25 million hectare from surface water and additional 10 million hectare from increased ground water recharge), which will be over & above the ultimate irrigation potential of 140 million hectare envisaged from the conventional irrigation projects.

As brought out earlier, this programme will augment and extend water availability of the order of 1100 BCM from conventional and traditional means to about 1300BCM. The programme does not preclude continued expansion of water resources development from present level of about 700 BCM to 1100 BCM. In fact, as the whole water resources development is long gestating, it is necessary that implementation of the desired expansion is started right in earnest. The country needs to develop all possible water resources as soon as possible to come out of the status of a developing nation and take its rightful place in the world as a developed nation.

How is such concept implemented in other countries?

Not only in India but in other countries one finds numerous examples of inter-basin water transfers. Such major international water transfer programmes are seen in more than a dozen and a half countries. The examples demonstrate that the ILR in general, is a successful concept practised all over the world to ensure the usage of water in an optimal manner.

INTERNATIONAL SCHEMES OF INTER-BASIN & MAJOR SUB-BASIN WATER TRANSFER

S.No.	**Country**	**No. of Schemes**		**Annual transfer (BCM)**	
		Completed	**Proposed**	**Completed**	**Proposed**
1	Australia	1	-	-	-
2	Brazil	-	1	-	1
3	Canada	37	9	268	1
4	Chile	2	1	3	-
5	China	-	3	-	45
6	Czech Rep.	6	-	6	-
7	France	1	-	-	-
8	Germany	2	-	1	-
9	India	7	30	10	200
10	Iraq	6	-	45	-
11	Japan	1	-	-	-

12	Malaysia	-	1	-	1
13	Morocco	1	-	-	-
14	Pakistan	7	-	50	-
15	Portugal	-	1	-	N.A
16	Romania	4	-	-	-
17	Russia	-	2	-	37
18	Spain	3	-	1	-
19	USA	49	6	45	376
	Total	**137**	**54**	**429**	**661**

While so many successful schemes of inter-basin transfers have been implemented round the world, critics point out some cases where the ILR concept was given up or shelved. Obviously, such cases were not embedded in adequate hydrologic assessments. It is better to give up schemes, which are infeasible at the right time. In case of present ILR programme, in-depth pre-feasibility and feasibility studies have been conducted over the last 20 years and the link schemes show promise of technical feasibility as well as economic viability. Still, presently a critical review is being conducted of such established feasible links after which DPR work will be taken up. In case any study shows that a particular link is infeasible it might not be pursued.

The example of the effect of diversion of waters for agriculture from Amu-darya and Sir-darya Rivers of Central Asia emptying into the land-locked Aral Sea has been cited by some as a warning for the ILR programme. The cited diversions have been responsible for the life supporting agriculture in this area, without which the societies would not be economically sustainable. At the same time, they have caused reduction of water level of Aral Sea and consequent ecological degradation. In reality the land-locked Aral sea is not comparable to the Arabian Sea and Bay of Bengal in which Indian rivers fall. Also, the scale of diversion in the two cases is not comparable. However, the Aral Sea depletion is being considered seriously by the Central Asian States for reversal as best as possible in consonance with agricultural needs. A shelved project for transfer of water by ILR is also being considered to ameliorate the difficulties. The ILR programme envisages in totality, a diversion of about 200 BCM out of 1900 BCM of runoff in the country, which is not expected to cause any significant impact. It must be understood that the country is planning to develop only about 1300 BCM out of 1900 BCM of runoff.

8. PRESENT STATUS OF THE INTERLINKING RIVERS PROGRAMME:

8.1 Time Schedule for the Completion of the Feasibility Studies

The NWDA has identified on the basis of detailed studies, 30 links in all: 14 in the Himalayan Component and 16 in the Peninsular Component. For each of these links, studies were undertaken sequentially - Pre-feasibility study followed by Feasibility Study. NWDA first completed all the pre feasibility studies and has prepared Feasibility Reports (FRs) for 8 links by now: one (Sharda - Yamuna) out of 14 of the Himalayan Components and 7out of 16 of the Peninsular Component.

The work of feasibility studies is on-going for 16 links. Work of preparation of FRs on the remaining 6 identified links is yet to take off. FRs for all the 22 links are planned for completion by December 2005. Out of these, FRs for 12 links are to be completed in the year 2004 and for 10 links in the year 2005.

Meanwhile, a critical review of the 'logic' and 'planning' for each of the proposed link has been initiated by the TF with active participation in the process by the concerned NWDA officials. The review aims to modify the proposals to be more in tune with the needs of the concerned States, to make them more cost-effective in order to enable reaching consensus. The review steps comprise a fresh look at the assessment of availability of water at identified locations for diversion, the water needs in the downstream, en-route needs and needs of the area receiving the supplies. It also gives a re-look to the need and extent of lift involved for the diverted waters without compromising on the benefits, the alignment of the link and the state schemes incorporated in the proposals.

The outputs of this review are under discussion in the NWDA and MoWR to reach a common understanding and agreement about the parametres involved. The TF is expected to take up the revised version of each proposal for discussion with the concerned State starting at the highest political level, to cut short the process and arrive at early acceptance of possible revisions. Some of the completed and the on-going FRs, would need modification as a result of this review. The extent of modifications and time required for the revision of the FRs would depend upon the acceptability of the revised proposals. The process to build such consensus could take a few months. The TF considers this as a key process to reach the next milestone of "Convening the CMs Meeting to Deliberate over the Project and to Elicit their Cooperation".

8.2 Norms of appraisal

The Task Force is engaged in drawing up a comprehensive terms of reference for the DPR. Advice is being obtained from experts in different fields and from specialized institutions to ensure that the terms of reference provide the necessary guidance to the agencies engaged for preparing the DPR as also to obtain data and information on all relevant aspects of the respective link projects. The project reports will have to be of a quality that will contain not only the necessary information so as to establish the technical feasibility of the project but also to determine their economic viability, their socio-economic impacts, their environmental impacts, the mitigatory and compensatory measures to be adopted, as also the estimated cost of such measures, including the cost of resettlement of project affected persons. Thus it is expected that the TOR will provide the necessary guidance on norms of appraisal for these projects. Some of the institutions/experts contacted include (i) the National Environmental Engineering Research Institute (NEERI), Nagpur; (ii) National Council of Applied Economic Research (NCAER), Delhi; (iii) Forest Research Institute (FRI), Dehradun; (iv) Wildlife Institute of India (WII),Dehradun; (v) Indian Space Research Organisation (ISRO), Bangalore; (vi) Tata Energy Research Institute (TERI), Delhi; (vii) Tata Institute of Social Science (TISS), Mumbai etc. The Terms of Reference will specifically address the multi disciplinary nature of the linkages with its implications and impact on the country's economy, its potential for poverty reduction, employment generation and overall growth.

9. ESTIMATED BENEFITS AND COSTS OF THE PROGRAMME:

The benefits of drought mitigation from inter-basin water transfers will accrue to an area of approximately 25 lakh hectares in the states of West Bengal, Bihar, Uttar Pradesh, Haryana, Rajasthan, Jharkhand, Madhya Pradesh, Gujarat, Andhra Pradesh, Karnataka and Tamil Nadu. Addition of 35 Mha of irrigation potential could mean enhanced food production of at least 70 M tonnes which could help in continuing food sufficiency in the country.

The environment in downstream in benefited areas and in deltas will be greatly improved by facilitating maintenance of minimum flows in the rivers due to regeneration and regulated releases from hydropower stations.

Most of the cities, urban centres and rural habitations in our country are already water short. Future requirements of cities and villages will be supplemented by inter-basin transfer of water. Water supply to cities and villages could be about 15 BCM.

Most of the proposed link canals are wide and deep to facilitate the inland navigation facilities across the country. An expert group is working on study of the possibilities for enhanced navigation, which will reduce fossil fuel consumption thus reducing the adverse environmental impacts.

Hydropower potential increase will be 34,000 MW. It would stabilise the power systems taking care of peak loads and bringing about a favourable hydro/thermal mix.

Peak flood moderation due to dams will be significant (about 30%) and due to diversion will be about 5%.

The tendency of migration of rural population to urban complexes due to lack of employment activities in rural areas would be arrested as the inter-linking of rivers would generate scope for employment not only during the construction period but also subsequently, due to various agricultural and allied activities, ushering in prosperity in rural areas as well.

It is estimated that about 4.50 lakh people may get displaced due to creation of reservoirs and canals. The cost of rehabilitation of these people is planned to be included in the project cost and the displaced persons will be provided proper rehabilitation and resettlement packages to ensure that their socio-economic condition improves after their resettlement at new places.

It is also expected that due to construction of storages, about 79,000 Hectares of forest land will come uder submergence. Sufficient provisions are being made for conservation of forest resources by means of raising compensatory afforestation, watershed treatment and alternate land and water management programmes.

10. SUMMARY:

Inter and intra basin transfers have been undertaken with great benefits not only in many other countries such as Canada, the USA, France, Germany, Spain, Japan, Iraq and Czechoslovakia, but also in India on a smaller scale, earlier. The three Gorges project in China transferring 45 BCM of water of Yangtse river to Huang He (Yellow river) from south to north is the most current endeavour. With 51 million hectares of our land being drought-prone and 40 million hectares being flood-prone, we need a comprehensive plan of action to mitigate the recurring problems of our people and to create a congenial life and environment for them. Moreover, we need to address the issue of increasing need of food of a growing population; potable drinking water for our rural and urban people; as well as growing need of energy, transportation and employment. The programme of interlinking of rivers offers an opportunity to address most of these issues in a comprehensive fashion. In fact, such a programme should have been taken up much earlier. We should not get bogged down by the argument that water-harvesting and water-shed management, taken up on a mass scale, would offer a solution to our perennial problems of flood and drought. In fact we need to and we have planned, to use these programmes along with the present programme of interlinking of rivers to find a solution to our problems caused by skewed distribution of water in India and to address our future needs of food, energy and water in a more comprehensive fashion. We also hope that this mammoth programme will set an example for a large number of developing countries to find a possible solution to their problem of development.

GROUNDWATER SUSTAINABILITY AND DYNAMICS II

(Session 5)

Chairpersons

B. Kumar
India

K. Rozanski
Poland

HOW CAN SUSTAINABILITY FOR GROUNDWATER USE BE DETERMINED?

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For groundwater management the question of SUSTAINABILITY is getting more and more important. This question contains two components: can the amount of extracted water be kept constant? and; will the concentration of possible contaminants remain below official limits? The understanding of water budgets and more over how they change in response to human activities is a key issue in this context.

Although forecasts of future evolutions that are based on calibrated numerical flow models are imprecise, they nevertheless may represent the best available decision making information available. The predictions are expected to be surveyed by appropriate monitoring programs.

In the following the question of sustainability will be discussed separately for three age ranges of the extracted groundwater:

a) for water younger than about 50 years

b) for waters in the age range between about 50 years and several thousand years and

c) for waters older than several thousand years.

Each time range will be illustrated in the talk by corresponding case studies.

Young groundwaters (age less than about 50 years)

The dominant drinking water resources in Europe are shallow and relatively recent groundwaters. These may be water from river infiltration, water from recent precipitation and infiltration with a considerable recent interaction between unsaturated and saturated zones.

Quality and quantity of the extracted young water may show relatively fast temporal variations. The water composition is usually far away from the natural (baseline) conditions and man made contaminants may already be present in the water. Because of the short timescales involved, effects of overexploitation may even be reversed and a system may recover from contamination within a few years. Therefore the questions of water balance and of sustainability are of minor importance for water authorities. However, predictions on water quality and quantity are still needed; predicting models should include reactions of the flow system, if the extraction rate is changed.

Tools to answer these questions are on one side direct measurements of effective or possible contaminants. On the other side chemical, physical and isotopic parameters are useful for model calibration and for the detection of trends. For instance: nitrates, salt contents, pressure heads and man made isotopes are indicators of a change of the flow system. He-3/H-3, SF6, Kr-85 and CFCs can be used for the detection of changes in the age structure, in the mixing components and in the origin and flow path of the water. Time series of these parameters and their gradients help to quantify on-going changes of the flow system and may induce restriction of groundwater extraction.

WATER WITH RESIDENCE TIMES BETWEEN ABOUT 50 YEARS AND SEVERAL THOUSAND YEARS

Sustainability for use of waters in this age range is the main criterion for water management: Man made tracers are absent and the risk of their appearance should be low enough to guarantee high water quality also in the future. Extraction and infiltration rate should be in a steady state. Groundwater managers should be aware of the high quality of these water reservoirs; information and education are important aims.

Calibrated flow- and geochemical models will allow to predict future water quality and to estimate water balances. Time information for the flow models are obtained from Ar-39, C-14 and He-4, whereas the presence of man made tracers like nitrates or Freons would indicate a shift of residence time distribution to the youger side. Monitoring programs and measured time series are useful for early warning: a change of the age structure and/or of the admixed components are clear signals to re-evaluate the model predictions. A difficulty in using chemical tracers are their large natural variations in time and space; the talk emphasises the distinction between real trends and natural variations. In an ideal situations natural “Baseline” concentrations of chemical compounds remain constant.

WATER OLDER THAN SEVERAL THOUSAND YEARS

Sustainability is not a good criterion for exploitation of so old waters. Water authorities should be aware that such a reservoir of water with excellent qualities is limited and that the exploitation of these groundwater is very often a “mining of a resource”. Tools for the identification of such old waters should be based on a dating and a climatic information: for dating long lived isotopes like He-4, C-14, Cl-36 and Kr-81 can be used, stable isotopes and noble gas recharge temperatures are main climate indicators. Changes of these tracers are strong signals for water authorities for overexploitation.

ISOTOPE HYDROGEOCHEMISTRY OF GROUNDWATER IN PURNA RIVER BASIN, MAHARASHTRA, INDIA

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Purna river basin, mainly located in Akola and Amaravati districts of Maharashtra in India, is an east-west elongated river valley ($20^0$10'-$21^0$25' N latitude & $76^0$00'-$77^0$55' E longitude). About 3000 km^2 area out of 7500 km^2 area of the inland basin is underlain by saline and brackish groundwater. The Quaternary sediments cover much of the area while the basin margins and the basement is composed mainly of the Deccan Traps. In the alluvial belt, the soil (derived from parent basaltic rock) has dense fabric, fertile but poor hydraulic conductivity with high degree of shrink-swell potential. Na^{+1} is the dominating cation in the soil and Ca^{+2}, Mg^{+2} decrease with depth. The electrical conductivity of the groundwaters of the area varies from 400 to over 30000 µS/cm. Some of the earlier studies in the area regarding the origin of salinity suggested intrusion of ancient seawater through Son-Narmada lineament, digenetic alterations, irrigation practices causing accretion and subsequent dissolution of salts in the soil horizons as well as dissolution of salts through the rock matrix. No conclusive inferences could be drawn from these studies.

In this study, the problem is tackled by employing isotope and hydrogeochemical techniques. Two sets of water samples from Purna river (Surface water), Dug wells (Shallow aquifer) and tube wells (Deep aquifer) and six piezometer samples were collected from different parts of the Purna river basin and analysed for environmental isotopes as well as major, minor, and trace ions. The interpretation of the results was carried out in the light of other geological information to decipher cause of salinity and delineating recharge & discharge zones of the fresh groundwater in the area.

The Piper trilinear plots for fresh waters and saline waters showed that fresh waters are generally Na-HCO_3 type whereas saline samples are predominantly Na-Cl type. The hydrochemical facies in saline waters change from HCO_3 to Cl type. No linear trend in salinity and depth were observed. It is observed that wherever groundwater flow is less, flushing is less and salinity is more. Computation of molar ionic ratios of the samples suggested that the salts have been derived as a result of weathering of the basalt present in the vicinity. Contribution of local precipitation to groundwater as a direct recharge is insignificant except in hard rock area. The foothills of the Satpura range, which is situated in the north of the basin, act as a recharge zone for fresh groundwaters in the area. Here the alluvium cover is quite thick and it becomes thinner and thinner as it progresses towards Purna River. Ultimately, the alluvium acts as discharge zone along the depression of Purna.

The deep aquifers of the area have saline, brackish and fresh waters. The δD-$\delta^{18}O$ plot indicates evaporative enrichment. The fresh waters fall near GMWL with a slope of about 8. Brackish waters, falling between saline and fresh waters seems to be mixture of the two waters. This is further inferred as well by the ^3H values of the waters.

Purna river water samples showed evaporative enrichment. It also indicates contribution of groundwater to the river at some places. A depleted starting isotopic composition for saline groundwater samples compared to present day river water sample indicated either source of saline waters is different from river water or a different climatic conditions existed at the time of recharge in comparison to the present era.

$\delta^{18}O$ – Cl^{-1} plot showed that the salinity in the deep aquifers could be due to leaching of salts from the formation as well. The ^3H values of the samples showed that the saline aquifers are isolated and not getting modern recharge. However, the brackish water aquifers do get partial recharge from a distant source. The ^{14}C results of the highly saline groundwater samples suggested their uncorrected ages about 4 - 7 ka BP. The $\delta^{34}S$ values of the aqueous sulphate samples indicated their non-marine origin.

From the study it was concluded that, the deeper saline waters are old waters; their salinity is predominantly Na-Cl type. The mechanism of salinisation appears to be owing to evaporation, dissolution, and leaching of salts from formation. The isotope study also indicates their non-marine origin of salinity.

ORIGIN AND TEMPORAL EVOLUTION OF THE GROUNDWATER IN THE FONTAINEBLEAU SANDS AQUIFER (FRANCE) INVESTIGATED USING ^{3}H, ^{85}KR, ^{39}AR, ^{14}C AND STABLE NOBLE GASES

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The Fontainebleau Sands aquifer is located in the Paris Basin, France, and constitutes the main exploited reservoir of this multi-layered formation. The aquifer is embedded by two clayed limestone layers. 99 percent of the sands are constituted by a very fine silica of 100 μm average diameter. Water table depths between 20 and 45 meters and a mean porosity value for the saturated zone of 20% were reported as representative parameters for this aquifer [1]. The aquifer is characterised by a mean hydraulic gradient within the sands of 2 ‰ and transmissivities between 5 10^{-4} and 11 10^{-3} m^2 s^{-1}; these values are susceptible to variations with the proportion of clays or with the granulometry [1,2]. The annual mean infiltration rates vary between 87 and 205 mm per year, with higher values in the outcrop areas and lower but still considerable values elsewhere [3,4].

Seven wells from the Fontainebleau Sands aquifer were sampled to investigate the age structure and origin of groundwaters. According to the spatially extended recharge, a broad range of residence times from decades to thousands of years and mixing ratios could be expected. Consequently a large set of tracers with corresponding dating ranges were adopted. Measurements of ^{3}H, ^{3}He, ^{85}Kr, ^{39}Ar and ^{14}C confirmed the expectations of a heterogeneous age distribution. Concentrations of dissolved stable noble gases (He, Ne, Ar, Kr and Xe) were used to distinguish water infiltrated under different recharge conditions e.g. caused through variations of water table depths. Transport through the relatively thick unsaturated zone was also taken into account for the interpretation of age indicators of younger water components.

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GROUNDWATER SALINIZATION MECHANISM OF AQUIFERS BENEATH HO CHI MINH CITY AREA (VIET NAM)

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Water supplying for domestic and product activities in Hochiminh City is being taken from two both sources: surface water and groundwater. Due to the amount of surface water did not satisfy the water demand, groundwater is extracted ever more.

In this area there are more than 1000 large production wells and about 83000 tubewells now tapping groundwater mainly in two aquifers: Q_{I-III}, Pleistocene in age and N_2, Pliocene in age. The over extraction causes the water level depression continuously. The observation data of DHES from 1991 to 1998 shown that water level depression of 7m in Q_{I-III} aquifer and 12m in N_2 aquifer were found in comparison with those in 1991.

In the past (1960s) saline groundwater (TDS $\geq$1g/L) was observed in Saigon area when the amount of groundwater exploited was 170,000 cubic meters per day. The ever more groundwater exploitation caused aquifers salinization. The enlargement of saline water is not able to shirk and becomes a hard problem for the exploiting groundwater manager. Therefore to study and assess the groundwater salinisation using suitable techniques is very necessary for water resources managers in establishing better exploitation strategy. In this situation, environmental isotopes technique is emphasized to determine the salinisation mechanism of groundwater. The objectives studied are groundwater of two aquifers mainly being exploited (Q_{I-III} and N_2) in Hochiminh City area.

Based on the national water monitoring wells existing in the studied area and the hydrogeological setting a network of 70 sampling points for both two aquifers was set up. Water samples were collected two times (in rainy season of 2001 and in the end of dry season of 2002). All collected samples were analyzed for hydrochemical and stable isotopes. 30 of them were analyzed for tritium and 15 of them were done for ^{14}C.

Analyzing hydrochemical results of collected samples show that the quality of groundwater varies from fresh to saline, soft to very hard and high iron contents in some regions (TDS: 17.0-33000mg/L; Salinity: 0-25%; Cl^-: 4.6-16600mg/L; Na^+: 0.75-5230mg/L; K^+: 0.10-176mg/L; HCO_3^-: ND-319mg/L; Ca^{2+}: 0.2-410mg/L; Mg^{2+}: 0.18-732mg/L; SO_4^{2-}: 1.15-1613mg/L; NO_3^-: ND-40.4mg/L). Groundwater quality problem in a half of studied area is due to high chloride, total dissolved solids, iron contents and sulfate. The analyses of cations and anions by Piper Trilinear Diagram show that in aquifers where saline groundwater distributed the cations are mainly sodium, calcium, and magnesium type while the anions are mainly chloride and sulfate type but in the part where fresh groundwater the cations are mainly sodium, calcium, and type while the anions are mainly bicarbonate, carbonate and nitrate type.

According to TDS values the distribution of fresh and saline groundwater in studied aquifers is mapped and fresh-saline groundwater boundaries in 1990 and 2000 is also demonstrated.

The stable isotopes data show that the isotopic compositions scatter widely (values of δD range from –7.72 ‰ to – 50.55 ‰ and values of $\delta^{18}O$ range from –2.18 ‰ to –12.3 ‰) along the GMWL and a part of them fall on the mixing with sea water line. The distribution of groundwater samples collected along the GMWL show that groundwater in this area is recharged directly by rainfall and surface water. High tritium contents and ^{14}C relative radioactivity of groundwater in the area also support this process.

Delta values of ^{18}O and Chloride contents plot show that it exists two main salinisation mechanism. The first one is the leaching process and the second one is mixing with seawater process and both these mechanisms are always accompanied by evaporation process. Each process dominates in different region: In the southwest part of area groundwater salinisation caused mainly by leaching process and in the southeast is dominated by mixing with seawater.

There is a small brackish region in the northeast of studied area in which the salinisation was caused by mixing with sea water too but the relation between ratios of Na^+/Cl^- and Cl^- contents show that the refreshing is taking place. It could be explained that groundwater salinisation in this region was happened in the past by infiltration of seawater coming inland through Dongnai river and its distributaries (due to the tidal effect, especially in dry season) but now when Trian reservoir constructed on the upstream, fresh river water push seawater far towards downstream and the infiltration of fresh river water makes groundwater fresher and fresher. This is one of evens proving that groundwater in studied area is recharged by surface water.

The study results are new and useful for water resources managers to make better groundwater exploitation plan for limiting the enlargement of saline groundwater in aquifers as well as make faster the refreshing of brackish in aquifer in the northeast part of Hochiminh City.

USE OF ENVIRONMENTAL ISOTOPES TO STUDY THE RECHARGE MECHANISMS AND ARSENIC POLLUTION OF BANGLADESH GROUNDWATER

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Groundwater is the main source of drinking water supply for over one hundred million inhabitants in Bangladesh. About 1.5 – 2.5 million wells are estimated to be contaminated with arsenic according to Bangladesh Standard 50 µg/L [2]. It is now widely believed that the source of arsenic is geological in origin, not anthropogenic. But the actual release mechanisms are yet to be known. The young (Holocene) alluvial and deltaic deposits are most affected, whereas the older alluvial sediments in the north-west and the Pleistocene sediments of the uplifted Madhupur and Barind Tracts normally provide low arsenic water.

Environmental isotopes like ^{2}H, ^{18}O, ^{13}C, ^{3}H and ^{14}C are the suitable tools for investigating a series of problems linked with the management of water resources in the alluvial and deltaic sediments of Bangladesh. Isotope Hydrology of Groundwater in Bangladesh: Implications for Characterisation and Mitigation of Arsenic in Groundwater (BGD/8/016), a Technical Cooperation Project sponsored by IAEA, carried out in 1999-2000. Total 56 nos. water samples from shallow and deep tubewells, ranging in depth 10 to 335 meters, located mostly in south-west, north-west and partly in south-east of the country were collected. Results of isotope techniques have provided adequate information on recharge conditions and age of groundwater in the basin, that is very important and open up prospects for further investigations using isotope techniques.

Shallow groundwaters (<70 m) have oxygen, hydrogen, and carbon isotope patterns that are distinct from those of deep groundwaters. These isotopic patterns indicate that shallow groundwater is being continually recharged with a residence time of 10s of years. Deep groundwater may be either recharged on a long time scale of 100s or 1000s of years (Faridpur and Burir Char), or nor recharged at all with 20000-30000 years old water (Barisal). Arsenic contamination is found to be present mostly in shallow groundwater to depths of less than 70 meters. Groundwater samples from deep wells containing elevated arsenic concentrations are found to contain water mostly from shallow aquifers and do not indicate arsenic contamination of deeper aquifers. However, depth itself is not a safe criterion that can be reliably or easily used to find arsenic-free, safe drinking water.

The groundwaters sampled in this study have stable oxygen and hydrogen isotope ratios ranging from –2.4 to –7.5 ‰ and –11 to –51 ‰, respectively (**Fig. 1**). All samples plot on or slightly below the meteoric water line, indicating an origin from local rain and rivers, with or without some evaporation before infiltration. The large range and depth trends of isotopic values indicate that groundwater at different depths has been impacted by one or more of the following processes: mixing with seawater, direct recharge from local rivers, and recharge under different climatic conditions. Most of the shallow samples (<70 m) have stable oxygen isotope values between –3.0 and –5.5 ‰. This range of values is similar to that expected for recharge from present day rain and flood waters in Bangladesh. BGS and DPHE studied the stable isotope technique in Chapai Nawabganj, Faridpur and Lakshmipur areas[2]; and apparently found similar compositions to the findings of this TC project.

The $\delta^{13}C$ of As-bearing shallow waters range mostly from –3.0 ‰ to –15.0 ‰. Higher arsenic concentrations are associated with higher carbon isotopic values, indicating that organic matter oxidation is not likely to play a role in arsenic mobilization in the aquifer. The carbon isotopic data indicate that the most likely process of arsenic mobilization may involve desorption from the sediments as a result of the relatively rapid and continuing (natural) renewal of shallow aquifers with arsenic free water. According to the study of BGS and DPHE, the large $\delta^{13}C$ variations observed in Bangladesh groundwaters reflect derivation of the DIC from the multiple sources; such as soil zone CO_2, oxidation of organic matter, potential oxidation of CH_4, dissolution of minerals and in places mixing with seawater[2]. It is concluded that depth itself is not a safe criterion for considering a deep tube well to be arsenic-free now or in the future.

As a consequence of challenging results from the previous study, BAEC has the on-going IAEA-TC project entitled ‘Isotope Techniques for Mitigating Arsenic Contamination in Groundwater (BGD/8/018)’, implemented in the year 2001-2002. The detailed field campaigns were accomplished during August (monsoon season) 2001 in the nested wells at Savar and Brahmanbaria; and during November (dry season) 2002 in the 16 nos. shallow and deep wells in Chandpur area. New data of stable isotopes from eastern regions (**Fig. 2**) are found similar to those from the central and southern regions.

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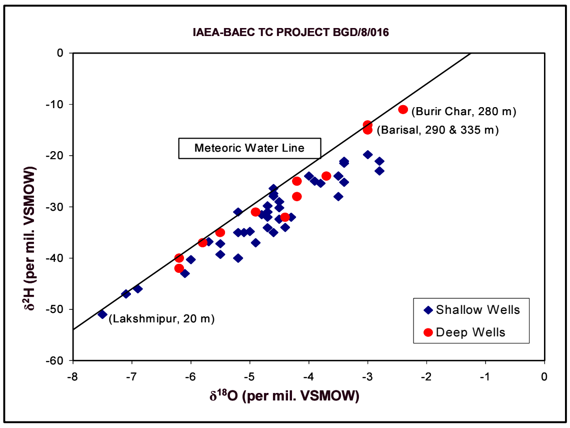

Fig. 1. Stable oxygen and hydrogen isotope compositions of Bangladesh groundwaters in 1999 - 2000

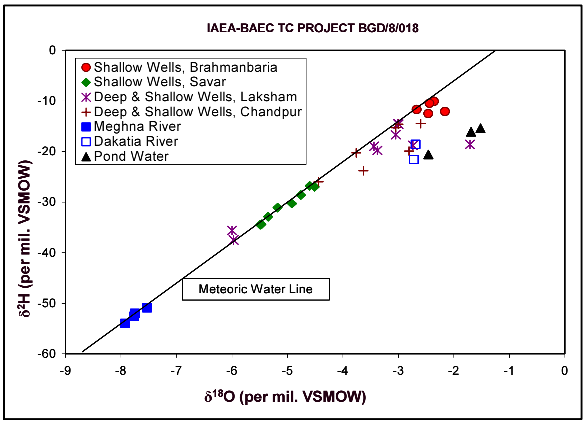

Fig. 2. Stable oxygen and hydrogen isotope compositions in groundwaters of eastern region in 2001 - 2002

UNSATURATED ZONE PROCESSES AND ARTIFICIAL RECHARGE

(Session 6)

Chairpersons

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STABLE HYDROGEN AND OXYGEN ISOTOPE BEHAVIOUR OF SOIL WATER IN SAND DUNES, AND ITS RELATIONSHIP TO SHALLOW GROUNDWATER, SOUTHERN GREAT LAKES REGION, CANADA

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The stable hydrogen- and oxygen-isotope compositions of soil water from seven profiles, up to 200 cm in depth, were measured ten times over fourteen months for a sand dune complex located on the southeastern shore of Lake Huron, southwestern Ontario, Canada. The profiles represent settings ranging from stabilized dunes covered by oak savannah to unstabilized dunes (both barren and grass-covered, with separate sites for C_3 versus C_4 vegetation), and topography varying from dune crest to slope to slack (the low area between dunes).

The stable hydrogen- and oxygen-isotope compositions of the soil water commonly show measureable differences from incoming precipitation each month. The soil water is generally, but not always, enriched in ^{2}H and ^{18}O relative to precipitation. The soil-water compositions fluctuate widely with depth and season (δ^2H = -132 to –13‰; $\delta\,^{18}$O = -18.0 to +0.6‰). By comparison, monthly composite precipitation samples range from delta^{2}H = -97 to –26‰, and $\delta\,^{18}$O = -14.1 to –4.8‰, and describe a local meteoric water line of δ^2H = 7.8($\delta\,^{18}$O) + 9.1. During the year, the stable hydrogen and oxygen isotopic compositions of Lake Huron ($\delta\,^2$H = -57±3‰; δ^{18}O = -7.3±0.3‰) and shallow groundwater (δ^2H = -77±4‰; $\delta\,^{18}$O = -11.1‰) remained relatively constant.

The results illustrate the complexity in the seasonal distribution of soil-water stable isotope compositions in a temperate, humid, continental setting, and the difficulty in estimating precipitation compositions from such data. Understanding seasonal variability is particularly important when assessing the stable isotopic compositions of proxies for climate that utilize soil water in their formation. For example, average annual stable isotopic compositions for soil water may be more relevant to interpretation of results for pedogenic carbonates and clay minerals than they are to silica phytoliths, which form only during certain parts of the growing season. The depth and timing of pedogenic mineral formation is also important, given that soil water can show significant depth-dependent variations in stable hydrogen and oxygen isotopic compositions. Likewise, rooting depth can be important to understanding the stable hydrogen and oxygen isotopic compositions of phytoliths and other phases formed in plant tissues.

The stable hydrogen and oxygen isotopic compositions of soil water in the study area reflect mixing between precipitation recharge and antecedent soil water, plus the processes of evaporation and (to a lesser extent) transpiration, particularly during summer months. Mixing causes the wide seasonal variations in the isotopic composition of precipitation to be attenuated with depth in the soil profile, but the downward movement of significant precipitation events can still be tracked from month to month. For most months, enrichment in ^{2}H and ^{18}O from evaporation is evident only in the top 10 cm of each profile. However, during the periods of highest average temperature (~25°C) and average minimum daily relative humidity (~50%), some effects of evaporation can be discerned to depths of 60 cm, depending on the amount of monthly rainfall and the timing of sampling relative to the last major rainfall event. Uptake of soil water by plants does not result directly in a change in the isotopic composition of the soil water, but it has a modest indirect effect by reducing the volume of soil water, rendering it more susceptible to evaporative enrichment in ^{2}H and ^{18}O.

The presence of vegetation tends to decrease the amount of direct evaporation from the soil surface, and through its subsurface root and rhizome network, promote mixing within the soil-water system. Systematic variations in soil-water content are most closely associated with rainfall amount, slope, vegetation extent and tree canopy cover. Some variations are also associated with seasonal differences in productivity of C_3 versus C_4 grasses. However, variations in the stable isotopic composition of soil water between heavily vegetated and lightly vegetated sites are not as large or as systematic as the differences in water content. Instead, the stable hydrogen- and oxygen-isotope compositions of soil water from all profiles describe similar patterns for a given month. For each season, there is a distinctive shape to the depth-dependent variation in soil-water stable isotopic values. This reflects characteristic seasonal differences in the relative influence of spring snowmelt, precipitation, antecedent soil water, evaporation and transpiration on soil-water composition.

LONG TERM VADOSE ZONE PROCESSES AT THE NEVADA TEST SITE, USA

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The nuclear weapons testing program of the United States of America has released radionuclides to the subsurface at the Nevada Test Site. Some of these tests have been used for long-term studies of hydrologic transport of radionuclides and identification of hydrologic transport processes in groundwater and the deep unsaturated zone. The studies conducted at one such test referred to as the Cambric event continue to provide unique data on water and radioisotope transport processes in the deep vadose zone typical of arid climates. The extensive data sets offer additional opportunities for research under controlled conditions.

The 1965 Cambric weapons test was a low yield event (0.74kt of TNT) that was detonated 298 m below the land surface and 73 m below the water table in alluvial material. In 1975, pumping of the aquifer was initiated 90 m from the cavity and continued steadily over the next 16 years to elicit information on radionuclide migration in the saturated zone. The pumping well flow and effluent – containing mobile radionuclides such as tritium, ^{36}Cl, ^{85}Kr, ^{129}I, and ^{106}Ru – were monitored, discharged to an unlined ditch, and allowed to flow towards a dry lake bed. It has been suggested that over 90% of the (decay-corrected) tritium inventory released by the test was recovered in this fashion. Flow monitors revealed approximately a third of the water introduced into the ditch infiltrated along its 1.6 km length. This created an unexpected second experiment in which the fate of the effluent and radionuclides in the deep unsaturated zone could be studied. A shallow vadose zone monitoring program was initiated in the late 1980s that observed the horizontal migration of the wetting front and radionuclides from the ditch. The tritium levels were measured at monthly intervals during the experiment and tritium migration was quantified in the vadose zone at seven locations within 11 m of the ditch over a multi-year sampling effort. Non-native vegetation also grew along the ditch and contributed to water and tritium loss from the ditch during the summer months. Measurements of radionuclides in a water table monitoring well 100 m away from the ditch indicate rising levels of tritium since 1993.

The Cambric Ditch experiment is providing opportunities to study field scale water and radionuclide migration in the vadose zone. The tritium level in the pumped groundwater uniquely labeled the date that the water infiltrated from the ditch into the soil. Water movement through the vadose zone is traced by tritium levels in the soil and at the nearby groundwater monitoring well. Within the near-surface vadose zone, tritium levels in the soil water are analyzed by a simple one-dimensional, analytical wetting front model and a much more sophisticated multidimensional vadose zone numerical transport model. In addition, the use of helium-3 accumulation following tritium decay permits assessment of the travel time for the infiltrated water to reach the water table and migrate to the monitoring well.

The Cambric Ditch experiment illustrates the necessity of long time series of hydrologic data to better understand contaminant transport processes in the deep vadose zone. These data sets combined with appropriate levels of modeling are used to quantify the dominant transport processes in the shallow and deep vadose zone. Such models can then be applied with more confidence to other sites where radionuclides have been released and pose a potential threat to humans and ecosystems.

RESULTS OF LONG TERM INVESTIGATIONS ON ^{18}O IN THE UNSATURATED ZONE IN COMPARISON TO THE RESULTS OF TRACING EXPERIMENTS AND NUMERICAL MODELING

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An observation station of infiltration water is in operation at Wagna in the porous groundwater field of Leibnitz in Southern Styria (Austria) since 1991. Numerous parameters are being measured continuously in the unsaturated zone in different depths under two fields of different agricultural cultivation, the infiltration water being sampled under disturbed and undisturbed conditions [3].

Tracer investigations has been done in 1993 [1], 1997 and 2001 using bromide and ^{2}H to detect the residence time of infiltration water from the surfase to the groundwater table (mean average: 4.5 m below surface) and to evaluate transport parameters for the different compartments of soil and unsaturated gravel and sand [2] as a basis for the calibration of numerical solute transport models [1], [2].

From 1991 to 2000 the content of ^{18}O has been detected in precipitation water and in seepage water in different depths of the unsaturated zone as well as in the groundwater itself. The time series of the concent of ^{18}O in precipitation (mean weighted monthly values from sampling site Graz-Universität) and in the soil water at the research station of Wagna 0.4 m below surface is shown in Fig. 1. As an example it is visible that the amplitude of ^{18}O in soil water is lower than in precipitation water and that the curve is shiftet of about +4 months at the time scale.

Due to the intensive investigations on tracing experiments and on numerical modeling at the test fielt Wagna it will be possible to discuss isotope data evaluation methods used in the unsaturated zone in comparison to the results of tracing experiments and modeling results. On the other hand the long term observation at different depths will give the possibility for better calibration of the numerical transport models on the behaviour of nitrogen from agriculture.

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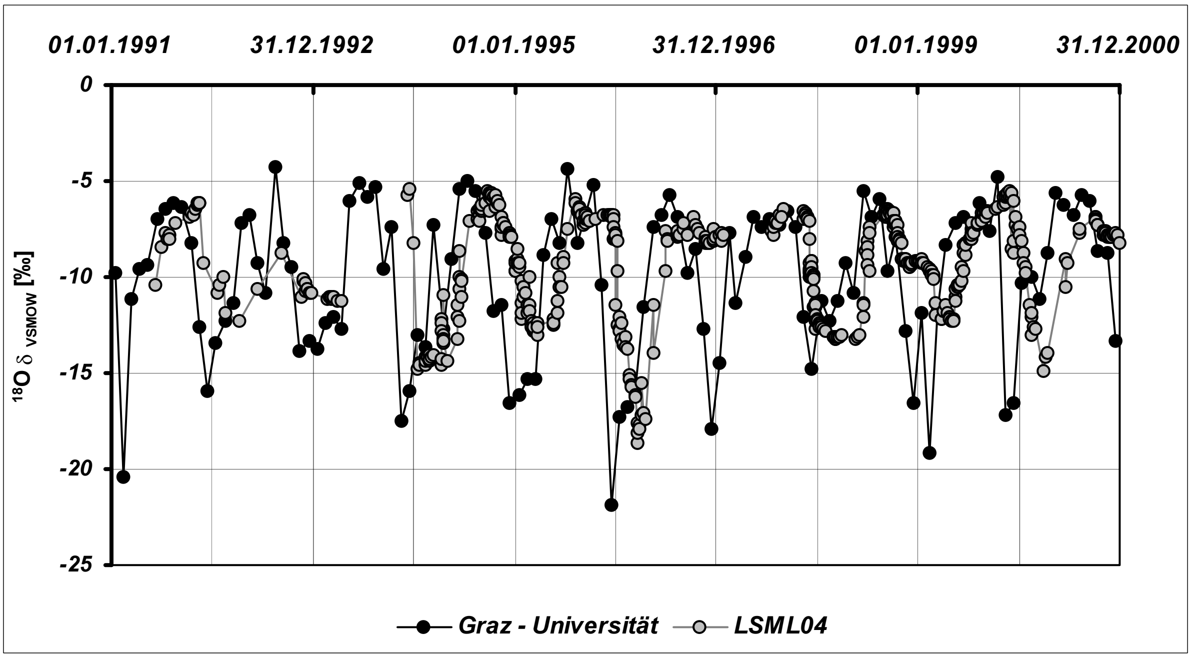

Fig. 1. Concentration of ^{18}O in seepage water 0.4 m below surface at research station Wagna (LSML04) in comparison to ^{18}O in precipitation (Graz - Universität) for the period 1991 to 2000)

USE OF ISOTOPIC TRACERS TO STUDY PATHWAYS FOR MIGRATION OF CONTAMINANTS THROUGH THE UNSATURATED ZONE IN IRRIGATED AGRICULTURAL SITES IN SOUTHWESTERN KANSAS, USA

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The Great Plains of the United States is a major agricultural region which produces corn and grains. The High Plains aquifer underlies a major portion of the Great Plains and extends from the panhandle of Texas through Nebraska. Since the mid-1950s, irrigation has been utilized in many parts of this region, with water being drawn from the Ogallala Formation. Irrigation has resulted in a draw-down of the water table over most of the system and has introducted agricultural contaminants into the groundwaters, most likely by movement through the unsaturated zone. In the late 1990's, the US Geological Survey NAQWA program began a study of the High Plains aquifer to determine recharge rates and potential contamination problems throughout the system. As part of this program, unsaturated zone studies were carried out at several sites. Included were physical measurements, tritium, stable isotopes of water, and various contaminants in soil waters as well as the concentrations of chlorofluorcarbons in vadose zone gasses. This paper discusses results obtained for unsaturated zone studies at three sites in the central section of the High Plains aquifer in Southwestern Kansas.

Two of the sites are agricultural fields (CAL-121 and CAL-122) that grow row crops and have been irrigated with groundwater pumped from the aquifer system since the mid-1950s. Initially, irrigation was carried out by flooding of furrows in the field but the methodology was changed in 1989 to a sprinkler system which is still in use today. Information about crop rotation, chemical usage and the quantity of water used for irrigation is available for both fields. A third location (CNG), about 60 miles southwest of the irrigated sites, was choosen as a control site. This location is a grassland and it has never been irrigated or used for agriculture. Groundwater levels have declined at all sites, although the decline has been greater at the two irrigated sites with depth to water ranging between 45-50 meters at the time of the study. Soil cores were collected using an ODEX drilling method at all sites and sealed samples were returned to the laboratories for extraction and measurement of various parameters. Wells were also installed at all sites to sample the local groundwater.

Results from groundwater samples collected at the three sites indicate that recharge to the water table has occurred since the advent of irrigation at the two irrigated locations. Tritium concentrations indicate the presence of bomb-produced tritium in groundwater at both irrigated locations whereas the tritium concentration at in groundwater at CNG was below the detection limit (0.3 Tritium Unit). There were also elevated concentrations of nitrate (up to 24 mg/L as N) and atrazine (0.9 micrograms/L) in the groundwater under the irrigated sites. Concentrations at the control site were 1.2 mg/L and >0.01 micrograms/L respectively for nitrate and atrazine. As there is no possibility of direct recharge for the groundwater, both the tritium and agricultural chemicals must have reached the water table through the unsaturated zone.

Tritium analyses on water extracted from core material indicate that water moves through the unsaturated zone at the two irrigated sites much more rapidly than at the control site. Tritium concentrations at the control site dropped from about 7-8 TU to below the detection limit at a depth of about 6 meters. No measureable tritium was found below this depth. Stable isotope results also changed very little below the surface layer at the control site, with ^{18}O averaging about –8.5 o/oo throughout the profile. At the irrigated sites, measureable tritium concentrations were found at various depths throughout the core, indicating that post-bomb water was moving through the unsaturated zone. At both irrigated sites, tritium concentrations varied from below the detection limit to over 4 TU at various depths in the profile, indicating that water was not moving down in a simple piston-like fashion. Estimated recharge rates are 54 mm/yr and 39 mm/yr at CAL-121 and CAL-122 respectively, compared to a recharge rate of < 5.4 mm/yr determined at CNG. Atrazine was occasionally detected in core material at the irrigated sites, usually close to layers where tritium was also present. CFC concentrations at the irrigated sites were above concentrations expected from gas diffusion or diffusion with recharge. An advective gas flux must be present, either due to the drop in the water table or irrigation processes. The CFC profiles at the control site could be explained by simple gas diffusion.

TRACING THE DECOMPOSITION OF DISSOLVED ORGANIC CARBON IN ARTIFICIAL RECHARGE BY CARBON ISOTOPE RATIOS

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One of the challenges in artificial recharge for drinking water purposes is to decrease the relatively high content of dissolved organic carbon (DOC) in surface waters. Two processes have been suggested to have an effect on diminishing the concentrations of DOC in infiltrated water during artificial recharge: 1) Either organic matter is adsorbed on the surfaces of soil particles, or 2) DOC is oxidized and decomposed by bacterially mediated processes. Geochemical concentration and microbiological activity data have, however, proved to be insufficient for getting quantitative evidence for comparison of these models. We applied the isotopic composition of dissolved inorganic carbon (DIC) in the recharged water as a tracer for redox processes and decomposition of DOC.

The study site is an artificial groundwater plant at Jäniksenlinna in southern Finland. Surface water is artificially recharged into an unconfined shallow aquifer by pond infiltration. Infiltrated surface water is derived from Lake Päijänne, a large lake in middle Finland. Water samples were collected from infiltrated surface water and groundwater at varying distances from the infiltration plant. The samples were analysed for the contents of the major dissolved components, DOC and the isotopic composition of carbon in DIC. In addition, the $^{18}O/^{16}O$ and D/H ratios of water were determined in order to calculate mixing ratios between local groundwater and infiltrated surface water. The $\delta^{18}O$ and δD end member compositions for mixing calculations were based on a monitoring period of two years.

The $\delta^{13}C_{DIC}$ value in recharge waters was -10.4 ‰, which differed significantly from the composition of local groundwaters, with $\delta^{13}C_{DIC}$ at -20.8 ‰. The recharged water recorded a considerable decrease in $\delta^{13}C_{DIC}$ from –10.4 ‰ in the pond to –16.3 ‰ in the first observation well, at a distance of 30 metres (FIG. 1A). No admixture of local groundwater was observed in this well based on oxygen and hydrogen isotope ratios, and the drop in $\delta^{13}C_{DIC}$ cannot therefore be addressed to mixing of two different waters. The shift in $\delta^{13}C_{DIC}$ was accompanied by a decrease in the DOC content from 0.43 mmol/l to 0.31 mmol/l and an equal increase in DIC content from 0.28 mmol/l to 0.40 mmol/l (FIG. 1B). The decrease in DOC is proportional to the increase in DIC to a distance of 350 metres from the infiltration pond. Because no other sources for carbon in DIC are known, the carbon isotopic composition of DIC in the artificial groundwater can be modelled as a mixture of carbon from two isotopically distinct sources:

$$\delta^{13}C_{DIC} = f_{org}\,\delta^{13}C_{org} + (1-f_{org})\,\delta^{13}C_{isw},$$

where org refers to dissolved organic carbon, isw to infiltrated surface water and f_{org} to the fraction of carbon in DIC resulting from oxidation of DOC. If a typical terrestrial $\delta^{13}C_{org}$ value of –27 ‰ [1] is assumed for DOC and f_{org} is estimated from the relative quantities of DIC in the infiltrated surface water and the drop in DOC contents, the model yields $\delta^{13}C_{DIC}$ values agreeing with the measured ones. It can be concluded that the main factor diminishing the content of dissolved organic matter in the early stage of infiltration is oxidative decomposition of DOC in the infiltrated surface water. Retention of DOC on mineral surfaces appears to be of minor importance, which is in contrast to conclusions reached in previous studies. Within a distance of 300 m from the infiltration pond, the infiltrated surface water is the dominant water component and the change in $\delta^{13}C_{DIC}$ may be totally explained by decomposition of DOC. However, at a distance of 700 m from the infiltration pond, the proportion of the local groundwater has increased to 51 %, based on oxygen and hydrogen isotope ratios, which adds a third carbon source to the mixing relation. (FIG. 1).

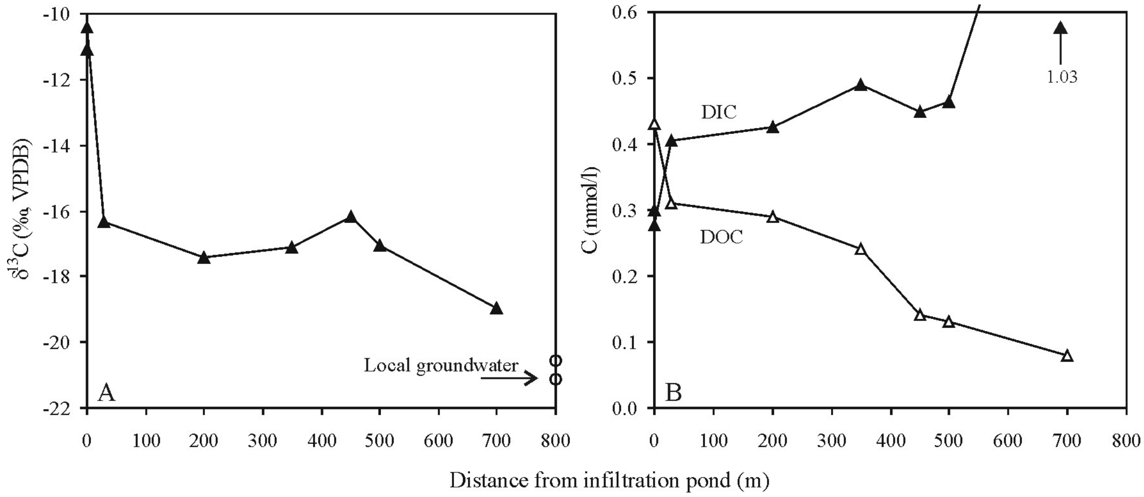

FIG.1. Changes in $\delta^{13}C$ of DIC (A) and the concentrations of DIC and DOC (B) along the groundwater flow path.

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ISOTOPE CONTRIBUTION TO GEOCHEMICAL INVESTIGATIONS IN AQUIFER STORAGE AND RECOVERY

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Aquifer Storage and Recovery (ASR) is an important resource management tool. An available water source; such as surface water, seasonal rainfall, or sewage effluent, is stored in a suitable aquifer for reuse when required to balance the seasonal demand for irrigation supply, thus relieving the pressure on groundwater resources. In ASR schemes, geochemical and biogeochemical reactions play an important role, impacting on both the aquifer matrix integrity and the recovered water quality. Understanding the driving processes that trigger these reactions is essential for determing the feasibility of new schemes and to adequately manage operating schemes. However the resulting geochemical signature is often due to a complex suite of reactions that is difficult to unravel. Few studies analyse the potential of isotopic tracers to contribute to the understanding of the biogeochemical reactions induced by ASR [1-4]. This paper investigates the potential of the stable isotopes of the water molecule, carbon-13 and carbon-14 and sulfur-34 to contribute to our understanding of the geochemical processes involved in reclaimed water ASR. The field trial at Bolivar, South Australia is investigating the viability of reclaimed water i.e. nutrient rich water, as an injectant.

The stable isotopes of the water molecule, can be used as conservative tracers to calculate the extent of mixing [1,3,4] as the stable isotopic signature of the reclaimed water and the native groundwater of the carbonate aquifer are significantly different. The δ^2H and δ^{18}O of native groundwater are fairly constant at -26 ± 1 and -4.4 ± 0.1 ‰ vs. SMOW respectively, while the injectant signature is more enriched and more variable, with δ^2H ranging from –10.6 to –3.6 ‰ and δ^{18}O from –1.74 to –0.21 ‰. The variation in the injectant signature is attributed to seasonal variation in the degree of evaporation occurring in storage lagoons [4]. The seasonal signature variation is maintained as injectant penetrates observation wells 4m and 50m from the point of injection. This can be utilised in mixing calculations to constrain the portion of injected end-member that is penetrating an observation well and reduces uncertainty with using an average representation of the variable injectant quality.

The isotopes of carbon, carbon-13 and carbon-14, can help to characterise the source of oxidised organic matter and dissolved inorganic carbon [1-2]. In this study, carbon-13 and carbon-14 of TDIC are used to gain insight into two of the important processes involved with ASR, organic matter oxidation and calcite dissolution. The native groundwater δ^{13}C signature is –11 ± 3‰ vs. PDB and the ^{14}C activity ranges from 3-10 pMC. The injectant δ^{13}C signature is more enriched, ranging from –7.0 to +0.1 ‰, and has a modern ^{14}C activity of 100 ± 9 pmC. Upon injection, both organic matter oxidation and calcite dissolution are evident within 4m from the ASR well. This is reflected by a lowering of the carbon-14 activity in the 4m groundwater consistent with calcite dissolution (FIG. 1). This suggests the carbon-14 signature is sensitive to small additions of TDIC through reaction processes. The carbon isotopes behave differently upon breakthrough of injectant to the 50m radius, where the ambient signature dominates until the groundwater is 100% injectant. The final signature at 50m after full breakthrough, δ^{13}C –8.1 ± 0.2 ‰ and ^{14}C activity 58 ± 1 pmC, is somewhat lower than the injectant signature and may be attributed to additional reaction processes.

Sulfate isotopes, sulfur-34 and oxygen-18, can provide insight on sulfate reduction and pyrite oxidation reactions [1]. Sulfate reduction up to 1.5 mmol L^{-1} is evident in groundwater sampled from the ASR well during a period of aquifer storage, while sulfate concentrations 4m from the ASR well remain unchanged. Enrichment in residual sulfate, of around 12 ‰ vs SMOW, accompanied the decline in sulfate concentration, is typical of biologically mediated sulfate reduction. Stable sulfate and sulfur-34 signatures at the 4m observation well, indicate the sulfate reducing zone does not extend far from the ASR well.

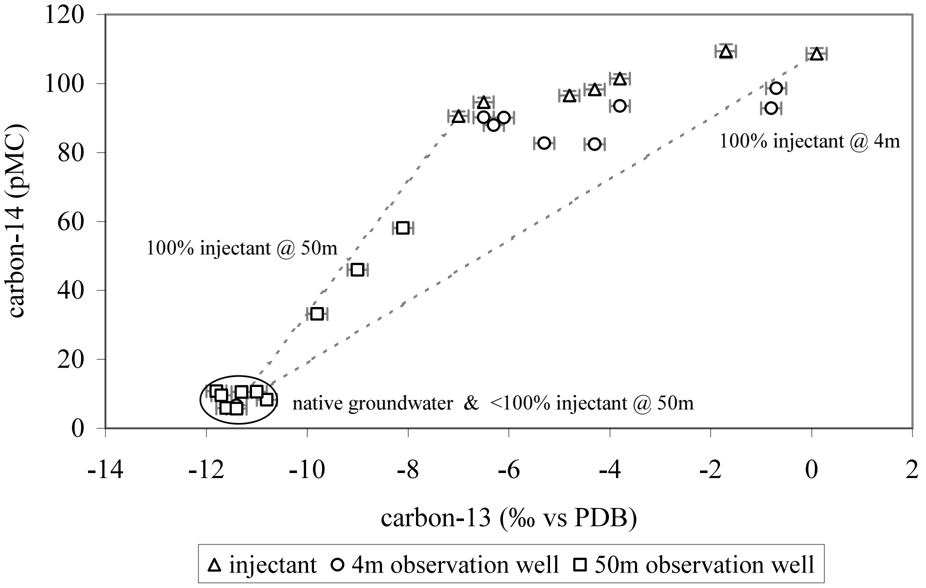

FIG. 1. Carbon-14 versus Carbon-13 from observation wells 4m and 50m from the ASR well.

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ENVIRONMENTAL ISOTOPE APPLICATION FOR DETERMINATION ARTIFICIAL RECHARGE EFFICIENCY, CASES FROM ARID AND SEMI-ARID AREAS OF JORDAN

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Jordan is one of the arid and semi arid regions where 90 % of the country receives less than 200 mm of annual precipitation. Artificial recharge and surface water harvesting has been given an importance and priorities in the last years.

Four dams have been taken under study of environmental isotope hydrology to define the efficiency of the artificial recharge to the groundwater, two dams are located in the highland areas (altitude ~ 740m above see level) and the other two dams at the main escarpment of the Jordan Valley graben (altitude is around -150m below sea level).

Monthly and several sampling campaigns from the dams and the surrounding wells of the stable isotopes oxygen-18 (^{18}O), Deuterium (^{2}H) and radioactive tritium (^{3}H) including complete chemical have been sampled and analyzed within the period 1995-2001 This has been existed within the framework of technical cooperation projects with the IAEA, RER/8/002 and RAW/8/007.

The aquifer, which is outcropping at upper dams, is formed from chert and limestone of campanian and turonian age as Siwaqa dam and overlies by Basalt at Khlidiya dam (upland areas) where the aquifer is formed from sandstone aquifer at Kafrain and Shueib dams at the Jordan valley.

The diagrams of ^{18}O and ^{2}H of Siwaqa and Khaldiya dams and some selected surrounding wells indicate that there is significant enrichment of the stable isotopes in the groundwater wells near the dams especially at the first years of dams operation which indicates a natural recharge of the enriched water from both lakes. The significant accumulations of silts and sediments at the bottom of both dams makes clogging and reduce the recharge, unless infiltration to the groundwater could occur through dam's escarpment after flooding and water rising.

The regression line of the diagram of ^{18}O and deuterium (^{2}H) of the four wells mentioned above including the dam water for the period 1995-2001 has high correlation coefficient, this is represented by the following equation of the evaporation water line:

$$\delta^{2}H = 4.91\,\delta^{18}O - 0.37 \qquad r^2 = 0.98$$

Concerning the two wells of Siwaqa dam well and Siwaqa dam observation well no.1 located around 100 meters downstream of the dam site show higher content of tritium and lower deuterium excess 13.5 $^{o}/_{oo}$ which is a strong indication of a leakage from a dam site to the groundwater where the deuterium excess in Siwaqa no.1 and Siwaqa no.6 pumping wells is 16-18 $^{o}/_{oo}$ closer to the Local Meteoric Water Line (LMWL) where the deuterium excess is 19 $^{o}/_{oo}$ and from the indicative Eastern Mediterranean Water Line (EMWL) where the deuterium excess is 22 $^{o}/_{oo}$.

This conclusion could be supported by the increasing tritium content in the groundwater monitoring wells as 4.3 T.U as an average where the initial groundwater is not tritiated due to the groundwater mining where the tritium content in 1987 within steadystate condition was 2.9-5.7 T.U in Siwaqa no.1 and 6 pumping wells where the average tritium content of the local precipitation is around 10 T.U for the period (1986-2002). The tritium content in the same well of Siwaqa no.1 has been analyzed thirty-five years ago in 1967 to be 9.8 T.U, which is considered low value, compared to the tritium content in the atmosphere, which reached locally in Amman Precipitation station to 330 T.U at the peak time of nuclear radioactivity in 1963.

Concerning the other two artificial recharge dams at the Jordan Valley escarpment, the occurance and behavior of ^{18}O, ^{2}H and tritium (^{3}H) content in the downstream wells indicates high recharge responses due to the cavities and high permeability of the unsaturated layers of the soil and rock matrix. This is valid also due to the high variability of groundwater level monitoring wells during dry seasons, flooding, water accumulation and release.

Diagram of ^{18}O versus Deuterium (^{2}H) of the three wells located downstream of Kafrein dam at the Jordan Valley for the period (1995-1997) indicates very low correlation represented by the following equation for the same reason mentioned above, also this is due to the water accumulation and release from the dam, dry, wet years and seasons including the heterogeneity of the unsaturated zone where the infiltration and artificial recharge is taking place.

$$\delta^{2}H = 1.75\delta^{18}O-17.34 \qquad r^{2}= 0.05$$

Actually these data sets for Kafrain dam represents the period (1995-1997) before operating Wadi-Sir wastewater treatment plant upstream and before effluent water mix with the fresh water accumulated in the Kafrain dam.

One of the main conclusions indicates that tritiated groundwater recharged after 1963 in Siwaqa and Khaldiya dams present only in a thin layer overlying the old groundwater without tritium.

As main recommendation, protection of artificial recharge dams from silts and sediments is required. Accumulation of silt should be a major factor to be considered in the evaluation and design of artificial recharge systems in Jordan.

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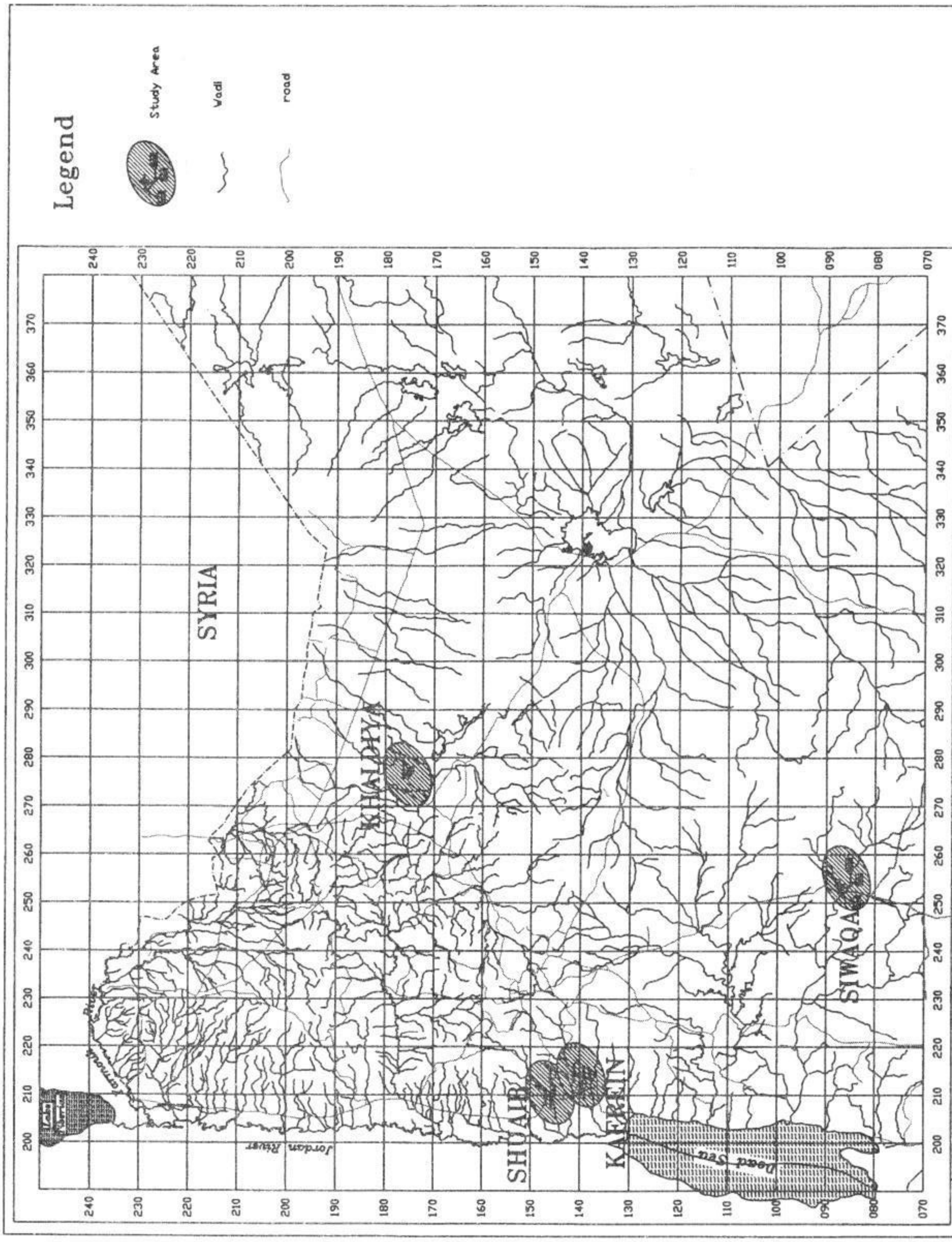

Figure (1) Location of Sampling Sites - Jordan

GEOTHERMAL SYSTEMS

(Session 7)

Chairperson

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USE OF ISOTOPIC AND CHEMICAL COMPOSITIONS OF THERMAL AND METEORIC WATERS TO INVESTIGATE RECHARGE FOR THE LARGE HYDROTHERMAL SYSTEM AT YELLOWSTONE NATIONAL PARK, USA

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Yellowstone National Park (YNP) is unrivaled for the abundance and diversity of its hydrothermal features, including geysers, fumaroles, mud pots and thermal springs. These extraordinary features are distributed throughout the entire 9,000-km^2 area of the Park, but are concentrated in several geyser basins located within the 0.6-Ma Yellowstone caldera and in the Norris-Mammoth corridor, a complex north-south subsidence structure, extending ~40 km from the Yellowstone caldera to the north of the Park. The hydrothermal features in YNP are the surface manifestations of very high fluid discharges that include, thermal water (~3-4 m^3/s), water vapor and gases, especially CO_2. The high discharges result from a favorable combination of climatic and geologic factors, including a huge magmatic heat source that is present at a relatively shallow depth of 4-8 km beneath the 0.6 Ma Yellowstone caldera, abundant supplies of recharge water primarily from melting snow and frequent seismic activity that creates new fractures and reopens clogged channels for fluid flow. The shallow magmatic heat driving this system is associated with a deep-mantle plume, a hotspot, that is presently centered beneath the Yellowstone caldera.

An intensive hydrogeologic investigation centered on the Norris-Mammoth corridor was conducted by USGS and other scientists during 1988-90 to determine the effects of using thermal water from a private well located north of the Park on the thermal springs of YNP, especially Mammoth Hot Springs. As part of this investigation, we carried out a detailed study of the isotopic and chemical compositions of meteoric water from cold springs and wells, thermal water, especially from the Norris-Mammoth corridor and of snow. Additional sampling of meteoric and thermal waters from YNP and surrounding region was carried out in 1991-92 to characterize the distribution of water isotopes in this mountainous region and to determine the origin and possible recharge locations of thermal waters in the Park.

The δD and $\delta^{18}O$ values for 40 snow samples define a well constrained line that is nearly identical to the Global Meteoric Water Line (GMWL). The δD and $\delta^{18}O$ values of 173 cold water samples range from –115 to –152‰ and –15.2 to –20.2‰, respectively, and exhibit a similar relationship although with more scatter and with some shift to heavier isotopes, due to evaporation effects. The data indicate that the groundwaters are derived predominantly from cold, isotopically light winter precipitation, and the spatial distribution shows a roughly circular pattern with isotopically lightest waters centered on the mountains in the northwest corner of YNP. The temperature effect due to altitude is the dominant control on water isotopes throughout the region; however, this effect is not observed locally in narrow 'canyons' and areas of high topographic relief. The effects due to distance (i.e. "continental") and latitude on water isotopes probably are relatively minor.

The pristine hydrothermal waters at the Norris and other Basins in YNP are sinter-precipitating Na-K-Cl type waters (salinity 1,000-2,000 mg/L), high in SiO_2, Li and B; they are commonly modified by boiling, silica precipitation and mixing with local meteoric water. The $^3He/^4He$ ratios relative to atmosphere (R/Ra) yield high values (up to 9 at Norris and 16 inside the caldera), indicating that the magmatic He, CO_2 and other volatiles have a "deep" mantle origin. The chemical and isotopic data, especially the $^3He/^4He$ ratios, in the travertine-precipitating Mammoth Springs indicate that water also derives its heat and some solutes (e.g., Cl, B, ^3He and CO_2) from a magmatic source. The higher salinities (2,000-3,000 mg/L) and concentrations of Ca, Mg, SO_4 and HCO_3 in the Mammoth water are obtained from reaction with Paleozoic carbonates at ~100°C.

The δD and $\delta^{18}O$ values for the thermal-water from YNP show significant δD and $\delta^{18}O$ shifts relative to the LMWL, but the origins of these shifts are complex and different for each area of the Park. Isotopic shifts may result from single-stage or continuous boiling, isotopic exchange between water and geologic materials and mixing between thermal water and shallow cold meteoric water. Detailed analysis of the isotopic and chemical data from several basins indicates that the hydrothermal system throughout YNP is recharged by meteoric water with δD and $\delta^{18}O$ values lighter than -149‰ and –19.9‰, respectively.

The isotope values of groundwater obtained from elevations above ~2.5-3.0 km in the Gallatin and northern Absaroka Ranges are light enough ($\delta D \leq -149‰$; $\delta^{18}O \leq -149‰$) to be the presumed recharge water for the hydrothermal system in the Park. However, estimation of the present-day recharge of this isotopically light water indicates that it is not adequate to supply the high (3-4 m^3/s) thermal water discharges from YNP, and cooler temperatures at the time of recharge would be required to provide an adequate volume.

The most logical conclusion from all the isotope and chemical data is that the hydrothermal water presently discharging from YNP was recharged in the Gallatin and northern Absaroka Ranges during the Little Ice Age (1350-1870 AD), when the mean annual temperatures likely were lower by 1-2ºC. The relatively short residence time is supported by the high fluid discharges and by model calculations of residence time (200-1000 yrs) obtained using tritium values and radium and radon concentrations in thermal water. See [1] for details and references.

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IAEA-CN-104/14

ISOTOPE AND CHEMICAL STUDIES OF THE THERMAL WATERS IN THE BUSAN AREA, REPUBLIC OF KOREA

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The geochemical and isotopic studies on thermal waters in the Busan city, on the southeastern tip of Korea, were carried out. The Haeundae and Dongrae geothermal areas are located in the Busan city. Haeundae is famous for the summer resort area, having the largest beach in Korea and the Dongrae area is located about to 10 km northwest to Haeundae. Both of the areas have been recorded as hot spring areas in the historical archives and characterized by high Cl content compared to other geothermal waters in Korea.

The TDS concentrations of the Haeundae and Dongrae waters tend to have positive correlations with pH. TDS of the Dongrae water is increased with well head temperature, whereas TDS of the Haeundae water shows distinctively a negative relationships with the well temperature. The relationships of major ions versus Cl show linear trends, indicating mixing process between a Cl-poor groundwater and a Cl-rich water at depth. Although most of the solutes do not fall close to the seawater dilution line, the linear relationship between Br and Cl strongly indicates that the solutes of the thermal waters in the Busan area is contributed by seawater. For the Dongrae water, the positive relationship between ion concentration and well head temperature can be explained by the mixing of cold fresh water during ascending of the thermal waters. In case of the Haeundae water, the ion concentration are decreased with the increasing of the measured temperature. It indicates that the Haeundae water is mixed with the cold seawater during ascending of thermal waters.

All available δ^{18}D and δD data for the study area are plotted to the worldwide meteoric water line, indicating that all waters are of a local meteoric origin. Although the isotopic data are plotted in the narrow range without a deviation to the seawater mixing line, the δ^{18}O-Cl diagram clearly show that the Haeundae water lies on a mixing line between a meteoric end member and the seawater from off-shore of Busan. The carbon isotope result shows very depleted values (-14.8 to –23.5 ™), indicating that the organic carbon was contributed to both thermal waters. The ^{14}C data (71.4 and 71.8 pmc, respectively) indicate large contribution of modern carbon. It indicates that the salinities of the Dongrae and the Haeundae water might be derived from the present seawater intruded beneath the Busan area. The overall hydrochemical features indicate that the sulfate in thermal waters is contributed by seawater. The δ^{34}S values of dissolved sulfate of the thermal water (+10.6 to +19.3 ™) support the mixing with seawater ($\delta^{34}S_{seawater}$ = +20 ™). However, the lower SO_4/Cl ratio compared with seawater should be explained. The sulfate reduction by bacterial activity is a possible explanation for decreasing of sulfate in waters, but cannot explain the low sulfur isotopic values of sulfate in water. As another possibility of explanation of SO_4 removal, the SO_4 and Ca in water can be transferred to solid such as gypsum in depth with high temperature.

The multicomponent mineral equilibrium approach [1] to the Dongrae water are applied to estimate the reservoir temperature at depth. This approach to determine equilibrium conditions can be limited by a lack of reliable Al analyses and dilution of thermal water through mixing with fresh water. The hypothetical Al concentration can be determined for each temperature by applying the FixAl method [2] and considering mixing ratio with fresh water. The mineral equilibrium geothermometer temperatures and therefore the probable reservoir temperatures are estimated to be about 110°C to 130°C. It is very complicate to apply the multicomponent equilibrium geothermometer fro the Haeundae water, due to high chemical disturbance of thermal water by the contribution of cold seawater. The mixing of thermal waters with cold seawater result in decreasing of temperature as well as enrichment of chemical constituents. Althogh the hydrogeochemistry of the Haeundae water shows the mixing with seawater of SiO_2 concentration, the Haeundae water still shows high silica content, showing that the reservoir temperature might be higher than temperature estimated by silica geothermometer.

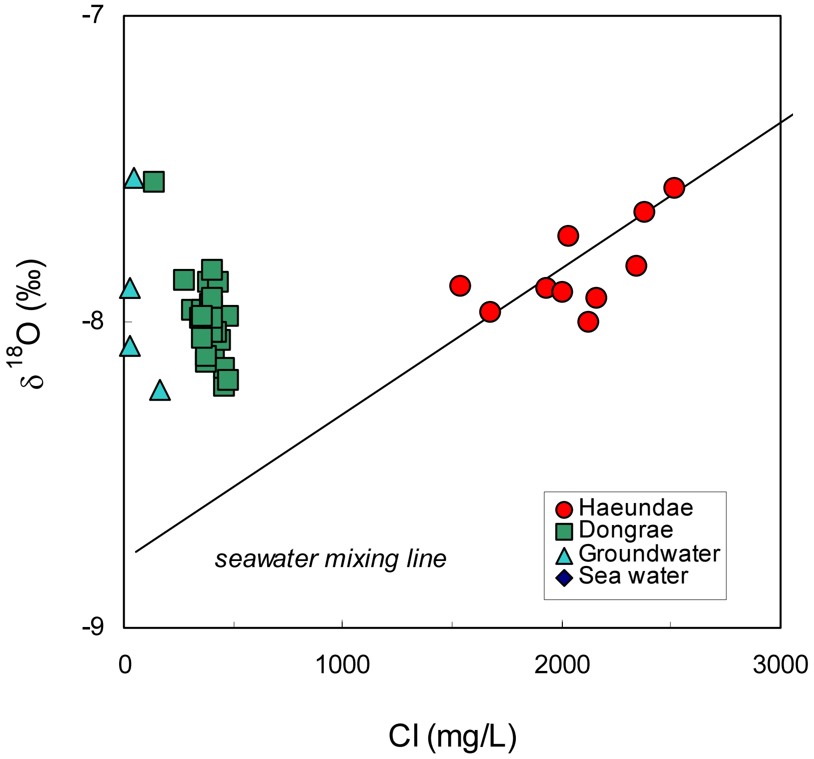

FIG. 1. $\delta^{18}O$ versus Cl diagram of water samples from the Busan area.

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INTERACTION BETWEEN THE GEOTHERMAL OUTFLOW OF SOUTHERN NEGROS GEOTHERMAL FIELD AND THE SHALLOW GROUNDWATER AQUIFER IN DUMAGUETE CITY, NEGROS ORIENTAL, PHILIPPINES

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Chemical and isotopic data indicate that significant quantity of mineralized thermal fluids are present downstream of the Palinpinon thermal spring areas that are naturally migrating into the shallow groundwater aquifer. Water district wells 49, 53, 54 and 55 located east from the Palinpinon springs, are tapping fluids that are relatively enriched in Na, K, Cl, SO_4, B and Li ions. Fluids appear to be diluted towards the Sibulan area as waters become diluted to Ca+Mg-Cl+SO_4 type. Shallow water southeast from the Palinpinon hot springs in the area of well 47 is composed of typical Ca+Mg-HCO_3 groundwater. Isotopically, the shallow groundwater in the vicinity of well 54 is relatively enriched in $\delta^{18}O$ and δ^2H while in the well 47 area the waters are relatively depleted. Isotopic dilution lines reveal that well 55, which is receiving groundwater recharged at relatively lower elevations, mixes with thermal waters from springs Pal3 and 40. The other wells 49, 53 and 54 are being recharged by groundwater at relatively the same elevation, and this groundwater mixes with the other Palinpinon hot springs resulting to the enrichment of heavy isotopes. Slight variations in the stable isotope composition of the shallow groundwater were observed from 1999 to 2002, but the difference is not as distinct as the variations of the heavy isotopes in rainfall. Isotopic altitude gradient for $\delta^{18}O$ and δ^2H are 0.28 and 2.1°/$_{oo}$ per 100 meters change in elevation, respectively. These correspond to a calculated recharge elevation of at least 1000masl for the shallow groundwater. Relative age dating using chlorofluorocarbon (CFC) reveals relative ages from 10 to older than 60 years old, which partly confirm the previous Tritium age of 50 to 100 years old.

Numerical simulation models confirm the migration of the thermal fluids from Palinpinon hot springs to the groundwater wells in the vicinity of well 54. Seasonal variation in isotope, Cl and SO_4 concentration indicate only minor dilution effect from precipitation. Drawdown in the deep geothermal reservoir have induced more than 500 meters of drawdown in the center of the resource but not enough to revert the naturally outflowing fluids from the Palinpinon thermal springs. Hence, there exists continuous natural migration of slightly mineralized geothermal fluids into the shallow groundwater aquifer of Dumaguete City.

TRACING THE SOURCES OF RECHARGE TO GROUNDWATER IN THE SPECIFIC METEOROLOGICAL AND GEOLOGICAL CONTEXT OF THE ETHIOPIAN RIFT AND BORDERING PLATEAU, USING ENVIRONMENTAL ISOTOPES

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The Ethiopian Rift valley is part of the Great East African rift valley. This area contains a lot of lakes and geothermal springs. The area is characterized by arid to semi arid climate with very high moisture deficit through out the year. Because of lack of ample rainfall, particularly in its northern sector, people mainly rely upon groundwater as major source of water supply. In some areas where groundwater is highly saline, people condense thermal steam as source of drinking water. The numerous lakes available in the region, except few, can not be used for water supply as they are very saline owing to high evaporation to outflow ratio. Due to these quantity and quality problems, nomadic people in the region are often move from place to place to search for fresh water.

Understanding the sources of ground water recharge and sources of salinity and tracing groundwater movement in this arid zone is therefore important to locate, to exploit sustainably and ultimately to change the life style of the people in the region.

The area has been subject to previous geoscientific studies. Sediments in the lakes have been used as paleoclimate proxies. Geothermal systems have been widely studied. Recently the IAEA through its TC projects conducted isotope hydrological studies. These studies and few other works produce a wealth of stable isotope ($\delta^{18}O$, δD) data (though very scattered).

No previous stable isotope data has been apparently available form the Ethiopian plateau until we recently gathered and analyzed over 45 isotope data from the Ethiopian plateau bordering the rift valley. This helped us to have a good picture on the groundwater dynamics in this arid region. Three sectors can be distinguished based on the isotope signature of meteoric waters. The Afar rift and Djibouti, the Main Ethiopian Rift and The Ethiopian Plateau. This difference in isotope signature (mainly in d excess) can be used as an opportunity to trace groundwater flow in the region (particularly the hydraulic continuity between the plateau and the rift and the influence of old groundwater on groundwater hydrology). These three zones have also different local Evaporation lines owing to different climate (humidity, isotopic composition of ambient vapor and/or temperature) or difference in sources of evaporating water. The role of lakes and surface waters in recharging the groundwater and the role of groundwater in recharging lakes and other surface waters has been obtained form the relation between $\delta^{18}O$ vs Electrical conductivity or δD.

There are however two limitations to fully benefit from stable isotopes of oxygen in the Ethiopian climate context. The first is the fact that strong altitude effect in the rift valley region is lacking, interpretation of variability in $\delta^{18}O$ in terms of altitude can not be made automatically. The fact that the rift valley region is located on the lee ward side of the two moisture sources seems to complicate the variation of $\delta^{18}O$ with altitude. The second is the fact that there is no strong variation in $\delta^{18}O$ with geographical position. To fully benefit from the isotope data one has to consider therefore d excess values combined with geochemistry and hydrological information.

We conclude with the following general points regarding recharge to the rift groundwater sytems:

- The presence of modern recharge from sporadic rainfall within the moisture deficit zone of the rift can not be ruled out.

- Deeper older (pre-bomb) and convecting thermal groundwater seems to exist in the northern sector of the rift (Afar and Djibouti). This deeper system seems to interacts with the relatively shallow cold groundwater systems.

- Meteoric waters on Ethiopian plateau plays a major role in the recharging the aquifers in southern and central sector of the rift valley.

- Source of salinity (>600mg/L) in many rift valley river waters comes from influx of saline groundwater than en route evaporation.

- Lakes in the central sector of the Ethiopian rift plays a major role in recharging adjacent aquifers.

- Based on deuterium excess the recharge of deep thermal water in Afar and Djibouti from present day Ethiopian plateaus meteoric waters can be ruled out. Many of these thermal waters plot on $8\delta^{18}O+0$ contrary to greater than 10 d_excess in Ethiopian plateau thermal waters.

- Limitations exist to fully utilize stable isotopes because of lack of strong altitude and/or latitude effect. These are mainly related to complex rainfall derivation mechanisms in Ethiopian region. The relationship between isotope variability and meteorological processes needs further investigation.

CLIMATE AND ATMOSPHERE

(Session 8)

Chairpersons

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STABLE ISOTOPES ON SEASONAL TO MILLENNIAL TIME SCALES AS RECORDED IN LOW-LATITUDE, HIGH-ALTITUDE ICE CORES

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This paper examines the stable isotopic ratios, $^{18}O/^{16}O$ ($\delta^{18}O_{ice}$) and $^{2}H/^{1}H$ (δD_{ice}), preserved in mid to low-latitude glaciers as tools for paleoclimate reconstruction. Ice cores are particularly valuable as they contain additional data (such as dust concentrations, aerosol chemistry, and accumulation rates) that can be combined with the isotopic information to assist with inferences about the regional climate conditions prevailing at the time of deposition. We use a collection of multi-proxy ice core histories to explore the stable isotopic climate relationship on seasonal, decadal, centennial, and millennial timescales. The paper looks closely at the relationship between temperature-precipitation and stable isotopes over these diverse time perspectives. Stable isotopic variations in ice cores from the tropics are highly correlated with sea surface temperatures (SSTs) across the equatorial Pacific Ocean, which are closely linked to ENSO variability. Therefore, a network of ice cores from selected locations offers the prospect of reconstructing low-latitude circulation.

Decadally-averaged stable isotopes records from three Andean and three Tibetan ice cores are combined in a composite in order to present a low-latitude stable isotope history for the last two millennium. Comparisons of this composite over the last millennium are made with the Northern Hemisphere proxy record (1000-2000 A.D.) reconstructed by Mann et al. (1999) and measured temperatures (1856-2000 A.D.) reported by Jones et al. (1999). The ice cores evidently have captured a great deal of the decadal-scale variability in the global temperature trends. The ice core record shows a 20th century isotopic enrichment that suggests that a large scale warming is underway at low latitudes. The rate of this isotopically-inferred warming is amplified at higher elevations over the Tibetan Plateau, while amplification in the Andes is latitude-dependent with enrichment (warming) increasing equator-ward. In concert with this apparent warming, *in situ* observations reveal that tropical glaciers are currently disappearing. A brief overview of the loss of these tropical data archives over the last 30 years is presented, along with evaluation of recent changes in mean stable isotopic values. The isotopic composition of precipitation should be viewed not only as a powerful proxy indicator of climate change, but also as an additional parameter to aid our understanding of the linkages between changes in the hydrological cycle and global climate.

REGIONAL ATMOSPHERIC MODELLING OF THE WATER ISOTOPE CYCLE

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In the present document, we introduce a new module handling the water isotope tracers $H_2^{18}O$ and HDO in the atmospheric regional circulation model (A-RCM) REMO, based on previous work with the ECHAM atmospheric global circulation model (A-GCM). Preliminary results over Europe (from Moroccan coast to the Barents Sea and from the Egyptian coast to South-East Greenland) are analysed, with particular emphasis on the comparison with an isotopic precipitation climatology compiled from GNIP station measurements.

The atmospheric ECHAM-4 GCM and REMO-5 RCM, both developed at the MPIM, use a similar physics schema, referred to as EC4-physics. An isotopic module was elaborated for ECHAM, accounting for isotope fractionating processes in stratiform and convective clouds, vertical diffusion, and evapo-transpiration from the surface with regard to sub-surface reservoirs. A centennial experiment was run in the T30 spectral truncature, corresponding to a horizontal resolution of 3.75°, i.e. ca. 450 km. This isotopic module was adapted in order to fit the REMO RCM; in its current settings, the standard resolution increased to 0.5°, i.e. ca. 50 km over Western and Central Europe. A rotated grid was applied, providing an equal grid cell area over the entire study domain, with its longitudes and latitudes comprised in [50°E; 70°W] and [30°N; 75°N] respectively.

The general aim of this study is to enhance the knowledge of water cycle obtained with REMO e.g. in the framework of the BALTEX project, by using water isotopes as a proxy for different hydrological processes. Preliminary results of REMOiso are compared to monthly means of meteoric isotopic measurements from the Global Network for Isotopes in Precipitation (GNIP). The sensitivity of the model output to the boundary conditions is discussed, with respect to ECMWF re-/analysis or alternate ECHAM forcing. Further investigations will test the model output against events measurements at several study sites in Germany monitored by the GSF.

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IAEA-CN-104/157

AUSTRIAN NETWORK OF ISOTOPES IN PRECIPITATION (ANIP): QUALITY ASSURANCE AND CLIMATOLOGICAL PHENOMENON IN ONE OF THE OLDEST AND DENSEST NETWORKS IN THE WORLD

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The Austrian Network for Isotopes in Precipitation (ANIP) started in 1972. Some stations have already been sampled since the 1960s. 72 stations are presently sampled all over Austria with some preference given to the Karst areas North and South of the Alpine mountain range. The network is run in co-operation between the Austrian Environment Agency (64 stations) and the ARC Seibersdorf Research (Arsenal:8 stations). The precipitation is collected on a daily basis in ombrometers (500 cm^2) and mixed to monthly samples at stations ranging from 120 to 2250 m in altitude (Fig. 1). So far about 8000 analyses of oxygen-18, deuterium and tritium have been made by the isotope laboratories of ARC (Arsenal, Vienna) and the Institute of Hydrology (GSF, Munich). All samples not measured immediately were stored in 1L bottles in a specially dedicated cellar (16000 samples) in Vienna and are available for analysis in the future.

The aim of the Austrian Network for Isotopes in Precipitation (ANIP) is to provide input data for hydrological and hydrogeological investigations and a data-base for climatological changes and trends in sensitive Alpine areas.

The amount of precipitation in Austria is highly influenced by the Alpine mountain range (400-3000 mm/y). The amount of annual precipitation increases toward the mountain ranges, in particular at the high altitude regions. However, strong regional differences exist between the windward and the lee side of the Alpine ranges.

Besides of the quality assurance of the analysing laboratories, which regularly take part at round robin tests of the IAEA, particular care has been taken for the quality control of the ANIP-Depot of the samples collected in 1 L polyethylene (PE) bottles and some of them stored in dark cellars up to 30 years. Mean temperatures (14° C) and relative humidity (70 %) data were recorded over time periods.

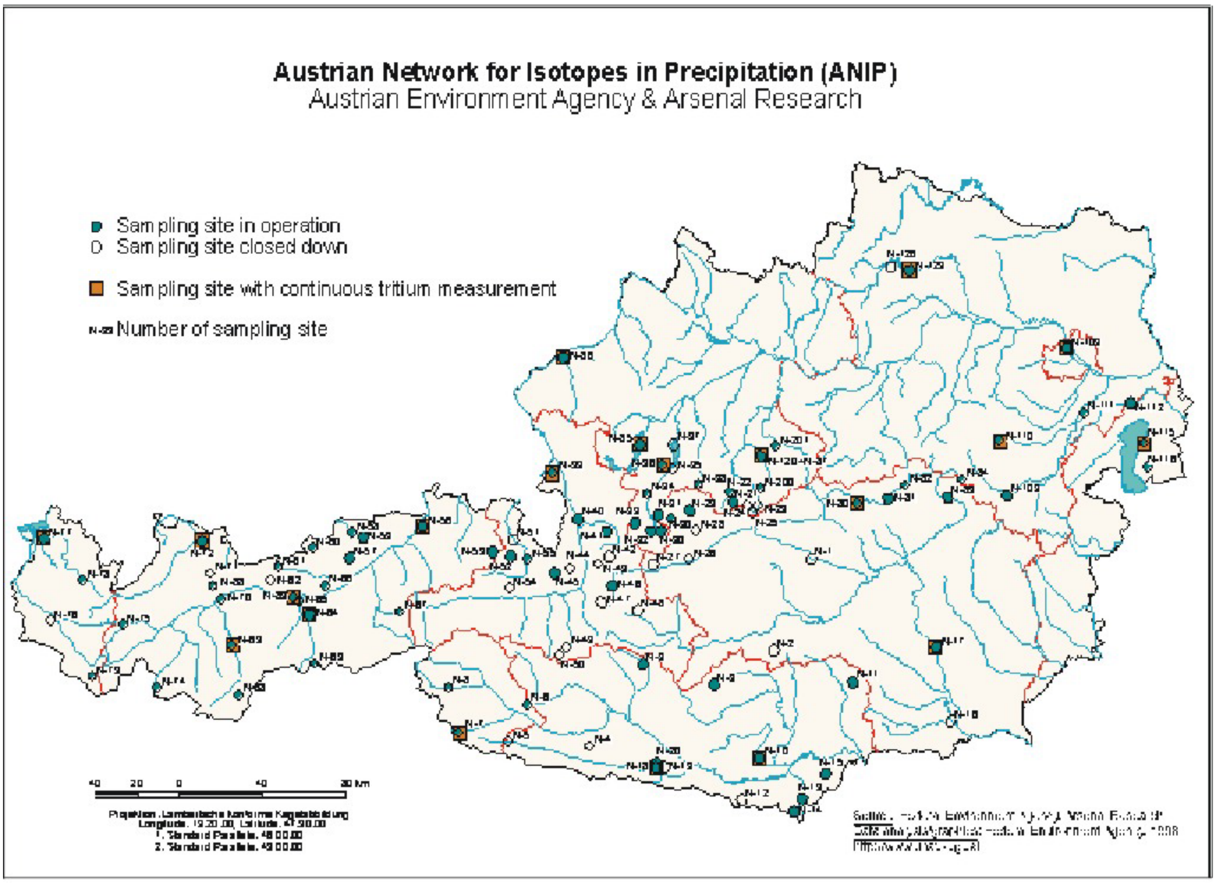

FIG. 1. 72 active sampling stations of the Austrian precipitation network

Control measurements (2002) of precipitation samples measured fairly regularly since 1973 and still stored in the original 1L PE-bottles were performed in 2002 (Institute of Hydrology (GSF, Munich). The results of 47 samples collected in 1973, 1975, 1985 and 1995 showed that results could be repeated with an mean error of less than 0.2 %o for oxygen-18 and 1 %o for deuterium (Fig. 2).

Just four samples showed an larger deviation in the direction of evaporation. Two 1L PE-bottles of 1973 filled to 200 and 250 ml only and two samples belonging to a charge of samples waiting about 3 years in 30 ml PE-bottles in laboratory environment (about 20-25° C) prior to original analysis showed larger deviations (0.7 to 2 per mil) indicating evaporation.

Wet periods are supposed to represent maritime phases. The Alps as a weather divide sharply distinguish precipitation events caused by different air flow directions. A study about the origin of the precipitating air masses in Austria showed that an Atlantic influence (moisture from NW) causes lower $\delta^{18}O$ values (e.g. Patscherkofel and Bregenz) than a Mediterranean one (e.g. Villacher Alpe and Graz) [1].

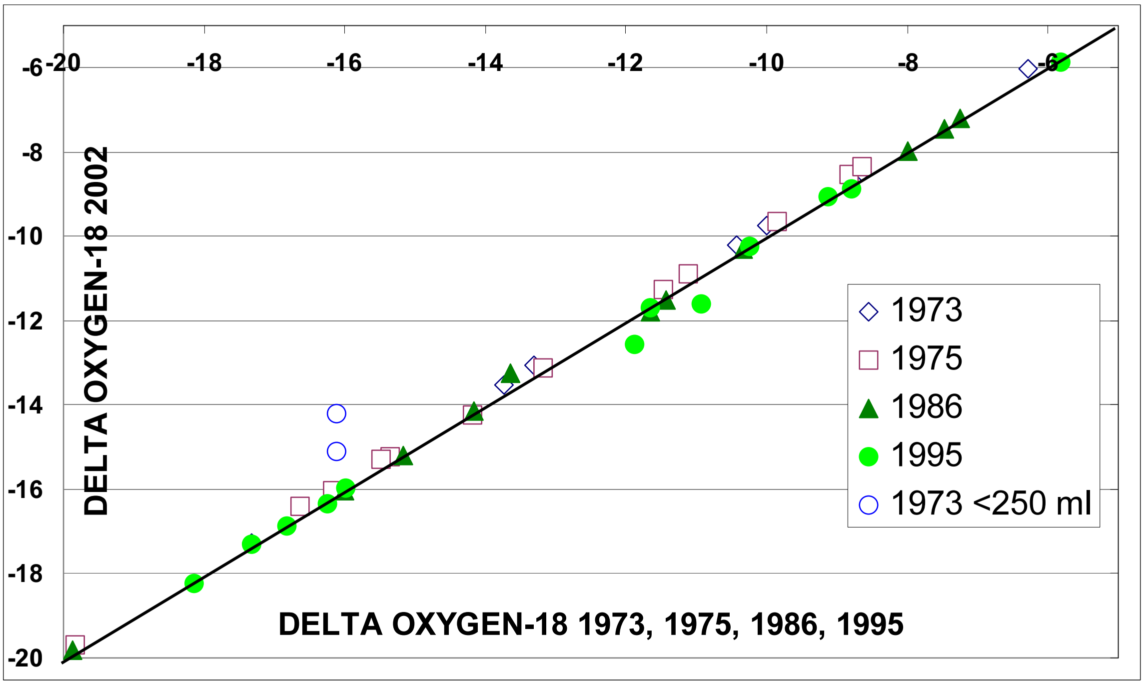

FIG. 2. Control measurements of rain water in 1L polyethylene bottles store in a cellar up to 30 years. Most results were repeatable within an error of δ O-18 0.2 ‰. Just 4 samples showed larger differences (see text).

In addition to the input measurements at the above mentioned meteorological stations 173 springs North and South of the weather divide were analysed for oxygen-18 and tritium four times a year in 1997/1998 in the framework of the Austrian Water Quality Network (AWQN). The mean O-18 values were plotted against the altitude of the recharge area calculated statistically as the half-height between the altitude of the spring and the potential maximum altitude of the recharge area. The correlation between the weighted mean of the O-18 values (1993-1997) and the altitude of the northern meteorological stations are in fairly good agreement with the spring trend in the North (Fig. 3).

It indicates a reasonable gradient of 0.21‰ oxygen-18 per 100 m altitude change. However, some of the meteorological stations and the springs in the south of Austria show clearly the Mediterranean influence as indicated by the station San Pellegrino [2] in Northern Italy. Also the altitude effect is small or not existing probably caused by the shielding effect of the Southern Alpine ranges in Northern Italy and Slovenia. As indicated by the study of [1] all stations and springs are influenced by Atlantic and Mediterranean origin to a variable degree and show therefore local mixtures, which may even vary in time.

There is a significant increase of the yearly mean of the deuterium excess in the mountain station above 1500 m altitude. But moreover, the seasonal pattern of the deuterium excess is quite different. While all valley stations exhibit the expected minimum in summer, the four mountain stations above 1500m, including the S. Pellegrino station in N-Italy, show a distinct maximum (12 - 15 ‰) between May and October. This is also the period with the seasonal maximum of precipitation

The possible physical and meteorological mechanisms causing these isotope patterns in the precipitation will be discussed.

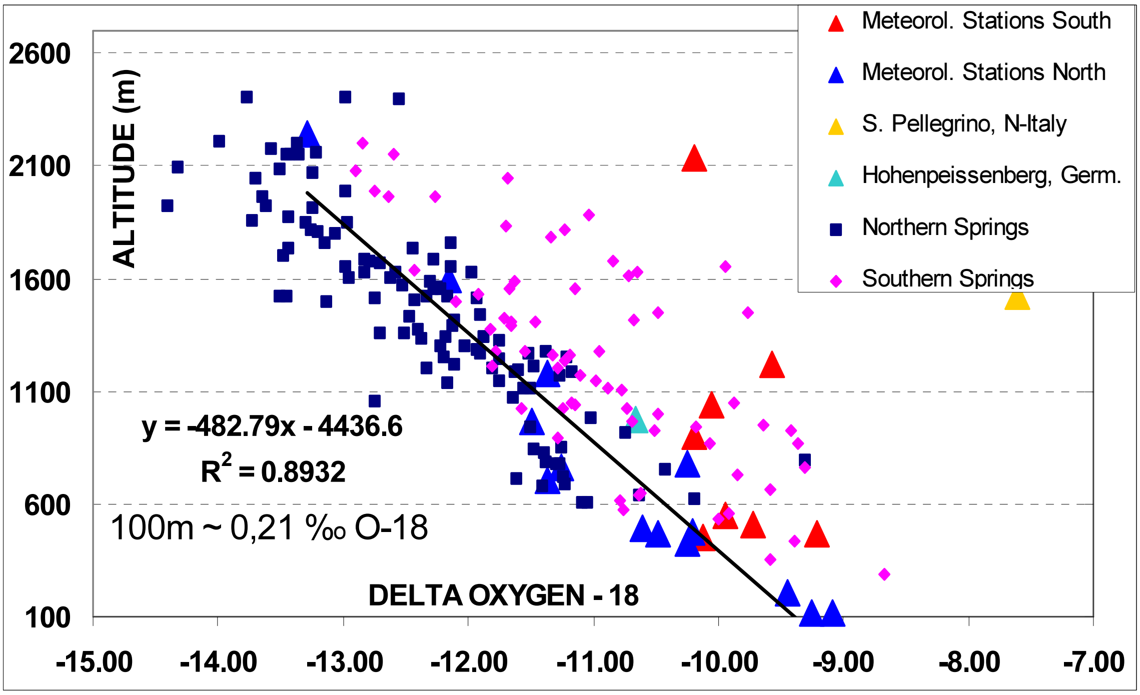

FIG. 3. Altitude effect at the northern front of the Eastern Alps in meteorological stations and springs (dark blue) in contrast to a very steep or nearly no altitude effect at the inner-alpine mainly Mediterranean influenced stations and springs in southern part of Austria (lighter red symbols).

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STUDY ON WATER VAPOR TRANSPORT TO TIBETAN PLATEAU USING STABLE ISOTOPIC COMPOSITION OF PRECIPITATION

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Southern edge of Eurasian continent is the place where the most prominent and strong monsoon is observed in the world. It is called Asian Monsoon. Many researchers pointed out that Tibetan plateau has an important role for heating of middle atmosphere due to its geographycal height (morethan 4000m in average). Development of convective clouds on the plateau also derives atmospheric heating through condensation of water vapor. These heating may be an essential process for monsoon system, and the process of water vapor transport to the Tibetan plateau is one of the most interesting question, because middle atmosphere is usually dry.

Precipitation samplings were made during intensive observation period of GAME-Tibet in 1998 summer at about 10 sites on Tibetan plateau. Rainwater was sampled daily, and hydrogen and oxygen isotope ratios were obtained.

There are several mountain ranges running west to east on the plateau. Isotopic compositions of precipitation sampled at many places on Tibetan plateau showed similarity depending on geographical distribution. Three areas are recognized from the isotopic composition of precipitation. The area between Himalaya and Nyainqentanglha, that between Nyainqentanglha and Tanggula, and that north of Tanggula showed different pattern in the isotopic compositions of rainfall during summer. The first area (between Himalaya and

Nyainqentanglha) usually showed lower delta values than the others. These differences in the isotopic composition of precipitation may be derived from the difference in the origin of water vapor.

Periodical variation in the isotopic composition of precipitation was also observed, corresponding on the active phase and break of indian monsoon. During the break period of indian monsoon, delta values decreased at most sites. On the other hand, delta values increased at the sites between Nyainqentanglha and Tanggula, during active period of indian monsoon. This difference may be caused by the different transport path of water vapor.

TEMPORAL VARIATION OF STABLE ISOTOPES IN PRECIPITATION AT BANGKOK, THAILAND

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Some studies discussed spatial and temporal variability of the stable isotope composition of precipitation in the Asia Pacific region. However, the relationship between isotope signature of precipitation and climate is not well understood, because the long-term isotopic data in precipitation is limited. The purpose of this study is to understand the temporal variation of stable isotopes in precipitation at Bangkok and precipitation mechanism in Monsson Asia region in response with El Niño/Southern Oscillation.

The monthly averaged stable isotopes (Oxygen-18, Deuterium) in precipitation and meteorological data for the period of 1968 to 1995 at Bangkok (13.73°N, 100.5°E), which are provided by the Global Network for Isotopes in Precipitation. The vertically integrated precipitable water and moisture flux datasets in NCEP/NCAR global atmospheric reanalysis with $2.5^\circ \times 2.5^\circ$ resolution are used to determine the circulation anomalies for the period of 1979 to 1995.

To consider the influence of El Niño/Southern Oscillation to precipitation in Bangkok, correlations between oxygen-18 of precipitation and SST in Niño-3 region (that is ENSO index) are considered for each month. The positive correlations with statistically 95% significant level are found only May and October, which is onset and offset period of Asian Monsoon in Thailand. The correlation coefficient is 0.39 for May and 0.62 for October. The isotopic low-phase years in May are 1981, 86, 88 and 91, and isotopic high-phase years are 1979, 80, 83, 87, 92, 94 and 95. Also, the isotopic low-phase year in October are 1988, 90 and 95, and isotopic high-phase years are 1979, 80, 82, 91 and 94.

The large-scale circulation fields are considered to elucidate the cause the variations of stable isotopes in precipitation and its relation to ENSO. Composite mean of precipitable water (PW) and moisture flux (UQ, VQ) anomalies for isotopic low and high phases in May and October are considered. An obvious positive (negative) anomaly of PW is found over the Indian Ocean and expands to the Indochina Peninsula in the low (high) phase of May. And also negative (positive) anomaly of PW is found the southern Pacific Ocean from the equator in the low (high) phase. Anomaly of moisture flux is eastward (westward) in the Indian Ocean and westward (eastward) in the Pacific Ocean in low (high) phase, respectively.

In case of October, strong negative (positive) anomalies of PW are found in the Indochina Peninsula and Indonesia Maritime Continent in the isotopic low (high) phase. And also negative (positive) anomaly of PW is found the Equatorial Pacific in low (high) phase.

The anomaly of moisture flux is westward (eastward) in the Indian Ocean and eastward in the Pacific Ocean, respectively. Anomaly of moisture flux is shown convergence (divergence) pattern centered in the Indochina Peninsula and westward (eastward) in the Equatorial Pacific in low (high) phase. These PW and moisture flux anomalies suggest the close connection to the ENSO.

UTILIZATION OF MONSOONAL RAINS BY PLANTS AND ISOTOPIC PARTITIONING OF EVAPOTRANSPIRATION IN TWO CONTRASTING SEMI-ARID SAVANNA ECOSYSTEMS

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Due to the episodic and localized nature of monsoonal precipitation, the exchange of water between the land surface and atmosphere in arid and semi-arid environments is temporally dynamic and spatially heterogeneous during the summer growing season. There are relatively few data on how monsoonal rains are used by plants and what proportions of these growing season precipitation are lost to transpiration by canopy and evaporation by vegetation surface in semi-desert ecosystem.

In this study, we applied stable isotopes of oxygen and hydrogen to study differential utilization of summer monsoonal rains by dominant plants and to partition evapotranspiration (ET) water fluxes in southern Arizona, USA and eastern Inner Mongolia, China. Both ecosystems are influenced by monsoonal rain events and threatened by invasion of woody shrubs due to climate and land-use changes.

Isotope compositions of stem water from dominant plants indicate that woody perennial plants showed limited utilization of summer rains while grasses and annual herbs rely on summer rains for their growth. In addition, "Keeling plots" (isotope mixing relationships) were generated from isotope ratios (δD and $\delta^{18}O$) of atmospheric water vapor collected along height profiles and the regression intercepts from these profiles to partition ET fluxes. Our results suggest that two semiarid savanna ecosystems have distinct patterns of ET fluxes following the monsoonal rain events because of differences in local climate conditions and species compositions.

ISOTOPIC LINKS BETWEEN THE WATER AND CARBON CYCLES

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Water, carbon and oxygen fluxes in the biosphere are tightly coupled physically and functionally. A unique aspect of these interactions is the transfer of 18-O label from the hydrological cycle to the carbon and oxygen cycles. Fractionations in the hydrological cycle results in large meridional and continental gradients in the 18-O content of meteoric water on land. This labeling is transferred to CO_2 via CO_2 dissolution in water and subsequent oxygen exchange; and to O_2 via the water splitting reaction in photosynthesis. The 18-O labeling of atmospheric CO_2 provides, in turn, a powerful tracer of sinks and sources of carbon in ecosystems. The 18-O label of O_2 provides, in addition, a global-scale indicator of ocean—land partitioning of biospheric productivity. In both cases, modifications in the 18-O label of the atmospheric gases are coupled to changes in the hydrological cycle. I will discuss the major developments in understanding the processes underlying the18-O links in the H_2O-CO_2-O_2 system and the insights they provide to hydrosphere–biosphere interactions.

STABLE ISOTOPES IN CHARACTERIZATION OF MOISTURE SOURCES IN PRECIPITATION

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Moisture source and transport dynamics in continental precipitation is an important component of understanding and simulating the energy and water balances of the earth. Seasonal prediction of water source strengths and transport pathways to predict fresh water availability could improve understanding, mitigation and response in many regions land use, management and the sustainability of fresh water resources and quality. The predictability of fresh water availability in a coupled land-atmosphere system could be improved by a better understanding of moisture source and transport patterns. Analysis of satellite data, particularly wind, temperature, and pressure anomalies, have been used to characterize moisture transport patterns. Passive water vapor tracers have been used in GCMs to estimate the source of moisture in local precipitation at various resolutions. Results of both of these methodologies, however, are difficult to validate with physical data. Stable oxygen and hydrogen isotope ratios of precipitation are an excellent tool for this purpose, but have rarely been used to characterize or validate moisture transport patterns inferred from meteorologic analysis. In this paper, we review isotope distributions in precipitation in the Asian Monsoon region and their significance for understanding moisture transport patterns.

The Asian summer monsoon (ASM) results from atmospheric convection in the inter-tropical convergence zone (ITCZ) over the western Pacific and Indian oceans (Lau et al., 2000). Temporal and spatial variations in the ITCZ and consequent changes in air circulation patterns and moisture sources determine the seasonal evolution and rainfall variability of the ASM. Distinct, spatially variable moisture source and transport patterns have been identified for rainfall in the ASM by using sea surface temperature and pressure fields, low and high level air pressure anomalies, and precipitation patterns (Lau et al., 2001; Kim et al, 2002).

Isotopes in precipitation in southeast Asia, including the ASM region, have more negative delta values in strong summer rains, in spite of higher temperatures compared to the winter rains, and have been interpreted to be controlled primarily by the amount of precipitation and rainout during moisture transport across the continental areas (Araguas et al., 1998; Hoffman and Heimann, 1996).

Stable isotope ratios in precipitation at island or coastal stations located between 70°E - 160°W longitudes and 10°S - 26 °N latitudes were obtained from the global network of isotopes in precipitation (GNIP) database (IAEA, 1992; 2002). Figure 1 shows that isotope values are not correlated with the amount of precipitation when all stations are compared together. Figure 2 shows a poor correlation between the long-term oxygen isotope record in precipitation at Bangkok and the El Nino anomaly, indicating a lack of broad sea-surface temperature control on isotope variations in this region.

Long-term, amount-weighted annual means of δ^{18}O values in the asian monsoon region are shown in Figure 3. Monitoring stations between 70°E - 96°E, located on the Indian subcontinent and Sri Lanka, display an easterly decrease in δ^{18}O values from -1.3 to -4.3. Precipitation between 100°E - 170°E has much lower δ^{18}O values (–5 to -7.5) with no discernible pattern across the longitudinal range. In the western Pacific, between 170°E – 160°W, precipitation δ^{18}O values (~-2.4) once again are much greater than those in the 100°E -170°E range. While delta values in the western Pacific stations are similar to those in the 70°E -100°E longitudinal range, they have a much narrower range of values that do not vary with latitude. There is a lack of correlation ($r^2<0.5$) between δ-values and the amount of precipitation or mean surface air temperature, either within or between the three sub-groups of data. In addition, similar amounts of precipitation in each of the sub-groups have different delta values.

The isotope distributions are consistent with the inferred source and transport of moisture in the Asian Summer Monsoon (Lau et al., 2000; Lim and Kim, 2002). Indian Ocean and the Bay of Bengal are the primary source of moisture for the Indian subcontinent, resulting in relatively high δ^{18}O values observed in this area.

Air circulation in the 100°E – 170°E region is derived from spatially and temporally variable sources. The cross-equatorial monsoon flow in this region facilitates moisture transport from the Indian Ocean and eastern China. During the initial stage of monsoon evolution, moisture from the Indian Ocean produces precipitation, whereas moisture from eastern China and more northern latitudes dominates the later stages (Lim and Kim, 2002). Moisture from the Indian Ocean and high-latitudes transported over northeast China to the South China Sea and the Pacific consequently has more negative δ^{18}O values due to rainout.

In the 170°E – 160°W region, moisture is derived from the Pacific and transported mostly over the ocean westward by trade winds. Isotopically, this moisture is similar to that from an oceanic source and is consistent with the relatively higher delta values of about –2.5 per mil.

The marked difference of about 3 ‰ in oxygen isotopic composition (and a corresponding difference in hydrogen isotope composition) of present-day precipitation in the Asian Monsoon system between ~100-170^{o}E is explained by differences in moisture sources and transport patterns to the east and west of this zone. While previous analyses of isotopes in precipitation have focused on the relationship between isotope content and climatic parameters, the correlation between moisture source and circulation pattern, particularly in the Asian Monsoon System, has not been recognized. In addition to explaining the spatial variability in isotopic composition, our study provides an explanation for the observed lack of correlation between isotope content and temperature or precipitation amount in tropical areas.

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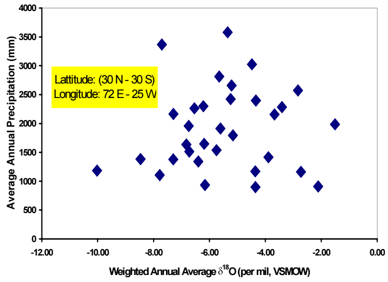

Figure 1.

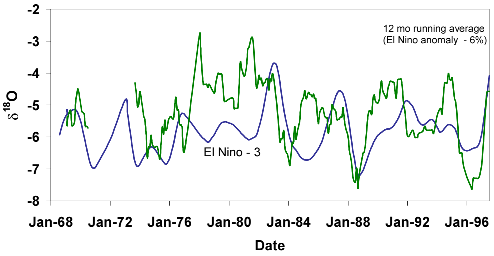

Figure 2

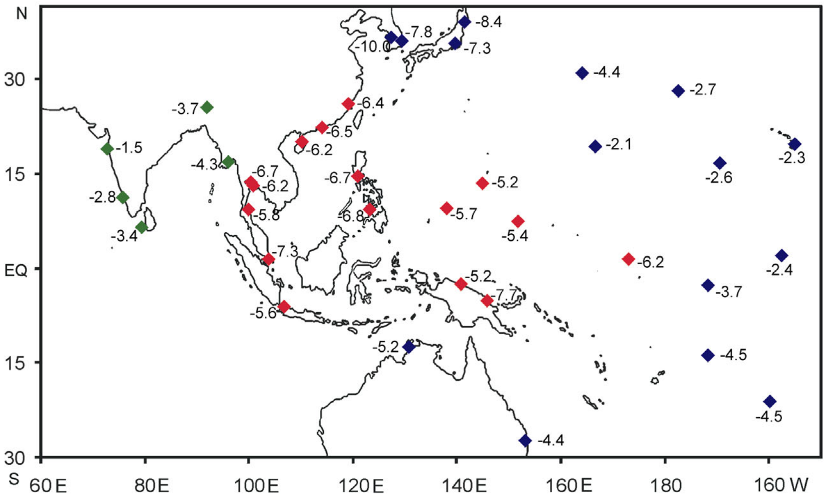

Figure 3

SELECTED APPLICATIONS OF ISOTOPES IN STUDIES OF OCEAN CLIMATE

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We present and discuss applications of isotope and other tracer data (^{3}H, ^{3}He, Ne and ^{18}O) to studies of ocean climate. Specifically, we address the variability of deep water formation the Greenland Sea, the variability in Arctic Ocean freshwater components, and the addition of glacial meltwater to the shelves around Antarctica. Changes in deep water formation rates in the Greenland Sea (ca. 80% from 0.5 to 0.1 Sv) were determined using a time series of tritium/^{3}He data. Reduction of the fraction of meteoric water along a section across the Eurasian Basin of the Arctic Ocean occupied in 1991 and 1996 were derived from $\delta^{18}O$ and salinity measurements. Ne and $\delta^{18}O$ data were used to calculate fractions of glacial meltwater (ca. 4 per mil) in plumes of ice shelf water flowing out from underneath the Ross Ice Shelf.

BIOGEOCHEMISTRY AND WATER QUALITY

(Session 9)

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IAEA-CN-104/106

HISTORIC AND CONTEMPORARY EXAMPLES FOR ASSESSING SOURCES AND TRANSFORMATIONS OF SULFATE AND NITRATE IN THE HYDROSPHERE USING ISOTOPE TECHNIQUES

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The isotoic composition of dissolved sulfate ($\delta^{34}S$ and $\delta^{18}O$) and nitrate ($\delta^{15}N$ and $\delta^{18}O$) in surface water and groundwater often provides information about the sources of these solutes (Kendall 1998, Krouse & Mayer 2000). Additionally, spatial or temporal patterns of increasing or decresing sulfate and nitrate concentrations in conjunction with changing isotope ratios may reveal biogeochemical processes occurring in the hydrosphere. This contribution summarizes historical and contemporary case studies, in which the isotopic compositions of sulfate and nitrate have been successfully used to determine sources and transformations of these solutes in surface water and groundwater.

The isotopic composition of dissolved sulfate in surface water and groundwater can provide information about sulfur sources, particularly if both $^{34}S/^{32}S$ and $^{18}O/^{16}O$ ratios are determined. The following three major sources of sulfate can often be distinguished isotopically:

- sulfate derived from dissolution of primary evaporites with relatively high $\delta^{34}S$ and $\delta^{18}O$ values;
- sulfate derived from pyrite oxidation usually with comparatively low $\delta^{34}S$ and $\delta^{18}O$ values;
- sulfate derived from atmospheric deposition with $\delta^{34}S$ often between 0 and +6 ‰ and high $\delta^{18}O$ values.

Additionally, anthropogenic point sources may contribute sulfate with characteristic isotope compsotions. Simultaneous monitoring of spatial or temporal trends in concentration and isotopic composition of sulfate is an effective approach for revealing sulfur sources and transformation processes in aqueous systems. Decreasing sulfate concentrations with increasing $\delta^{34}S_{sulfate}$ and $\delta^{18}O_{sulfate}$ values are indicative for dissimilatory bacterial sulfate reduction. Increasing sulfate concentrations accompanied by increasing $\delta^{34}S_{sulfate}$ values are often typical for admixture of sulfate from evaporite dissolution. In contrast, increasing sulfate concentrations with decreasing $\delta^{34}S_{sulfate}$ values may point to pyrite oxidation as a potential sulfate source. Finally, evaporation increases the concentration of dissolved sulfate without causing major shifts in its $\delta^{34}S_{sulfate}$ and $\delta^{18}O_{sulfate}$ values. Eventually, gypsum or anhydrite may form with $\delta^{34}S$ and $\delta^{18}O$ values similar to those of the dissolved sulfate, since isotope fractionation during precipitation of sulfate minerals is small for both sulfur (< 2 ‰) and oxygen isotope ratios (< 4 ‰).

The isotopic composition of nitrate in surface water and groundwater can provide information about nitrogen sources, particularly if both $^{15}N/^{14}N$ and $^{18}O/^{16}O$ ratios are determined. The following four major sources of nitrate can often be distinguished isotopically:

- nitrate from atmospheric deposition with variable $\delta^{15}N$ values and high $\delta^{18}O$ values (+25 to +80‰);
- nitrate from synthetic fertilizers with $\delta^{15}N$ values often around 0‰ and $\delta^{18}O$ values near +23‰;
- nitrate from soil nitrification with $\delta^{15}N$ values < +5‰ and $\delta^{18}O$ values < +15‰, and
- nitrate from sewage and manure with $\delta^{15}N$ values > +7‰ and $\delta^{18}O$ values below +15‰.

Simultaneous monitoring of spatial or temporal trends in concentration and isotopic composition of nitrate is an effective approach for revealing nitrogen sources and transformation processes in aqueous systems. Decreasing nitrate concentrations with increasing $\delta^{15}N_{nitrate}$ and $\delta^{18}O_{nitrate}$ values are indicative for the process of denitrification. In contrast, increasing nitrate concentrations accompanied by relatively high $\delta^{15}N_{nitrate}$ values (> +7‰) are often typical for admixture of nitrate from sewage or manure. Concentration and isotope patterns indicative of other processes such as nitrate assimilation will also be discussed.

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USE OF ENVIRONMENTAL ISOTOPES TO EVALUATE NATURAL AND ANTROPIC SOURCES OF GROUNDWATER IN AN AREA WITH MULTIPLE LAND USES, SANTIAGO NORTE BASIN, CHILE

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One of the key aspects, that has significant implications in groundwater resources management in urban areas, is the identification of the potential multiple sources of aquifer recharge. This paper will discuss data from an ongoing project aiming to develop a management strategy for groundwater development in the northern part of the Santiago Basin, Chile. The study area is densely populated with multiples land practices including urban (60%), agriculture and recreational (30 %), and industrial (10 %) uses. The aquifers are composed of sedimentary granular units related, genetically, to the evolution of the alluvial fan of Mapocho River (fig. 1a). Unconfined aquifers are developed in the proximal alluvial fan facies, while confined and semi-confined aquifers are associated to distal alluvial fan deposits. Naturally these aquifers must be recharged by infiltration from small local watershed asociated to basement outcrops and, in a more regional scale, from lateral recharge of upgradient aquifers, recharged in the upper part of the Mapocho River watershed. Potential antropic sources of recharge could be associated, with leakage from the old water supply network and sewage system in the urban area, and/or irrigation channels that exist within and in the margin of the basin. All these water networks are principally supplied with water from the Maipo River, located to the south of the study basin.

An extensive hydrogeological and geochemical study is being carried out in the study area to evaluate the groundwater flow system and the different sources of aquifer recharge. The evaluation of water sources is primarily being carried out using oxygen-18, deuterium and tritium. Sulfate-34 and oxygen-18 in sulfate are also being used to evaluate sources of groundwater sulfate, that could also provide additional information about water sources.

The results of more than 100 groundwater samples and more than 20 surface water samples are summarized on Figure 1b. The broad range of isotope values (-18 to -14 ‰ for $\delta^{18}O$ and -90 and -130 ‰ for $\delta^{2}H$) observed in river waters are due to seasonal variations represented by enriched isotope values for winter rainfall and isotopically depleted water associated to snow melting events in summer time [1]. The more isotopically enriched water in the basin are represented by springs recharged by low altitude precipitation in the basin. This pattern agreed very well with the isotope gradient with altitude documented for precipitation in the central part of Chile. The groundwater isotope signature in the study area shows a very wide range, with some overlapped within the isotope range for the Maipo and Mapocho River waters. The more isotopically enriched groundwater are observed in areas close to the low altitude hills, clearly representing water recharge by local precipitation. The groundwater in the aquifer located in the upper part of the Mapocho river basin has an isotope composition of –11 to –13 ‰ for ^{18}O and –80 to –100 ‰ for ^{2}H. Therefore, the predominance of more depleted isotope values in the aquifer that is part of alluvial fan of the Mapocho River, has to be related to a strong influence of Maipo type waters. This hypothesis is supported by the occurrence of high level of sulfate in most of the wells sampled (> 250 ppm). The Maipo River waters are characterized by sulfate concentration ranging between 250 – 350 ppm [1]. Much lower sulfate concentration are observed in the upgradient groundwater in the Mapocho basin (70 – 100 ppm) and in groundwater representing local recharge (40 – 60 ppm). A trend of decreasing sulfate concentration and a change to more isotopically enriched waters is observed with depth in the aquifers. Water collected from deep screened wells (> 140 m depth) shows a clear chemical and isotopic relationship with the groundwater present in the beginning of the alluvial fan of the Mapocho River.

Based on the sulfate concentration pattern, ^{34}S and ^{18}O in sulfate are being used to evaluate the source of the groundwater sulfate. This approach was based on the different isotope composition expected for sulfate originated in the Maipo River basin compared to sulfate from the Mapocho River basin. The Mapocho River sulfate should come mainly from oxidation of sulfate minerals [2], while sulfate in the Maipo basin is coming from dissolution of Jurasic marine evaporites [3]. Preliminary data tend to support this hypothesis. The Mapocho river sulfate has an isotope composition of +3 ‰ for ^{34}S and -4 ‰ for ^{18}O, meanwhile the Maipo River sulfate is characterized by +12 ‰ for ^{34}S and +6 ‰ for ^{18}O. Based on this relatively high differences, ≈ 9 ‰ ^{34}S and ≈ 10 ‰ ^{18}O, it will be possible to determine and quantify the influence of Maipo water types in the study area. These water could be associated to leakage of the water supply and sewage systems and irrigation channels. The combined use of hydrogeological, geochemical, and isotopic tools has provided valuable information about the groundwater flow system and sources of aquifer recharge.

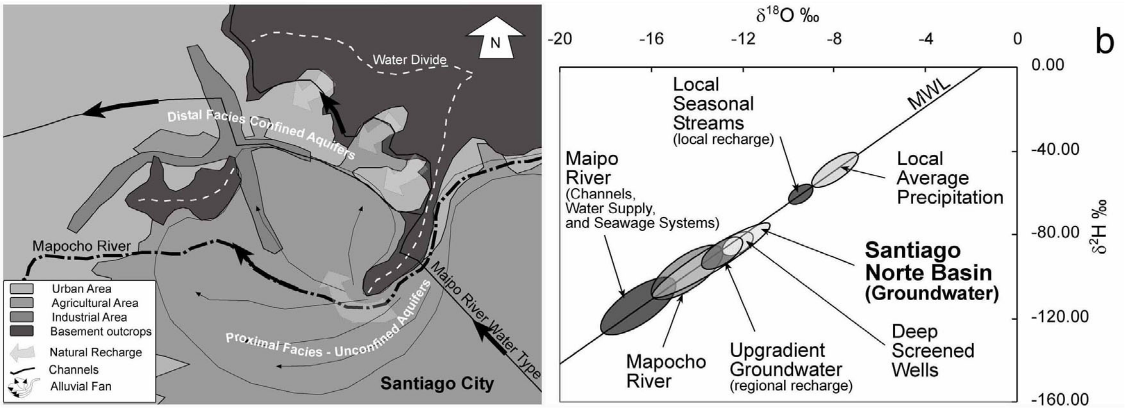

FIG. 1.

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TEMPORAL TRENDS IN THE CHEMICAL AND ISOTOPIC COMPOSITION OF SURFACE WATER NITRATE WITHIN THE OLDMAN RIVER BASIN, SOUTHERN ALBERTA, CANADA

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Temporal variations of concentrations and isotope ratios of riverine nitrate from the Oldman River watershed were monitored over more than two years. This basin, located in Southern Alberta, Canada, has almost pristine headwaters in its western part and increased urban/industrial/agricultural activities in its eastern part. The objective of the study was to assess nitrate sources and their impact on surface water quality throughout the different seasons. Monthly sampling of the main stream of the Oldman River (OMR) and some of its tributaries (T) commenced in December of 2000, and a total of 14 sites (5 OMR & 9 T) were sampled until March 2002. Presently samples are taken from 21 sites every two months.

In the tributaries, [NO_3^- - N] ranged from < 0.003 to 8.810 mg/L, $\delta^{15}N_{nitrate}$ values varied between -2.5 and +23.4‰ (Figs. 1a and 1b), and $\delta^{18}O_{nitrate}$ values ranged from -15.2 and +3.4‰. Tributaries located in the upstream-western portion of the watershed (< 100km) had low and invariable nitrate-N concentrations (≤ 0.5 mg/L) throughout the seasons. In contrast, some tributaries in the downstream-eastern part (> 100km) had high nitrate-N concentrations (> 1 mg/L) in the fall-winter and low concentrations in the spring-summer (Fig. 1a). Western sites (< 100km) had in general lower $\delta^{15}N_{nitrate}$ values (~ +2‰) than eastern sites (~ +15‰), and the $\delta^{15}N_{nitrate}$ values showed no seasonal variations at the respective sampling sites (Fig. 1b).

In the Oldman River, nitrate-N concentrations ranged from < 0.003 to 0.339 mg/L, $\delta^{15}N_{nitrate}$ values varied between -1 and +14‰ (Figs. 1c and 1d), and $\delta^{18}O_{nitrate}$ values varied between -10 and +6‰. Oldman River sites located in the upstream portion (< 100km) of the basin had low and constant [NO_3^- - N] (≤ 0.15 mg/L) throughout the seasons. Eastern sites had somewhat elevated nitrate-N concentrations in the fall-winter and low concentrations in the spring-summer (Fig. 1c). $\delta^{15}N_{nitrate}$ values appeared to be constant with time at the respective sampling sites, but there was a trend of increasing $\delta^{15}N_{nitrate}$ values from the western-upstream sites (~ +3‰) to the eastern-downstream sites (~ +8‰) (Fig. 1d).

Chemical and isotopic data suggest that nitrate in the western part of this watershed was mainly derived from soil nitrification ($\delta^{15}N_{nitrate}$ < +5‰), whereas significant portions of nitrate in the urban/industrial/agricultural eastern part were derived from manure or sewage ($\delta^{15}N_{nitrate}$ > +10‰) [1]. The latter anthropogenic sources caused high nitrate concentrations in the tributaries particularly in the non-irrigation season. This suggests that the local hydrology (e.g. water level in irrigation canals) has a major influence on the amount of agricultural nitrate reaching the streams and hence on their water quality. To what extent biological activity contributes to the low nitrate concentrations in the irrigation season is currently under investigation.

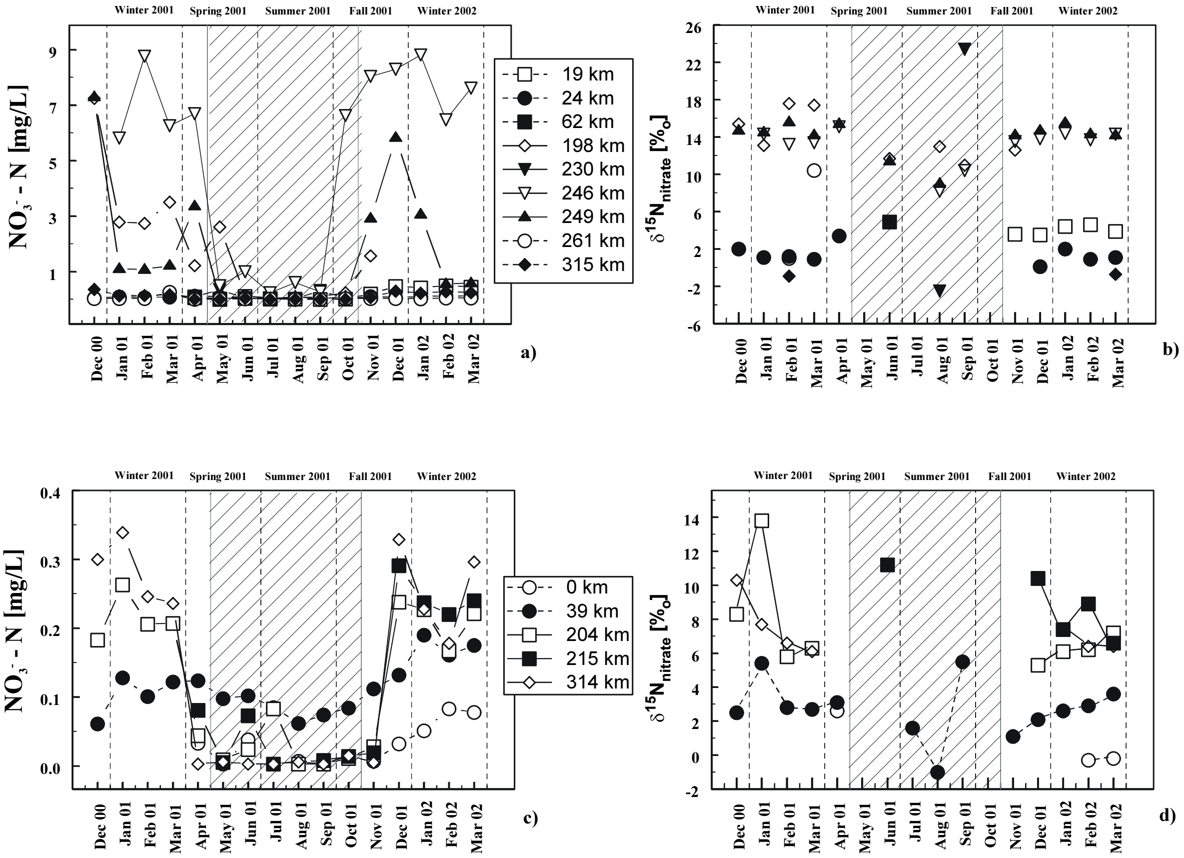

FIG. 2. a) [NO_3^- - N] versus sampling month for the tributary sites; b) $\delta^{15}N_{nitrate}$ values versus sampling month for the tributary sites; c) [NO_3^- - N] versus sampling month for the Oldman River sites; d) $\delta^{15}N_{nitrate}$ values versus sampling month for the Oldman River sites; hatched area represents irrigation season; distances in km downstream of Oldman River site (0 km).

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^{15}N AND ^{18}O ISOTOPES AS TRACERS OF AGRICULTURAL GROUNDWATER CONTAMINATION IN OSONA (NE, SPAIN)

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The Osona District (NE Spain) is classified as *vulnerable zone* of nitrate contamination from agricultural sources by the Directive 91/767/CEE. In this region (1,263.8 km^2) more than 1000 pig farm exploitations exist, most of them situated in the central part of the area. In 1999, livestock in the area consisted of 927,250 pigs, 90,024 cows and 57,391 sheep. This intensive activity produces large quantities of manure, mainly coming from the pig farms; a small part of them is processed in treatment plants and the rest is spread onto the fields as organic fertilisers. This practise produces a diffused contamination in the aquifers of the area with high concentrations of nitrates, up to 365 ppm, which is more than 7 times the permitted concentration in drinking waters. Additionally, synthetic fertilisers are also used in the area, contributing to the groundwater contamination.

An area of 31 km^2 is used in order to study the complexity of its groundwater hydrodynamics, to characterise the nitrate contamination, to evaluate the contribution of each pollutant source (i.e. fertilisers and pig manure) and to identify the fractionation processes of ammonium volatilisation, nitrification and denitrification. To do this, 38 groundwater samples were collected during October 2001 and chemical and isotope data ($^{15}N_{NO3}$ and $^{18}O_{NO3}$) were determined.

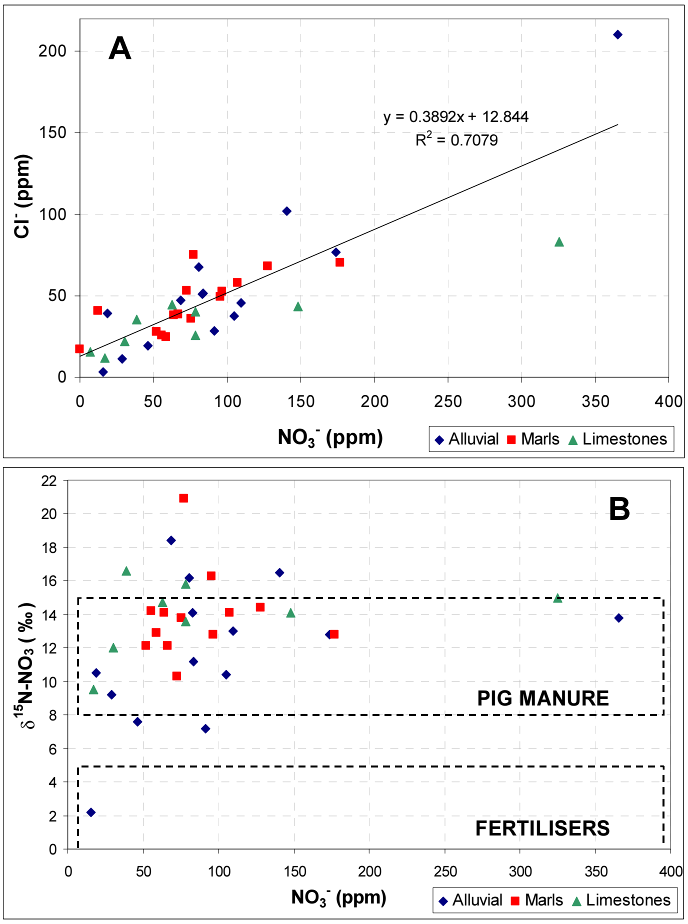
A correlation between chloride and nitrate concentrations exists (fig. 1A), indicating that they have the same origin. Their spatial isoconcentrations are distributed comparably to the piezometry showing an accumulation of nitrates and chlorides downflow. Therefore, as chloride is a conservative ion, it can be used as tracer to know where the maximum inputs of nitrogen have been applied and/or to study the hydrodynamics of the pollutant constituents.

Isotopic values range from +2.2‰ to +21.0‰ for the $\delta^{15}N_{NO3}$ and from +5.1 to +11.8‰ for the $\delta^{18}O_{NO3}$. Most of the groundwater samples have $\delta^{15}N_{NO3}$ values heavier than +8‰ (fig.1B), corresponding to nitrates coming from the pig manure ($\delta^{15}N_{NH4}$ between +8 and +15‰, [1]). Only three samples have lower values corresponding to synthetic fertilisers contaminated waters (fertilisers have a $\delta^{15}N_{Ntotal}$ near the 0‰, [2]) or by a mix of the two inputs.

As the pig manure or the synthetic ammonium fertilisers are spread onto the fields, two reactions take place: the urea hydrolysis and the ammonium volatilisation increasing the residual ammonium isotopic composition. In the unsaturated zone ammonium is nitrified into nitrates. Samples with higher isotopic values ($\delta^{15}N_{NO3}$ from +15 to +21‰ and $\delta^{18}O_{NO3}$ from

+8 to +12‰) are affected by the denitrification process, which produces an enrichment of the isotopic compositions $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$. Denitrification in the area is believed to be caused principally by the oxidation of pyrites present in the aquifer materials, mainly marls and limestones. Denitrification caused by the organic matter oxidation is difficult to be observed as the high natural bicarbonate concentrations buffers any relation between this concentration and the nitrates or carbonates isotopic compositions.

The $\delta^{15}N_{NO3}$ have permitted to determine that the groundwater contamination in the area is mainly due to the high rates of pig manure used as organic fertilisers in agriculture. The chloride concentrations in waters are also due to this agricultural practise and can be used as a tracer of the pig manure contamination. The $\delta^{15}N_{NO3}$ together with the $\delta^{18}O_{NO3}$, permit to identify the fractionation processes that affect groundwaters (volatilisation, denitrification). The use of other isotopic values ($\delta^{34}S_{SO4}$, $\delta^{18}O_{SO4}$, $\delta^{18}O_{H2O}$ or $\delta^{13}C_{HCO3}$) could permit a better evaluation of the denitrification process.



Fiure 1. A) Chloride versus Nitrate concentrations in ppm. B) Nitrogen isotopic composition of nitrates versus nitrate concentration in ppm.

ACKNOWLEDGEMENTS

This study has been financed by the CICYT project HID99-0498 of Spanish Government and the SGR01-00073 of Catalonian Government.

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STABLE ISOTOPES OF DISSOLVED OXYGEN AS AN INNOVATIVE TOOL FOR WATER QUALITY PARAMETER ESTIMATION

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The concentration of dissolved oxygen in surface waters is an indicator of the water quality and the impact of pollutant loads from various sources of discharge. Dissolved oxygen concentrations and $\delta^{18}O$ of dissolved oxygen in a river are controlled by gas exchange with the atmosphere (reaeration), respiration (biological and sediment oxygen demands), and photosynthetic production. When respiration dominates over photosynthesis, dissolved oxygen will be undersaturated and $\delta^{18}O$ of dissolved oxygen will be greater than 24.2‰. When photosynthesis exceeds respiration, in contrast, dissolved oxygen will be supersaturated and $\delta^{18}O$ will be less than 24.2‰. When gas exchange dominates over photosynthesis and respiration, dissolved O_2 is close to saturation and the $\delta^{18}O$ will be nearly 24.2‰ [1].

Direct measurements of the rates of these processes are difficult and laboratory or empirical estimates are commonly used for predictive modeling of water quality. An innovative approach to site-specific estimation of parameters for water quality modeling and validation of predictive models is to use the stable oxygen isotope ratio of dissolved oxygen as a unique tracer of the source and consumption of oxygen.

The concentration and $\delta^{18}O$ of dissolved oxygen along with other physico-chemical parameters like pH, Electrical conductivity, temperature, chlorophyll, BOD and COD were measured in three lakes and a river. The water samples were also collected for the measurement of $\delta^{13}C$.

Electrical conductivity of Rawal lake vary from 306 to 462 µs/cm, the pH varies from 6.65 to 7.84 temperature varies from 15.6 to 32.2 °C. $\delta^{18}O$ of dissolved oxygen ranged from 24.15 to 29.5 ‰ and indicate that gas exchange dominates photosynthesis and respiration at the surface of water both in July and December. However in December, EC, temperature, DO concentration and $\delta^{18}O$ of dissolved oxygen have no variations with depth. In July, DO concentration decreases and $\delta^{18}O$ increases with depth. Respiration dominates over photosynthesis at 5 meters and 10 meters of depth as dissolved oxygen is undersaturated and $\delta^{18}O$ is greater than 24.2‰.

In Kalar Kahar Lake, EC varies from 3100 to 3410 µs/cm, temperature ranges from 15.8 to 17.7 °C and dissolved oxygen concentration varies from 11.1 to 14.9 mg/l. $\delta^{18}O$ values of 19.15 to 20.87 ‰ indicate that photosynthesis dominate respiration and exchange rate.

From River Ravi, the samples were collected from four locations, 0 km, 4 km, 25 km and 50 km downstream. The first location that is considered as unpolluted is taken as first sampling point (i.e. 0 km). EC values of the river Ravi vary from 202 to 463 µs/cm, pH ranges from 7.16 to 8.58 and the temperature have values from 23.1 to 32.5 °C. $\delta^{18}O$ of river water has variations from –7.80 to –7.13 ‰. The DO concentration varies from 0.3 to 8.4 mg/l. At first location (unpolluted), DO concentration is 8.4 mg/l and $\delta^{18}O$ of dissolved oxygen is about 24‰ showing the gas exchange domination over photosynthesis and respiration.

After mixing of sewerage water, DO concentration decreases to 5.8 mg/l and $\delta^{18}O$ increases to 27.20 ‰ at 4 km downstream. The respiration dominates both gas exchange and photosynthesis. At 25 km downstream, the DO concentration is as low as 0.3 mg/l and $\delta^{18}O$ of dissolved oxygen is around 24‰ showing that after traveling 25 km, the microbiological activity dies out and the dissolved oxygen again starts rebuilding its concentration through gas exchange. Here the concentration is very low but the $\delta^{18}O$ is close to 24‰ showing that gas exchange is dominant over respiration and photosynthesis. At 50 km, the DO concentration becomes 6.7 mg/l and $\delta^{18}O$ remains near to 24.00‰ showing gas exchange domination. Depleted values of $\delta^{13}C$ show the effect of pollution. Where there is dominance of gas exchange $\delta^{13}C$ values are near to the atmospheric CO_2 value of about –8.00 ‰.

A cruise of the Ravi river was also performed in the month of June, when the river was in medium flood. The samples were collected from 14 locations within a span of 50 km along the left bank and across the river at some locations. EC varies from 151 to 596 µs/cm, temperature from 27.6 to 30.9 °C, concentration of dissolved oxygen from 1.9 to 6.2 mg/l, COD from 4 to 107 mg/l, BOD from 2.7 to 23.9 mg/l and $\delta^{18}O$ of DO ranges from 23.78 to 29.55 ‰. The results of dissolved oxygen for the cruise are presented in figure 1.

The $\delta^{18}O$ and dissolved oxygen concentrations were used to determine the ratio of community respiration (R) to gross photosynthesis (*P*) rates. *R* : *P* varies between 1.6 and 2.6 for the cruise of the Ravi River. The $\delta^{18}O$ indicated the presence of photosynthetically produced oxygen, with the highest proportion occurring in unpolluted water. The $\delta^{18}O$, through determination of R:P, provides a means of quantifying the heterotrophic state of freshwaters.

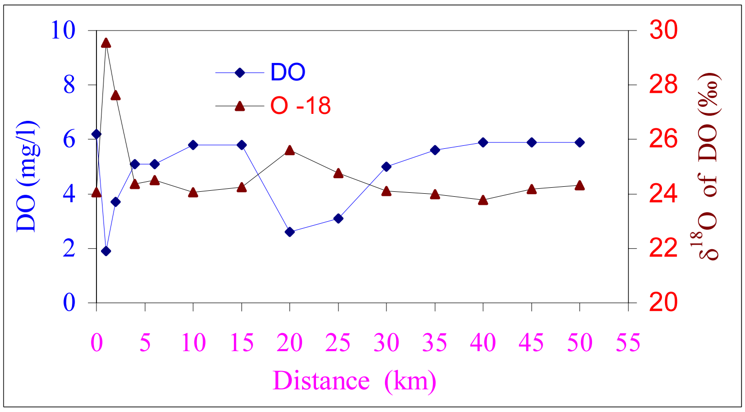

Fig. 1: The variation of dissolved oxygen concentration and $\delta^{18}O$ of dissolved oxygen in Ravi River.

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IAEA-CN-104/188

UNDP'S GLOBAL ENVIRONMENT FACILITY INTERNATIONAL WATERS PORTFOLIO: POSSIBLE LINKAGES TO ISOTOPE HYDROLOGY TOOLS AND APPLICATIONS

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The Global Environment Facility (GEF), in addition to serving as the financial mechanism for the Biodiversity, Climate Change, POPs and Desertification Conventions, is also a major source of funding for programs that assist groups of countries to manage their shared water resources -- river basins, groundwater, enclosed seas and Large Marine Ecosystems -- more sustainably and equitably. The GEF assists countries with improving their understanding of the functioning of transboundary waters to inform governance reforms targeting priority environmental issues. The United Nations Development Programme (UNDP) is one of the Implementing Agencies of the GEF and has a GEF International Waters portfolio totaling over $500 million, including co-financing. This presentation will provide an overview of UNDP-GEF's International Waters portfolio, highlighting key waterbodies, issues and strategies being developed and implemented to address transboundary environmental problems. The focus will be on waterbodies where isotope hydrology applications are already being applied or could prove useful to improve scientific understanding of critical waterbody processes.

POSTER SESSION I

DYNAMICS OF GROUNDWATER

PRELIMINARY INTERPRETATION OF ENVIRONMENTAL ISOTOPE DATA IN THE CHAD BASIN AQIUIFERS, NE NIGERIA

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The Chad Formation is the youngest stratigraphic unit of the hydrographic Chad Basin which occupies the North Eastern part of Nigeria and stretches into neighbouring countries like Chad, Niger, Cameroun and even as far as Sudan. It is a Plio-Pleistocene mainly argillaceous sequence with three well defined arenaceous horizons referred to as Phreatic (Upper), early Plaocene (Middle) and Continental Terminal (Lower) aquifers.

Most of the area of Chad Basin is Sahelian with mean annual rainfall below 500mm and characterized by high evaporation of more than 2000mm per annum and virtual absence of perennial rivers/streams except the surface water of the Lake Chad which has drastically reduced in volume due to recurrent droughts over the years.

Competing demand for water in the Basin range from domestic through irrigation to industrial uses and there is increasing reliance on groundwater to meet these water requirements. Consequently, some of the aquifers of the Basin are subjected to tremendous stress and irrigation practices are characterized by heavy reliance on agrochemicals. This is against the backdrop of lack of adequate information on recharge of the aquifers and agricultural impact on groundwater resources in the basin which are crucial issues in sustainable development and environmentally sound management of the scarce water resources of the fragile ecosystem of the Chad Basin.

This paper undertakes a preliminary interpretation of isotope data acquired so far under the IAEA sponsored TC Project No NIR/8/006: Isotope-based Investigations in Chad Basin Aquifers in an attempt to address some of these problems. The presence of pseudo fossil to completely fossil waters in the Middle and Lower aquifers has been inferred while Upper aquifer water shows evidence of meteoric recharge (see Fig. 1).

Data assemblage is continuing and other issues like estimation of recharge (infiltration) rates, age correlation of the aquifers, water dynamics and modeling of flow regime and contaminant transport will be addressed in a later paper.

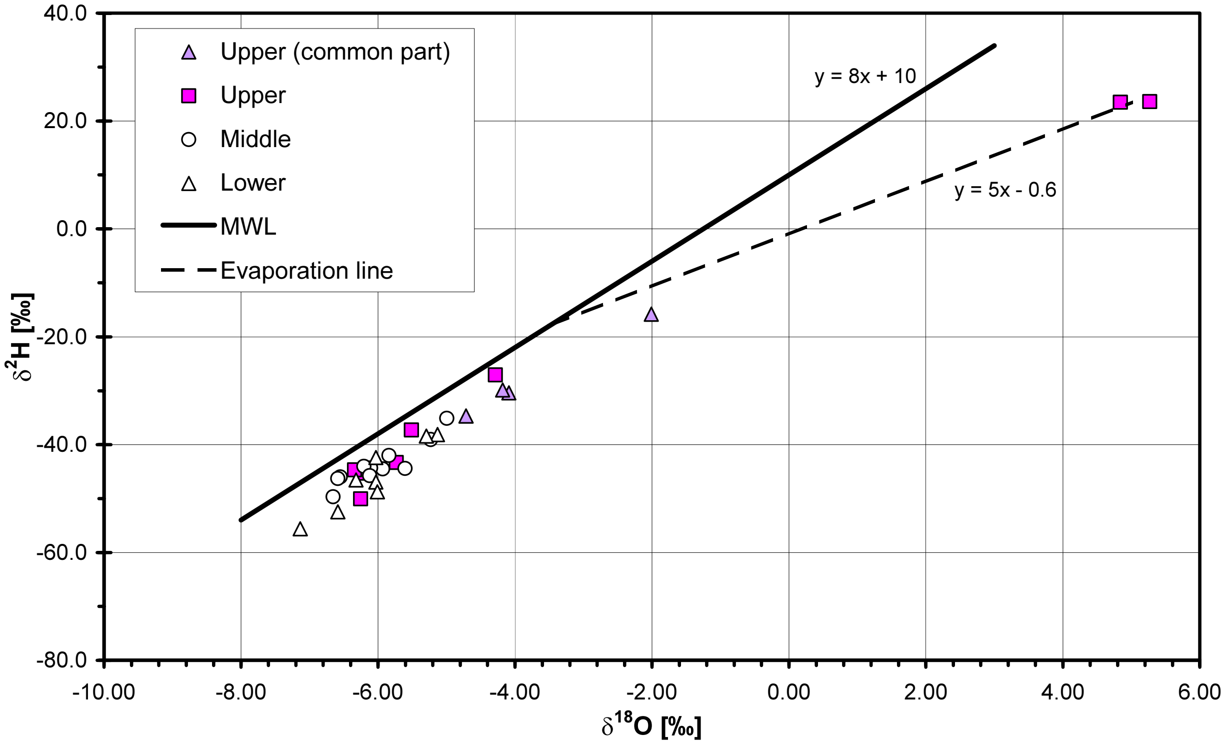

Fig. 1. Results of stable isotope measurements in Chad Basin Aquifers.

A RADIOISOTOPE TRACER STUDY OF ESTUARINE GROUNDWATER MOVEMENT ON THE EASTERN AUSTRALIAN COAST

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Groundwater discharge to coastal waters, and the associated transport of nutrients and contaminants, is believed to have a significant impact on coastal ecosystems. However, complex boundary conditions and rapidly changing short-term fluxes make net flows resulting from local or regional groundwater discharge difficult to quantify. Such boundary conditions include beach face wave run-up and storm set-up, sub-surface tidal forcing, frequent surface inundation and tidally driven surface/groundwater interactions in estuarine and coastal areas. Tracer techniques can complement hydrological and geochemical studies of such systems and help distinguish longer-term net fluxes from the highly variable short-term fluxes.

At Hat Head, NSW, on the eastern Australian coast, a comprehensive study of hydrogeology and hydrogeochemistry has been conducted in an estuarine/coastal sand dune aquifer (Figure 1). A scheme currently under construction will dispose of treated sewage effluent from the small coastal community by injection into the sand dune aquifer. Hat Head is characterised by a 10m high sand dune separating freshwater and estuarine wetlands from the Pacific Ocean. The wetlands are linked to the ocean via Korogoro Creek, which has a 1.5m maximum tidal range. The underlying aquifer extends to a depth of >30m below sea level. It consists of well-sorted fine sands (K=20m/d) with a zone of poorly cemented ‘coffee rock’ sands (K=<1 m/d) occurring at 10-11 m depth. Geophysical and geochemical data have shown that there is an extensive mixing zone between fresh and saline water near the creek. Saline intrusion is limited by the coffee rock base and appears to vary over time. Fresh regional and local groundwater discharges to the creek around the saline water at shallower depths. Tritium data indicate that regional groundwater is modern and stable isotope ratios have been used to distinguish between salt flat and sand dune dominated systems where evaporative and seawater mixing processes are observed. Storm wave set-up and beach wave runup have been shown to elevate the water table near the coast leading to flow reversal and potential discharge of effluent to the estuarine zone.

Whilst short-term changes in hydraulic head can be measured, variations in salinity make it almost impossible to translate head gradients into flow rates in tidal environments. A radioisotope tracer study of groundwater flow in response to tidal forcing was conducted in the variable salinity zone adjacent to Korogoro Creek at Hat Head. Using the short lived conservative radioisotope tracer ^{82}Br ($T_{½}$=35h), groundwater movement was tracked in-situ over a period of ~5 days on two occasions, first during a spring tide (August 2001; 80 MBq ^{82}Br) and then during neap tides (July 2002; 200 MBq ^{82}Br). The tracer was injected into a borehole screened at 5 m and gross gamma counts monitored over time from an adjacent borehole using NaI(Tl) detectors. Count rate was used to estimate average distance of the plume based on laboratory calibrations, vertical profiles were measured to determine the tracer depth and directional profiles monitored the changing direction. The technique allowed us to map the path of the slow moving tracer without sampling (Figure 2) and to distinguish net groundwater movement from short term tidally driven fluxes. During the neap tide period net groundwater movement of 0.15 m/d was observed with horizontal tidal fluctuations in the order of 0.04 m and no discernible vertical movement. This contrasts with the tidally dominated spring tide period where tidally driven fluctuations were up to 0.14 m, net horizontal groundwater movement was negligible but upward movement was ~0.1 m/d.

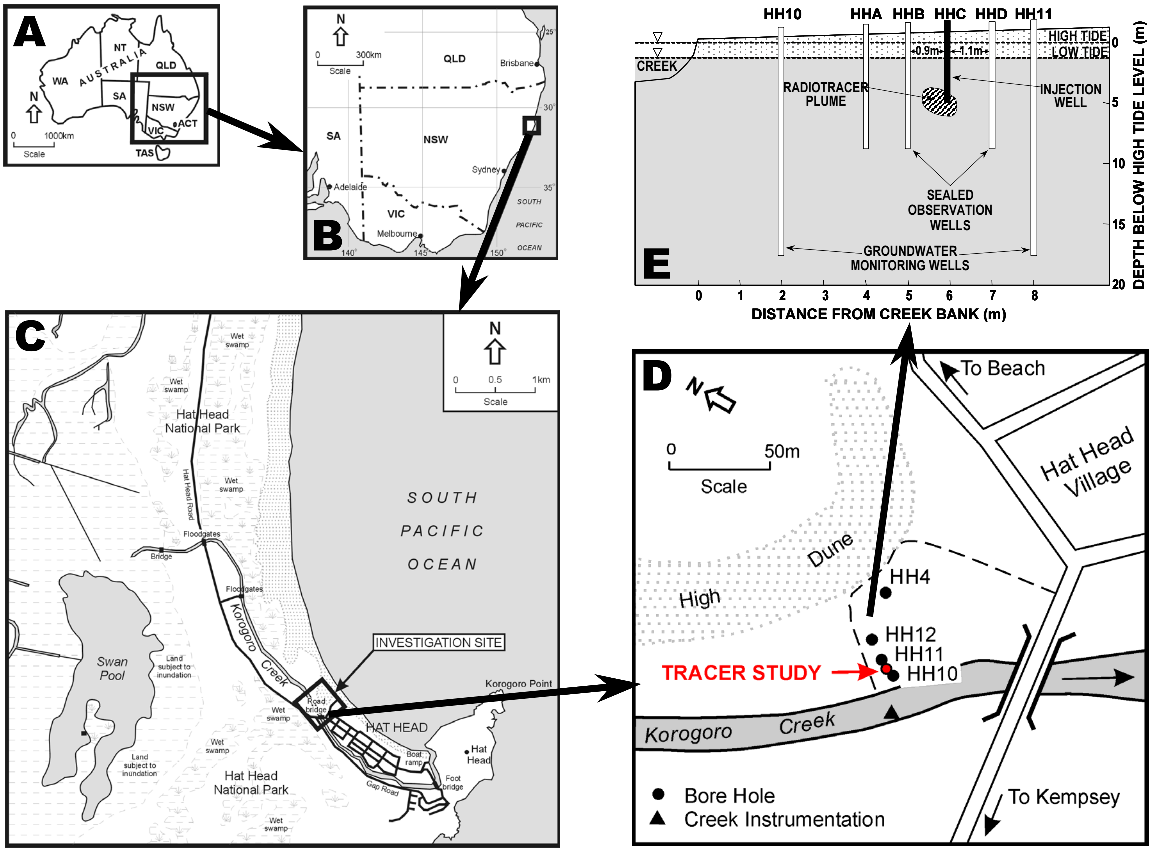

Figure 1. Hat Head study site: location maps (A-C), well locations (D) and site cross section (E).

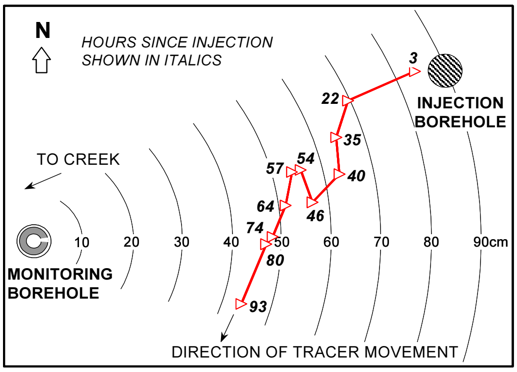

Figure 2. Radial plot of plume path during the tracer study. NB. The frequency of directional data collection is not sufficient to show all tidal fluctuations in direction.

CONCLUSIONS

During spring tides horizontal fluctuations are driven by the tides but observed net movement is upwards. This supports the hypothesis that saline intrusion drives upward circulation in the mixing zone.

During neap tides vertical movement is negligible and the tidally driven fluctuations are small. A net horizontal flow towards the creek is clearly observed supporting the hypothesis that fresh local and regional groundwater discharges to the creek above the high salinity zone.

ISOTOPIC AND HYDRODYNAMIC APPROACHES IN THE QUATERNARY AQUIFER OF LAKE CHAD BASIN IN NIGER AS INDICATORS OF PRESENT AND PAST HYDROLOGICAL PROCESSES

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The studied area is the Niger part of the Quaternary aquifer in the large endoreic Lake Chad basin. In a semi-arid to arid environment, it covers almost 200 000 km² between latitudes 13° and 14,5° N, in the South-eastern part of Niger and is the upper layer of a Plio-Quaternary continental reservoir. Because of the scarcity of surface water in the region, groundwater is the only permanent resource for the population.

We linked the environmental isotope and hydrodynamic approaches to understand the present state of the phreatic aquifer and its evolution with time. Groundwater samples were collected only from wells for chemical, stable isotope ($\delta^{18}O$, $\delta^{2}H$) and radioisotope ($A^{14}C$, $\delta^{13}C$) analyses during several field trips between 1997 and 2002. At the same time, depths to the water table were systematically measured to complete older information.

Groundwater flows slowly from the north and the west to Lake Chad, in the centre of the basin. All isotopic data are below the meteoric water line in a $\delta^{2}H$ *vs* $\delta^{18}O$ diagram, sign of evaporation. The results vary from –5,8 ‰ to +8,5 ‰ vs SMOW for $\delta^{18}O$ and –55 ‰ to +38 ‰ for $\delta^{2}H$. This important range and the heterogeneity of isotope distribution show that the recharge is not diffuse but mainly occurs in several areas and is highly variable.

Four regions were identified as getting a present significant recharge: (i) On the south west, the Manga grassland forms a late Pleistocene erg reworked by more recent aeolian processes with radiocarbon activity of groundwater between 80 pmc and 98 pmc. The hydrodynamic confirmation is the seasonal presence of small lakes in some interdune depressions in hydraulic continuity with the aquifer. (ii) The flooding of the Komadugu Yobe, a non perennial river, is a large source of recharge as shown by the seasonal piezometric variation and isotopic results (~ -1 ‰ *vs* SMOW for $\delta^{18}O$ in the aquifer 15 km away from the river bed, very similar to measurements in the river). (iii) The lateral seepage from Lake Chad is shown by local piezometry and also by enriched $\delta^{18}O$ values in the groundwater (between

+5,3 ‰ and +8,5 ‰), characteristic of the high evaporation of the lake. But the present recharge only exists in the vicinity of the lake. (iiii) Finally a recharge occurs also by vertical percolation of rain through the sand dunes, marked in groundwater by the lowest mineralisation of the area and isotopic values, close to the regional rainfall between –4,3 ‰ and –3,6 ‰.

Beside the ^{14}C values showing a present infiltration, most of the groundwater samples suggest a mixing between the recent recharge and old groundwater. The oldest groundwaters, all located in the Kadzell, have ^{14}C activity from 23,5 pmc to 36 pmc (fig 1). The Kadzell is a clayey plain close to the lake and the river. The water table forms locally a piezometric depression of 40 m deep, a common feature through the Sahel. The centripetal distribution of ^{14}C activities, where the oldest water are in the center of the hollow aquifer, shows the predominance of the lateral recharge from the peripheral zone. The $\delta^{18}O$ values in the center, the lightest of the aquifer, vary between –5,8 ‰ and –5 ‰ *vs* SMOW. They indicate a recharge during the last humid period, 9200-12700 years ago, when the temperature was lower and the rainfall higher. At that time, according to some previous studies, Lake Chad would have covered the plain and saturated the phreatic aquifer.

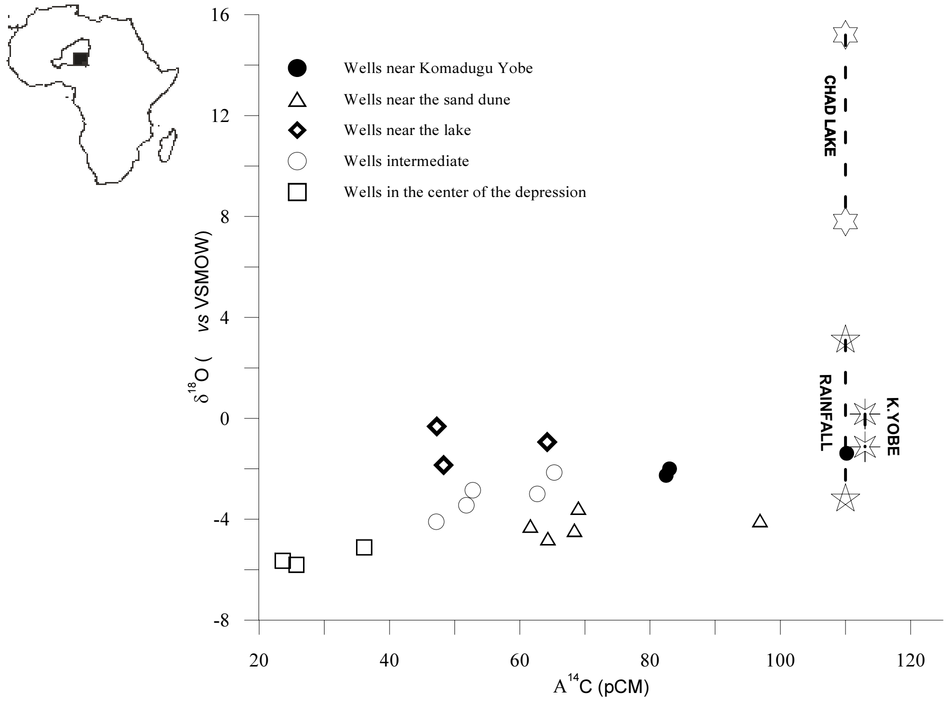

Figure 1: $\delta^{18}O$ versus A ^{14}C diagram for groundwater samples in the Kadzell plain ($\delta^{18}O$: ± 0,2 ‰ and A ^{14}C: ± 0,5 pmc)

We decided to simulate the deepening of the water table since the last climatic optimum to confirm the isotopic interpretation. We firstly calibrated the groundwater numerical model with the recent piezometric state. We simulated the aquifer behaviour during the last decades and specially the impact of the droughts in the 70s and the drying up of the lake. Numerical results suggested a low renewal rate of about +1mm.an^{-1} for the whole Quaternary aquifer, in good agreement with ^{14}C values, with the exception of an evapotranspiration assessment between -0,7 to -0,4 mm.a^{-1} in the Kadzell plain, in spite of an unsaturated zone up to 50 m thick.

The origin of the piezometric depression requires two parameters: (i) low permeabilities and (ii) a water balance negative in the plain. The results from the numerical modelling and from isotopic interpretation are in close agreement and allow the reconstruction of interactions between surface water and phreatic aquifer for their present state and their changes since the last climatic optimum.

ISOTOPE INVESTIGATIONS AS A TOOL FOR WATER RESOURCE MANAGEMENT IN LJUBLJANA CITY (SLOVENIA)

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For almost 15 % of Slovenia's inhabitants living in Ljubljana, the capital of Slovenia, two groundwater sources of drinking water are of great importance. An abundance of groundwater is hidden inside the sandy and gravely Sava river aquifer underneath the urban city area, called Ljubljansko polje, which is one of the largest underground reservoirs of drinking water in Slovenia. Ljubljansko polje is a tectonic basin by its origin and is, together with the second important groundwater resource - Ljubljansko Barje - a part of the Ljubljana basin. Ljubljansko Barje is highly complicated from the hydrogeological point of view - the variety of unconfined and unconfined aquifers stretching along the city suburbs in the South give us just a misty figure of the processes taking place in the sandy layers, in places covered by impermeable clayey layers and surrounded by karst mountains [1].

The Ljubljansko polje aquifer is one of the most investigated Slovenian areas, because its groundwater has been used for public drinking water supply since 1890. Together with the increasing number of Ljubljana's inhabitants and consequently rising withdrawal quantities, groundwater quality began to show unacceptable deviations from the quality standards. The question of acceptable exploitation quantities that would not cause further decrease in groundwater quality was opened. The aim of isotope investigations was to determine the origin of the abstracted groundwater in more detail. The results served as helpful tools in determining priority tasks in planning future water exploitation and protection.

Isotope investigations had not been applied in groundwater researches of Ljubljansko polje until recently. As an additional tool for understanding the groundwater recharge and flow of Ljubljansko polje groundwater, oxygen isotope composition was being determined during the period from autumn 1997 to autumn 1999. On the basis of results of previous hydrogeological investigations it was concluded that only two important sources of the Ljubljansko polje groundwater exist, local precipitation and the Sava river water. The two sources showed a noticeable difference in oxygen composition, which served as the basis of groundwater origin determination. The pumping wells included into the public water supply system were used as sampling points. Isotope investigations showed that the share of the river water and of local precipitation strongly depend on the sampling point location, namely on its distance from the Sava river recharging area. As a consequence, the values of physical and chemical parameters show annual changes according to the variations in the portion of the two sources. The sampling points with a high proportion of the recharging river water show better groundwater quality. In other words, human impact in the urban city area is the main reason for deterioration of groundwater partly flowing below the urbanised area of the Ljubljana City.

Encouraging results of isotope investigations of the Ljubljansko polje led to the decision to start investigations on the second part of the Ljubljana basin – Ljubljansko barje. The exploitation of the aquifers located south of the city started in the mid-eighties of the previous century. It has been expected that this water resource with its mostly not urbanised recharge area could be protected from the anthropogenic influences more easily than the water resource in the close vicinity of the city.

The main aim of the research, based on stable isotope (oxygen, devterium) techniques, was to confirm the existence of different aquifers determined by former geological investigations and hydrogeological observations and to determine the differences in their recharge dynamics. The investigations started immediately after the conclusion of the Ljubljansko polje research in the autumn of 1999 and took place for two years. The results of isotope composition and chemical parameters, observed simultaneously, contribute to the understanding of groundwater origin, mean altitude of the recharge area, aquifer recharge dynamics and the relation between surface waters and groundwater [2].

Two recent investigations, based on the determination of the stable isotope composition, give important results and form the basis for the decision of the future protection and exploitation of the Ljubljansko polje and Ljubljansko barje aquifers.

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STABLE (O, H AND C) AND RADIOGENIC (TRITIUM & ^{14}C) ISOTOPES STUDIES OF SHALLOW AND CO$_2$-RICH GROUNDWATER FROM THE FOREZ GRABEN (EASTERN MASSIF CENTRAL, FRANCE)

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The Forez basin, which is located in the eastern part of the Hercynian Massif Central in France, is a non-symmetric Tertiary graben filled with 600 to 700 meters clastic sediments. It is surrounded by Palaeozoic granites ranging from 350 to 320 Ma. Volcanic activity in the basin during Miocene times was related to peri-Alpine tectonic activity.

This tertiary basin is known for its rare thermal and more numerous bicarbonate-rich springs. For more than two years, groundwater (springs) and rainfall waters have been collected for measurements of temperature, pH, conductivity, alkalinity, dissolved element concentration and stable isotope ratios. A subset of samples were analyzed for tritium content and dated using the ^{14}C method.

Stable isotopes values on rainfalls and snowfalls define a Local Meteoric Water Line, $\delta D = 7.7\ \delta^{18}O + 4.2$ ($r^2 = 0.92$; 180 values). From those records, weighted mean $\delta^{18}O$ and δD values of rain range respectively from -3.5‰ and -25‰ during summer months to close to -13‰ and -90‰ at snow period of time. A mix of 6 months rainfalls (July 2002 to January 2003) was analysed by ICP-AES. These rainfalls contained dominantly Na, K, Ca close to 0.5 mg.l^{-1} each, with less than 0.05 mg.l^{-1} of Mg and Si elements. A year of rainfalls (from July 2001 to July 2002) and a largest rainfall (November 2002) were measured for tritium activity to define current rainfall contents. Results are respectively 9 ±1 and 2.9 ±0.9 TU.

Perennial springs located on arenite-basement unconformities (770-1200m a.s.l.) range in $\delta^{18}O$ values from -9 to –11‰, and in δD from –55‰ to –70‰, with significant seasonal differences. These springs have progressive depletion of $\delta^{18}O$ (0.2‰ /100m) and δD (1.4‰ /100m)with temperature- geographic variations.

The tritium content goes from 7 to 9 TU (October 2002) indicating a short-time of recharge. Moreover, carbon isotope ratios ($\delta^{13}C = -19$‰ to –24‰) indicate an important contribution of unevolved organic compounds, whose ^{13}C signature is dominated by C3 plants in regions of temperate climate ($\delta^{13}C_{average} = -27$‰). Enriched chemical compositions of fluids, compared to rainfalls, confirm an interaction with surrounding silicated rocks (arenite, schists and granite). All samples contain, by descending order (concentration: one to tens of mg.l^{-1}) Na, Si, Ca, Mg and K; Sr and Ba are always present (<0.1 mg.l^{-1}) with traces of Al, Mn and Fe.

Rivers near some of the mineral springs show similar carbon isotope composition ($\delta^{13}C$ from -21 ‰ to -24 ‰) and, as they flow on granitic environments, they present similar ion concentration than those previously described.

Coupling geological criteria and ICP-AES results, there is a relation between mineralization and space-location. The highest spring, located in granitic environment, is the less element-rich, whereas springs in the basin (i.e. lying in the sedimentary units) have higher content. Moreover, each spring has different major ion concentrations, but admits with the following trend (ranging by progressive depletion): Na (up to 900 $mg.l^{-1}$), Ca, Mg, K, Si (10 to 20 $mg.l^{-1}$), and in lesser proportions Li, Sr, Ba (several $mg.l^{-1}$). Sometimes Fe and Mn are also present.

CO_2-rich springs and the thermal springs have close oxygen and hydrogen isotope ratios ranging from -8.5 ‰ to -10 ‰ ($\delta^{18}O$) -60 ‰ and -70 ‰ (δD) than shallow springs, with no seasonnal variations. C isotope ratio of the rich total dissolved carbon mineral waters gives $\delta^{13}C$ values from -2 ‰ to -6 ‰ excepted for one thermal spring ($T \approx 30°C$) that has a $\delta^{13}C$ value of –12 ‰ (Fig. 1). Enriched $\delta^{13}C$ are probably influenced by degassing and hence linked to peri-Alpine tectonic activity in the basin.

Most of mineral springs have tritium activity ranging from < 1 to 3 TU. Among these springs two have a relative important tritium activity (5 to 6 TU), probably related to a variable proportion of surface water. ^{14}C activities were also measured on those mineral springs; the thermal one has a pMC equal to 38.2, whereas all the other waters have few content, ranging between 3.9 and 7.3 pMC (Fig. 2).

To access ^{14}C ages, we use on field observations and $\delta^{13}C$ results. They give us a range of 20.000 – 25.000 years BP, except the thermal one which is younger (< 8.000 years). Using Tamers' model and assuming a constant stock of atmospheric CO_2, no exchange between old and recent water (few tritium content), calculated age is near 2.500 years BP.

The mineral springs from low Tritium and ^{14}C activity have then experienced long-time residence in reservoir rocks. To approach a maximum temperature reached by these waters, we use silica and cation geothermometres. Studied mineral waters appear immature whereas thermal ones are partially equilibrated, considering Giggenbach's diagram (1988). Calculated temperature using silica thermometre (Quartz) gives from 55 to 75°C, Li-Mg: 130 to 220°C and Na-Li: 210 to 280°C, with low values for thermal waters. These last waters have ^{14}C age of 20.000 and 2.500 years B.P., for Na-Mg-K partially equilibrated waters at ca. 150°C in agreement with Li-Mg temperatures. These similar temperature for different residence-time correspond to different type of water-rock interaction in silico-clastic sedimentary rocks and fractured granitic basement.

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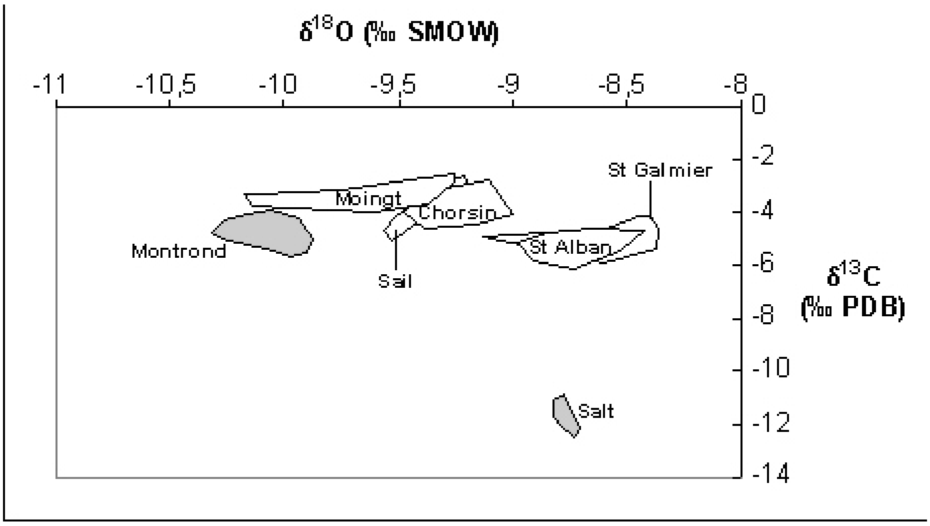

Fig. 1: C and O isotope ratios of CO_2-rich waters (white domain: water with gas) showingtwo groups: one ($\delta^{18}O$ > -9‰) including waters in granite domain, the other ($\delta^{18}O$ < -9‰) comprising waters flowing at the limits of the Forez sedimentary basin. Thermal waters are in grey.

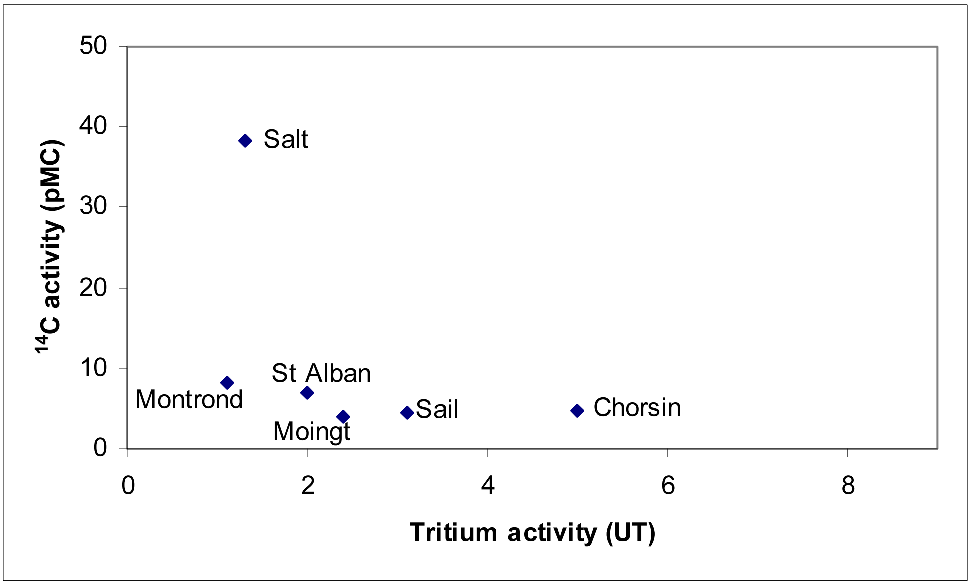

Fig. 2: ^{14}C (pMC) vs Tritium (UT) activities of mineral waters; low ^{14}C content give close residence time form 20.000 to 25.000 years: recent water influxes (see Tritium content) does not affect ^{14}C activity. In grey, Tritium activity of perennial shallow springs. Arrows indicate the limits of current Tritium content in rainfalls.

THE URANIUM DISEQUILIBRIUM OF GROUNDWATER AT GOBI DESERT IN THE ARID ALXA PLATEAU, INNER MONGOLIA, CHINA

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The dissimilarities in geochemistry of U and the complementary half-lifes of its radioisotope provide one of the most reliable dating methods for Quaternary materials. The method is based on measurements of the $^{234}U/^{238}U$ acitivity ratio in a smaple, which will be equal to 1 if secular equilibrium has been reached. The degree of disequilibrium provides a measure of time. Until recently, the $^{234}U/^{238}U$ activity was determined by α-spectrometry. Thermal ionization mass spectrometry (TIMS) now provides higher precision analyses with mg-size samples. The disequilibrium of uranium series of groundwaters within Alxa Plateau with annual mean precipitation of about 50 mm is used as a means of providing information related to the hydrogeological framework of its aquifer system. Sampling area including Gobi, dune desert and grassland covers approximately 60 000 km^2 since 1997.

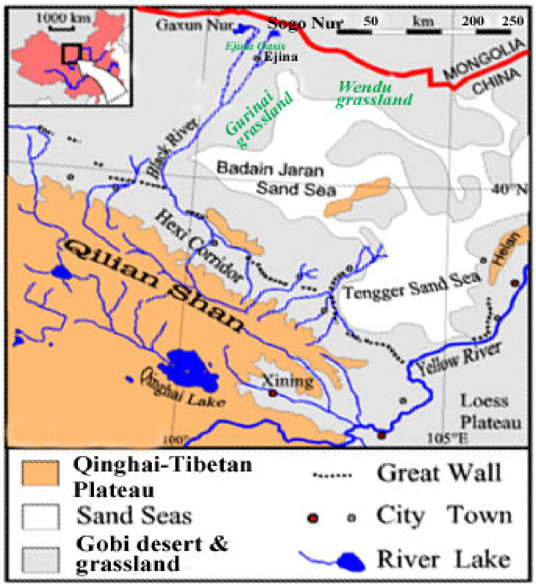

Fig. 1 Location of sampling sites, Alxa Plateau, Inner Mongolia (follow Prof. Steffen Mischke)

Variation of uranium content and the environment of groundwaters

The concentration of dissolved uranium (UC) in phreatic groundwater ranges from 0.65 µg/l to 37.5 µg/l while that in confined groundwater including springs ranges from 2.7 µg/l to 28.76 µg/l. The highest values are found from the phreatic groundwater in Badain Jaran Dune Desert. For the variation of activity ratio $^{234}U/^{238}U$ (or AR) which is a measure of the fractionation of ^{234}U from ^{238}U, different from the case of UC, both confined and phreatic groundwater hold a similar range from 0.96 to 2.92 of deep groundwater and 0.94 to 2.81of phreatic groundwater. For the inflow Black River water, UC ranges from 1.20 to 5.55 µg/l and AR from 0.58 to 1.22 according to the water stages.

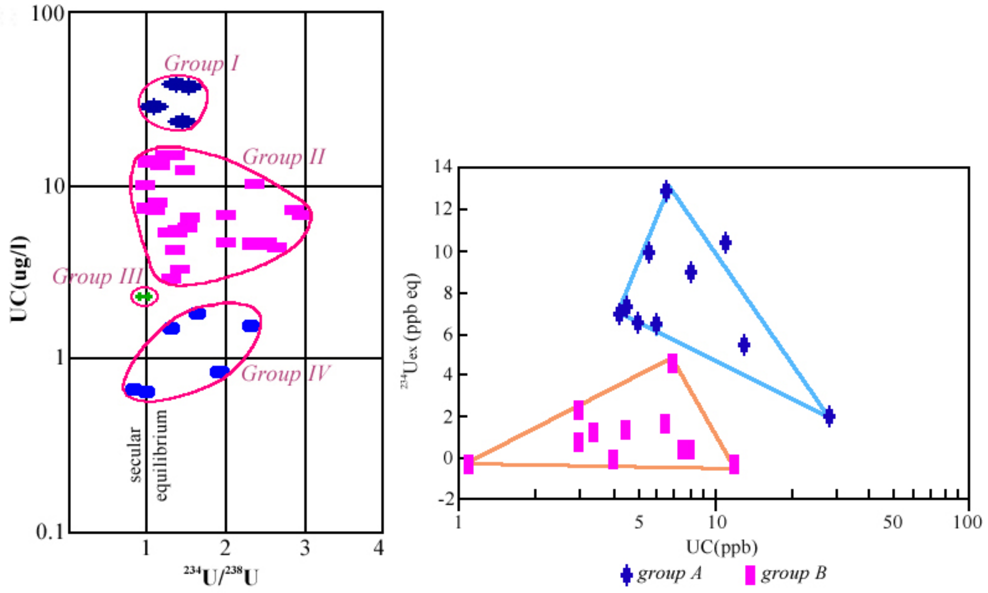

Fig. 2 The results of analyses in groundwater samples

The changing of the above isotopic characters is mainly due to the differing aquifer histories and its environment, the occurrence of isotopic re-equilibrium. It leads to the possibility for grouping the regional circulation patterns of groundwaters. Three circulation patterns from the UC versus AR relationship are grouped including (a) Group of active circulation and oxidizing-like environment characterized by high UC values more than 20 µg/l accompanied by lower AR values. It reveals an intense exchange with relative high transmissivity. (b) Group of weak circulation and reducing-like environment characterized by lowermost UC values less than 2 µg/l accompanied by a varied AR values. It reveals a stagnant-like environment. The low UC is due principally to the increasing insoluble quadrivalent ion of uranium in reducing-like environment. The relative high values of AR are due to the recoil transfer process. However, the mechanism of the lowermost AR of 0.94, which is lower than the secular equilibrium, is still not clear. (c) Group of moderate circulation characterized by mediocre UC of 2-20 µg/l with large variation of AR, nearly all the deep groundwater and spring water fall into this group. It reveals a mediocre mixing mechanism, the paleowater accepts with varying degrees the meteoric recharge water from its overlaying formations. For example, the palaeowater with ^{14}C age of about 10 000 BP and AR near to the secular equilibrium, but it holds a moderate UC of 7.29 µg/l.

Sources of groundwaters

A measure of the disequilibrium of uranium series i.e., the excess of ^{234}U, ^{234}Uex = (UC)(AR-1) is used. Three sources of confined groundwater are identified from the ^{234}Uex versus UC and pMC relationships. For that of the Gurinai grassland within Gobi desert covering an area of about 4500 km^2, they are: (a) The meteoric water originated from percolation of shallow groundwater; (b) The palaeowater with ^{14}C age of 9575±165 BP and TU less than 2.2 [1, 2] sourced from the Badain Jaran Dune Desert to the south of Gurinai and (c) Another kind of palaeowater with ^{14}C age of 12435±295 BP and TU < 2.1 sourced from the dune desert to the east. For that of the Ejin area, they are: (a) The recharge from the vast Gobi area situated to the east; (b) The palaeowater with ^{14}C age of 12000±270 BP, TU < 2.1 [1, 2, 3]; and (c) underground recharge from Gobi desert area of Mongolia situated to the north. Using mixing ratios[4], contributions of these source waters are evaluated quantitatively.

Local systems of phreatic groundwater are differentiated also from ^{234}Uex, together with water isotopes, the precipitation recharge and the leakage of palaeowater are identified as the main sources even another source originated from the percolation of Black River and Gobi area is deduced.

ACKNOWLEDGEMENTS

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ISOTOPIC HYDROGEOLOGY AS A TOOL TO DEFINE "GOOD STATUS" OF GROUNDWATER BODIES: EXAMPLE OF THE VALRÉAS MIOCENE AQUIFER (FRANCE)

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The European Water Framework Directive makes necessary to identify and define every groundwater system across European countries. The concept of groundwater body, according to the Water Framework Directive, imposes to estimate a "good status" of groundwater and thus encourages restoring this initial good status in places where strong deterioration is occurring. Isotopic techniques might be useful to define such pre-exploitation conditions and particularly in complex systems were paleowaters preserved in confined aquifers can provide pristine waters.

The Miocene aquifer of Valreas is located in Provence close to the Rhône valley. It consists of multilayered sandstones of approximatly 600m depth in the central part of the basin. The structure of the aquifer is complexe and the southern part of the system is confined under a marly Pliocene cover of around 100m depth. Recharge takes place in the northern part of the basin through the outcropping area of the Miocene sediments. The groundwater flow direction in the aquifer is from north-east towards south-west. The paleo-flow conditions in the aquifer were presumably controlled by the presence of the Pliocene cover, causing a rapid flow in the unconfined part of the aquifer compared to the confined part of the aquifer. At the boundary between the two systems, several springs were present. Since the 1950's, extensive abstraction of groundwater has been carried out from the confined part of the aquifer for irrigation purposes. As a result, the springs at the confined/unconfined boundary are now dry, and groundwater flow takes place at a more uniform velocity of around 2 m/yr in the entire aquifer.

More than 100 boreholes were sampled, and stable isotopes of water molecule (^{18}O, deuterium) as well as ^{13}C concentrations were measured on each sample. In addition, 25 boreholes located along the main flow line were sampled for radiocarbon dating in order to evaluate groundwater residence time and to precise groundwater velocity [3]. Major ions and trace elements concentrations were also investigated with a special interest in arsenic concentrations. These results have been used to set up a conceptual model of the functioning of the aquifer [1]. Some of the most interesting results are the evaluation of groundwater residence time which is clearly over 30,000 years, and the reconstruction of paleotemperatures prevailing during the recharge of waters at the end of the Pleistocene [2].

Owing to the large number of isotopic data available it has been possible to draw maps covering the whole area and showing the distribution of ^{18}O, deuterium and ^{13}C (FIG. 1 &

FIG. 2). These documents are useful and allow locating the recharge area with accuracy and thus potentially sensitive areas. It can also be used for the estimation of groundwater dynamic or to detect the intrusion of young waters under the Pliocene cover. These waters are particularly difficult to identify especially when they are deprived of any strong anthropogenic influence. In the case of the Valréas basin, stable isotopes and especially ^{13}C can be of major interest. The age of groundwater increases gradually from the recharge area towards the confined aquifer. Along the down gradient direction, the increasing in ^{13}C, related to matrix exchange reactions with carbonates, can be considered as a good qualitative age indicator. Thus a strong enrichment in ^{13}C will indicate the occurrence of old pristine waters in the aquifer. This can be easily realised and at low cost compared to radiocarbon. ^{18}O distribution maps were used to locate long residence time waters thanks to the strongly depleted signature of paleowaters. ^{18}O data were also used to precise the extension of the recharge area by comparison with modern precipitation content.

The chemical data obtained from paleowaters can be considered as the baseline concentrations of the aquifer and they will be used as a goal towards restoration of water quality especially in the unconfined Miocene aquifer. The methodology developed here might be applied in other cases, and would be of help towards achievement of good groundwater status.

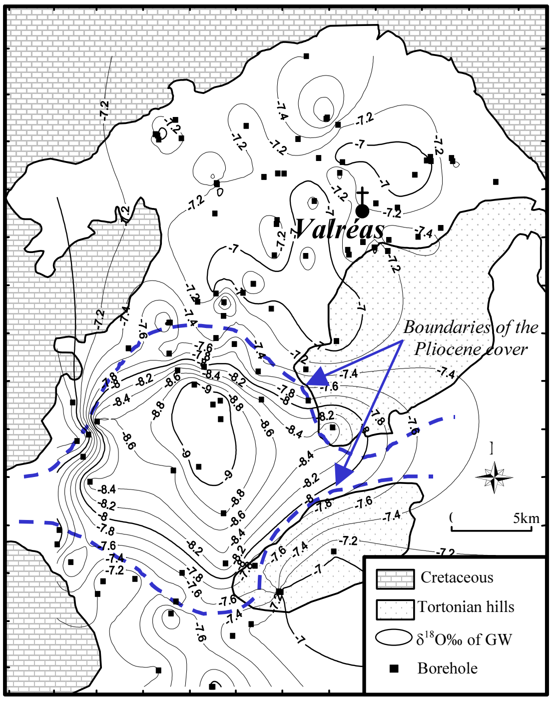

FIG. 1: Distribution of ^{18}O in the aquifer.

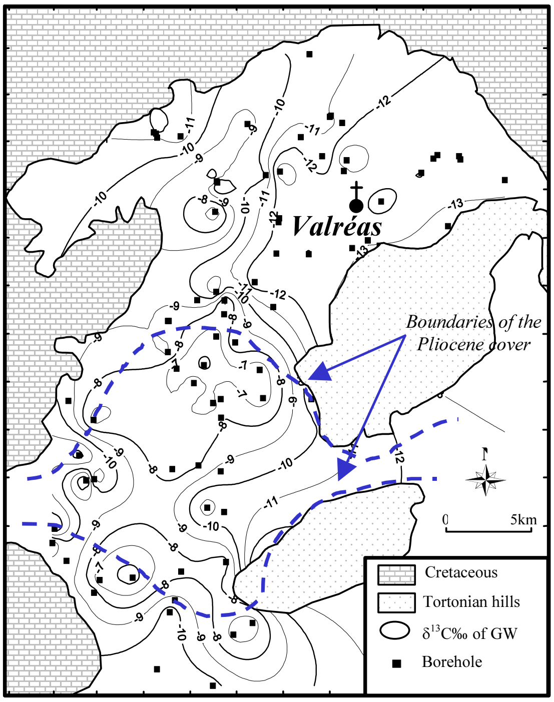

FIG. 2: Distribution of ^{13}C in the aquifer.

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HYDROCHEMISTRY AND ISOTOPE GEOCHEMISTRY AS MANAGEMENT TOOLS FOR GROUNDWATER RESOURCES IN MULTILAYER AQUIFERS: A STUDY CASE FROM THE PO PLAIN (LOMELLINA, SOUTH-WESTERN LOMBARDY, ITALY)

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The Po plain, located in Northern Italy, hosts a multi-layer alluvial aquifer of Quaternary age constituted by sands interbedded with clays. The plain supports most of the agricultural and industrial activities of Northern Italy, which are associated with groundwater pollution in the shallower portions of the aquifer. The increasing demand of water for industrial and domestic use has led to the exploitation of deeper layers of the aquifer, without a rational management of the resource. Only in the last decade, the government agencies have started a global evaluation of the quality standards of pumped groundwater, urged by the increasing need for clean water for domestic use. The task is particularly difficult because of missing or approximate well logs and the presence of multi-filter wells tapping in different aquifers. In this case the chemical and isotopic characterisation of groundwaters is the only reliable tool to reconstruct the geometry, the interconnections and the characteristics of the aquifers.

This study, promoted by the local agency for groundwater management and protection (Amministrazione Provinciale di Pavia, settore tutela e valorizzazione ambientale - U.O.C. Acqua) focused on a limited portion of the Po plain, the Lomellina region, of approximately 900 km^2. The region is bound to the South by the Po river, to the East and West by the Sesia and the Ticino rivers respectively, and to the North by the administrative boundary. The study aimed at the hydrogeological, hydrochemical and isotopic characterisation of the aquifers, allowing to serve as basis for the correct management of the groundwater resource.

A preliminary reconstruction of the hydrogeological asset of the Lomellina plain was performed through the analysis of the stratigraphic data from 102 municipal wells. On this basis, a shallow phreatic aquifer, reaching depths of about 50-60 m from the surface, and two groups of aquifers containing confined groundwater, were distinguished. All data were georeferenced and integrated in a GIS database. Subsequently, 40 wells and natural outflows were selected for the hydrochemical and isotopic characterisation. The selection was performed in order to cover homogeneously the studied region both in terms of extension and depth. Analyses included major ions, trace elements, pesticides, stable isotopes of the water molecule, ^{13}C and ^{14}C of dissolved inorganic carbon. Shallow waters containing high levels of nitrates were considered for the isotopic analysis of ^{15}N and ^{18}O of NO_3^-.

Hydrochemical analyses defined the hydochemical facies as calcium-bicarbonate. Groundwaters generally show a decreasing conductivity and mineralisation with depth. The phreatic aquifer displays evidence for groundwater pollution from agricultural activities, namely high nitrate, sulphate and chloride contents and, locally, detectable levels of pesticides. Deep confined aquifers contain groundwater of excellent quality standards. Activity diagrams clearly allow the distinction between the phreatic aquifer and the confined aquifers, which display a higher degree of interaction with the aquifer matrix.

Stable isotopes of the water molecule are in agreement with the results form adjacent sectors of the Po plain (Pilla, 1998), evidencing the lateral continuity of the aquifers. The phreatic aquifer and the different confined aquifers may be distinguished on the basis of their isotopic composition, which also allowed to verify their hydraulic confinement of deeper aquifers. Intermediate aquifers are in part recharged by the shallow phreatic aquifer, which in turn is fed by local infiltration and by streams and irrigation channels.

The isotopic analysis of nitrates of 10 waters samples from outflows and shallow wells confirms the agricultural origin of contaminants in the phreatic aquifer. The isotopic signature is typical for the nitrification of synthetic fertilisers (Clark and Fritz, 1997). A correlation of the isotopic composition with nitrate concentrations (and consequently with depth) is also observed.

Carbon-14 activities and ^{13}C data for DIC indicate a possible input of dead CO_2 coming from the decomposition of the organic matter at depth, affecting the age corrections and precluding a precise dating. This is particularly observed for deep aquifers and is in agreement with what evidenced in similar hydrogeological situations in the Po plain (Zuppi and Sacchi, 2002). Nevertheless, ^{14}C indicates long residence times for deep waters, in the order of thousands of years. This information, coupled with the high quality standards of groundwater raises some concern about their exploitation for use other than domestic.

All hydrochemical and isotopic data, included in a georeferenced GIS database, provide the local administration with a powerful management tool for monitoring groundwater quality, enforce better agricultural practices, implement remedial actions for local pollution problems and plan a rational development of the groundwater exploitation.

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ISOTOPES HYDROLOGY OF SIMBRUINI MOUNTAINS (CENTRAL APENNINES, ITALY)

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The combined study of oxygen and hydrogen isotopes in karst groundwater is an excellent tool for exploring hydrological fluxes and meteorological variabilities at a regional scale. The interest for the hydrological and isotopic studies in the carbonatic Apennines (Central Italy) is explained by the large exploitation of the aquifers for several different purposes (civil, agricultural and industrial).

Limestones and dolostones of Mesozoic age form the axis of the peninsula in Central Italy. The carbonates are and fractured and karstified and provide good conditions for infiltration. It has been shown (Boni and Bono, 1982; Boni et al., 1986) that the structural geology of the area is complex and that discontinuities at regional scale are abundant. Preferential deep circulations are linked to those structural systems. Because of the tectonic features one can assume that water circulation in depth is rather slow, and the signals of natural tracer are smoothed.

The objectives of the study are: (1) to identify recharge zones and flow patterns, calculate recharge rates or mixing ratios, and to discern hydraulic connections between aquifers; (2) to characterize the hydrogeochemical features of the karst groundwater system as a typical case in central Italy; and (3) to show the effectiveness of geochemical analysis techniques to extract hydrological information from hydrogeochemical data. As a major diagnostic tool in groundwater hydrology, hydrogeochemical data have been used to identify recharge zones and flow patterns, calculate recharge rates or mixing ratios, and to discern hydraulic connections between aquifers.

Water chemistry and isotopes in springs have been used extensively to study aquifers, based on samples and data collected from 10 rain gauges on a transect West – East from the Tyrrhenian Sea and 10 springs. Typically, studies have focused on either: long-term rainfall data collected at biweekly or monthly intervals or higher resolution analysis of single storm events. Analysis of $\delta^{18}O$ in spring waters has yielded, indirectly, information about groundwater residence times.

In the Italian peninsula, rainfall and groundwater samples show differences in their isotopic composition. These differences are related to the contrast existing between water vapour of Atlantic origin and water vapour of south-western Mediterranean origin and indicate a strong correlation between isotope contents and altitude. However, the complexity of the hydrologic situation cannot be appraised by the study of single event, since the isotopic records from the Italian meteorological stations, and the literature review by Celle et al., (2000) suggest the continuous change of the influence of the Mediterranean and Atlantic Ocean on isotopic composition of the rainfall.

The determination of recharge altitudes can be estimated both through the use of the isotopic content of infiltrated water, and the isotope composition of shallow groundwater. In fact, the latter must be representative of the mean local composition of the present-day precipitation.

The data from the Simbruini Mountains and those of the local GNIP stations give a ^{18}O-altitude gradient close to – 0.0020.The good correlation of ^{18}O with altitude ($r^2 = 0.98$) shows that an orographic effect is present whatever is the origin of air masses.

As previously mentioned, the groundwater isotopic composition indicates that precipitation reflects the origin of air masses participating to the aquifer recharges on the Apennines and the mean elevation of infiltration areas. This can be questioned, since only a single rain event is used to characterise the isotopic signature of the precipitation in an area, which is known for the occurrence of precipitation of both Mediterranean and Atlantic influences. Isotopic studies on rainfall in the central and western Mediterranean basin, and the relative proportion of south-west and north-west precipitation has been determined in several stations and state that precipitation are typically aligned in a ^{2}H–^{18}O diagram on a local meteoric water line with a deuterium excess varying between +12 and + 14.5 (Chery, 1988; Panichi et al., 1992; Celle et al., 2000). The distinct isotopic signature of precipitation with a Mediterranean origin has been used, already, in hydrological studies in the Central Apennines (Zuppi and Bortolami, 1982; Governa et al.,1989). However, these studies do not address the spatial variation in isotopic signature inside a large aquifer system, for which source and age interpretations are known to be difficult.

The differences related to the contrast existing between water vapour origins are reflected in shallow groundwater characterised by a fast circulation. On the contrary the signal homogenisation is dominant in deep groundwater. Firm conclusions on the causes of this pattern are drawn at this stage, because the isotopic signatures of rainfall events are extreme and in agreement with the air masses movement above Mediterranean regions. The fact that groundwater has very different oxygen-18 values means that circulations are short and fast and seasonal signals could be maintained. In such a case, the isotopic content can provide also a useful tool for analysing in detail the characteristics of the recharge.

Accurate dating of deep groundwater is not possible due to the lack of a long-term record of the tritium transient in this area, as well as the slow change in tritium concentrations over the precipitations in the past years. Moreover the measured tritium concentrations in groundwater are affected by hydrodynamic dispersion and mixing of different age waters over the length of the screened sampling interval. However, the tritium concentrations appear to be compatible with the estimates of high recharge rates and high transmissivity of the Mesozoic aquifer in the study area.

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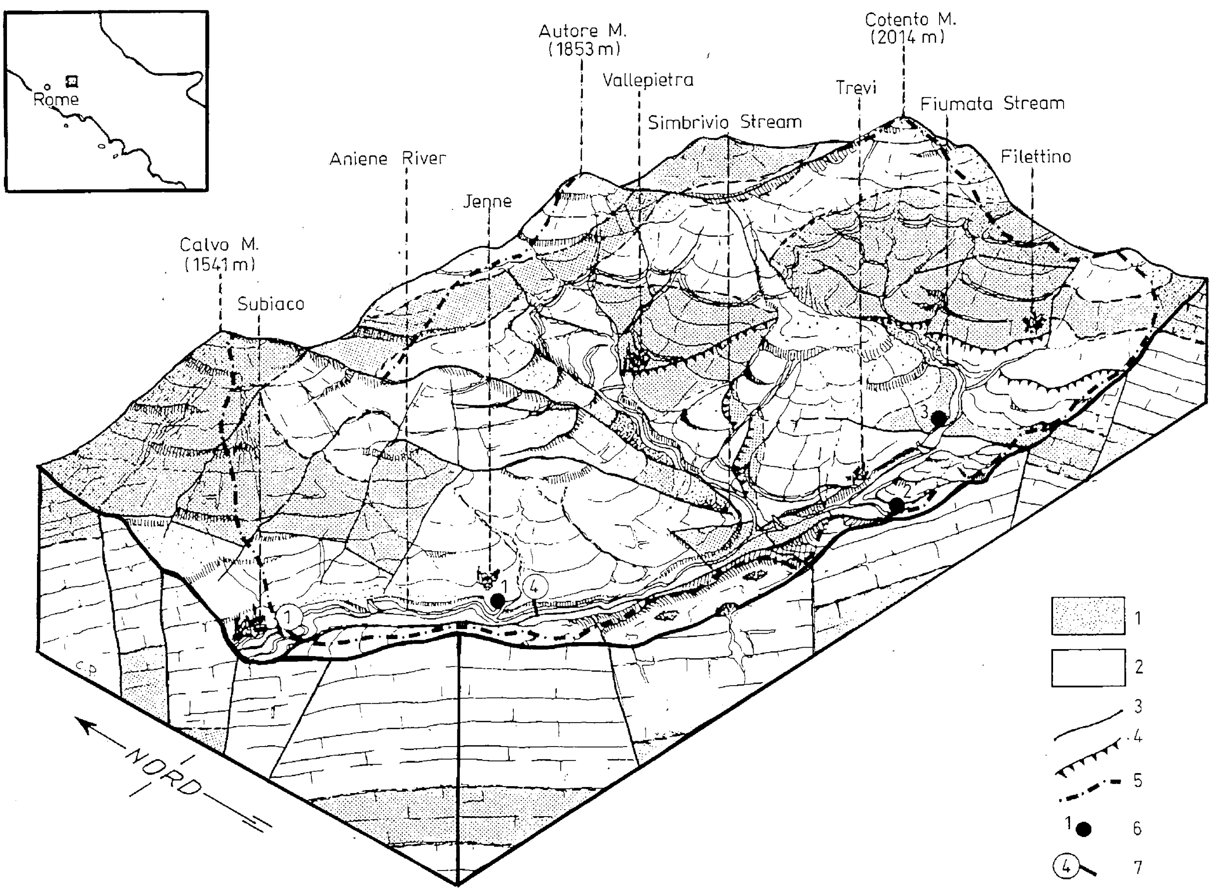

FIG. 1 – Mounts Simbruini karstic range: Schematic geological and hydrological setting. 1, Undifferentiated dolomitic complex (Upper Triassic; Lower Cretaceous); 2, Undifferentiated limestone complex (Jurassic; Upper Cretaceous; Lower Miocene); 3, Fault; 4, Overthrust; 5, Watershed area; 6, Major permanent karst springs (1:. Inferniglio, 2: La Foce, 3: Pertuso); 7, Flow gauging station and monitoring reference point of chemico-physical parameters. (From Bono P. and Percopo C., 1996)

DEUTERIUM AS REFERENCE IN A MULTITRACING EXPERIMENT IN A KARST SYSTEM – A COMPARATIVE STUDY

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Deuterium was used as a reference tracer for a multitracer experiment in a karst cave system in the Central Styrian Karst, Austria. As tracers two fluorescent dyes (Na-Fluorescein and Sulphorhodamine G), one inorganic salt tracer (Sodium Bromide) and one isotopic tracer (Deuterium) were used in a comparative study.

The karst cave system which is situated in paleozoic limestone allows access to open underground galleries with active channel flow, and therefore offers a good opportunity to control the boundary conditions during injection, such as the flow conditions during the experiment and the specific details of channel topology.

The objective was to compare different types of tracers, their behaviour during transport and the degree to be classified as conservative or non-conservative. The tracer transport in the underground channel was monitored with different systems, but also water samples were collected by automatic samplers for later laboratory analysis. Fluorescent dye tracers were measured online with a 2-channel fiber optic fluorometer with built-in data-logger and the sodium bromide tracer was measured for Bromide with a Br-selective electrode. To have parallel sample records the collected water samples were analyzed quantitatively with a laboratory scanning-fluorometer for the dye tracers, separately for Sodium and Bromide by ion-chromatography and for Deuterium by mass spectrometry.

In addition to the tracers of interest flow conditions (water level with a pressure probe) and physical parameters (electrical conductivity and water temperature) were monitored. The latter as well as the Bromide data were recorded with data-loggers.

The achieved breakthrough-curves of individual tracers were compared to each other and analyzed for shape and characteristic time-marks (e.g. first appearance, peak and center-of-gravity), for retardation and mutual cross-over effects.

The result was, that Deuterium and Bromide showed the highest degree of conservativeness. Na-Fluorescein and moreover Sulphorhodamine G showed retardation compared with Deuterium and Bromide. A direct comparison was difficult due to the different sensitivity of the analytical procedures, because sensitivity of dye tracer analytics as well as Bromide and Deuterium analytics differ from each other over several order of magnitudes.

ISOTOPE HYDROLOGY OF THE MULTI LAYER AQUIFER IN N.E. BUENOS AIRES PROVINCE, ARGENTINA

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The study area is located in populated areas of the coastal plain of the Rio de la Plata between Buenos Aires and La Plata (figure 1). Water supply of the region is done both by groundwater and by Rio de la Plata treated water. Suburban areas are mainly served by groundwater pumped from the Puelche, regional semi-confined aquifer, although domestic wells exploit the Pampeano free aquifer, containing the phreatic layer. On the contrary Buenos Aires metropolitan area is served by river water.

The coastal plain is characterized by elevations ranging from 0 to 5 metres above sea level and by a width of 1.5 to 7 km. This is an area where small differences in elevation (0.15 – 0.30 m) lead to the development of marshes that catch the rain and runoff from the high areas. Moreover, under certain metheorological conditionss (atlantic storm “Sudestada”), with strong wind blowing form SE, generally accompanied by heavy rains, the plain is partially flooded by the Rio de la Plata.

In the coastal plain, groundwater from the phreatic and Puelche aquifers is brackish due to a marine transgression occurred at *ca.* 9000 years BP. ^{2}H and ^{18}O contents of surface water and from both aquifers present distinctive characteristics. River water is isotopically enriched with respect to ground water (although seasonal variations does exist, Panarello and Dapeña, 2001), whereas tritium contents in the river water are significantly high because of the upstream existence of a nuclear power station.

The saline / fresh water interface is well known and described for the inland environment by several authors (Hernandez, 1978, EASNE, 1972, Panarello *et. al* 1994). The aim of this work is to investigate the (brackish) groundwater / (fresh) river water interface in the coastal zone, in the Puelche and Post Pampeano/Pampeano hydrogeological units by using environmental isotopes, geochemical analysis and geophysical techniques.

RESULTS

Geophysical survey VES-1, and VES-2 show an increase of resistivity corresponding to the Puelche aquifer. The first profile, performed on the sand bar, shows high values in the upper part of the curve (Post-Pampeano unit), whereas the second profile suggests a lateral migration (landward) of the interface. 1-D interpretation model suggest a four layer arrangement

Tritium concentrations indicate that the Puelche aquifer is partially recharged from the Rio de la Plata. In fact, tritium content of qpc-3 well is 14.3 TU, and at the same time Cl^- concentration is very low.

Within the Post-Pampeano aquifer, groundwater stratification exists. Water from qpc-2 and hpc-3 wells and water pumped in the upper levels of the aquifer show higher tritium contents than water from hpc-2 and qpc-5 and that collected at the deepest levels. In other words, the Post-Pampeano aquifer receives an active recharge, at least, in the upper part.

The geochemistry confirms the stratification within the Post-Pampeano unit (table 1).

CONCLUSIONS:

In the sand bar level, the hydraulic conductivity is higher than in other zones of the coastal plain, as result of its sedimentological characteristics.

Surface water level increase due to tide and metheorological events, favours an active recharge of the phreatic aquifer from the river (bank storage phenomena), as indicated by changes in hydraulic head and, sometimes, temporary inversion of the hydraulic gradients.

The result is a dynamic stratification of groundwater with an upper zone of the aquifer containing less mineralized young groundwater grading to brackish old water from the marine transgression, through a thick interface where diffusion and hydrodynamic dispersion occurs.

In the Puelche aquifer the influences of tidal movements should be presents; but they are negligible considering the groundwater exploitation occuring in land. Permanent inversion of the landward hydraulic gradients (originally coastward) generates recharge from the river that acts as a “positive” barrier, and a lateral migration of the interface.

Besides, the Puelche aquifer receives active recharge from the river, with water circulating within sediments containing levels of organic matter that turns redox potential to negative values.

well name	hpc-2	hpc-3	qpc-2	qpc-3	qpc-5	rq-1	rh-1
well depth (m)	10	2.9	8	25	15	river	river
Aquifer	Phreatic	Phreatic	Phreatic	Puelche	Phreatic		
λ(μS/cm)	4100	141	1850	1400	10300	290	500
Cl (ppm)	974.26	5.1	124.84	83.4	4276.4	59	38
Tritium (TU*)	4.2	9.3	7.4	14.3	0.0	25.9	38.0

* Table 1

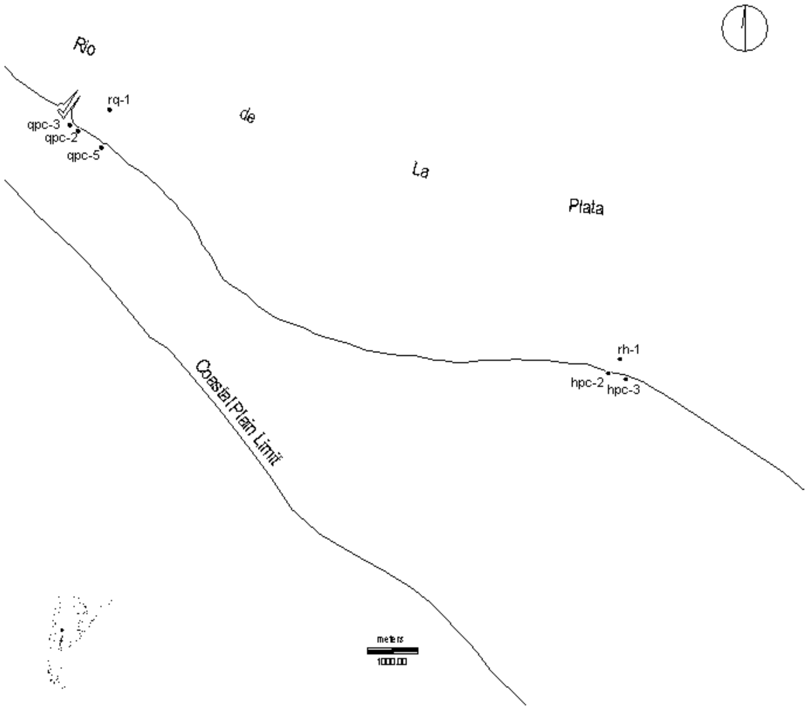

Fig.1

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CAVE LEVELS, SAFE YIELD AND TURNOVER TIME IN KARST AQUIFERS

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The presence of cave levels where ground water flow is organized is a typical feature of karstic carbonate aquifers. These cave levels are high conductive paths within a capacitive matrix that differentiates flow velocities, transit times and therefore, the chemical and isotopic composition of groundwater. These two extreme transmissive end points allowed the application of double porosity models to solve flow and transport equations although actually karst aquifers are multiple-porosity systems where flow is rigorously hierarchised.

The application of environmental stable and radioactive isotopic models to several Cuban karstic aquifers have shown a well defined stratification of flow varying from three months to 100 years. These so large transit times for ^3H suggest that - isotopically - the system is far from steady state conditions and, therefore, the exploitation of the aquifers horizons is strongly restricted by these low renewable resources. While associated with well defined cave systems, transit time of groundwater in karst aquifers is a variable to be considered in the estimation of safe yield and in the engineering measures, as artificial recharge, designed for improve the sustainability of water resources. Depletion of water resources in karst aquifers of the humid tropics could be associated to the exploitation of isotopic “old” waters not linked with the present hydrologic cycle.

CAT: AN INTEGRATED GEOLOGICAL, GEOPHYSICAL, GEOCHEMICAL AND ISOTOPE HYDROLOGICAL APPROACH TO STUDY THE MARINE–GROUND WATER INTERACTION

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The Coastal Aquifer Test Field (CAT) is situated in northern Germany between the Elbe and Weser estuaries. Here the Leibniz Institute for Applied Geosciences (GGA) and its research partners study the interaction between ground water and seawater in a geologically complex and anthropogenically influenced environment.

The site extends 50 km. in the N-S and 30 km. in the E-W direction. The geology is dominated by quaternary glacial and periglacial deposits of till, silt, gravel and sand. Topography is generally flat, reaching 40 m. above MSL where coarse glacial material is found at the surface, called “Geest”. Postglacial fine clastic tidal flat, lagoonal and peat deposits are found in very flat areas, few meters above and below sea level, called “Marsch”. Outside the dikes recent fine clasic tidal flat sediments are deposited by the North Sea.

On the Geest ridge ground water infiltrates and flows towards the Marsch areas which are drained by artificial ditches and towards the tidal flats. The seawater-freshwater interface is found close to the surface in the Marsch, sometimes off shore in the tidal flats and reaches deeper than 100m in the recharge regions of the Geest. The drinking water supply of the cities Bremerhaven and Cuxhaven and several smaller communities are based on the deep fresh ground water resources beneath the Geest.

Two helicopter borne surveys were conducted during the years 2000 and 2001. Frequency domain electromagnetic data were inverted to electrical resistivities. The data identified the saltwater-freshwater interface and gave a three-dimensional insight into the geology. The lateral extent of a freshwater lense in the tidal flats of the North Sea was mapped for the first time. This survey was ground truthed with vertical electrical soundings, seismic transects and samples. It constrained the positions and hydraulic properties of glacial channels created during the quaternary by the "Elster" and later glaciations. Several exploration boreholes were drilled and various geological, geophysical and hydraulic tests were applied at these boreholes. Sediment samples for geochemical investigations were taken and five multilevel wells were installed, some of them at the saltwater freshwater interface.

The talk concentrates on the isotope hydrological investigations using D, ^{18}O, Tritium, ^{3}He, CFCs, SF_6, ^{85}Kr, ^{39}Ar, ^{13}C, ^{14}C and ^{4}He on a total of more than 170 samples. Age-depth profiles in the ground water from $T/^{3}He$ and ^{85}Kr quantify the magnitude of ground water recharge in the infiltration areas. CFCs and SF_6 only allow age estimates, due to contamination from industrial areas and a military airport, and due to anaerobic degradation in the marshes. Tritium in the fresh water springs of the tidal flats shows a fast component of ground water outflow towards the North Sea. ^{13}C and ^{14}C analysis in ground waters dated by $T/^{3}He$ and ^{85}Kr gives new insight into the geochemical and isotopic evolution of the total dissolved inorganic carbon (TDIC). In this complex geochemical system with timescales for ground water flow in the order of several centuries to a few millennia the weakness of radiocarbon ground water dating becomes evident. It was tried to address this problem by the use of ^{4}He and ^{39}Ar.

A future goal of the studies is the development of a three dimensional numerical model for the entire ground water system, simulating coupled density dependent ground water flow and transport. The model will be calibrated by geophysical and isotope hydrological methods. For the vicinity of the city of Bremerhaven in the southern part of the study area, such a model is in the calibration process.

STUDY OF ^{2}H AND ^{18}O IN THE KOURIS CATCHMENT (CYPRUS) FOR THE DESCRIPTION OF THE REGIONAL GROUNDWATER BALANCE

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The Kouris catchment covers 300 km^2 on the southern side of the Troodos Massif of Cyprus and bounded on the South by the Mediterranean Sea. Elevations range from 2000 m to sea level within a distance of 30 km. The basin consists of an ophiolitic complex in the North (ultramafic rocks, gabbros, sheeted dykes and pillow lavas) and an overlying sedimentary complex in the South (chalks, marls, calcarenites and limestones). The ophiolites highly heterogeneous and contain the major groundwater resources in Cyprus.

While the geology of the Troodos Massif is very well documented, the hydrogeology of the area is much less known. The aim of this study is to apply 144 new and 72 published analysis of δD and δ^{18}O in groundwater as well as as new and reported in IAEA database analysis of rainfall samples for better understanding of main mechanisms of ground water flow and for checking the assumptions of the groundwater model, developed at the previous stage.

^{2}H AND ^{18}O IN PRECIPITATION

^{2}H and ^{18}O contents in rainfall over the Kouris catchment samples are linearly related by the equation of the local regression line:

$$\delta D = 6.5*\delta 18 + 10.6$$

that differs from the equation of the Global Meteoric Water Line and indicates partial evaporation of rain drops prior to infiltration. Seasonal variations were 36‰ for δD and 5.5‰ for δ^{18}O in 2000/2001. Averaged monthly mixed rainfall samples for October-February 2000/2001 at the two meteostations and some data from springs at the highest altitudes suggest the regression equation for δD(‰) and the altitude (m):

$\delta D = -0.012H(m) – 24{,}86$ (1), where H(m) – the altitude of the rainfall

^{2}H AND ^{18}O IN GROUNDWATER

Almost all points at the ^{2}H versus ^{18}O diagram (except some in the ophiolites) are displaced from the local meteoric water line due to evaporation. Samples taken from the sedimentary rocks seem to be more affected by evaporation than those in ophiolites. Seasonal changes due to evaporation in ground water over the whole catchment are clearly illustrated by the stable isotopes contents.

In order to analyze the stable isotopes altitude effect in the aquifer, we eliminated samples with the clear evidence of evaporation; 108 remaining samples were used for further analysis. For every sample of groundwater the altitude of the rainfall was calculated as a function of δD (Eq.1). Fig. 1 shows the scatter diagram between altitudes of sampling points, obtained from the Digital Elevation Model and altitudes of the recharge areas, calculated from the ^{2}H content. Three groups of groundwater can be clearly distinguished: sedimentary complex, ophiolitic complex and alluvial aquifer. Sedimentary and ophiolitic complexes seem to contain the groundwater from the local recharges at the low and high altitudes respectively, although uncertainty due to evaporation effect might be high, especially at the low altitudes. On the contrary, alluvium complex in the lower part of the catchment contains water from considerably higher altitudes, than the altitudes of the sampling points.

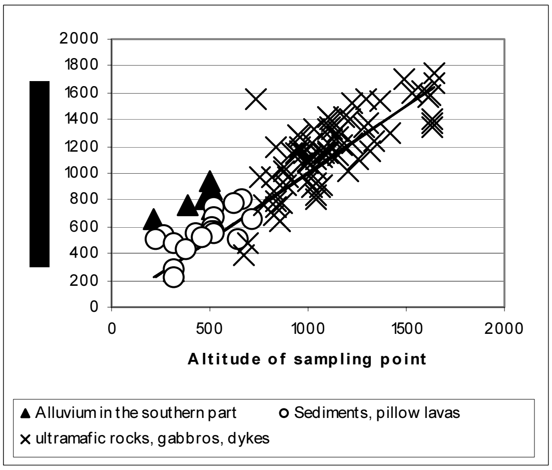

FIG.1. Scatter diagram between altitudes of sampling points and altitudes of their recharge areas; crosses – ophiolitic aquifer, triangles – sedimentary aquifer, circles – alluvium aquifer

The analysis proved the result of the groundwater model, carried out at the previous stage, that only negligible amount of water flows from the ophiolites to the sediments. Additionally the δD data were input in the model for the calibration of the recharge rates. The model calibration only by piezometric heads resulted in several reasonable variants with different input recharges. Using stable isotopes for calibration allowed to choose the optimal variant with the recharge rate 90-130 mm per year (Fig. 2).

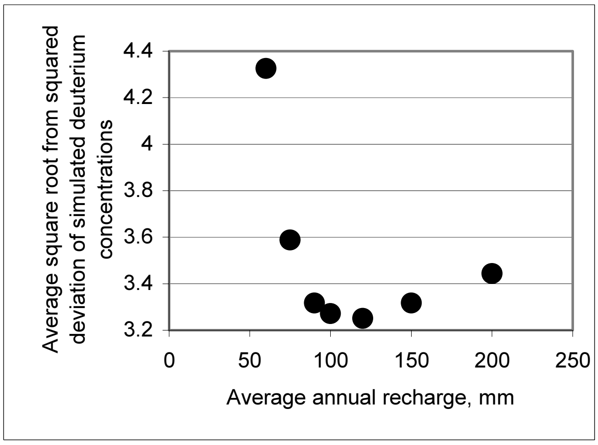

FIG.2. Average deviations between observed and simulated deuterium concentrations, plotted against the annual recharge for 7 simulation variants

USE OF ENVIRONMENTAL ISOTOPES TO CHARACTERIZE THE GROUNDWATERS FROM TERTIARY AQUIFERS OF KUTTANAD, KERALA, INDIA

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Kuttanad area commonly known as the 'rice bowl' of Kerala is of importance as it contributes to the majority of rice production of the state. Even though more than 75% of the area is covered by surface waters and wetlands, groundwater is the only source of potable water supply to the nearby Alleppey town and the rural areas of Kuttanad because of contamination and inherent water quality problems in surface waters. Due to large-scale exploitation of groundwater resources for almost five decades, it is important to understand the sustainability of aquifers in this area in view of the increasing demand for domestic and irrigation requirements. Since the hydraulic gradient is mild and owing to the lowering of piezometric heads over the years, seawater ingression and deterioration of water quality in some parts of this coastal aquifer is apprehended. More over, the impact of agricultural pollution by the excessive use of fertilizers and pesticides need to be dealt with for the protection and mitigation of pollution in aquifers.

As a pre-requisite to address the above problems, a systematic environmental isotope (δD, $\delta^{18}O$, ^{3}H ^{13}C and ^{14}C) study is carried out to understand the flow pattern, source & process of replenishment and possible hydraulic interconnection between aquifers and surface waters of this region. From the hydrogeological settings, it is seen that Kuttanad is a multi-aquifer system of formations of Eocene to Recent age. Quarternary Alluvium and Laterite form the top phreatic aquifer and is underlain by Tertiary sediments that are under confined condition. Archaean crystalline rock forms the basement and is exposed at the eastern periphery of the area. There are four distinct groups of formations in Tertiary sediments namely, Warkali bed, Quilon bed, Vaikom bed and Alleppey bed of which Vaikom and Warkali are potential aquifers [1]. Pre-monsoon (May, 2000) and post-monsoon (November 2000) samples were collected from tube wells tapping different aquifers, surface waters like tributaries of Pamba River and Vembanad Lake for the analysis of environmental isotopes and hydrochemistry. Precipitation samples were collected from two stations namely Alleppey and Kottayam. Field parameters like temperature, pH, EC, dissolved oxygen etc.were measured in-situ.

Analyses show that the water quality of Alluvial aquifer is fresh (chloride <100 mg/L) where as that of Warkali varies from fresh to slightly brackish (chloride 10-400 mg/L) and Vaikom aquifer is fresh in the southern parts and brackish (chloride ~1200 mg/L) in the northern parts. Hydrochemical data shows that waters from alluvial aquifers are basically fresh Ca-Mg-HCO_3 type. These waters are chemically quite distinct from tertiary waters. Within Warkali bed itself, there is a variation in chemical species of water. Ca-Mg-HCO_3 type occurs in the southern part of this aquifer. The water type changes to Na-Cl-HCO_3 in the central region. This probably indicates that as recharging water moves from south towards northwest direction, it gets mineralised. Water samples from Vaikom and Quilon beds are in general, Na-Cl type. Trends in piper diagram show that subsequent increment of Na^+ in waters of Warkali to Quilon bed is caused by cation exchange.

The δD - $\delta^{18}O$ relationships of groundwaters is shown in Figure 1. Most of the shallow and deep groundwater samples fall on or close to the GMWL indicating that these waters are of meteoric origin and are not affected by secondary isotope effects such as evaporation etc. Stable isotope composition of Alluvial aquifer is slightly depleted compared to deep tertiary aquifers. Tritium content of groundwaters from Alluvial aquifer varies from 3-4 TU, which is similar to the present day precipitation values indicating modern recharge. The seasonal variation of stable isotope content in precipitation is well preserved in groundwaters of this aquifer. In δD - $\delta^{18}O$ plot, most of the samples from alluvial aquifer and Warkali aquifer forms distinct clusters showing that these two aquifers are not interconnected while samples from Vaikom and Warkali forms a single group indicating that they are interconnected at few places through Quilon beds which is a Limestone aquifer. Tertiary aquifers like Warkali, Quilon and Vaikom beds contain negligible tritium and their ^{14}C values are in the range of 56 to 1.6 pMC, 2.4 pMC and <1 pMC respectively. This indicates that these waters are very old. Progressive increase in ^{14}C age is observed along the flow paths in Warkali aquifer. $\delta^{13}C$ of deep groundwaters are in the range of –10‰ to -15‰ and the depleted $\delta^{13}C$ values could be due to oxidation of organic matter within the aquifer matrix.

From the study it is concluded that the presence of thick clay beds below the Lake and the wetlands prevents the infiltration of polluted water to the groundwater. Hence contamination of shallow aquifer is remote. Since there is no hydraulic connection between the shallow and deep groundwaters, the tertiary aquifers are devoid of vertical recharge. Hence, owing to the lowering of piezometric levels and deterioration of water quality in paleowaters of this tertiary aquifers, further exploition of groundwater should be done carefully.

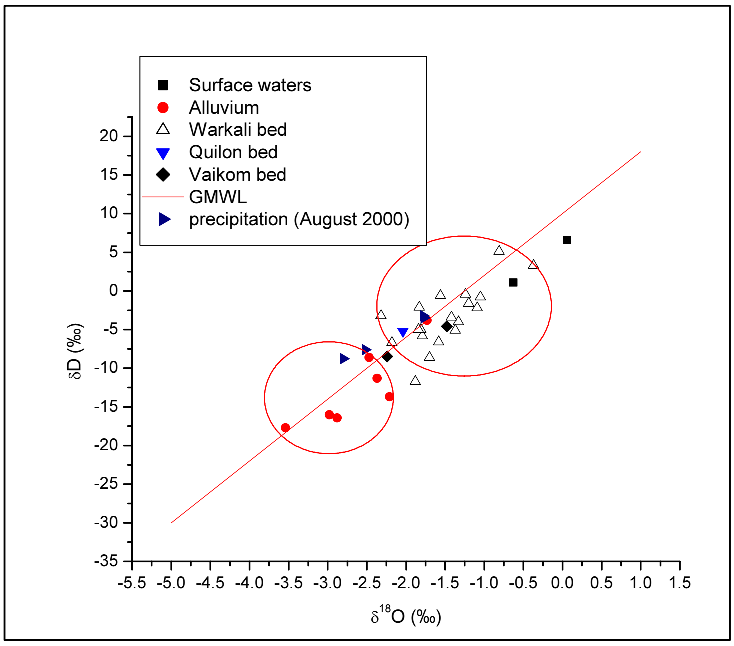

FIG 1. δD - $\delta^{18}O$ relationships in groundwaters of Kuttanad (May 2000)

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HYDROGEOLOGICAL FRAMEWORK OF THE NORTHERN DRÂA-CATCHMENT, MOROCCO: RESULTS OF LOCAL AND REGIONAL SCALE INVESTIGATIONS

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In the framework of the BMBF (Federal Ministry of Education and Research) project "Global change of the water cycle", IMPETUS West Africa focuses on water as a scarce resource. IMPETUS is an interdisciplinary and application-orientated approach from a research group of the universities Bonn and Cologne. As one of the investigation areas the Drâa-Catchment in Morocco has been selected.

Within the overall goal of IMPETUS: "An integrated approach to the efficient management of scarce water resources" groundwater is of significant importance. In order to develop a conceptional hydrogeological model of the Drâa-Catchment different scale approaches have been applied. Together with other disciplines investigations have been carried out in local test sites representative for geological and hydrological catchment areas and situated along a gradient of aridity and elevation. Based on natural labeling combined with classical hydrogeological and hydrological investigations for those testsites storage and discharge behavior of the various geological units have been defined. Besides local scale (*IMPETUS test sites)* regional scale approach was selected to understand the hydrogeological framework.

The purpose of *local scale* investigation is to define the hydrogeological characteristics of each IMPETUS's test site commonly selected as a representative for the specific geological areas of the Drâa catchment. In a further step this side specific information will be applied to a hydrogeological regional scale model. Basic requirements for a reliable hydrogeologic characterization are information on the geological structure as well as on the groundwater quantity/quality including hydrodynamics. Based on detailed geological mapping in the framework of master thesis geological and structural maps (1:25000), geological profiles and lithological description are available for four testsites. Accompanied by chemical and environmental isotope measurements, carried out during base (autumn 2000, 2001) and high water flow conditions (spring 2001, 2002) the investigations allow a preliminary hydrogeological classification of the groundwater types in respect to their geogene mould, their seasonal variations and the origin of the water. More chemical and environmental isotope measurements are on the way to testify the classification.

As an intermediary step in upscaling, hydrogeological investigations will focus on one important catchment area (*sub regional scale*). As a representative, the Asif n´Ait Ahmed catchment (60 km^2) in the High Atlas is chosen. This catchment includes two test sites, already mapped. The geological mapping was accompanied by measurements of the groundwater quantity/quality, surface runoff and discharge of the receiving water course.

Taking the size of the Upper Drâa-catchment into account a different investigation strategy was chosen for the regional scale. The necessary geological and structural framework has been elucidated by both existing geological maps and geological evaluation of remote sensing data, added by selected ground checks. These information result in a first hydrogeological characterization. For a better understanding of the aquifer systems in respect to catchment area, age and groundwater recharge sampling campaigns have been carried out.

Hydrogeological screening of the area between High Atlas – Basin of Ouarzazate – Anti-Atlas has been carried out in four profiles trending more or less N-S. The groundwater chemistry deviate considerably in both within and between the profiles. Observation points near the mountain rim hydrochemically exhibit a clear dependence on the nearby mountain geology. However, the hydrochemical pattern could not be used to solely determine the catchment area of the springs or wells. The environmental isotope measurements which have been performed show a reasonable correlation of $\delta^2H/\delta^{18}O$-data with the meteoric water. Deviations are partly due to enrichments by evaporation effects. Hence the regular sampling of rainwater in the new climatological stations started in autumn 2001, establishment of the local input function for the $\delta^{18}O$- and δ^2H-content of the rainwater is still in progress. But first distinction of some catchment areas of the springs is possible. Currently performed tritium and carbon-14 sampling as well as the ongoing sampling for the stable isotopes will be used to validate those hypotheses.

PCO$_2$–^{13}C: AN INTERESTING TOOL TO CHARACTERIZE TYPES OF KARSTIC AQUIFERS

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Carbon-13 is an interesting tracer in studying water transit within karst systems. It can also be used to characterize the different types of waters which participate in the karstic flow ([4] fast and slow infiltration in the unsaturated zone and water from saturated zone). The $\delta^{13}C_{TDIC}$ (Total Dissolved Inorganic Carbon) at the outlet of a karstic system originates from the influence of the three Carbon-13 end-members : (1) atmosphere, -8 ‰ VPDB [1], (2) carbonates, 0 ± 2 ‰ VPDB [2], and (3) biogenic CO$_2$, values varying from –20 to –27 ‰ VPDB for C$_3$ pathway plants [8]; and the aqueous carbonate species equilibria under closed or open conditions.

Several systems were studied from springs of the experimental site of Vaucluse (Southeastern France) : *Fontaine de Vaucluse (FV), Notre-Dame des Anges (NDA), Grozeau (GRO), Font Gillarde (GIL), St-Trinit (TRI), Millet (MIL), Font d'Angiou (ANG), la Nesque (NES)*. The aquifers characteristics are already known thanks to several works ([6], [7], [5] et [3]). A new sampling campaign has recently be conducted, including: temperature, electrical conductivity, anions and cations, total organic carbon and $\delta^{13}C_{TDIC}$. The different springs were sampled twice a month, during an hydrological cycle (from 1999 December to 2001 January).

Observed variations of $\delta^{13}C_{TDIC}$ versus partial pressure of CO$_2$ (pCO$_2$) highlights two kinds of evolution for these systems (Fig. 1):

Evolution 1 corresponds to strong variations in pCO$_2$ but strong variations in ^{13}C and gathers the Font Gillarde, the Grozeau, Fontaine de Vaucluse and Notre-Dame des Anges. Each springs show strong variations for both pCO$_2$ (mean value from $4.7.\ 10^{-3}$ to $1.8.\ 10^{-2}$ atm) and $\delta^{13}C_{TDIC}$ (mean value from –10.8 to –12.1 ‰). This first relation expresses the thickness increase of saturated zone. Indeed, the Font Gillarde and the Grozeau are poorly karstified systems, with a limited saturated zone, whereas Fontaine de Vaucluse and Notre-Dame des Anges, show a well-developed karstification with saturated zones of respectively 300 and 100 m thick. Saturated zone works as a closed system relative to the gazeous phase inducing high values of pCO$_2$ because a lack of degasing processes. Moreover, carbon-13 contents of waters from this environment evolves towards to enriched values due to a long contact with the carbonate rock.

Evolution 2 expresses low variations for the two parameters and includes the Font Gillarde, Millet, Font d'Angiou and St Trinit springs. This one present weak variations in pCO$_2$ (mean value lower than $1.\ 10^{-2}$ atm) and $\delta^{13}C_{TDIC}$ (mean value from –11 to –13 ‰). These aquifers are superfical systems with different degree of karstification. There is no fast infiltration in Font Gillarde and Millet systems because of their hydrodynamic behaviours, characterized by a net difference between transfer and transit of water. Fast infiltration can be possible in the Font d'Angiou system. Then, St Trinit is a typical epikarstic aquifer, that is to say that infiltration of recent water is very fast (several hours). Evolution 2 highlights an increasing influence of infiltration zone on the aquifer behaviour.

This classification of the karstic systems from the experimental site of Vaucluse corresponds to those established with others parameters and tracers of residence-time such as Mg, and work with others karstic aquifers from the Jura mountains (Eastern France) and Larzac (Southeastern France). The study of the pCO_2 and $\delta^{13}C_{TDIC}$ variations is a relevant tool to characterize karstic systems.

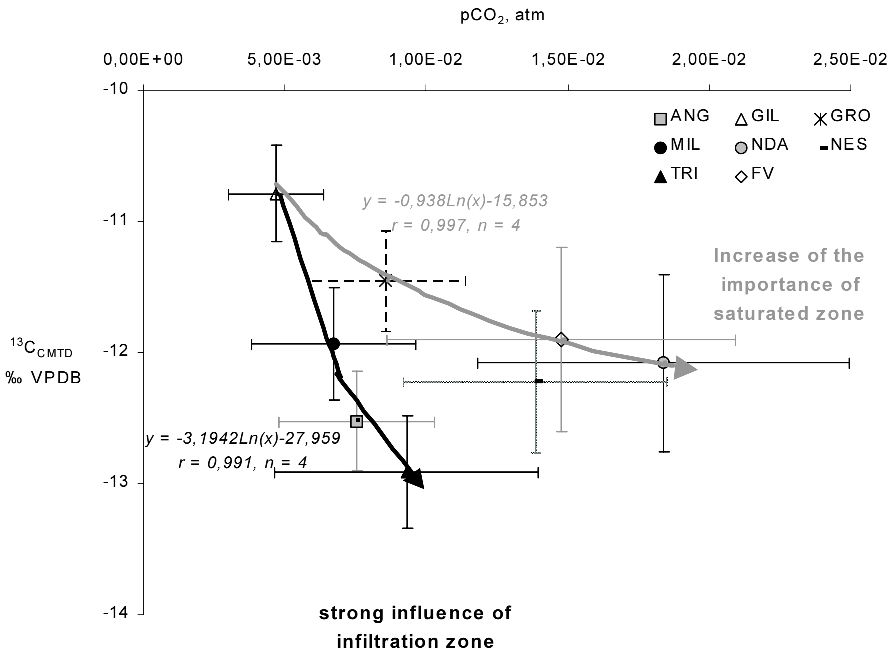

FIG. 1. pCO_2 - $\delta^{13}C_{CMTD}$ relation at the karstic outlets (mean values and standard deviations).

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APPLICATION OF ISOTOPE TECHNIQUES TO GROUNDWATER INVESTIGATION IN THE ERDOS BASIN, CHINA

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The Erdos Basin is located in the eastern part of Northwestern China and extends over parts of 5 provinces: Shaanxi, Gansu, Ningxia, Inner Mongolia and Shanxi. The basin is surrounded by the Yellow River to the west, north and east and the Weihe River, the largest tributary of the Yellow River, flows through the southern basin from west to east. The Erdos Basin covers an area of about 400 000 km^2 and is a plateau depression basin caused by structural uplift. The early Cretaceous sediments which form the artesian basin consist of six primary hydrostratigraphic units with a total thickness of 1 000m. Generally, Ordovcian carbonate rock formations form karstic aquifers that flank the east, south and west of the basin distributed in a U-shape forming the peripheral mountains and hills with an area covering about 100 000 km^2.

The groundwater resources of the basin are strategically important and this ongoing IAEA TC-project (CPR/08/12) was undertaken in 2001-2002, with the major tasks being to evaluate the availability of groundwater resources, especially the recharge process and recharge rate, to understand the inter-relationship between groundwater system and surface water and between different groundwater aquifers, to determine the age of groundwater, and explore the possibility of utilizing deep groundwater. The objective is to improve groundwater investigation and management in arid and semi-arid regions in China through integrating isotope techniques.

This paper reports upon work in progress through collection, collation and analysis of climatic, geological, hydrogeological hydrochemical data, water sampling and laboratory analysis, isotope technique training. A double-packer sampling system is being used to collect discreet-level water samples from target hydro-stratigraphic units via uncased boreholes up to 1000m in depth.

Four rainfall stations for rain collection have been set up in the Erdos Basin and 50 water samples for D, ^{18}O, T were collected. 420 groundwater samples for D, ^{18}O, T, ^{13}C, ^{14}C, ^{34}S, ^{36}Cl, ^{4}He and CFC were collected, and analyses have been completed. Some preliminary isotopic results and interpretation are as follows:

The isotopic features of rainfall in the Erdos Basin give the weighted average δ^{18}O of -7.38‰, and δD of -50.22‰, and T is 34.6 TU. The average δD and δ^{18}O of shallow groundwater (depth is less than 100 m) ranges from -62.90‰ to -61.80‰, from –7.81‰ to -9.60‰, and tritium value from 8.5 to 16.6 TU. The most deep groundwater is confined or artesian water with depths of more than 100 m to 900 m, and the δD and δ^{18}O range from -76.01‰ to -81.29‰ and from -9.42‰ to -10.94‰ respectively, tritium value is less than 8 TU.

The D and ^{18}O values of groundwater and precipitation are mostly located below and near the Global Meteoric Water Line. That means the deep groundwater in the Erdos Basin originated from the precipitation and shows some isotopic effects of enrichment by evaporation. The groundwater in different regions and depth maybe was recharged from different rainfall in different areas and different time. With the depth increasing, the value of D and ^{18}O clearly decreases.

For most of the deep groundwater in the Basin, the ^{14}C ages are more than 5,000 years. The oldest age of deep groundwater can reach more than 20,000 years.

Some of the pending questions relate to the deep groundwater in Erdos basin including the origin and circulation patterns of groundwater, including brackish groundwater, relationships between the different aquifers, recharging mechanism and the recharge quantity of water in the desert area to north part of basin. These factors are critical to groundwater resources management and the long-term sustainable groundwater yield from this strategically important water resource in a large sedimentary groundwater basin.

USING ISOTOPIC AND CFC METHOD TO STUDY THE RIVER WATER AND GROUNDWATER INTERACTION IN THE GUANZHONG BASIN, SHAANXI, CHINA

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An isotopic hydrological study was carried out on the Wei River water and shallow groundwater in the Guanzhong basin, Shaanxi, China. The study area is bordered by the Qinling Mountain in the south and by the North Mountain in the north, by the Yellow River in the east. Wei River is located in the middle of the basin and converges eastward into the Yellow River. The water supply for the major cities like Xi'an, Xianyang, Baoji and Weinan is from river and groundwater resources. Wei River and nearby shallow groundwater is largely used for fresh water supplies. With increasing use of the surface and groundwater, the water quality and groundwater table is decreasing. The over-exploitation of water resources is resulting in serious hydrogeological damage, such surface land depression and surface fracturing etc. The groundwater over 300 m depth is fresh from the foothill of the Qinling Mountain northward to the Wei River. The groundwater is brackish from the northeast foothill of the North Mountain southward to the Wei River, the salinity is decreasing westward and eastward. This hydochemical trend was the foundation of a hydrogeological model in which the groundwater is recharged mainly in the Qinling Mountain and is transported relatively quickly northward and resulting in some discharge into the Wei River. Groundwater in the north bank of the Wei River is recharged in the North Mountain and move slowly southward. New isotopic and CFC data are presented to improve the interpretation for interaction between Wei River and groundwater in the Guanzhong basin. The oxygen isotopic ratios in the shallow groundwater lie within –7‰ to –10‰, these are different from the more rich values of surface water, which reflect the weak link between the surface and groundwater. Deeper, warm groundwaters show a significant ^{18}O shift due to isotope exchange with lithologies, indicating long groundwater residence times, confirmed by ^{14}C data. Most of CFC concentrations for groundwater are very low near the Wei River, but high near the Qinling Mountain foreland alluvial fan and the North Mountain. Ratio of CFC data indicate that the groundwater near the Qinling Mountain, the North Mountain and Wei River may contain respectively as much as 20-50%, c.a. 20% (age less than 12 years), and <10% young water mixed with old regional water. Some high fraction of young water near the Wei River is related to heavy pumping. The relative high fraction of young water near the mountain areas and the Wei River in the inner basin indicates that foreland mountain areas are the recharge sources of the shallow groundwater and discharge to the Wei River.

HYDRAULIC COMMUNICATION AND IMPACT ON THE QUALITY OF GROUNDWATER IN THE NORTH DJEFFARA COASTAL AQUIFER, TUNISIA

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The studied aquifer system is located in the south east of Tunisia bordering on the Gulf of Gabés. It extends over an area of 1000 km^2 [1]. This coastal Djeffara basin is characterized by an undulating landscape with a semi arid climate. The average annual rainfall is about 180 mm, the potential evaporation is about 1300 mm/year, and the average monthly temperature ranges from 16°C (coldest month) to 30 °C (warmest month). Two sandy layers between 0 and 120 m depth, which belong to the Mio-Pliocene, form the aquifers.

The paper is related to a technical cooperation project with the International Atomic Energy Agency, Vienna, Austria, aimed at the utilization of saline groundwater to grow salt-tolerant plants. In this connection, isotope and geochemical groundwater investigations were carried out[5]. The results of these geochemical and isotopic studies are presented in this paper and evaluated in terms of replenishment and flow regime of the groundwater as well as evolution of its salinity. Fig. 1 is one of the plots used to discuss the measured stable isotope values of samples taken from the El Hicha study area. This plot and other indications discussed in the paper [2]-[4] show that the groundwater in the south of the study area (El Hicha) originates mainly from the Djeffara aquifer. The groundwater is replenished by discharge of the Continental Intercalaire in the fault system of the El Hamma region. North of a drain that crosses the El Hicha area at Oued el Akarit, the groundwater contains varying proportions of additional local recharge, which range between about 10% and more than 50%. At some sites the presence of bomb-tritium indicates a modern component of recharge in the groundwater. This suggests that the aquifer is unconfined, at least in its upper layer. ^{14}C data have been used to estimate the rate of local recharge (in the order of 1mm/a). The salinity of the groundwater appears to originate from dissolution of minerals in the aquifer system. The higher values of the dissolved anions and cations in the northern part of the El Hicha area are due to higher sodium and chloride concentrations. The changes of the latter concentration seem to be associated with changes of the proportion of local recharge.

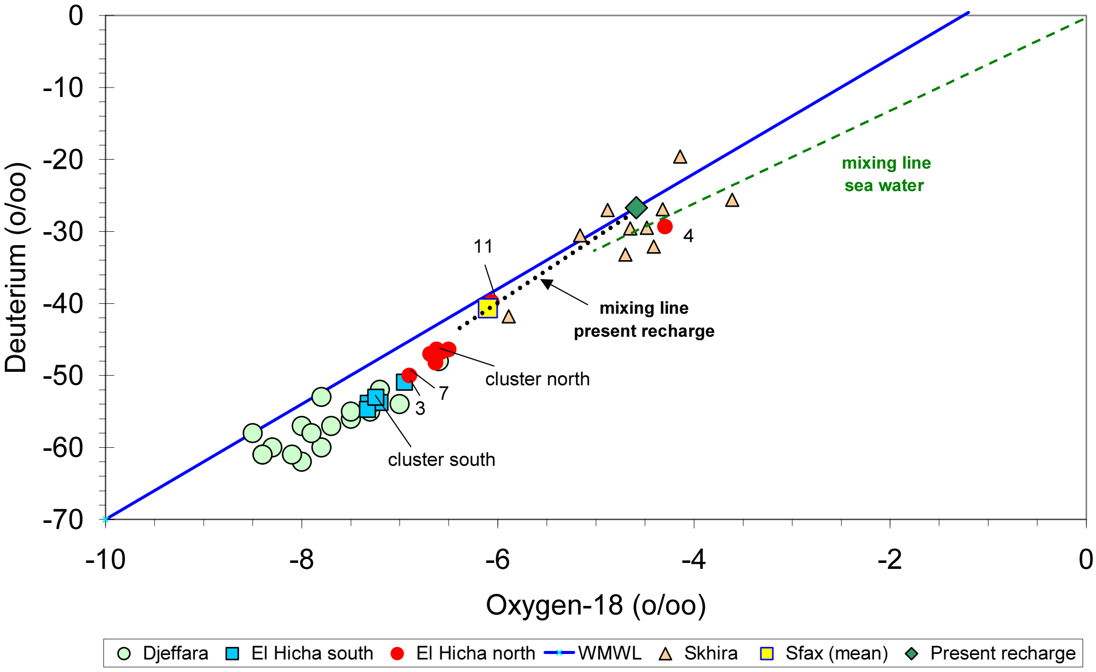

Fig.1: Plot of δ^2H versus δ^{18}O of groundwater from El Hicha and other neighbouring aquifers

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THE USE OF STABLE ISOTOPES AND HYDROGEOCHEMICAL STUDIES TO CHARACTERIZE WATER RESOURCES IN THE SEMI-ARID SOKOTO BASIN, NIGERIA

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The Sokoto hydrological basin in Northwestern Nigeria belongs to a larger geographic unit, the Iullemmeden Basin in West Africa covering an estimated area of 700,000 Km^2 [1]. It is a semi-arid region with mean annual rainfall (over a period of 90 years) ranging from 350mm at Kalmalo in the extreme north and 670mm (at Sokoto). The potential evapotranspiration at Sokoto is calculated to about 2,500mm/a, thus exceeding precipitation by as much as a factor of 5. The aim of this study is to characterize water resources in the basin and investigate the risk of pollution. This is to aid the planning and management of water resources in the semi-arid areas of northwestern Nigeria to meet the demands of the growing population.

In order to achieve the aim of the present study more than 190 samples were taken from dugwells and tubewells, boreholes, lake as well as rivers Rima and Sokoto in four major sampling campaigns in the Federal Ministry of Water Resources (Nigeria) under the joint RAF/08/22 project with the International Atomic and Energy Agency, Vienna (Austria) and three fieldwork in the University of Ilorin (Nigeria) in collaboration with Technical University, Darmstadt (Germany). As a reference to groundwater 10 rainwater samples were collected from 3 different stations (Goronyo, Wurno and Sokoto) for isotope analyses.

Physical parameters like temperature, pH, electrical conductivity (EC), dissolved oxygen and alkalinity were measured in the field using potable meters and "AquaMerck" titration kits. Main chemical components and the environmental isotopes H-2, H-3, C-13, C-14 and O-18 have been analyzed. Stable isotopes ratios are expressed as delta in per mil (δ‰) relative to VSMOW (Vienna Standard Mean Ocean Water). The isotope precision of measurement based on VSMOW is ±0.15 ‰ for ^{18}O and ±1 ‰ for ^{2}H.

Results of field analysis of the water samples have shown a pH range of 5.5 – 8.3; electrical conductivity of 45 -1, 155 µS/cm and total dissolved solids (TDS) between 16 to 1, 063 mg/l. The dominant anion is bicarbonate although places of significant concentration of sulphate were recorded depending on where the sample was taken. It is generally difficult to find any significant criterion in the chemical solutions of groundwater for distinction of the different aquifer types. However, five groups of water samples were formed to plot the equivalent concentration of the major ions and ionic combinations [2]. These groups, with their distinguishing chemical composition, are as follows:

(I) deep groundwater from boreholes ($HCO_3>SO_4>Cl$),

(II) shallow groundwater mainly from dug wells outside the irrigation area ($SO_4>HCO_3>Cl$),

(III) shallower groundwater from tube wells and some dugwells around the Wurno Irrigation Scheme, ($Cl>HCO_3>SO_4$), (IV) Lake and Carnal waters ($HCO_3>Cl>SO_4$), (V) Rivers Rima and Sokoto ($HCO_3>SO_4>Cl$).

The study of stable isotope contents (^{18}O, ^{2}H) also identified the five groups (Fig. 1). Group I-III is of groundwater origin while group IV and V represent surface water. It is obvious that, between the deeper groundwater (group I) and the overlying water bodies, no transition zones are known, as they can be clearly separated. For the shallower groundwater, however, admixtures of groups II, III, with groups IV and V are obvious. Group II and III stem mainly from direct recharge by precipitation. However, due to lack of sufficient information on the position of the screens the depth penetration of recharging water is not known.

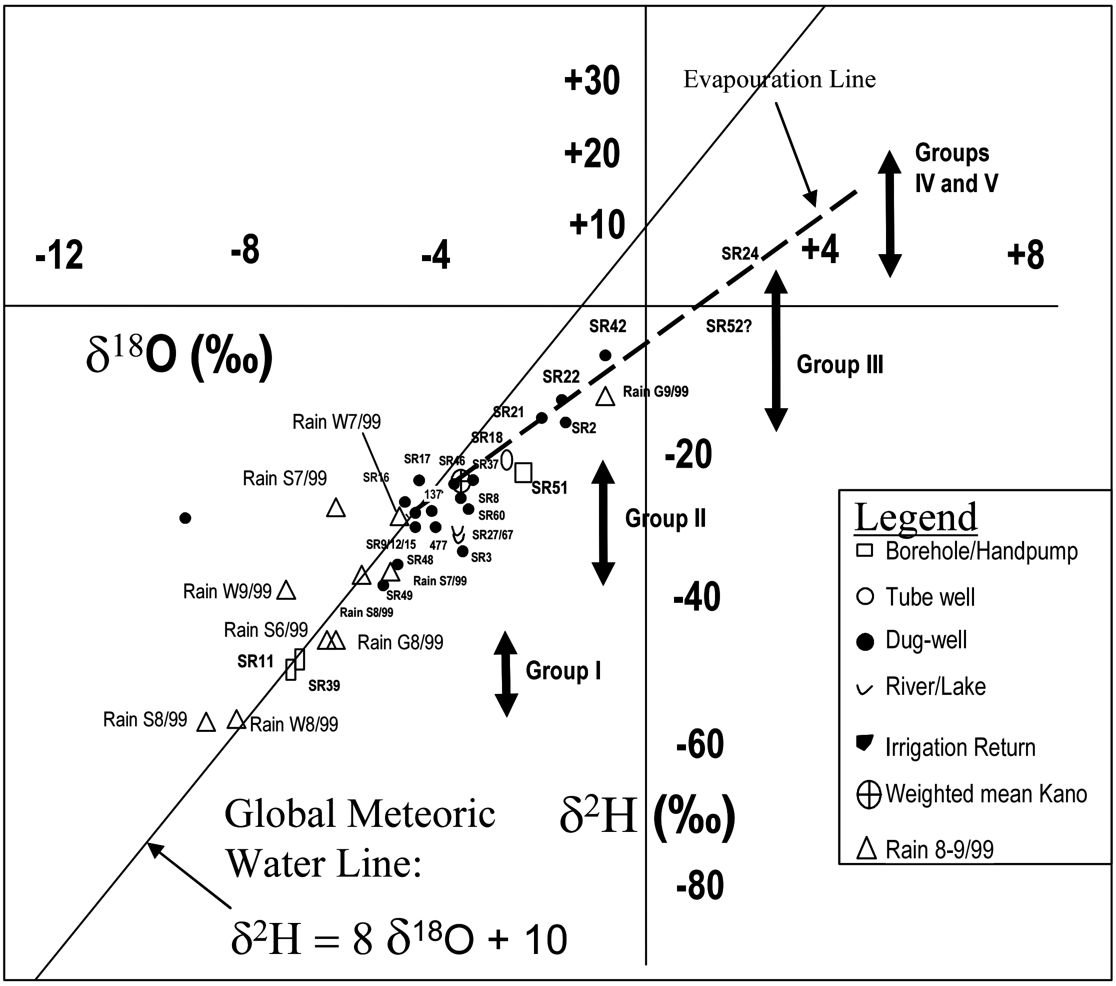

Figure 1: Relationship between δ^2H and $\delta^{18}O$ in groundwater and surface water.

Except few samples of shallow and surface water which defined a local evaporation line of slope 5.1, no signification evaporation was found to occur during infiltration; most of the points plot close to the Global Meteoric Water Line (GMWL) and the weighted mean of precipitation in Kano [3]. A combination of the hydrochemical and isotope data (^{14}C, ^{13}C and ^{3}H) reveals the Sokoto basin aquifers generally contains good quality groundwater of Holocene age (100 to 10,000 years Bp).

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AGE DATING OF HYPORHEIC GROUNDWATER WITH RADON (RN-222)

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Radon (Rn-222; Rn) has been used as a tracer for the dating of very young groundwater that has recently infiltrated from a river [1]. The radon method uses the fact that minerals in rocks contain traces of the radium mother isotope, ^{226}Ra. As an inert gas, radon (Rn) emanates from rock surfaces after the decay of ^{226}Ra. River water usually contains little Rn and the Rn activity is in equilibrium with the atmosphere. During the recharge of aquifers by downwelling river water, the Rn activity increases in the flowing groundwater, with time and distance. Under plug flow conditions, the law of radioactive ingrowth governs the Rn activity of the recharge water {$\tau = -1/\lambda \ \ln [(A_\infty - A_t)/ (A_\infty - A_0)]$; τ, radon water age; $\lambda = 0.182$ d^{-1}, decay constant for ^{222}Rn; A_∞, Rn activity at steady state; A_t, Rn activity of a sample; A_0, non-zero initial activity (some rivers may contain traces of radon from groundwater that exfiltrated into the river upstream the sampling site)}. A maximum Rn concentration indicates that a steady state has been reached between ingrowth and decay. About 90 per cent of this steady state is reached after about 15 days (4 half-lives of Rn). Often groundwaters of different residence times are mixed in aquifers and plug-flow conditions do not apply. In the case of a binary mixing of very young groundwater that has recently infiltrated from a river and older groundwater, the residence time of the young water component can only be assessed with Rn, if the actual mixing ratio is known. To this end, mixing must be determined through additional measurements with non-reactive mixing tracer.

Aquatic habitats in flood plains are characterized hydrologically by a strong interaction between river water and groundwater of alluvial sand-and-gravel aquifers. The transition zone between surface and subsurface waters is a hydrological continuum and an ecotone characterized by the hyporheic zone. If the riverbed is in direct contact with well-permeable aquifer material, and if the ground-water level is deeper than the river stage, the river can lose water to the subsurface (downwelling river). The freshly infiltrated water from losing reaches of the river is called “hyporheic” groundwater. Hyporheic groundwater is distinguished from older alluvial groundwater by a very short residence time in the subsurface of up to a few days [2].

Radon-222 (Rn) activities were measured in hyporheic and alluvial groundwaters of two perialpine flood plains in northern Switzerland (river Töss, and river Thur). The studied rivers were subjected to rehabilitation operations. At the sites of rehabilitation operations, piezometer wells were drilled at different depths. Ages of older alluvial groundwaters were calculated with the tritium/helium-3 (^{3}H/^{3}He) dating method and compared with those of the Rn method [3]. Mixing tracer measurements (chlorofluorocarbons, specific electric conductivity, temperature, and chloride) in these wells were interpreted as mixtures between river water and older groundwater. The fractional mixing with water that has recently infiltrated from the river Töss seemed to be higher in summer than in winter. Where the rivers were allowed to reshape banks and beds following rehabilitation operations, measurements in wells near the bank revealed differences in Rn activity before and after the rehabilitation of more than a factor of two.

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USE OF ISOTOPES IN THE MANAGEMENT OF KISORO TOWN WATER SUPPLY, UGANDA

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Environmental isotopes in combination with hydrochemistry have been used to determine the source and flow path of Chuho spring water, the only source of Kisoro town water supply, in order to protect it from pollution. The town is located in the catchment of the spring and is expanding with so many pit latrines and other possible sources of pollution raising concern about possible pollution of the spring water. This concern has been aggravated by the fact that the source and flow path of this water is not known.

The geology of the area is dominated by basic volcanic rocks which are associated with lava flow caves and other volcanic vents which act as good conduits for water and have major impacts on underground drainage system. Previous hydrogeological studies involving geological mapping, geophysical surveys and groundwater tracing carried out with the aim of delineating the source and flow path of this water were unsuccessful because of the complicated geology and groundwater flow systems. Isotope hydrology methods were employed to resolve these uncertainties since conventional hydrogeological methods had not succeeded.

Based on assessment of hydrogeological, hydrochemical and stable and radioactive isotope data, a good understanding of the possible source and flow path of water supplying Chuho springs has been obtained.

It has been found that drainage in Kisoro district follows a northerly to north- westerly direction and that the only drainage to Chuho springs should either be from the southern or eastern parts of the town.

Chuho springs consist of six spring lets which all have very similar hydrochemistry, and stable and radioactive isotope content suggesting that they have similar origin and flow paths resulting in similar residence times. Based on stable isotope results it has been found that Kigyezi swamp is a possible source of recharge to Chuho Springs because it has similar isotopic content with no evaporation signature and the storage of water in the swamp creates a permanent water source that is probably responsible for the almost constant discharge of Chuho springs.

From hydrochemistry, the water that discharges at Chuho seems to flow through Leucite basalt and Leucite basanites located in the southeastern direction of Chuho. This is the direction in which Kagyezi swamp is located thus confirming the observation that Kagyezi is likely to be the source of Chuho springs.

Carbon-14 and tritium results indicate that Chuho water is quite old and has a long residence time and thus low flow rate. This therefore indicates that no active recharge is taking place in the area and thus there is no direct relationship between rainfall and spring discharge. This has water quality and quantity implications in that if environmental degradation occurs in the wider catchment and specifically in areas around Kagyezi, it may have long term impact on the quality and quantity of Chuho springs although this would be seen after along time. However, pollution in the immediate catchment of Chuho springs is of more concern because if it happens, it will affect the water discharging at Chuho much faster because of short flow distances and also because of high permeability of volcanic rocks close to Chuho.

Based on the conclusions reached a number of recommendations have been made for sustainable management of Kisoro town water supply.

The area in the southeastern direction of Chuho springs should be protected from pollution. Initially an area 10km long and 2 km wide upstream of Chuho springs should be protected by limiting activities to only those that have no impact on groundwater. There should be no pit latrines in the area and application of any fertilizers or pesticides within this area should be avoided.

Similarly, while the rate of flow of water from the recharge point to the discharge point is low, any serious pollution of Kagyezi swamp and its surroundings will eventually have an impact on the quality of water of Chuho. In addition, environmental degradation of areas around Kagyezi swamp could result in reduction in water storage volume and hence have an impact on the discharge of Chuho springs. Areas around Kagyezi swamp be thus be protected from environmental degradation and any other activities that may have an impact on the quality and quantity of water.

Regular monitoring of the water quality and discharge of Chuho springs should be done to assess any variations. This will not only be necessary for water supply purposes but will ensure that any impacts on the spring are detected well in advance to enable necessary actions to be taken.

The findings of the study and the recommendations made are based on activities carried out over a one and half year period. The data collected is therefore limited and the results need to be verified. This could be done through two more rounds of sampling campaigns involving all the water sources and most especially the swamps and Muhavura crater in order to assess the consistency of the data used in reaching the conclusions and the validity of the recommendations.

GROUNDWATER POLLUTION

ENVIRONMENTAL ISOTOPE STUDIES OF MARINE COASTAL POLLUTION IN PAKISTAN

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The International Atomic Energy Agency (the IAEA), Vienna launched a five years (duration: 1998 – 2002) Joint Project on “Better Management of the Environment and Industrial Growth Through Isotopes and Radiation Technology (RAS/97/030) in co-operation with the RCA (Regional Co-operative Agreement) office-Vienna, and UNDP (United Nations Development Programme). The Marine Sub-project entitled “Management of Marine Coastal Environment and its Pollution (RAS/8/083)” is a key component of this joint project. Pakistan has significantly contributed in the marine sub-project by demonstrating the potential use of environmental isotope techniques such as stable isotope ratios of oxygen ($\delta^{18}O$ ‰ V-SMOW) in water molecules, carbon ($\delta^{13}C$ ‰ PDB) in total dissolved inorganic carbon (TDIC), carbon ($\delta^{13}C$ ‰ PDB) in total dissolved inorganic carbon (TDIC) as well as marine plant (leaves and tree rings), nitrogen ($\delta^{15}N$ per mil. Air) in marine plants and animal shells, and sulfur ($\delta^{34}S$ ‰ CDT) in aqueous sulfate for tracking the transport of pollutants in marine coastal environment. This paper/poster highlights the innovative use of these environmental stable isotope techniques in relation to conventional physiochemical techniques for tracking fate and behaviour of land based domestic / industrial pollution inventory in to the marine coastal environment of Pakistan.

1. INTRODUCTION TO THE PROBLEM

There are a number of environmental issues in the coastal zone of Pakistan and amongst these the disposal of domestic wastes and industrial effluent causing marine pollution problems along the urban centers are the most significant. The coast of Pakistan is about 960 km long and borders the Arabian Sea. Administratively, the coast is divided into a 745 km long strip called the Baluchistan/Makran coast and a 215 km long strip called the Sindh coast. Very serious environmental pollution problems exist along the Sindh Coast due mainly to the indiscriminate discharge of untreated domestic sewage and industrial effluents into the marine coastal environment through natural outfalls. The coastal city of Karachi has an estimated population of ~13 million, and is the biggest industrial base in the country. The sewage waste generation in Karachi is more than ~300 million gallons /day out of which 40% is domestic waste and 60% is industrial waste. This sewage is dumped into the Karachi sea via Malir River (Ghizri-Korangi Creek area), Layari River (Manora Channel/Karachi Harbour area) and small waste drains mainly along Clifton Coast and Korangi Coast. In contrast, the Baluchistan coast has small towns with a population of about one million. Due to lack of industry and population, the Baluchistan coast is relatively free of pollution. Gwadar is the key coastal dwelling along Baluchistan coast. Stable isotope ratios of oxygen ($\delta^{18}O$ ‰ V-SMOW) in water molecules, carbon ($\delta^{13}C$ ‰ PDB) in total dissolved inorganic carbon (TDIC) as well as marine plant (leaves and tree rings), nitrogen ($\delta^{15}N$ per mil. Air) in marine plants and animal shells, and sulfur ($\delta^{34}S$ ‰ CDT) in aqueous sulfate are used as innovative tools to address the marine coastal pollution issues along Pakistan coast.

2. RESULTS AND DISCUSSIONS:

Application of Environmental $\delta^{18}O$ (water) and $\delta^{34}S$ (Aqueous Sulfate) as Tracers of Pollution Transport

Investigations were made to explore the potential and suitability of stable isotopes of oxygen ($\delta^{18}O$) in water molecule, and sulfur ($\delta^{34}S$) in aqueous sulfate as a tracer of pollution inventory. Water samples were collected during low tide conditions from down stream polluted Layari Riverprior to its outfall into Manora Channel, various locations within the Manora Channel/ Karachi Harbour, as well as the sea adjoining Karachi coast. These samples were analyzed for $\delta^{18}O$ (water) and $\delta^{34}S$ (aqueous sulfate). Using the chemical mass balance equation and the isotope balance equation for mixing of two water bodies (two component mixing system), the polluted mixture of seawater and Layari river water across a mixing profile opposite KPT Shipyard in Karachi Harbour area was analyzed to identify the % contribution of inorganic pollution/ inorganic carbon coming from Layari River Outfall Zone, as well as the amount of Layari River water in the mixture (Table 1). Results indicate that within the measuring precision limits for oxygen isotopes, $\delta^{18}O$ (water) can be used as a reliable tool to identify the amount of water coming from either of the water sources (sea or polluted river outfall zone) for modeling purposes. Results on $\delta^{34}S$ (aqueous sulfate) also gave a good clue on the input percentages of sulfur from the polluted Layari River. However, the applicability of both these isotopes is restricted to narrow navigational channels and backwater zones.

Stable Carbon Isotope Analysis of Total Dissolved Inorganic Carbon as a Tracer of Marine Pollution

Environmental stable isotope ratios of carbon ($\delta^{13}C$ ‰ PDB) in total dissolved inorganic carbon (TDIC) have been successfully used as a natural tracer of domestic and industrial pollution inventory from selective coastal dwellings into the shallow seawater along 960 km long coastal strip of Pakistan. 83 seawater samples (sea depth range: < 20 meters) were collected from two locations off Sindh Coast (Karachi and Indus Delta) and five locations off Baluchistan Coast (Jiwani, Gwadar, Pasni, Ormara, Sonmiani). Physiochemical parameters such as pH, electrical conductivity, and salinity were measured in-situ. $\delta^{13}C_{TDIC}$ contents of collected water samples were measured using standard gas source mass spectrometric procedures. Significantly depleted $\delta^{13}C_{TDIC}$ values (as low as -7 per mill. PDB) coupled with measurable depletion in pH, electrical conductivity and salinity are observed in seawater samples collected off Indus Delta, Karachi coast, Gwadar coast and Sonmiani Bay (Table 2). This is indicative of inputs of pollution from industrial and/or domestic waste drains into the marine environment off these coasts. Other coasts like Gwadar and Pasni are relatively less polluted by domestic waste inputs as compared to Indus Delta, Karachi, Sonmiani. However, the mangrove ecosystem is also found to strongly control the $\delta^{13}C_{TDIC}$ composition of seawater in narrow channels of Jiwani Bay, Sonmiani Bay and in the backwaters of semi-closed Manora Channel.

Use of Mangrove Tree Rings as Indicators of Pollution Inventories

Studies were made to identify the potential of carbon isotopes of mangrove tree rings as qualitative tracers of pollution inventory in polluted zones off Karachi Coast. Mangrove tree rings pertaining to a profile of trees (growth age band: Years: 1918 – 1996) collected from Manora Channel Backwaters (Layari River Outfall Zone) and a profile of trees collected from Korangi Creek/South-east coast of Karachi/industrial area (growth age band: Years: 1948 – 1996) were analyzed for $\delta^{13}C$. Tree ring were separated with a fine chisel, freeze dried, grounded in a Whiley^{TM} Grinding Mill, combusted in a modified Parr^{TM} Oxygen Combustion bomb for conversion into CO_2 gas, and analyzed for stable carbon isotope ratios ($\delta^{13}C$ per mil. PDB) using a gas source mass spectrometer. Results indicate that $\delta^{13}C$ values of mangrove tree rings grown in Korangi Creek area are depleted by about 1 to 1.5 per mill in ^{13}C as compared to mangroves grown in the polluted outfall zone of Layari river outfall zone in Manora channel. This signifies the impact of industrial pollution (in addition to domestic waste) drained by the Malir River in to Ghizri/ Korangi Creek in contrast to mainly domestic wastes drained by the Layari River. The observed annular variations in $\delta^{13}C$ composition of mangrove trees have strongly suggested that stable carbon isotope composition of tree rings can be used as potential indicators of pollution inventory. It is now established that the year 1991-1992 are the minimum pollution years, where as, the years 1996 and 1990 correspond to maximum pollution inventories in the mangrove forests from domestic sources.

Stable Carbon and Nitrogen Isotope Contents of Seaweeds, Mangrove Leaves and Animal Shells as a Tracer of Marine Pollution

17 samples of mangrove *(Avecinnia marina)* leaves, 63 seaweed (various species) samples and 18 animal shell (*Perna virdus*) samples were collected from within 5 meter depth contour of polluted marine environment of Karachi sea namely: Layari River & Malir River mouth areas, Manora Channel, South-East Coast and North-West Coast. Stable carbon ($\delta^{13}C$) and nitrogen ($\delta^{15}N$) isotope ratios were determined by gas source mass spectrometry to evaluate prospects of these isotope techniques for establishment of pollution transport/fate in shallow marine environment off Karachi Coast-Pakistan. $\delta^{13}C$ values of mangroves range between -28.3 to -26.7 ‰ PDB and are quite in agreement with $\delta^{13}C$ values quoted for the tropical mangroves in Malaysia. $\delta^{13}C$ values of seaweeds lie in the range of -31.1 ‰ -4.9 ‰ PDB. Large of $\delta^{13}C$ variations in seaweeds of Buleji and Pacha areas suggest incorporation of carbon from local domestic waste drains. Mangroves in polluted Korangi Creek are more depleted in ^{13}C as compared to Backwaters of Sandspit. This depletion is attributed to input of industrial waste related organic chemicals in Korangi Creek. $\delta^{15}N$ values of mangroves and seaweeds range between +6 to +13 ‰ and +7 to +18 ‰ relative to air N_2 respectively. The $\delta^{15}N$ values of NH_4^+ & NO_3^- in manure/domestic waste range between +14 to + 17.3 ‰ and +11 to +38.4 ‰ respectively relative to air N_2. The present studies clearly document potential of stable carbon and nitrogen isotope ratios of marine plants and animal shells as indicators of pollution transport in shallow marine environment off Karachi coast. Further, the determined isotopic values will also serve as reference to identify any input of industrial pollution in their respective growth areas along the coast of Karachi.

3. CONCLUSIONS:

The environmental stable isotope contents of oxygen, carbon, sulfur, and nitrogen in water molecules, total dissolved inorganic carbon, aqueous sulfate, marine plants and marine shells can be potentially used as innovative tracers of pollution as well as fate of pollutants in shallow marine waters that receive domestic and industrial pollution.

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TABLE 1. Environmental isotope and chemical evaluation of mixing characteristics of polluted Layari River water with non-polluted seawater in Manora Channel across a mixing profile opposite KPT Shipyard /Karachi Harbour

Profile Description	**E.C. (mS/cm**	**δ^{13}C per mill. (PDB)**	**δ^{18}O** per mill. **4. SMO W**	**EC Based % Contribution of Inorganic Pollution from**		**δ^{13}C Based % Contributic of Carbon from Layari Outfall**	**δ^{18}O Based % Contribution of Water from 5. Layari River**
				Pure Layari River	**Layari Outfall Zone**		
Arabian Sea, Manora Channel Break Waters	**55.6**	**- 0.88**	**-0.08**	**-**	**-**	**-**	**-**
Layari River (At Gulistan Colony, Mirza Adam Khan Road, Near Tanga Stand, Middle of Layari Channel, 1230 hrs.)	**2.6**	**-5.90**	**-6.67**	**-**	**-**	**-**	**-**
Layari RiverOutfall Zone	**36.0**	**-10.22**	**-1.79**	**-**	**-**	**-**	**-**
Prior to apparent mixing boundary of Layari Channel near Shipyard	**53**	**-4.42**	**0.13**	**4.9**	**13.3**	**37.9**	**1**
Prior to apparent mixing boundary of Layari Channel near Shipyard	**52.8**	**-5.64**	**-0.22**	**5.3**	**14.3**	**24.2**	**2**
At apparent Mixing boundary of Layari Channel in Shipyard	**53.8**	**-9.72**	**-1.24**	**3.4**	**9.18**	**94.7**	**17**
Extreme of Layari Channel in shipyard	**45.6**	**-8.6**	**-1.76**	**18.9**	**49**	**82.7**	**25**

TABLE-2: Stable carbon isotope (TDIC) analysis of Pakistan's marine coastal waters (Period: Nov-Dec., 2000)

Coastal Belt	**Coastal Location (n= No. of samples)**	**$\delta^{13}C_{TDIC}$ (‰ PDB)**
Baluchistan Coast (Pakistan)	Jiwani (n=5)	-1.9 to -0.3
	Gwadar (n=9)	-1.8 to - 0.2
	Pasni (n=5)	-1.9 to -0.5
	Ormara (n=5)	-1.1 to 0.6
	Sonmiani (n=7)	-3.7 to - 1.4
Sindh Coast (Pakistan)	Manora Channel / Karachi Harbour (n=9)	-7.3 to -2.4 (Low tide) -12 & -5.8 to 0.1 (High tide)
	South-east Coast (n=7)	-2.8 to 0.6 (Low tide)
	North-west Coast (n=7)	-5.3 to 0.5 (Low tide)
	Korangi Coast (n=8)	-6.6 to -2.7 (Low tide) -5.5 to -1.9 (High tide)
	Indus Delta (n=6)	-2.3 to -1.4

ISOTOPE HYDROCHEMICAL EVALUATION OF GROUNDWATER IN COASTAL KARACHI, PAKISTAN

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Abstract:

ISOTOPE HYDROCHEMICAL EVALUATION OF GROUNDWATER IN COASTAL KARACHI, PAKISTAN

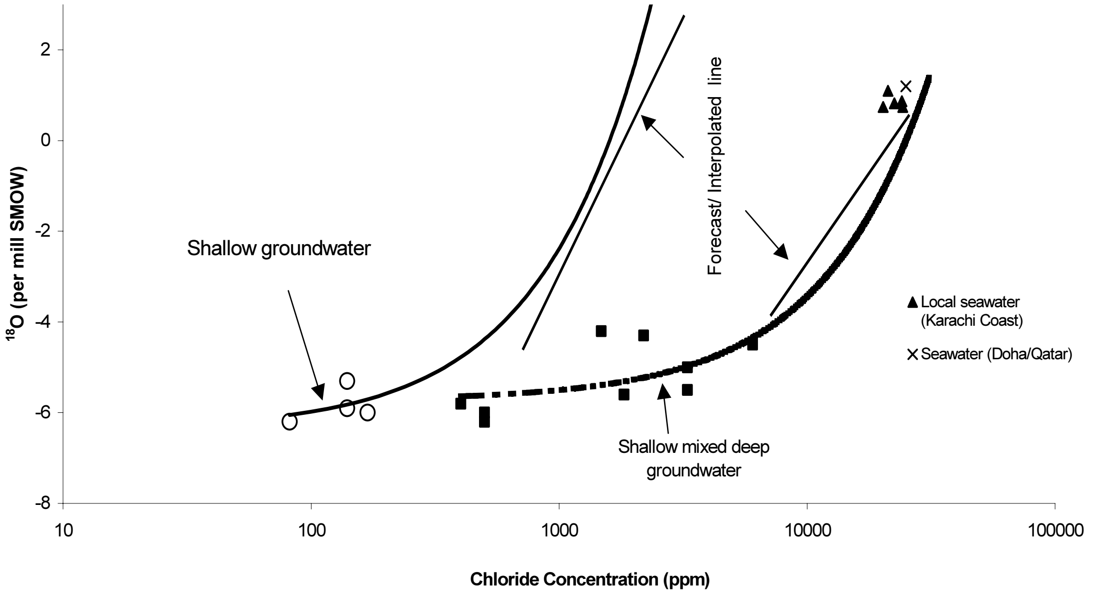
Karachi Metropolis is the most populous *(more than 10 million inhabitants*) and the biggest industrial base in Pakistan. It is also the largest coastal dwelling in the country with a coastline of ~80 km. Potable groundwater salinity has become a problem of great concern in Karachi. Environmental stable isotope techniques have been used in conjunction with physiochemical tools (temperature, dissolved oxygen, pH, redox, electrical conductivity, salinity) and biological tools (Fecal Coliform bacteria) to delineate: (i) isotopic & chemical input functions and biological labeling of various recharge sources (rain, polluted streams, rivers, lake, seawater) and the shallow / deep groundwater; (ii) potable water quality; (iii) extent and origin of saline groundwater in the coastal aquifer system with special reference to the role of seawater intrusion and/or trapped seawater in the coastal belt of Karachi. In total, 12 surface water samples and 59 groundwater samples were collected in the study area. To-date all surface water samples and 18 selective groundwater samples have been analyzed for $\delta^{18}O$ (water molecules), $\delta^{13}C$-TDIC (TDIC=Total Dissolved Inorganic Carbon) by gas source mass spectrometry and for aqueous contents of HCO_3^{-1}, SO_4^{-2} and Cl^- by standard chemical techniques. Measurements of δ^2H (water), $\delta^{34}S$ (aqueous sulfate), tritium (^3H) and radiocarbon (^{14}C) content in surface water and groundwater samples are in progress and will be completed shortly.

RESULTS AND DISCUSSION:

Groundwater recharge characteristics: The five sources of recharge to groundwater reserves in coastal Karachi are: (i) rainfall, (ii) Indus River water supply, (iii) Hub-River / Hub Lake water supply; (iv) Layari / Malir Rivers and their contributory channels that drain domestic, industrial and agricultural wastewater; and (v) seawater. Contribution to groundwater recharge by local precipitation seems very small due to very poor frequency of rainfall events and high evaporation rates in coastal Karachi. The long term (15 years annual record) mean monthly average precipitation for Karachi is between 0-15 mm during the months of January to June, 23 - 91 mm during the months of July to September and 0-7 mm during the months of October to December [1]. However, the remaining four sources play a significant role in recharge to shallow and deep groundwater system in coastal Karachi.

Isotopic, chemical and biological labeling of recharge sources: The long term weighted mean δ^{18}O (rainfall) in Karachi as used for interpretation purposes are: - 3.93 ± 1.94 per mil. V-SMOW. The δ^{13}C-TDIC and δ^{18}O (water) indices for the Indus River (IR) water are: δ^{13}C-TDIC (IR)= + 1.7 per mil. PDB and δ^{18}O (IR)= - 8.2 per mil. V-SMOW. The Indus River waters have electrical conductivity values below 500 µS/cm and salinity levels below 1ppt. The SO_4^{-2} concentrations in the Indus River water is 86 ppm. The range of variation in δ^{13}C and δ^{18}O (water) content of Layari River (LR) water are: δ^{18}O (LR)= -5 to -2.7 per mil. V-SMOW and δ^{13}C-TDIC (LR) = -7.2 to -0.2 per mil. PDB. The range of variation in δ^{13}C-TDIC and δ^{18}O (water) content of Malir River (MR) water are: δ^{18}O (MR)= -4.9 to -4.6 per mil. V-SMOW and δ^{13}C-TDIC (MR)= -8.4 to -0.2 per mil. PDB. In relatively non-polluted seawater along Karachi coast, δ^{18}O (seawater) lies in the range: + 0.3 to + 1.1 per mil. V-SMOW while δ^{13}C-TDIC (seawater) lies in the range: - 3.9 to + 0.8 per mil. PDB. The chloride content of non-polluted seawater is ~23000 ppm. In polluted seawater along Karachi coast, δ^{18}O (seawater) lies in the range: -1.3 to + 0.1 per mil. V-SMOW. The biological quality of all river waters w.r.t. population of Fecal Coliform is quite poor (> 64 to 2420 E.Coli/100 ml) and renders these waters subject to treatment prior to supply for domestic purposes/drinking purposes.

Figure -1 :Chloride versus ^{18}O trend line for shallow and shallow mixed deep groundwater, Coastal Karachi (Pakistan)



Isotopic, chemical and biological labeling of groundwater:

In general, biological quality of shallow groundwater (SG) w.r.t. population of Fecal Coliform (E.Coli Counts/100 ml) is generally quite poor (> 1 – 252 E.Coli/100 ml) and renders the water unfit for direct drinking purposes. The concentration of HCO_3^- (356 - 514 ppm), Cl^- (82 - 169 ppm) and SO_4^{-2} (38-117 ppm) in shallow groundwater is very reasonable. The mean chemical concentrations of Cl^-, SO_4^{-2} and HCO_3^- in shallow groundwater is in the range: Mean Cl^- (SG)= 132.8 ± 36.5 ppm; Mean SO_4^{-2} (SG)= 63.3 ± 36.7 ppm; Mean HCO_3^-

(SG)= 423 ± 67.4 ppm. The range of variation in δ^{13}C-TDIC and δ^{18}O in shallow groundwater is: δ^{18}O (SG)= -6.3 to -5.8 per mil. V-SMOW and δ^{13}C-TDIC (SG)= -16.5 to -5.5 per mil. PDB. The mean δ^{18}O (SG)= -5.9 ± 0.32 per mil.V-SMOW and the mean δ^{13}C-TDIC (SG)= -10.1 ± 3.3 per mil. PD. The δ^{18}O (water) results indicate that freshwater phreatic/ semi-unconfined aquifer is recharged mainly by rainwater. The shallow confined aquifers are recharged by a mixture of polluted waste waters from the Layari and Malir rivers and their feeding drains (both under natural infiltration conditions and artificially induced infiltration conditions) and local precipitation. In general, deep groundwater (DG) is mostly saline and has high electrical conductivity (range: 1.9- 19.1 mS/cm) and salinity (range: 1.7 - 7.4 ppt) as compared to shallow groundwater. The sampled deep groundwater from pumping wells is in fact a mixture of various proportions of shallow groundwater from freshwater phreatic/ unconfined aquifer and actual deep groundwater from the confined aquifer. The mean chemical concentrations of Cl^-, SO_4^{-2} and HCO_3^- in shallow mixed deep groundwater (DG) is: Mean Cl^- (DG)= 2169.2 ± 1828 ppm; Mean SO_4^{-2} (DG)= 458.4 ± 691.4 ppm; Mean HCO_3^- (DG)=353.6 ± 215.4 ppm . The mean stable isotope content of ^{18}O in shallow mixed deep groundwater is: Mean δ^{18}O (DG)= -5.3 ± 0.7 per mil. V-SMOW and Mean δ^{13}C (DG)= -10.5 ± 3.7 per mil. PDB.

Origin of groundwater salinity:

In order to postulate the origin of groundwater and related salinity in shallow and deep aquifer system, the stable isotope composition of oxygen (δ^{18}O per mil. V-SMOW) and hydrochemical data (ppm of $Cl_{(aq)}$ and $SO_{4(aq)}$) of groundwater samples are statistically evaluated. In principle, the discharge (with extremely high values of $Cl_{(aq)}$, $SO_{4(aq)}$ and a trend towards seawater δ^{18}O values) obtained from pumping wells installed in the vicinity of coastline should represent contributions from seawater intrusion. However, for pumping wells located comparatively far from the coast and representing high values of $Cl_{(aq)}$ and $SO_{4(aq)}$, the high salinity values of groundwater may be attributed to a possible upward diffusion from the freshwater-seawater interface as a result of fluctuation of groundwater table in response to continuous pumping of the local aquifer system for domestic, agricultural and industrial usage. In the present investigation, pumping wells installed near the coastline and tapping both the shallow and deep aquifers, represent relatively high values of $Cl_{(aq)}$ and $SO_{4(aq)}$ but their δ^{18}O values are comparable with those of the shallow groundwater and the polluted rivers draining Karachi. This suggests that these pumping wells are withdrawing significant quantities of water from the shallow aquifer system which also hosts recharge of seawater gushed into the coastal zone during summer monsoon period and infiltrates into the soil. However, possibilities of direct seawater intrusion in these wells under prolonged pumping conditions is yet to be verified. Noteworthy are the pumping wells that are discharging groundwater with negative redox values, significantly high $Cl_{(aq)}$ contents but relatively low $SO_{4(aq)}$ contents (Well No. G-001, G-017). It is speculated that the lower sulfate contents in these samples are due to biological reduction of $SO_{4(aq)}$. Sulfur Isotopic analysis (δ^{34}S) of aqueous sulfate in these samples is in progress to document this observation. The relatively deep groundwater (representing confined aquifer) sampled from three pumping wells: No. G-006, G-012, G-014, have a mean δ^{18}O value of -4.3 per mil. V-SMOW and excessively high contents of $Cl_{(aq)}$ and $SO_{4(aq)}$. Groundwater obtained from well No. G-006 has δ^{13}C-TDIC value of -0.3 per mil. PDB which is very close to the δ^{13}C-TDIC value for seawater adjoining Karachi coast (-0.6 to -8 per mil. PDB). Groundwater samples collected from other two wells No. G-012 and G-014 have δ^{13}C-TDIC values of -10.4 per mil. PDB and -13.2 per mil. PDB respectively. Similar depleted $\delta^{13}C$-TDIC values have been reported for deep saline groundwater tapped from confined aquifer in the coastal zone of Orissa- India [2]. It is concluded that the discharge from these wells mainly represent a mixture of recharge of rainfall in the hinterlands, flood water, and the spring water drained by the Malir River Basin and the Hub River Basin in coastal Karachi; and partly the seawater. For Well No. G-006, we speculate direct seawater intrusion by excessive pumping of the local aquifer. However, the excessively high contents of SO_4^{-2} and Cl^- in deep groundwater from two pumping wells No. G-012 and G-014 located away from the coast, suggest possibilities of trapped seawater. To verify possibilities of seawater intrusion in shallow groundwater / shallow mixed deep groundwater and/or existence of trapped seawater in deep groundwater, the concentrations of aqueous SO_4^{-2} (in milligrams per liter, log scale) are plotted against SO_4^{-2}/Cl^- ratios (in milli equivalents per liter, log scale) for the water samples analyzed to-date. Interestingly, the shallow groundwater and deep groundwater plot along two distinct lines (Figure 1). This is further justified by the trend of Cl^- concentrations (in ppm, log scale) versus $\delta^{18}O$ values (in $^{o}/_{oo}$ V-SMOW, linear scale) in shallow / deep groundwater and seawater adjoining Karachi Coast, as well as seawater from Doha-Qatar in Gulf Area [3]. It may be realized from Figure 1 that the extrapolated or forecast trend for shallow groundwater samples (with low SO_4^{-2} content) do not fall on the data points for local seawater (or other tropical seawater from Doha/Qatar). However, the extrapolated or forecast trend for deep groundwater samples (with high SO_4^{-2} and Cl^- contents and enriched $\delta^{18}O$ values) falls in the vicinity of the data points for the local seawater / other tropical seawaters (for example from Doha/Qatar). This observation strengthens the possibilities of seawater intrusion in the coastal zone/ build-up of salt-water up-coning in the confined aquifer; and existence of trapped seawater salinity in coastal Karachi. However, the postulation of trapped seawater will be validated upon analysis of tritium (^3H) and radiocarbon (^{14}C) in formation representative groundwater samples.

CONCLUSION:

Stable isotope contents of various groundwater recharge sources in coastal Karachi are determined for hydrogeological implications. The biological quality of potable shallow groundwater is not satisfactory in general. The conjunctive use of stable isotopes of oxygen (in water molecule) and carbon (in TDIC) as well as conventional hydrochemical analysis of SO_4^{-2} and Cl^- contents in selective surface water and groundwater samples has provided a preliminary valuable information on dynamics of groundwater, origin and mechanism of groundwater salinity in shallow and deep aquifer systems in coastal Karachi. The phreatic groundwater system is found to host mainly the local precipitation (rainwater). The shallow aquifer system mainly hosts recharge from local rainfall, infiltrated polluted river water (Layari/Malir River Water) as well as intruded seawater. The confined deep groundwater is quite saline and is believed to host trapped seawater. The postulation of seawater intrusion or build-up of salt-water up-coning and/or existence of trapped seawater salinity in the deep confined aquifer will be validated upon additional isotopic analysis such as $\delta^{34}S$ (aqueous sulfate), tritium (^3H) and radiocarbon (^{14}C) content, as well as hydrochemical analysis of the remaining surface water and groundwater samples in coastal Karachi. These updated results will be presented at the conference.

ACKNOWLEDGEMENTS

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ISOTOPIC AND HYDROCHEMICAL APPROACHES TO STUDY THE SALINITY AFFECTED AREAS IN AMARAWATI DISTRICTS OF MAHARASTRA STATE IN INDIA

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Inland salinity of groundwater in parts of Purna alluvial tract is a very interesting phenomenon because it lies 800 km away from seacoast and no remnants of irrigation practices have been observed. Out of the total area of about 7500 km^2, the salinity affected area is about 2956 km^2, which is confined mainly in the northern and central parts of the Purna alluvium in Amravati, Akola and Buldhana districts of Maharashtra. The thickness of saline aquifer varies from 50 m to 420 m deepest in the basin.

Different types of land forms, viz. older flood plain, piedmont zone, alluvial fans, pediplain with alluvial cover, interfans, dissected alluvial platform are identified within the alluvial plain: Rock types exposed in the area are Upper Gondwana, Infra trappean bed, Deccan trap and Quaternary sediments. Quaternary sediments cover much of the area while basin margins are mainly of Deccan Trap.

The Groundwater Surveys and Development Agency (GSDA) of Maharashtra State carried out a “Induced Recharge Project”, whereby the river water of good quality was intended to be used for recharging the groundwater in the aquifers adjoing the river courses. A large number of wells were drilled along the river banks and operated to create a reverse groundwater level gradient.

In the present paper presents the results of the work that was carried out to understand the causes of groundwater salinity in parts of the Purna river basin using chemical and isotopic approaches. Also the evaluation of the performance of the wells drilled and being operated under an ongoing induced recharge project of the GSDA is presented.

A detailed study of available information on the hydrogeology, hydrochemistry, soil characteristics, hydrometeorology, land use pattern, and hydrology was carried out prior to the collection of river and groundwater samples from 37 locations in the study area. The samples were subjected to hydrochemical analyses for major ions such as Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, HCO_3^{-}, SO_4^{2-}, and Cl^{-}, trace elements such as Sr and Li, environmental tritium, carbon-14, and stable isotopes of oxygen and hydrogen (^{18}O and D).

Fig. 4.2 δD - $\delta^{18}O$ plot for the study area

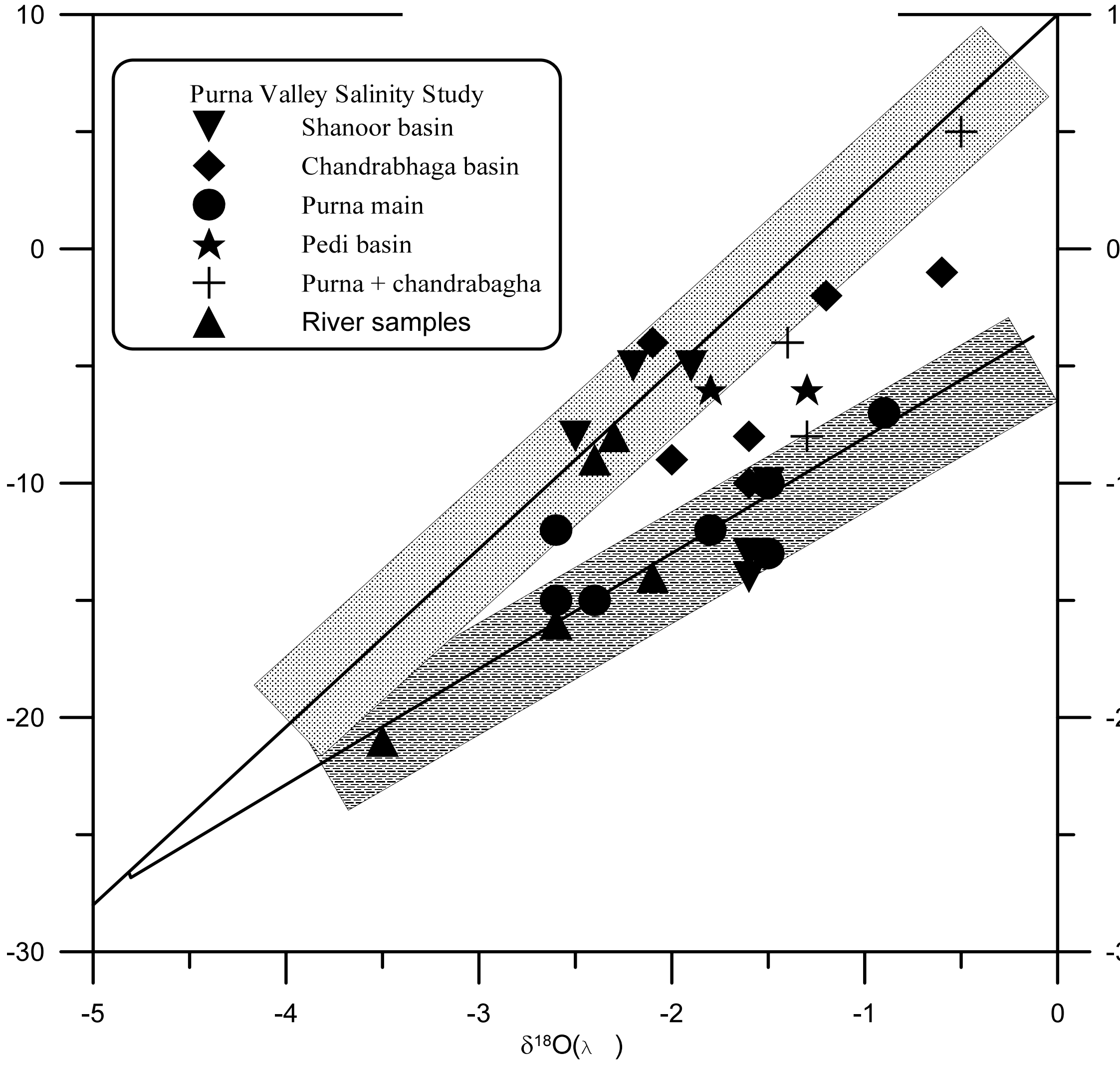

Figure 1. δD - $\delta^{18}O$ plot of groundwater samples from parts of the Purna alluvial basin. Two distinct trends are seen, with one being the local meteoric water line and the other the evaporation line.

The hydrogeological and hydrometeorlogical data reveal that the thick clayey soil strata, low annual rainfall and very low transmissivity and specific yield of the aquifers have probably lead to groundwater quality problems in the study area. The groundwater level contours indicate the regional slope trending to southwards, indicating the regional recharge zone probably lies in the northern part of the study area. Groundwater level contours also indicate the effluent nature of river Purna in a selected reach.

The hydrochemical and stable isotopes ($\delta^{18}O$ and δD) data indicate that salinity in the study area is due to the combined effect of a) evaporative enrichment of ions during the process of infiltration in the fine grained soil layers (Fig. 1) and b) dissolution of host formations as a result of longer residence time (Fig. 2). The longer residence time is probably due to poor groundwater drainage conditions. This negates the hypothesis that the salinity is a result of drying-up of an inland lake filled with seawater, as proposed by some earlier investigators.

Integrated use of hydrochemical and environmental isotopes indicate that about 72% of the induced recharge project wells being operated by GSDA are performing better and are reflecting improved recharge. The water quality in most of the project wells is also tending to become less saline.

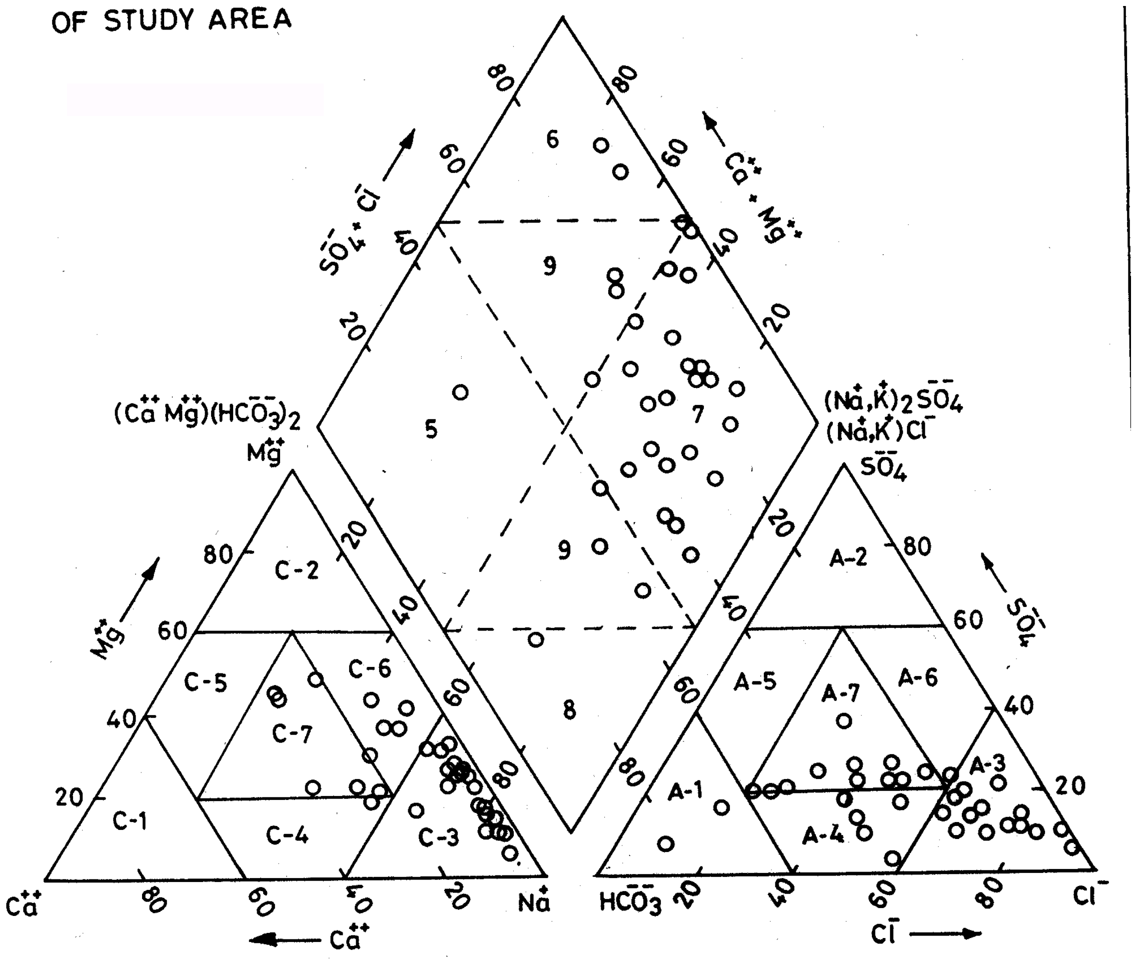

Figure 2. Piper trilinear diagram showing the chemical characteristics of the groundwater from parts of the Purna alluvial basin. The salinisation process as deduced from the figure is due to the longer residence time.

IAEA-CN-104/P-32

NEW CONTRIBUTIONS TO THE ISOTOPIC CHARACTERIZATION OF THE COASTAL AQUIFERS AND THEIR RELATIONS WITH THE SALINE INTRUSION IN THE COSTA DE HERMOSILLO, SONORA, MEXICO

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The area of study is located in the coast of the Gulf of California, at the Northwestern of Mexico. It is an Quaternary alluvial plain of continental origin. A new hydrogeologic model is described for the area, consisting of a single unconfined aquifer with an average thickness of 200 m, as well as some located semiconfined zones. We found no evidence of a deep aquifer suggested by previous authors, but there is a deep trap old water. Beneath the unconfined aquifer there exist marine sediments containing Miocene fossils. These marine sediments are more than 500 m thick that fill and cover a number of tectonic basins and horst system (Basin and Range) of variable size and depth. The regional basement is underlying the Miocene sediments, it consist of granites and volcanic rocks. Oxygen-18/deuterium and tritium data support this hidrogeologic model and the origin of the fresh groundwater stored in the aquifer. There is no evidence of modern water infiltration, even by agriculture return flow, because of the very high real evapotranspiration (>1220 mm/year) and the depth of the groundwater table (135 m). Enough evidence is present in this paper to affirm that the sea water is intruding into the upper part of this aquifer up to 32 km inland. The excesive pumping since 58 years ago depleated the potentiometric surface forming a cone with the actual deepest point in 65 meters under the sea level. The saline intrusion has created a interface zone of 5 to 15 km width and 80 km length of brackish water. As a consequence of the tectonic setting, there is also a fringe zone, which is protecting small areas of the aquifer from the sea water intrusion near the coast, in this place the impervious rock is present, and helps to configure the geometry of the interface zone. Radiocarbon data suggest an average age of 3000 years for the fresh water and the existence of a paleowater stored in both the marine sediments and the volcanic rocks with an age of 30,000 years.

GEOCHEMICAL EVOLUTION AND TIME SCALE OF SEAWATER INTRUSION INTO THE COASTAL AQUIFER OF ISRAEL

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The dynamics of seawater intrusion into a coast is commonly estimated by a rise in salinity and/or by theoretical hydrological models. Estimations using radioactive isotopes are reported only in several works. Here we present an attempt to quantify the geochemical processes and the time scale of seawater intrusion into a coastal aquifer from the changes in the major ions composition of the waters and the natural distribution of the cosmogenic isotopes ^{14}C and ^{3}H.

Saline and brackish groundwaters were sampled from observation and pumping wells in the Israeli coastal aquifer. In addition, detailed profiles across the fresh-saline groundwater interface (resolution of 10 cm) were provided using a Multi Layer Sampler (MLS) that was installed three times in this zone. All groundwater samples were analyzed for their chemical composition, stable carbon and oxygen isotopes, $^{14}C_{DIC}$ (^{14}C in the dissolved inorganic carbon) and tritium activity. The coastal rock was analyzed for its chemical contents and stable and radioactive carbon isotope composition of the carbonate and of the organic matter.

The chemical and the stable isotope data revealed three distinct water types (end members) that are placed in different zones in the coastal aquifer: 1. Slightly modified Mediterranean seawater with its salinity (SWS); 2. Slightly diluted (with up to 20 % fresh groundwater) saline groundwater (SDS); and 3. Fresh groundwater (FGW).

The SWS waters show in most cases excess in total alkalinity and DIC and depletion in ^{13}C and ^{14}C with respect to normal seawater, indicating that anaerobic oxidation of organic matter is the first diagenetic reaction that affect seawater during its penetration into the bottom sediments. Later on, the SWS waters dilutes, gain Ca^{2+} and Sr^{2+} and deplete in K^{+} suggesting that mixing with fresh water and cation exchange are the main diagenetic processes that transforms SWS into SDS. At the fresh-saline water interface, SDS waters show conservative mixing with FGW in most cases.

Inspection of chemical data from coastal aquifer around the world indicates that these main paths of seawater during its evolution into saline groundwater, intensive ion exchange and slight dilution with fresh groundwater, are globally important phenomenon.

Most saline waters contain substantial amounts of ^{3}H suggesting that penetration of Mediterranean Sea water and its travel inland to a distance of at 50-100 meter onshore occurred 15-30 years ago. Therefore, the relatively low $^{14}C_{DIC}$ activities measured in the saline groundwaters resulted mainly from diagenetic processes and not from simple radioactive decay.

STUDY OF THE POLLUTION IMPACT FROM THE USAGE OF SEWAGE AND DRAINAGE WATERS ON THE GROUNDWATER OF THE QUATERNARY AQUIFER, WEST CAIRO, EGYPT

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The aim of this study is to assess the water quality of surface and groundwater in the western part of Cairo and to estimate the sources of pollution as salinisation, nutrients, trace elements and microbiological activity as a result of re-use of partially treated drainage and sewage waters for irrigation.

In the studied area fresh water problems that need for irrigation arise from the limitation of water resources, high degree of use for cultivating in different seasons and the extension of the reclamation lands. Recently new applications were applied by mixing fresh and wastewater to substitute this decline. Two sewerage stations (Zinen and Abu-Rawash) are located in the area of study for collecting and partially treating wastewater from Giza area. The poorly treated effluents that discharge from these stations in open channels or mixed with fresh water in some canals are flowing through the cultivating land for agricultural irrigation. This could lead to direct pollution to the surface and ground waters in this area, which is the point that needs to detect in this work.

The studied area is located in the western region of greater Cairo at latitudes 30o 00` and 30o 15` N and longitudes 31o 00` and 31o 15` E Fig (1). About 97 water samples were collected from canals, drains and groundwater from the Quaternary aquifer in the area of study. The estimated values of total dissolved solid for most surface and ground waters samples don’t exceed 1000 mg/l except about 12% have salinity>1000mg/l. This increase in salinity could be attributed to the ion exchange process between Na- Ca as a result of water-rock interaction, or from the recycling of drainage water containing excess of fertilizers that used in cultivating practices. The predominant water types of surface and groundwater samples are $NaHCO_3$ and Na_2SO_4 representing meteoric and mixed water type. Few groundwater samples have MgC_{l2} (marine water type), these samples are located in the east and middle parts of the studied area. The results of the stable isotopes (fO18O, fOD) of most groundwater samples having nearly the value of the Nile water, which is considered as the main recharge source to this aquifer plus the infiltration of the excess irrigation water Fig (2). The slight depletion that presents in fO18O and fOD of some groundwater samples in the east and middle parts of the studied area could reflect the mixing with paleowater from lower aquifer as a result of extensive pumping of groundwater.

The Tritium content of the selected surface and groundwater samples varies from 0.6 to 10 TU. Samples with low tritium values confirm the mixing with paleowater where the recharge process occurred before the tritium peak time [1]. High Tritium content detected in few groundwater samples north of Abu- Rawash station indicates the absence of paleowater and the direct recharge by recent surface water.

The intensive use of fertilizers and wastewater in agricultural practices in the studied area led to increase in nitrate, phosphate, trace elements and high quantities of microbial organisms in some surface and groundwater samples. High concentration of NO-3 than the maximum recommended limit for drinking water (> 45 mgl-1NO-3, WHO, 1993)[2] was found in groundwater samples north of Abu- Rawash. The concentration of trace elements (Mn, Fe, Zn, B, Cd, Cu, Ni and Pb) in surface water samples are higher than that present in groundwater whereas most metal shave fairly limited mobility in soil and groundwater due to cation exchange or sorption of these elements on clay surface. High concentrations were detected more than the maximum recommended limit for drinking water in Mn, Fe, Cd, Ni and Pb of some surface and groundwater especially in east and middle parts of the studied area are attributed to the presence of sewage effluent in the surface channels. From the microbiological analyses, all sites of surface water and some groundwater especially shallow wells near by the sewerage stations are contaminated with all microbial indicators. So the use of effluent, drainage water and sludge in agricultural practices for long run will threat the surface water bodies and it's under laying aquifer as well as the human health.

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LANDFILL POLLUTION CONTROL WITH ISOTOPE TECHNIQUES

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1. INTRODUCTION

Groundwater and surface water contamination by sanitary landfills is being monitored since 1989 in Italy by using isotope techniques combined with chemical analyses. The results obtained are considered mostly satisfactory for identifying sources of contaminants and predicting their behaviour (see, for example, [1] and [2] and [3]). We present in this work the results of chemical and isotopic measurements performed on rainwater, surface water and groundwater samples, with the aim of investigating the fate of contaminants released from some landfills located near Ancona, Central Italy. The isotope determinations included $\delta^{18}O$, $\delta^{2}H$ and tritium (^{3}H).

2. METHOD

The first objective of these investigations is establishing the base concentration level of the main environmental parameters related to contamination, and obtaining indication about source and residence time (age) of groundwater in the landfill proximity. In particular, the methods used for detecting groundwater and/or surface waters contamination derived from the landfill, are based on the occurrence of tritium activity anomalies and chemical concentration changes. These methods are based on the environmental tritium content and isotopic composition of water in the region, and the subsequent evaluation of the data measured in the groundwater inside (leachate) and outside landfill.

In order to estimate the regional base level of environmental tritium in shallow groundwater, we measured the tritium content of monthly rainwater samples collected in stations on the Apennines in proximity of Ancona. In recent years, the tritium concentration ranged from 3 to 6 TU in winter months (October to April), and reached the maximum values (up to 14 TU) in summer months (Fig. 1).

TABLE 1. Tritium, ^{18}O and ^{2}H content in landfill areas.

LANDFILL	Sample	δ^{18}O ‰ SMOW	δ^{2}H ‰ SMOW	^{3}H (TU ± 1)
Landfill n. 1	Leachate	-5.23	-22.2	249
	Well P3	-6.53	-35.75	8.4
	Well P4	-6.46	-34.75	11.7
	Well P5	-7.73	-41.4	12.7
	Well P7	-6.80	-43.3	4.1
	Well P8	-5.60	-31.75	10.7
Landfill n. 2	Leachate	-7.55	-45.0	30
	Internal well	-7.34	-41.7	20.2
	External well	-7.02	-41.3	8.2

The investigations of groundwater and surface water contamination were undertaken on landfills dismissed from 1986 to 1998. The isotopic and chemical monitoring was started one year ago and was carried out on leachates, surface waters and groundwater (the last sampled in several downstream wells). The isotope determinations are reported in Table 1.

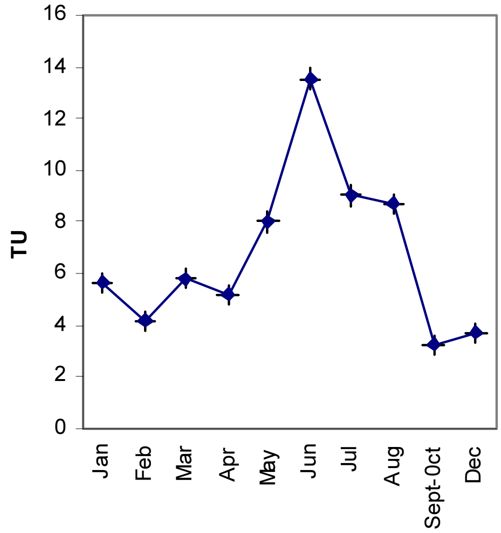

FIG. 1. Seasonal variation of rainwater tritium content in rainfall on the Apennines

3. RESULTS

The tritium concentration in leachates can be very high, due to a still active tritium release from the landfill. In principle, therefore, is possible to identify the contamination of groundwater from the tritium increase with respect to the base level, and also estimate the mixing ratio with the landfill leachate [4].

In the younger Landfill 1 (Fig. 2), which was dismissed in 1999, the leachate tritium concentration is still high (about 250 TU). However, only the downstream wells P4 and P5 show a tritium content above the natural base level, thus showing that groundwater may be currently contaminated by the landfill in a significant degree (leachate fraction 2-3 %). It should be noted also that groundwater in well P5 has a recharge source different from other wells, as indicated by stable isotopes (Fig. 3).

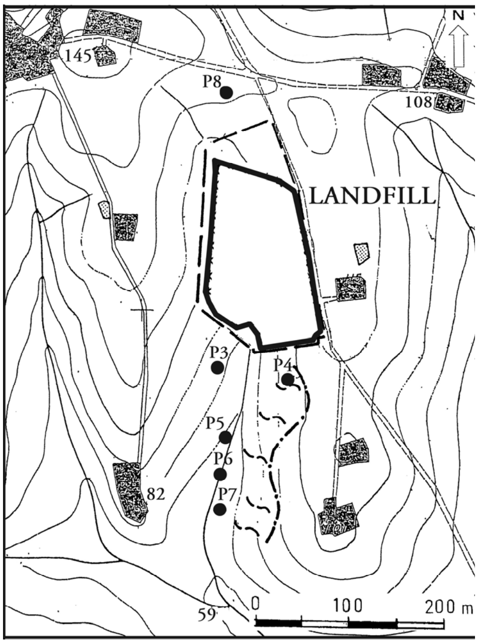

FIG. 2. Location of Landfill n. 1 and wells

In the older Landfill 2, dismissed in 1986 (Fig. 4), the tritium content of leachate is nowadays about 30 TU only, as most tritium has been washed out by the percolating precipitation. However, in the deep well located in the perimeter of the landfill, the tritium activity is higher than the present natural level, probably indicating contamination from the above landfill deposits. The stable isotopes indicate that the recharge of this groundwater derives from precipitation at elevation of 500-600 m asl (Fig. 5). In fact, other wells in the area which are recharged by local precipitation, have a $\delta^{18}O$ close to –5 ‰.

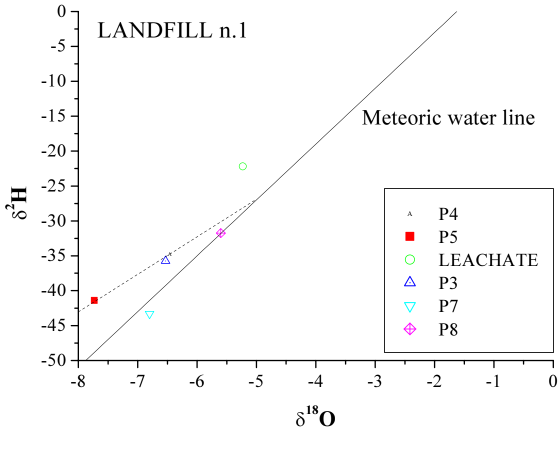

FIG. 3. Conventional plot of δ^2H against $\delta^{18}O$ for leachate and groundwater in Landfill n.1

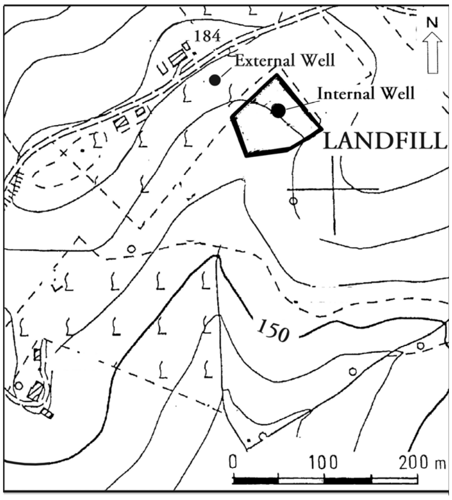

FIG.4. Location of Landfill n. 2 and wells

Several other landfills which have been investigated, show no significant contamination of the surrounding groundwater, whose tritium content is within the limits of the natural base leves (4-6 TU).

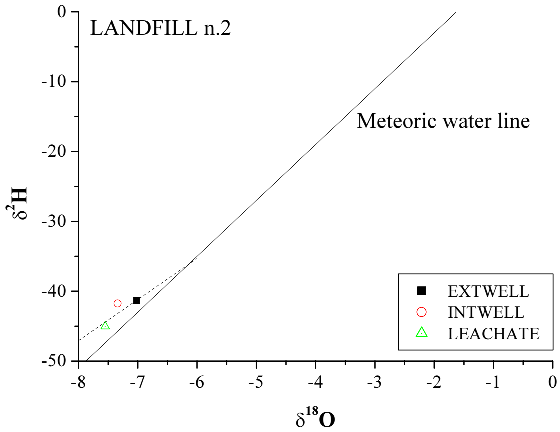

FIG. 5. Conventional plot of δ^2H against δ^{18}O for leachate and groundwater in Landfill n.2

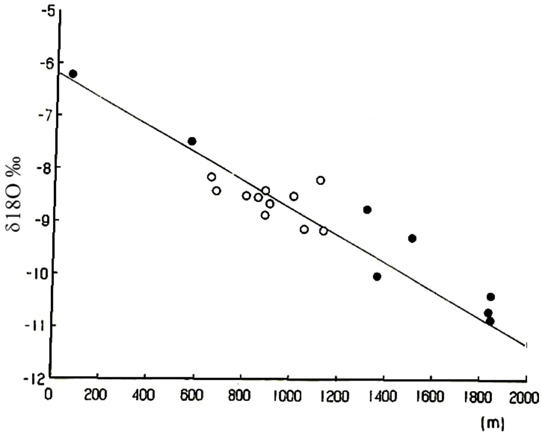

FIG. 6. Relationship between δ^{18}O ‰ and the altitude of springs, in the Apennines

4. CONCLUSIONS

The stable isotope composition of groundwater around landfills is in most cases similar to that of rainwater (Fig. 3, 5). The deuterium and oxygen-18 of leachates always appear to be somewhat different with respect to the groundwater values; but they can be used as contamination index only in cases of high fraction of leachate. Tritium is usually much more useful as contamination index, and enable us to identify the contamination deriving from mixing with landfill leachate.

The stable isotope composition is used to estimate the elevation of the groundwater recharge area. The relationship between isotopic composition and altitude in the Apennines was derived from springs (Fig. 6).

Our future investigation programs include isotopic measurements of $\delta^{13}C$ in dissolved carbonates, bicarbonates and carbon dioxide, $\delta^{34}S$ ‰ in dissolved sulfates, and $\delta^{15}N$ ‰ in nitrate, which will be performed on leachates and groundwater. The aim is to establish their isotopic ranges, and to assess if these isotopes can also be used in groundwater contamination studies by landfills.

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EVOLUTION OF THE CHEMICAL (NH4) AND ISOTOPIC ($\delta^{15}N_{-NH4}$) COMPOSITION OF PIG MANURE STORED IN AN EXPERIMENTAL PIT

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In the Catalonia Region (NE Spain), pig farming is a very important activity in the agricultural economy. In 1999, livestock in the region consist of 690,903 cows, 870,817 sheeps and 6,019,632 pigs, with more than 16,700 farm exploitations. Most of these farms are concentrated in some agricultural areas, where livestock densities are up to 64 sheeps/km^2, 79 cows/km^2 or 1057 pigs/km^2. This intensive activity produces large quantities of manure, mainly coming from the pig farms; a small part of them is processed in treatment plants and the rest is spread onto the fields as organic fertiliser. This practise produces a diffused contamination in the aquifers of these areas with high concentrations of nitrates, up to eight times higher the permitted concentration (50 mg/l) for drinking water. Moreover, synthetic fertilisers are also used in the agricultural areas, contributing to the nitrate groundwater contamination. In 1998, following the Directive 91/767/CEE, the Catalan Government classified six areas as vulnerable zone of nitrate contamination from agricultural sources. At present they are preparing a new governmental Act to add three other areas into this classification.

The nitrogen stable isotopes have already been used as tracers of nitrate source in groundwaters [1]. However, this technique requires a previous isotopic characterisation of the most significant pollutants, i.e. synthetic fertilisers and manure. The nitrogen isotopic composition of the pig manure is believed to vary during the period of time that they are stored in the deep pits before being spread onto the fields. The volatilisation of the ammonium is the cause of this isotopic change. The aim of this study is to know the variation of this isotopic composition in order to determine the isotopic signature of the pig manure.

In the present study, the conditions of a deep pit have been reproduced at smaller scale using a 125-L open plastic canister, which was filled with “fresh” pig manure and stored during eight months, from November 2001 to July 2002 at atmospheric conditions. Ammonium concentration and its nitrogen isotopic composition were analysed weekly during the first six months and every ten days during the last two months.

Ammonium concentration oscillates between 3000 and 4000 ppm, with no progressive decrease in time as it would be expected in a volatilisation process. This is caused by the loss of manure volume due to evaporation (50 % in eight months) which compensates the ammonia volatilisation and keeps the ammonium concentration stable.

The nitrogen isotopic composition of the ammonium is controlled by the volatilisation process. During the first ten days, the pig manure has an isotopic composition between +8 and +10‰, and after eight months, it raises up to +25‰ (Fig. 1). However, the pig manure is not stored in the deep pits more than six months; consequently, the range of $\delta^{15}N_{NH4}$ values to be considered for pig manure as an input of nitrogen contamination should be from +8 to +15‰.

Still, this isotopic composition can be higher if manure is stored during the summer time since the higher temperatures may increase the volatilisation rate and raise the ammonium isotopic composition in a shorter period of time (Fig.1).

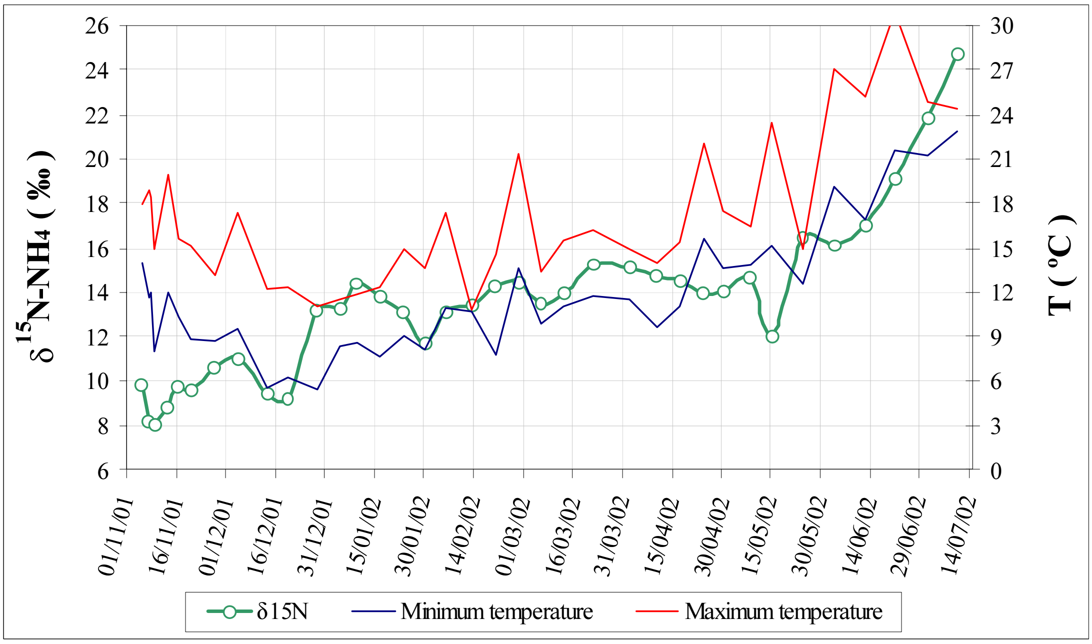

Figure 1: Evolution of the isotopic composition of the ammonium versus atmospheric temperature.

Unlike synthetic fertilisers, which are characterised by a δ^{15}N close to the 0‰ [2], the organic fertilisers (pig manure) are enriched in ^{15}N (δ^{15}N from +8 to +15‰). Therefore the nitrogen isotopic composition is a valuable tools to evaluate the origin of nitrate agricultural contaminations. As an example, nitrate nitrogen isotopic composition has been used in some areas in Catalonia [3] to confirm that pig manure is the main contributor to the nitrate pollution in groundwaters.

ACKNOWLEDGEMENTS

This study has been financed by the CICYT project REN2002-04288-CO2-02 of Spanish Government and the SGR01-00073 of Catalonian Government.

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STABLE ISOTOPES OF DISSOLVED SULPHATE AS TRACERS OF THE ORIGIN OF GROUNDWATER SALINIZATION IN THE LLOBREGAT RIVER (NE SPAIN)

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In the middle section of the Llobregat Basin (NE Spain) several potash mines exist. This activity produces large salt tailings, with an estimated mass of 61Mt, which are stored around the mining sites, with no waterproofing. Some aquifers near the mining zones are highly salinized (chlorine up to 14%), and the origin of the salinity is controversial, as it can be related either to contamination from mine tailing effluents or to natural water interaction with saline formations. Moreover, with less intensity fertilisers could also contribute to groundwater salinization, as agriculture is an important economic activity in the Llobregat Basin. These three sources, natural, mine effluents and fertilisers, where chemical and isotopically ($\delta^{34}S$) characterised in a previous paper [1], in addition, samples of uncertain origin were analysed and the sources of salinization were determined coupling chemical with $\delta^{34}S$ data.

On the basis of the previous results, the analysis of the $\delta^{18}O_{SO4}$ and $\delta^{18}O_{H2O}$ of the same samples is presented in order to: (a) asses the extent of redox processes, and (b) quantify the contribution of each source using a $\delta^{18}O_{SO4}$ - $\delta^{34}S_{SO4}$ diagram. The $\delta^{18}O_{SO4}$ was determined by TC/EA-IRMS, and the $\delta^{18}O_{H2O}$ was measured by CO_2 equilibrium and IRMS. Notation is expressed relative to V-SMOW.

All samples plot away from the field of sulphate produced from sulphide oxidation in a $\delta^{18}O_{SO4}$ vs $\delta^{18}O_{H2O}$ diagram [2] therefore oxidation processes are discarded. Results of $\delta^{18}O_{SO4}$ vs $\delta^{34}S_{SO4}$ are shown in Fig.1. Values for natural samples and mine effluents are in accordance with the $\delta^{18}O_{SO4}$ of bedrock evaporites and Potash Unit respectively [3], ranging from +12.2‰ to +14.6 ‰ the natural samples; and from +7.6‰ to +9.8 ‰ the mine effluents. Fertiliser oxygen isotopic composition is +9.5 ‰ for ammonium sulphate, and +14.6 ‰ for NPK. The $\delta^{18}O_{SO4}$ allows to discriminate natural and mine samples, but NPK plot within the area of natural values and ammonium sulphate coincides with mine effluents. Despite the overlapping of the $\delta^{18}O_{SO4}$ values, the $\delta^{34}S_{SO4}$ is different, and quantification of the contribution of each source can be done.

Fig. 1 shows the mixing lines between the end members considered. These models allow to quantify different source contribution for samples of uncertain origin (see [1] for sample characterisation). Samples from site 9 are in accordance with sulphates from the bedrock. Samples from site 7 are a mix between mine effluents and natural values, the contribution of mine effluents varies from 60 to 30% and fertilisers are discarded. For samples from sites 8 and 10, a better characterisation is possible, with a distinction of different fertilisers. At site 8 samples are a mix of NPK fertiliser with natural values, and at site 10, samples are mainly controlled by ammonium sulphate, in both cases fertilisers contribution is up to 90 %.

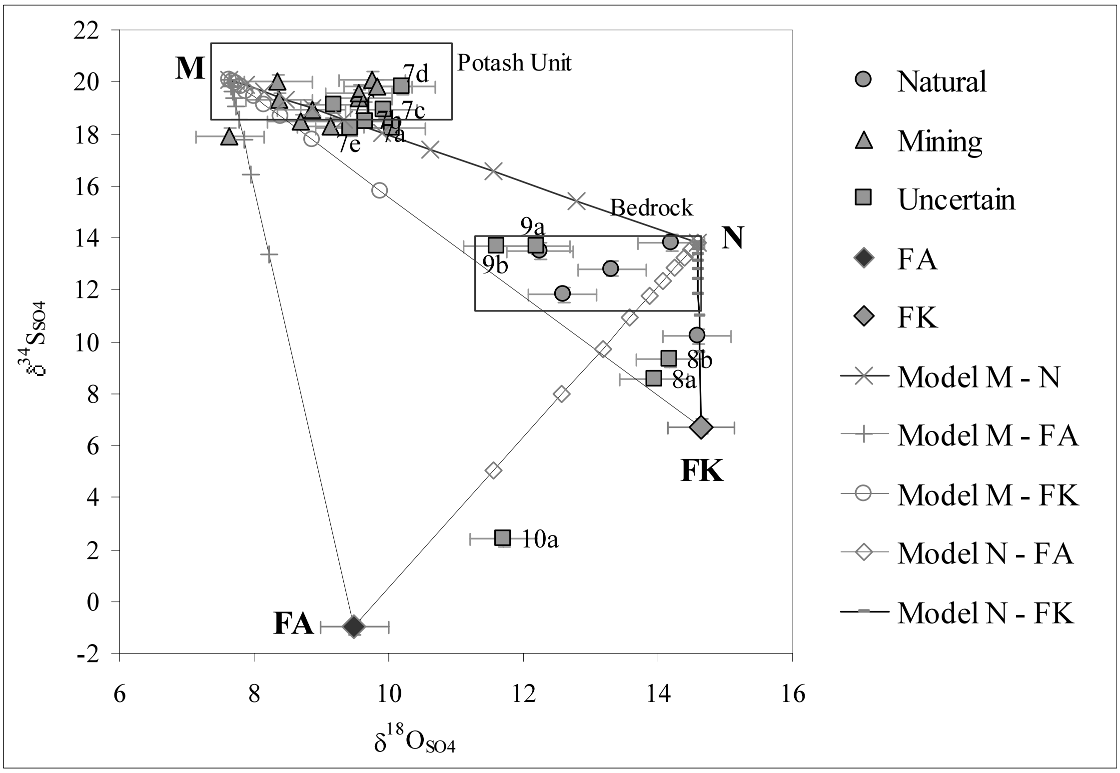

FIG. 1 Plot of $\delta^{18}O_{SO4}$ *vs* $\delta^{34}S_{SO4}$*. Symbols represent sample values; boxes show bedrock evaporites and Potash Unit ranges. Lines are mix models between the end members considered:* **M**=*mine effluents* ($\delta^{34}S$ = +20‰, $\delta^{18}O$ = +7.6‰), **N**= *natural springs* ($\delta^{34}S$ = +13.8‰, $\delta^{18}O$ = +14.6‰), **FK**= *NPK fertiliser* ($\delta^{34}S$ = +8‰, $\delta^{18}O$ = +15‰) *and* **FA**=*ammonium fertiliser* ($\delta^{34}S$ = -1‰, $\delta^{18}O$ = +9.5‰).

This study confirms the usefulness of isotopic geochemistry to trace the origin of water salinization in the middle section of the Llobregat River. As dilution processes do not affect isotopic composition, coupling the analysis of $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$ in waters provides an excellent tool for quantifying the anthropogenic inputs existing in the area, potash mine effluents and fertilisers.

ACKNOWLEDGEMENTS

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A NEW APPROACH BASED ON ENVIRONMENTAL TRACERS TO BETTER CONTROLE GROUNDWATER EXPLORATION AND EXPLOITATION

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The immediate availability of groundwater recharge decreases significantly with depth. Mathematical modelling showed, that as an average more than 85% of the groundwater recharge of a landscape is turned over in the upper decametres of aquifer systems (active recharge zone) and less than 15% penetrates the great depth (passive recharge zone). The passive recharge zone occurs above connate waters that did not return to the biosphere since these waters have been included in the sediment during sedimentation [5].

As a rule, groundwater of the active recharge zone has low turn-over times (< 50 years), is tritiated and contaminants have easy access; contrary, groundwater from the passive recharge zone has high turn-over times, a significant dilution, chemical and microbial reaction potential, is free of tritium and has ^{39}Ar- and ^{14}C-contents lower than initial concentrations [5].

The active recharge zone reaches a thickness of a few meters to 100m according to the amount of groundwater recharge and the hydraulic properties of the aquifer system; the passive recharge zone reaches several hundred meters in thickness.

All these modelling results have been confirmed by isotope related, hydrochemical and hydraulic field research in humid, tropical and semiarid climates [2, 3, 5].

For a sustainable water supply, from both the active and passive recharge zone adapted exploration, protection and exploitation strategies have to be applied, which are mostly disregarded.

As a consequence of depth related groundwater recharge and susceptibility of aquifer systems towards contamination and natural attenuation, respective data sets should be available; since these are often missing and since predictions based on mathematical models often suffer from geologic and hydrologic uncertainties to make a real long-term statement, a new method has been developed, using environmental tracers for a better calibration, prediction and assessment of hydrodynamic changes in the exploitation floor and his surroundings. Such tracers can be

- chloride, the concentrations of which indicate the intensity of evaporation losses of precipitation and the respective changes in geologic times as fare as no lithogenic chloride sources exists,
- Deuterium and oxygen-18, which both indicate climate changes during groundwater recharge and
- The radioactive environmental tracers ^{39}Ar and ^{14}C.

Under undisturbed hydraulic conditions, all these tracers occur either in fixed horizons or prove a continuous concentration decline with depth. Once groundwater abstraction starts, this natural stratification gets disturbed according to the abstraction depth, rate and duration, because hydraulic short cuts with neighbouring aquifers are initiated.

These man-made hydraulic short cuts lead to a long-term transient behaviour of aquifer systems [4] and the depth of exploitation produces a special inflow constellation to the screen of the well, which are both difficult to predict and mostly neglected. As an alternative to the usual monitoring of the arrival of contaminants, it is proposed to

- Control the changes in the natural isotope and chemical stratification of aquifers, which express changes and mixing in the hydrodynamic system and
- Use these analytic results to calibrate numerical models on flow and non-reactive transport.

These measures create an effective early warning tool to assess the consequences of hydrodynamic changes and prevent in time any contaminant access to the exploitation floor.

Mathematical models to do so have been set up showing that the exploitation well and its downstream area are the most sensitive areas for such an isotope survey; Tritium was not a good early warning tracer, because it behaves like the contaminants, contrary ^{39}Ar and ^{14}C are very sensitive in the time range till several 100 years, respectively of more than 1000 years. With mathematical modelling it could also been shown that an environmental tracer monitoring all 3 to 5 years was sufficient to efficiently control and asses in time any groundwater abstraction from the passive recharge zone [1].

Groundwater exploration and exploitation in connection with the proposed environmental tracer survey methods could be favourably used to guarantee a sustainable drinking water supply from areas, which are highly susceptible to contaminations like in urban areas [3] or intensive agricultural areas [2].

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CHEMICAL AND ISOTOPIC SIGNATURE OF GROUNDWATER AFTER SEA WATER ENCROACHMENT IN COASTAL AQUIFERS OF THE CORNIA RIVER BASIN (TUSCANY, ITALY)

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Groundwaters in several regions within the Mediterranean basin exhibit a boron concentration which often exceeds the potability limit of 1 mg/L. The origin, fate and geochemical processes of boron in groundwater is now being investigated in Israel, Greece, Cyprus and Italy within the framework of the coordinated research project BOREMED, financially supported by the European Union. We report here the current status of the BOREMED investigations on groundwater of the Cornia Valley in Western Tuscany, Italy. Although high boron (up to 4 mg/L) is observed in inland groundwater as well, the emphasis of this presentation is on aspects related to the boron content of coastal aquifers of the Cornia Valley, which may attain 8 mg/L. This high boron concentration, although often well above that of seawater (5 mg/L), appears to be connected with sea water encroachment due to groundwater overexploitation. A geochemical explanation is proposed here, on the basis of the behaviour and contents of various chemical (Na, K, Ca, Li, B, Sr) and isotopic ($^{18}O/^{16}O$, $^{11}B/^{10}B$ and $^{87}Sr/^{86}Sr$) tracers.

The Cornia basin, a small catchment area of 527 Km^2 only, is formed by the Quaternary alluvial deposits of the Cornia River. The shallow aquifer of the upper basin evolves, moving towards the coast, into a semi-confined and then a well-ordered multilayer aquifer consisting of gravel, sand and silt levels alternated with clay levels.

In the upper part of the basin, the groundwater has a Ca-bicarbonate facies, resulting from leaching processes of the aquifer alluvial sediments by the recharge waters (including those from cold springs at the foot of the hills bordering the basin). This groundwater is characterized by $\delta^{11}B$ values ranging from +3 to +9‰ *vs.* NBS951 and δD and $\delta^{18}O$ values of about -36 and -5.5‰ *vs.* VSMOW respectively, which are typical of meteoric waters.

In the coastal aquifers, chemical and isotopic interactions between salty water and the aquifer matrix occur in the mixing zone of groundwater with seawater, which determine the release of chemical tracers through exchange reactions. This process is capable to modify significantly the chemical composition of groundwater and the isotopic composition of some dissolved trace elements.

The $\delta^{18}O$ signature, and the Br/Cl and Cl/SO_4 ratios indicate the seawater fraction present in of groundwater may attain up to 30-40%. The marine intrusion typically produces the Na-Ca-Chloride facies occurring all along the coast, as shown by GIS maps. In spite of their unquestionable marine fingerprint, these waters display negative $\delta^{11}B$ values associated with high B concentrations, indicating the occurrence of more complex processes than simple mixing with sea water ($\delta^{11}B \sim 40$ ‰). This conclusion is also supported by the B, Li, K, Ca, Mg, Sr enrichments and Na depletion with respect to seawater.

The peculiar chemical and isotopic composition of coastal groundwater is explained by cation exchange processes between brackish waters and sediments. The process is based on the adsorption capacity of the clay minerals (including their amorphous companions such as allophane) present in the aquifer that release the adsorbed elements when groundwater salinity increases. Thus, the contribution of desorbed boron could explain the high boron contents observed and its negative $\delta^{11}B$ values. According to its isotopic composition, the boron originally adsorbed on the clayey fraction of the aquifer material and released during subsequent groundwater-rock interaction, seems to have a continental origin rather than marine. The rather homogeneous $^{87}Sr/^{86}Sr$ ratio of dissolved strontium (mean value 0.7089, standard deviation of the mean 0.00003, n = 47) suggests a dominant contribution from carbonate dissolution and/or exchange.

The combination of different geochemical and isotopic fingerprints shed light on various aspects of groundwater encroachment by sea water, and allow us to delineate the complex saline water-aquifer interactions which are triggered in the groundwater-sea water mixing zone.

ISOTOPIC IDENTIFICATION OF PROCESSES RESPONSIBLE FOR INCREASING SULFATE CONCENTRATIONS IN AN AQUIFER NEAR MANNHEIM (GERMANY)

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Dissolved sulfate is a common constituent in groundwater. Sulfate concentrations range typically between less than 10 mg L^{-1} to more than 50 mg L^{-1} in aquifers without significant lithogenic sulfur sources (Robertson et al 1989, Edmunds et al 1996). Throughout the last few decades, an increase in sulfate concentrations has been observed in many aquifers particularly in industrialized regions of the northern hemisphere. Elevated atmospheric sulfur deposition rates in the 1960's and 1970's have been suggested as a possible reason for increasing sulfate concentrations in groundwater. Widespread use of fertilizers such as ammonium sulfate or potassium sulfate, industrial point source pollution, but also natural processes such as oxidation of reduced inorganic sulfur compounds (e.g. pyrite) are alternate candidates which may cause increasing sulfate concentrations in aquifers.

The Käfertal aquifer near the city of Mannheim (Rhine-Neckar region, SW Germany) is an example of a groundwater system, where increasing sulfate concentrations have been observed throughout the last three decades. Sulfate concentrations in the shallow portion of the aquifer increased from circa 100 mg L^{-1} in 1970 to more than 150 mg L^{-1} at the end of the 20th century. Continuation of this trend would eventually necessitate the costly construction of a water treatment plant. The objectives of this study were (1) to identify the processes responsible for the increasing sulfate concentrations in the Käfertal aquifer near Mannheim (Germany) and (2) to suggest potential procedures to ameliorate this trend.

The investigated catchment is 67 km² in size and located NE of the city of Mannheim (320.000 inhabitants). The region is characterized by intense industrialization. Land use comprises forests (50%), farmland (37%), and urban developments (18%) predominantly in the eastern portion of the watershed. The waterworks at Mannheim-Käfertal, situated about 6 km northeast of the city of Mannheim, have been in operation for over 100 years. In 1998, 13.5 x 10^6 m³ of groundwater were obtained and used for public drinking water supply. Production wells tap an upper unconfined and a lower confined aquifer, both consisting of unconsolidated Quaternary sand and gravel separated by a 20 meter thick clay layer.

Precipitation water (bulk and throughfall), seepage water from the unsaturated soil zone, and groundwater were repeatedly sampled between September 1996 and September 1998. Concentrations and isotopic compositions of sulfate were determined using standard techniques (Krouse & Mayer 2000). Soil and sediment samples were obtained from three soil profiles and four drill cores completed in the Quaternary aquifer deposits. Concentrations and isotope ratios of total sulfur (ASTM 1993) and chromium-reducible sulfur (Canfield et al 1986) were determined.

δ^{34}S values of precipitation and seepage water sulfate varied between 0 and +3 ‰. δ^{34}S values of most groundwater sulfate samples were significantly more negative ranging between –1.4 and –8.8 ‰. Moreover, increasing sulfate concentrations in the aquifer were correlated with decreasing sulfur isotope ratios. This indicates that oxidation of sulfide minerals with δ^{34}S values as low as –25 ‰ in the aquifer sediments is the process responsible for the increasing sulfate concentrations in the groundwater. Since the highest sulfate concentrations (> 200 mg L^{-1}) and the lowest δ^{34}S values (< -8 ‰) occurred in the drawdown cone of the pumping wells, it appears that lowering of the water table due to increasing pumping rates triggered the oxidation of sedimentary sulfides via aeration of aquifer sediments. Hence, a reduction of the groundwater extraction rates was suggested as a potential measure to counteract any further increase in the sulfate concentrations of the produced groundwater.

BENZENE-CONTAMINATED GROUNDWATERS — TRANSPORT PARAMETERS AND ISOTOPIC EVIDENCE FOR NATURAL ATTENUATION

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The area of investigation is located on the site of a former hydrogenation plant in Zeitz (Saxonia-Anhalt, Germany). The plant was founded in 1938 to produce gasoline and lubricants originally for the German war industry and was subject of severe bomb strikes in 1944 and 1945 spilling about 250 m^3 hydrocarbons into soil. In 1946 it was rebuilt and in the beginning of the 1960's upgraded with a benzene production plant in the eastern part of hydrogenation plant. From 1963 till 1990 the latter produced more than 750,000 t of benzene with maximum production rate in 1979 (79,000 t per year). Leaks and production accidents contaminated groundwater.

Contaminations were found in two aquifers. The upper aquifer (I) is a 5-10 m layer of sandy and clayey deposits from the Pleistocene Elster-glacial. The Tertiary aquifer (II) is composed of gravel deposited by an Eocene river, partly overlain by a lignite seam or silt and clay layer of Tertiary age. The prevailing contaminants of aquifer I are BTEX, dominated by high benzene concentrations up to 500 mg L^{-1}. BTEX-concentrations in the aquifer of Tertiary age are considerably lower (100 mg L^{-1}), and benzene is again the dominant pollutant.

At three positions, groundwater samples for tritium and ^{3}He analyses were taken from both aquifers trying to match beginning, centre, and end of the contamination plume. Samples exhibit tritium contents of about 10 TU, the groundwater from deepest well 11.7 TU. Tritiugenic ^{3}He contents are in the upper aquifer between 0 and 3.3 $TU_{equivalent}$ (1 $TU_{equivalent}$ is the ^{3}He content yielded by the decay of 1 TU tritium) corresponding to ^{3}He/tritium ratios of 0.31 and less, whereas in the deeper aquifer tritiugenic ^{3}He was found between 19 and 37 $TU_{equivalent}$, i.e. ^{3}He/tritium varies in flow direction from 2.0 to 3.1. In terms of apparent groundwater ages these contents correspond to 3 – 5 years in the upper and 10 – 25 years in the deeper aquifer (comp. Figure 1). In case of samples from the deeper aquifer even increasing apparent ages in flow direction might be evident.

The upper aquifer is phreatic, and therefore ^{3}He contents there may be affected by diffusive losses. However, tritium contents in both aquifers indicate apparent ages of less than 15 years. The confinement of the deeper aquifer probably preserves most of tritiugenic ^{3}He. Apparent groundwater ages in Figure 1 indicate a recharge in 1975 or younger. Thus, it is probable that at least in the deeper aquifer the contaminant plume does not 'flow' together with the groundwater.

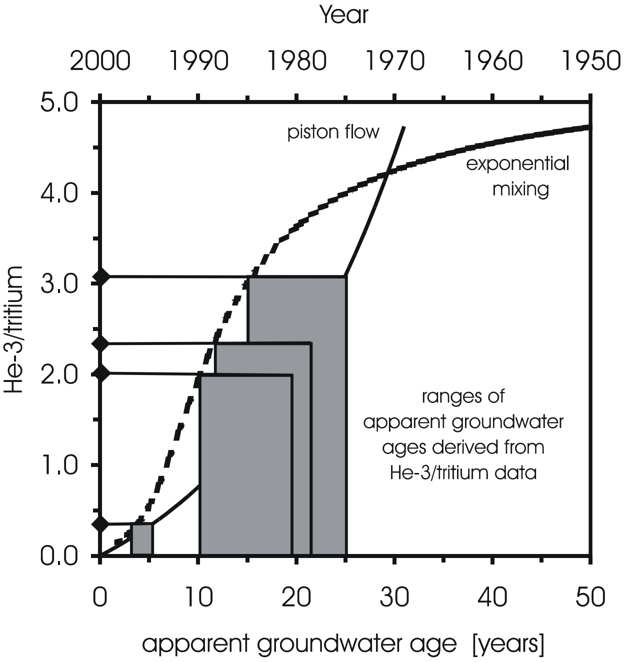

FIG. 1. ^{3}He/tritium ratios of groundwater samples and correlated apparent groundwater ages. The extreme situations piston flow and exponential mixing were assumed as flow conditions.

The energy consumption of natural attenuation processes may be covered by 'oxidizers' like nitrate and/or sulphate. Because in contaminated as well as non-contaminated groundwaters of the investigation area the nitrate level is very low, attention was focussed on the isotopic composition of sulphate (δ^{34}S) as possible source of energy and on dissolved inorganic carbon (*DIC*; δ^{13}C) as indicator of totally decomposed hydrocarbons. Fig. 2 shows sulphate content and its δ^{34}S along a flow path in aquifer I, reflecting isotopic enrichment in sulphate due to bacterial reduction. This trend corresponds to a slight decrease of δ^{13}C of DIC from -22.4 ‰ to -23.7 ‰ confirming the hypothesis of bacterial decomposition of

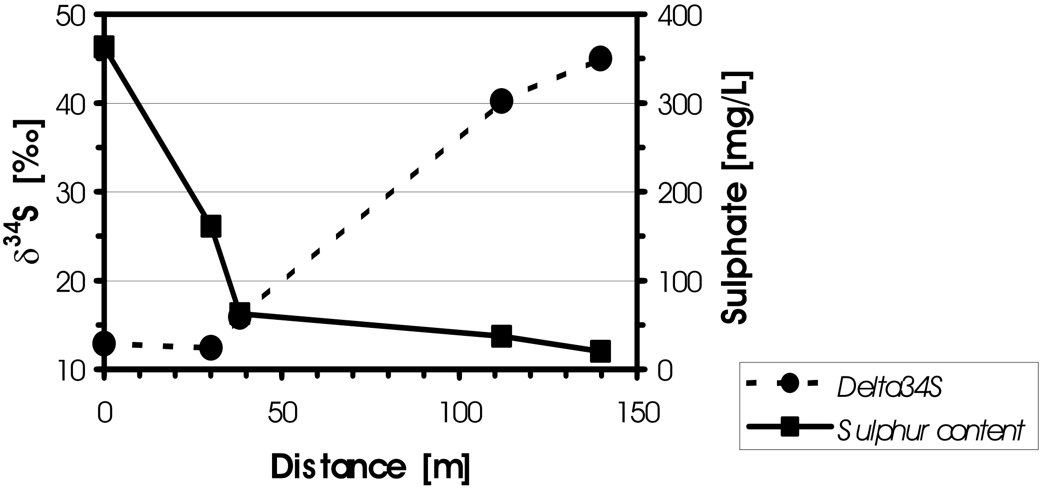

FIG. 2.Sulphate content and its $\delta^{34}S$ *along a flow path in BTEX contaminated aquifer I.*

CHARACTERIZATION OF BIODEGRADATION PROCESSES IN A KARST AQUIFER USING ENVIRONMENTAL ISOTOPE DATA

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The European community has recently adopted a new Water Framework Directive (WFD) that extends to protect all groundwater types and sets a legally binding objective of good status for those waters (6th Environment Action Programme 2001). Europe has only begun to address this issue, recognizing the importance of groundwater protection. While the increased and more efficient food production derived from chemical use the accumulative effect of adding more nutrients and persitant organic pollution can have adverse effects of the quality of water resources. The continuing pollution causes problems not only on the availability of high quality freshwater resources but generated also economic and social pressures due to increasing conflict between land use and the demands for protection of the water resources.

The presentation shows results of hydrograph separation technique in three karstified aquifers (Franconian Alb, South Germany) using isotopic (^{18}O) and geochemical tracers (Sr^{2+}). The main runoff components were characterized for better understanding of spatial and temporal distribution of runoff generation processes. Each of the three catchments within the Franconian Alb responsed differently to storm rainfall. The extent to which the runoff components contributed to stormflow varied among catchments as a function of the different drainage systems. Event water showing a contribution of 10 % to 68 % during flood peaks was identified by means of a detailed observation, stable isotopes and electrical conductivity variation. The high contribution of up to 68 % to stormflow could be explained if event water flows through the sinkholes directly and a significant part of the runoff flows horizontal (interflow) beneath areas of thin soil in a extended epikarst system to the sinkholes. The other two components originated from water stored in the shallow groundwater (soil zone, epikarst) and the deep groundwater and also contributed significantly to stormflow. The proportion of pre-event water which was stored in the soil zone and the epikarst before the event extends from about 16 % to 44 % in the three catchments.

Combined hydraulic, isotope- and tracer-based appraoches in one of the catchments chacacterize the flow paths and mean transit times of water indicating that low sulfate and nitrate concentrations can probably explained by biodegaradation processes in the saturated zone and soil zone. A multi-tracer experiment using artificial tracers with different pore diffusion coefficients was performed in the karst aquifer [1]. The results of the field experiment, environmental ^{3}H output concentrations, mathematical modelling and hydrograph seperation demonstrate possible existence of diffusion processes between mobile fracture water and immobile matrix water. δ^{34}S and $\delta^{18}O\text{-}SO_4^{2-}$ values reflect the existence of biodegradation as the key attenuation process of aquatic sulfate in the porous matrix and dead end pores of the saturated bedrock. A comparison of δ^{34}S and $\delta^{18}O\text{-}SO_4^{2-}$ values from deep wells with the calculated isotope composition of the residual sulphate from the observed karst aquifer probably documents the involvement of sulphite during the biologically mediated reaction supported by enzymatic activities [2]. Because $\delta^{18}O\text{-}SO_4^{2-}$ values of the residual sulphate approaches a constant value and the pertinent $\delta^{34}S$ values increase it was assumed that the $\delta^{18}O\text{-}SO_4^{2-}$ of the residual sulphate was controlled by isotope exchange with water [3].

Results of hydrograph separation can demonstrate that pre-event water showing a contribution of 16 % was stored in the soil zone of the karst aquifer. Increasing $\delta^{15}N$ and $\delta^{18}O$ values of nitrate reflecting changing in nitrate concentartion by denitrification processes. The isotope values of nitrate collected during storm runoff and baseflow conditions are in areas where different sources of NO_3^- typically plot [3]. The source of nitrate contamination in the karst could be determined and originates probably from synthetic fertilizer but influenced from atmospheric nitrate too. The two different sources of oxygen- atmospheric and synthetic fertilizer- could be pronounced in samples with highest $\delta^{18}O$ values$^-$of nitrate and simultaneously a observed dilution effect of nitrate concentrations influenced from areas covered by forests. $\delta^{18}O$ values in atmospheric nitrate reached values with a mean of 64.5 ‰ [4] and can influence isotope values caused by kinetic isotope effects accompanying denitrification of nitrate.

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PROCESS AND BALANCE ASSESSMENT IN LIGNITE MINING AREAS BY MULTI-ISOTOPE APPROACH

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The multi-isotope approach using stable isotopes of various light elements offers possibilities to recognize chemical processes within the aquifers, interactions between ground and surface water, quantification of the balance of water or dissolved compounds in anthropogenic stressed landscapes. Especially in mining areas, the quality of ground- and surface water is one of the main problems during and after remediation measures. Caused by lowering of groundwater level, sulfide oxidation and consequently acidification of surface and groundwater systems are common processes. Successful remediation strategies require knowledge of the chemical and physical processes proceeding in dump sites, and of the groundwater flow dynamic.

Experienced in using sulfur, hydrogen and oxygen isotopes in post-mining landscapes, we will present three key examples for assessing the sulfate reduction in dump sediments, the water balance of mining lakes, and sulfate input from different sulfur sources.

(i) Sulfate reduction: During the long time saturation process the groundwater system of dumps can turn to reducing conditions as indicated by S- and O-isotope signatures of dissolved sulfate. Mainly in the overburden dump sediments of Cospuden mining area (south of Leipzig, Germany) sulfate reduction follows a continuous trend in time from younger to older parts. The input of oxidizing solutions can prevent the reduction process. Evidently, sulfate reduction is still underdeveloped in the conveyor bridge dump caused by penetration of sulfate and iron rich solutions from the weathering zone. A spatial and temporal development was evaluated in different age structured dump sediments using the $\delta^{34}S$ and $\delta^{18}O$ values of sulfate.

(ii) Lake water and sulfate balance: The acidic mining lake 111 (Lusatia mining area, Germany, pH-value 2.6) exists for more than 40 years and reached stable hydrological and hydrochemical conditions about 30 years ago. Isotope data (H, O) were used to determine the annual groundwater in- and outflow of the lake and to calculate the amount of sulfate, iron, and acidity that is carried into the lake by groundwater. For the hydrological balance water samples for ^{18}O-analyses were taken from sampling wells around the lake representing the in- and outflow area, from springs at the lake shore, and from the lake itself. The calculation of the hydrological balance by $\delta^{18}O$-values was carried out by a hydrological model. Besides the acquired field data long-term average values for precipitation, evaporation, temperature, humidity, and isotopic composition of the precipitation were taken into account. The calculated balance proposed an average residence time of the lake water of about 20 years. Considering the lake water sulfate as a mixture of the dump- and aquifer-input, the $\delta^{34}S$-values of lake- and groundwater-sulfate combined with the established annual inflow was used to calculate the annual sulfate input, and based on the hydrochemical data of the inflowing groundwater likewise for the annual iron-input.

(iii) Sulfate balance during flooding: Different sources of sulfur have to be considered for the sulfur budget of mining lakes (in process of filling up): dissolved sulfate from aquifers in the surrounding, dissolved sulfate from water used for artificial flooding (river water or a drainage water from a neighboured mine), and sulfate from the interaction of lake water with aerated sediments bearing oxidized sulfides. Balance investigations can be supported by $\delta^{34}S$ if the contributing sulfur sources can be characterized by known and sufficient different isotope signatures. The accompanying flooding of an extended system of abandoned open pits north of Leipzig (Goitsche) with water from the river Mulde was monitored by sulfur isotopic composition. The starting point was the existence of uncovered sediments with high primary sulfide content in parts of the future lake bottom and a very low pH in the drainage water. Thus, acidification of the lake water was apprehended. Actually, the influence of highly depleted sulfides (-25 ‰ CDT) characterized the pre- and initial phase of flooding. In the later phase, $\delta^{34}S$ was controlled more by groundwater than by river water (about +4.4 ‰) due to the much higher mean sulfate concentration in groundwater. Because of a large variation of $\delta^{34}S$ values and sulfate concentrations measured in groundwater samples, only the $\delta^{34}S$ of the mean groundwater input can be estimated. Based on this result, the contributions of the three mentioned main sources in the sulfur balance have been estimated.

SULFUR CYCLING IN THE DRINKING WATER CATCHMENT AREA OF TORGAU-MOCKRITZ (GERMANY): INSIGHTS FROM STABLE ISOTOPE INVESTIGATION

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In the mid 1990's the annual drinking water production rate in the waterworks Torgau-Mockritz (Germany) was drastically reduced from approximately 36 million cubic meters to 10 million cubic meters. Simultaneously a significant elevation of the sulfate concentration occurred in the raw water from certain production wells especially in the water intake Mockritz I (Fig. 1). Due to its minor toxicity sulfate is normally not regarded as a major problem in drinking water production. However, higher sulfate concentrations influence the water hardness, cause corrosion in water pipelines, and impair the taste of the drinking water. Referring to those quality aspects, the EU Drinking Water Directive considers sulfate as an indicator parameter with a parametric value of 250mg/l.

The objective of this study is the determination of the reasons for the elevated sulfate concentrations by means of stable environmental isotope investigations. A variety of stable isotope species in the water, in dissolved components, and in the sediment matrix is examined to clarify hydrochemical and hydrodynamic aspects. In detail, the following isotopes ratios were studied: $\delta^{2}H$-H_2O, $\delta^{18}O$-H_2O, $\delta^{34}S$-SO_4^{2-}, $\delta^{18}O$-SO_4^{2-}, $\delta^{15}N$-NO_3^-, $\delta^{18}O$-NO_3^-, $\delta^{34}S$-S_{red}.

A basic requirement for the evaluation of sulfur pathways is the isotopic distinction of possible sulfate sources in the studied area (reduced inorganic sedimentary sulfur, sulfur from atmospheric deposition, sulfur from inorganic fertilizers, and sulfate from waste deposits). Sulfate from the oxidation of sedimentary sulfides shows clearly lower $\delta^{34}S$ values (-25…-5‰ CDT) and $\delta^{18}O$ values (-2…+5‰ VSMOW) than the sulfate from deposition fertilizers, and waste deposits (anthropogenic sources). However, a positive isotopic distinction between the single anthropogenic sources is not possible since those three sources occupy a similar range of isotope signatures ($\delta^{34}S$: 0…+12‰, $\delta^{18}O$: +6…+18‰). Depending on its primary source the isotopic composition of inorganic soil sulfate displays a wider range ($\delta^{34}S$: -25…+9‰).

Mobilization and transport of the sulfate are not accompanied by an isotopic fractionation. Therefore, each sulfate sample can either be related to the oxidation of sulfide or to the mobilization of sulfate from anthropogenic sources. However, due to the complicated flow regime in the aquifer mixing of sulfate from different sources is a common process which influences the isotopic composition of the sulfate and hence makes it more difficult to relate the sulfate to a certain source. Sulfate samples were taken from a total of 250 sampling wells covering various levels of the aquifer. Sulfur and oxygen isotope ratios of the dissolved sulfate range from -20…+10‰ and -2…+20‰, respectively.

Dissolved sulfate from the majority of samples from the middle and lower sampling level shows a similar isotope signature as the anthropogenic sulfate. However, samples from the groundwater surface and the upper sampling level are dominated by isotopically lighter sulfate indicating a greater influence of the oxidation of sedimentary sulfur. The large number of sampling sites enables the statistically proved interpolation of isotope distribution maps and cross sections that clearly illustrate flow paths and the local relevance of various sulfate sources.

The oxidation of sedimentary sulfides was found to be the key process for elevating the sulfate concentration in the extracted raw water. The investigation of the isotopic nitrate composition was intended to give information to what extend the sulfide oxidation is performed by autotrophic denitrification. The direct isotopic prove for the denitrification process cannot be given by the data obtained so far. However, it is assumed that the process plays an essential role for the mobilization of sedimentary sulfur. Another possible mechanism of the sulfide oxidation is the transport of free oxygen into the sulfide bearing layers. Sulfide oxidation by oxygen was identified by the oxygen isotopic composition of the mobilized sulfate.

A further process which characteristically affects the isotopic sulfate composition is the dissimilatory sulfate reduction. Sulfate influenced by reduction can be found on rare locations, especially in the lower sampling level.

Surface waters cannot be neglected in the sulfur balance of the study area. Evaporation leads to an enrichment of ^{2}H and ^{18}O in the remaining water. In case of an infiltration of surface water into the aquifer the isotopic composition of the groundwater should be altered significantly. In numerous sampling wells in the flood plain the δ^{18}O and δ^2H values are increased up to -4.5‰ and -40‰, respectively. Considering the average isotopic composition of the groundwater in the Tertiary upland (-9.2‰, -66‰), which is believed to be the main recharge area of the catchment, the clearly elevated values in the flood plain prove the massive influence of surface waters.

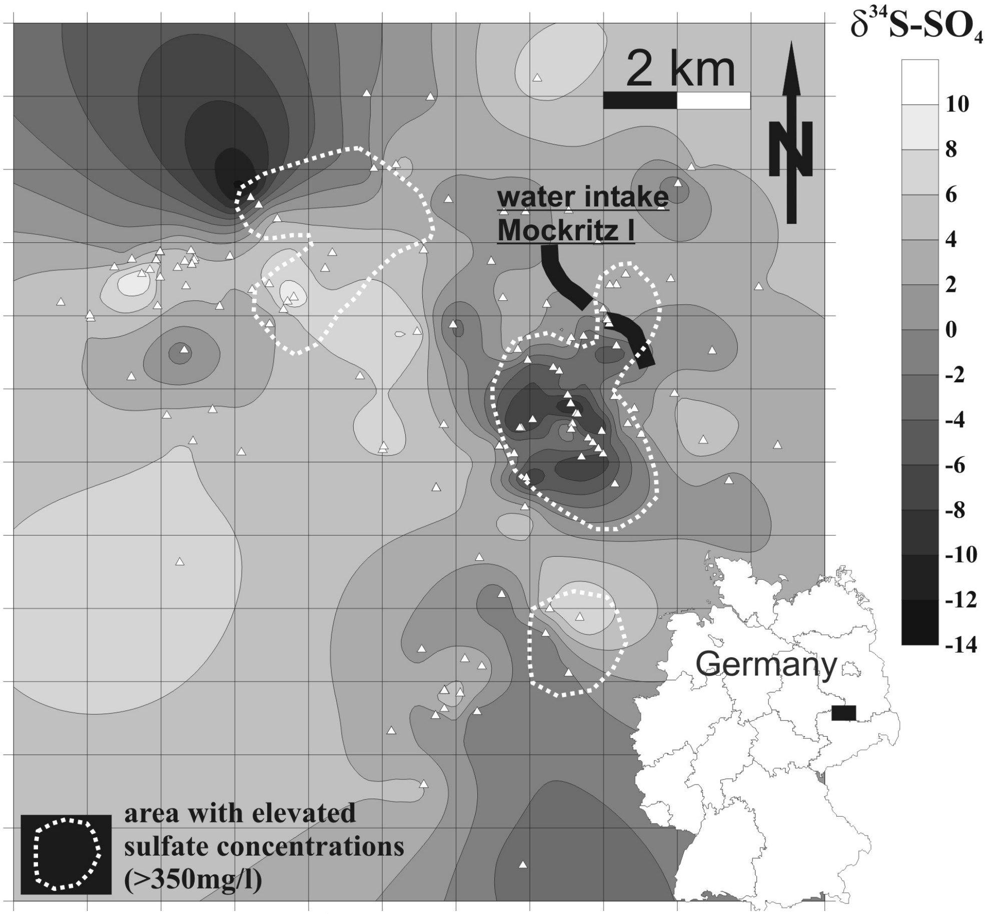

FIG. 1. Regional distribution of δ^{34}S at the groundwater surface in the catchment area of Torgau-Mockritz.

APPLICATION OF ENVIRONMENTAL ISOTOPES IN STUDIES OF BIODEGRADATION OF ORGANIC CONTAMINANTS IN GROUNDWATER

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Groundwater contamination by organic contaminants is of major concern for implementing efficient water management strategies in aquifers used for domestic and industrial uses. Monitored natural attenuation (MNA) has been chosen as a method to manage groundwater contamination at many sites. Biodegradation is usually the main process limiting the spreading of dissolved contaminants and protocols are required to assess biodegradation. Successful implementation of monitored natural attenuation (MNA) requires a monitoring strategy that does not only demonstrate diminishing contaminant concentrations but also provides insight into the processes responsible for contaminant attenuation. Analysis of compound-specific isotope ratios is a new approach to gain such process-specific information [1,2]. During microbial and chemical transformations, the reaction rate is often faster for molec ules with light isotopes compared to molecules with heavy isotopes. This leads to a characteristic pattern of isotope ratios of reactants and transformation products [3]. Stable isotope ratios can provide information on predominant biodegradation pathways in two ways: A degradation pathway may be identified based on an enrichment of heavy isotopes in the reactant as the reaction proceeds. Or, an intermediate of a degradation pathway can have a distinct isotopic composition, which makes it possible to distinguish it from other sources of the compound.

Most of the isotope research has concentrated on BTEX (benzene, toluene, ethylbenzene and xylenes) and chlorinated compounds, the two more important groups of compounds commonly found in groundwater. Several studies have been carried out under laboratory conditions (microcosm experiments) to evaluate carbon isotope fractionation during aerobic and anaerobic biodegradation of organic contaminants. These studies have shown the occurrence of large carbon isotope fractionation for biodegradation of chlorinated compounds such as cis-1,2-dichloroethene (cis-DCE) and 1,2-dichloroethane (1,2-DCA) [4]. In contrast small carbon isotope fractionation occurred during biodegradation of BTEX [5,6]. Recent studies have shown deuterium can be more sensitive than carbon-13 for BTEX biodegradation studies [7]. An example of microcosm studies is illustrated on Figure 1 that shows concentration and isotope pattern for biodegradation of cis-dichloroethene (cis-DCE) to vinyl chloride (VC) and final product, ethene. As the cis-DCE is transformed to VC, an enrichment trend is observed in the remaining cis-DCE. The formed VC is isotopically lighter than the primary product, but as the VC is transformed, the remaining VC becomes enriched in ^{13}C. The ethene is lighter than the VC and its isotope composition tend to the isotope composition of the primary substrate, cis-DCE, at the end of the experiment. The laboratory results have been confirmed at field sites.

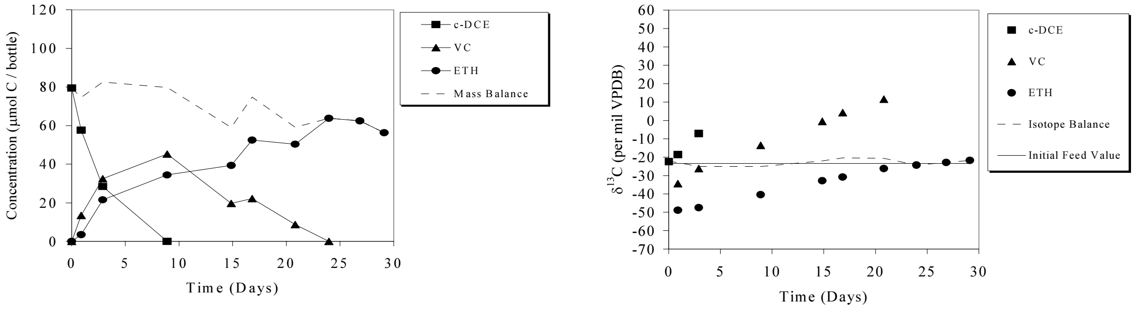

FIG. 1. Concentration and carbon isotope patterns for biodegradation of cis-DCE.

This paper will present a state of the art review on the application of environmental isotopes in biodegradation studies of organic contaminants in groundwater. Laboratories and field studies, and potential new applications of environmental isotopes in contaminant hydrogeology will be discussed during this presentation.

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CONTAMINATION OF GROUNDWATER UNDER CULTIVATED FIELDS IN AN ARID ENVIRONMENT, CENTRAL ARAVA VALLEY, ISRAEL

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The aim of this study was to understand the processes of contamination of groundwater in arid environments due to agriculture activity. A combination of physical, chemical and isotopic analyses was used to describe the hydrologic system and the trends in recharge of water and salts into the aquifer. The results indicate that intensive irrigation and fertilization substantially affected the quantity and quality of groundwater recharge.

The water levels of shallow groundwater (2-5 m depth) rose during the agriculture season (September – March) by about 35 cm, indicating a significant contribution of irrigation water. It should be noted that there was no significant flood during this period. It is estimated that low irrigation efficiency of about 50 % caused recharge of about 3-4 million cubic meter of recycled irrigation water per year in the Arava Valley.

Salt concentrations in soil profiles drilled down to depth of 2.5 m were low in cultivated fields and Wadi Arava, indicating that the irrigation water and intermittent floodwaters infiltrated and leached the salts downward. In contrast, there was an accumulation of various salts near the surface in undisturbed natural soil.

There are 2 main sources of salt in contaminated ground water: (1) salts dissolved in the irrigation water itself, and (2) human additions include nitrogen from fertilizers and sewage ponds, as well as K. Mixed lines of different ions against TDS indicate that the dominant source of salinization is irrigation water from the surface.

Nitrate concentrations increased in the aquifer, mainly in the last ten years. In parts of the aquifer that are closer to the surface, the increase was more rapid and the nitrate concentrations currently are higher. The nitrate concentration in the upper sub aquifer is over 50 mg/l and in a shallow local lens it ranges between 100-300 mg/l. The background nitrate concentrations, as found in the lower sub-aquifer, are 5-10 mg/l. Nitrate concentrations of drainage water at the depth of 60-120 cm below the cultivated fields range between 150-700 mg/l during the fertilization season.

The isotopic compositions of $\delta^{15}N\text{–}NO_3$ also imply that the main source of contamination of nitrate is the fertilizers in the irrigation water. Another local source could be, in places, from nearby sewage ponds.

Other evidence of contamination in groundwater includes high concentration of K (20-120 mg/l) and Total Organic Carbon (about 10 mg/l).

IAEA-CN-104/P-150

ISOTOPE DATA POINT TO NATURAL PROCESSES IN THE PRODUCTION OF HIGH NITRATE CONCENTRATIONS IN GROUNDWATER

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High nitrate concentrations sometimes in excess of 100 mg L^{-1} NO_3-N, are endemic in ground water in Limpopo Province of South Africa. The region is to a large extent dependent on ground water, especially in the rural areas. High nitrate in drinking water poses a considerable health risk, such as intestinal cancer in adults and methemoglobineamia in infants. Thus far, attention has been focused on potential anthropogenic sources such as agriculture and sewage disposal. However, a recent joint study on ground water resources, conducted by the Environmental Isotope Group and the Department of Water Affairs, suggests that important natural processes could also be responsible.

The area of study is underlain by the Karoo sedimentary sequence of sandstones and siltstones, which is capped by basalt. Except for fracture zones associated with a fault, the relatively shallow ground water levels stand in the basalt. Ground water development was therefore to a large extent restricted to the basalt aquifer.

Modeling radiocarbon and tritium data suggests an uncoupling of these two isotopes used for estimating ground water residence times. Deep-seated root systems of common phreatophytes in the area, such as acacia erioloba (camel thorn) amongst others, can transport significant amounts of biogenic CO_2 into the saturated zone of the basalt aquifer well below the water table. This results i.a. in ongoing chemical weathering and precipitation processes within the saturated zone, usually ascribed mainly to soil and vadose zone processes.

Correlations with other solutes such as silica and carbon-13 in TDIC are further indicators of the weathering process. Roots produce CO_2 not only by respiration but also through the decay of the functional (fine) roots which are seasonally discarded from the structural root systems. Bacterial decay processes liberate nitrogenous nutrients which support even macroscopic life forms observed in the basalt megapores, which can be mineralised to NO_3.

These proposed mechanisms are the subject of a follow-up study involving nitrogen isotope studies to assist in nitrogen source apportionment. As natural processes, they are not readily mitigated. Exploration prompted by the results of the isotope and hydrochemical studies point towards geohydrological and resource management strategies.

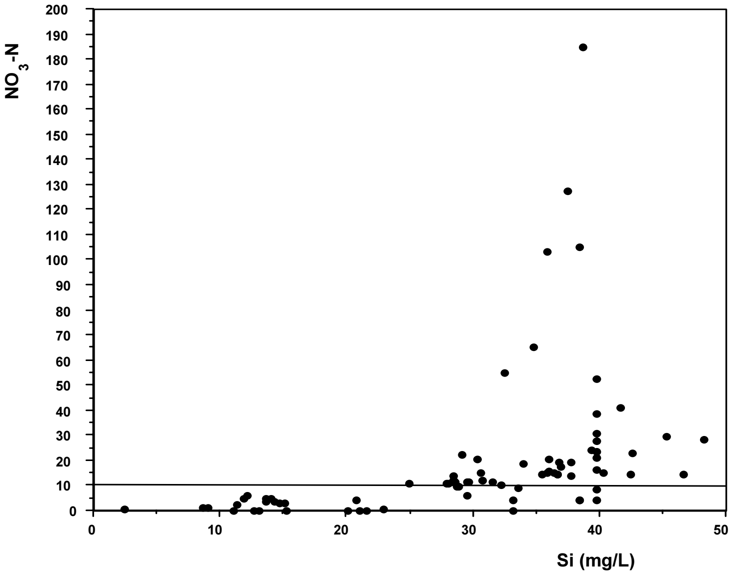

Figure 1. Correlation of NO_3- N against Si for mainly basalt ground water in the Taaibosch study area.

ISOTOPIC INVESTIGATION OF SALINITY AND WATER RESOURCES IN THE SOUSS-MASSA BASIN (MOROCCO)

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The Souss-Massa region has become over the years one of the major economic poles in Morocco. The Souss-Massa Basin, covers approximately 27,000 square kilometers. With a year-round growing season, irrigated agriculture in the river basin produces more than half of Morocco's exported citrus and vegetables. Total water use in the basin is about 965 million cubic meters per year; approximately 94 per cent of the water use is for irrigation. Although water used for irrigation is obtained from surface water and groundwater sources, these sources are not sufficient to sustain current agricultural practices, and groundwater resources are being depleted. The area is characterized by a semi-arid climate and by a marked seasonal contrast. The rainfall average amounts to 250 mm/yr in the plain area and 500 mm/yr in the mountain. Every river of the region, called "oued", has a temporary flow regime, because the drought period is very long (6 to 8 months) every year. The principal water resource is provided by the Souss-Massa Plio-Quaternary plain aquifer and by the dams. The sand and gravel aquifer, which was previously mainly exploited for irrigation, is becoming a source of increasing importance for the domestic supply of the Souss-Massa region. The aquifer with a variable transmissivity ranging from $2x10^{-4}$ to $6x10^{-3}$ m^2 s^{-1} flows from the east to the west, towards the sea. The aridity of the climate, the drought in these last years, the overexploitation and the deterioration of the water quality, induce serious problems for a sustainable water management in the area. On average, groundwater extraction in the basin exceeds recharge by an estimated 260 million cubic meters annually. This over-pumping of the alluvial aquifer has resulted in water level declines ranging from 0.5 to 2.5 meters per year during the past three decades. The water quality is very variable and in some areas, it presents a high salinity exceeding 4 $g.l^{-1}$ (Hsissou et al. 1997 1999; 2002; Boutaleb et al, 2000).

In order to improve the management of these precious resources several studies to better understand the hydrology of the aquifer system have been carried out during the last years including this multiple isotopes investigation being come out in the collaboration with IAEA. Seawater intrusion and other process that contribute dissolved solids to groundwater are a major threat to water quality in the heavily exploited Souss-Massa aquifer. A hydrogeologic investigation using several isotopes such ^{18}O, ^{2}H, ^{3}H, ^{87}Sr, ^{36}Cl, ^{11}B, ^{129}I, ^{14}C, ^{34}S and ^{4}He, is being carried out to determine the sources and mechanisms of recharge to the aquifer and the origin of salinity. The information gathered on the hydrology and the relative importance of various salinity and sources will be used to make informed decisions about water resource allocation and possible remediation strategies.

Stable isotope data (Bouchaou et al. 2002), indicate that the Atlas Mountain with high rainfall and impovrished values (-6 to –7.5 per mil delta ^{18}O), constitute the main source of recharge to the Souss-Massa shallow aquifer (Fig. 1). Deuterium and Oxygen-18 values show a westward gradient with more depleted values particularly in upstream part, suggesting altitude and continental effect. To the regional distribution in the irrigated perimeters (middle Souss plain, Chtouka and Massa part) suggests an evaporation phenomenon which can be explained by the water irrigation return. At the level of the irrigated perimeters in the middle Souss plain, Chtouka and Massa, the stable isotopes of the groundwater are enriched indicating possible irrigation return flow. Preliminary results of this study from nineteen groundwater samples collected on the middle and downstream (coastal area) part of the basin suggest that relatively old water is mined at some wells, and seawater intrusion is just one of the multiple sources of salinity present in these waters. Radiogenic excess ^{4}He ranges up to $2x10^{-7}$ cm^{3} $STPg^{-1}$ indicating ages as great as several tens of thousands of years. The long-lived isotopes of chlorine and iodine will be used to try to distinguish intrusion modern seawater, ancient seawater, agricultural water, and evaporite-derived water. The relative abundances of these anions along with bromide indicate that while dilution of intruded seawater from west to east is taking place, another significant source of salinity is water/rock interaction. The isotopic strontium indicates mixing of groundwater from different origin in this area (Fig 2).

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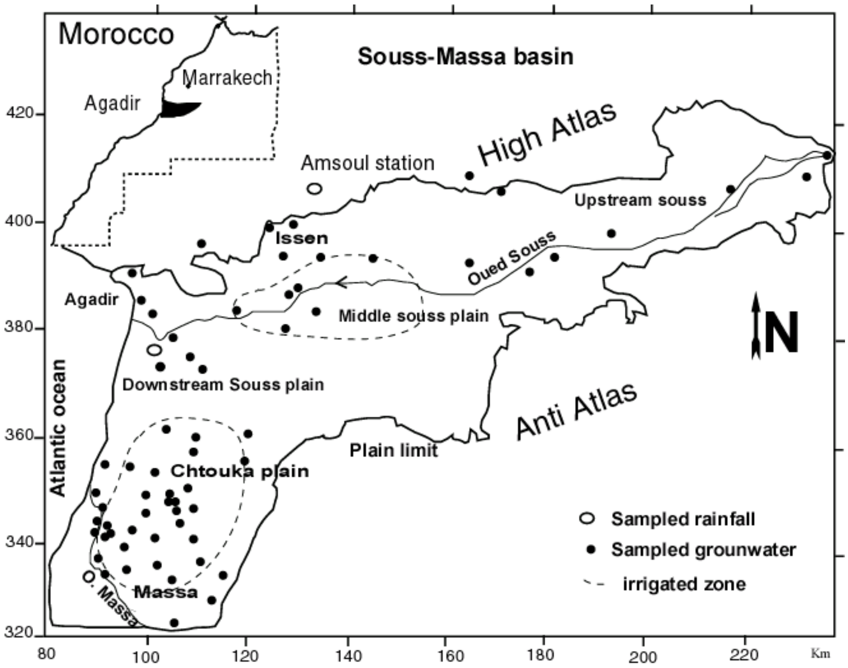

Fig. 1 – Situation map and sampled wells (Bouchaou et al., 2002)

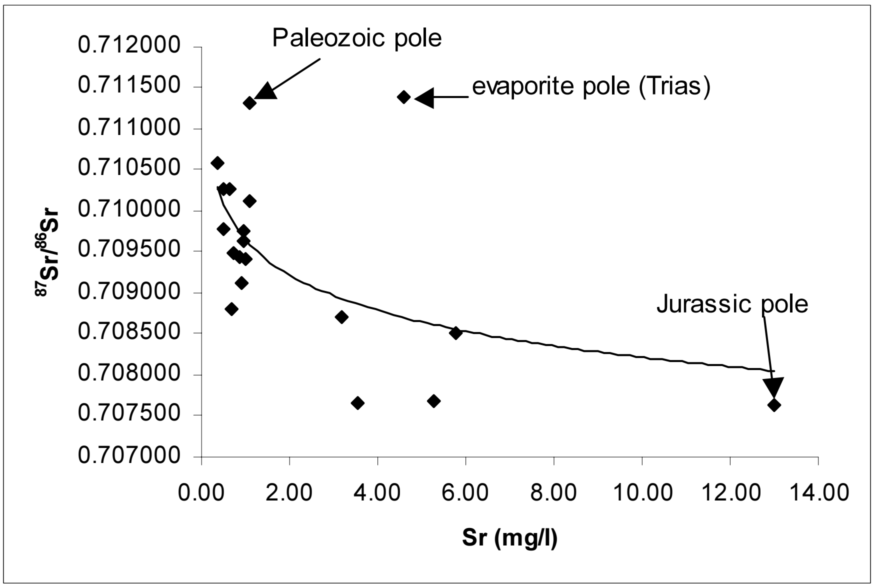

Fig. 2 - Relation between $^{87}Sr/^{86}Sr$ et Sr (mg/l).

MODELLING APPROACHES

RAPID METHOD FOR MEAN RESIDENCE TIME DETERMINATION

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Environmental isotopes (oxygen-18 and deuterium) are ideal independent tracers to obtain the dynamics of water transport in catchment area because they are constituents of water molecules. River water consists mostly from two main components; recent precipitation that has reached the river either by surface runoff, channel precipitation, or by rapid flow through the shallow subsurface flow paths and groundwater. Their relative contribution of these sources, differ in each basin and depend on the physical setting of the drainage basin (topography, soil type, depth to bedrock, vegetation, fractures), climatic parameters (precipitation amount, seasonal variations in precipitation, temperature, potential evapotranspiration) and human activities (dams, reservoirs, irrigation usages, clearing for agriculture, channel restructuring). During that time, water is a mixture of the past recharges with different residence times in the catchment, and the more appropriate term is the "mean residence time" (MRT). Different mathematical models were evolved based either on the matrix associated with the compartmental system or on the theory of the statistical moments. Those solutions require detailed information on the flow system (boundary condition, porosity, hydraulic conductivity, three-dimensional extent of catchment), which are mostly not available particularly for large basin.

The relation between input and output tracer concentrations could be formulated via the convolution integral [1]:

$$c_{out}(t) = \int_0^\infty c_{in}(t-\tau)g(\tau)d\tau \qquad (1)$$

where $g(t)$ represents the weighting function of the mathematical flow model (age distribution function), $c_{in}(t)$ and $c_{out}(t)$ are the input and output tracer concentrations, respectively, and t refers to time. We prefer exponential flow model, which is mathematically equivalent to a well-mixed reservoir. In this case $g(t)$ is one parameter function

$$g(t) = \frac{1}{T}e^{-t/T} \qquad (2)$$

where T stands for MRT. Any periodical function could be transform in a sum of sinusoidal function using the Fourier transform method [2]. The equation (1) is well presented by the first (dominant) harmonics of input and output functions. The average seasonal tracer concentration could be approximated with input (i=in) or output (i=out) sine functions:

$$C_i(t) = C_{0i} - C_i \sin(\frac{2\pi t}{12} + \phi_i) \qquad (3)$$

where $C_i(t)$ represents model function and C_{0i}, C_i, and ϕ_i are the mean of $\delta^{18}O$, amplitude of variation, and phase angle, respectively. This first harmonics has a period of one year. Solving equations (1) and (2) under the condition (3), T can be expressed in months as:

$$T = \frac{6}{\pi}\frac{\sqrt{1-A^2}}{A} \qquad (4)$$

where A is the amplitude attenuation, $A=C_{out}/C_{in}$.. The amplitudes of C_{in} and C_{out} are proportional to standard deviations of tracer concentrations [3]. Based on Tukey's work [4], we calculated values for A as the ratio of standard deviations for the input (precipitation), $c_{in}(t)$, and output (river water), $c_{out}(t)$, tracer concentrations

$$A = \frac{\sigma_{c_{out}}}{\sigma_{c_{in}}} \qquad (5)$$

This relation passed check on simulated sinusoidal curves and one-year periodical non-sinusoidal functions. The method is applied also for noise curves and shows that it is less sensitive on noise than sinusoidal fitting curve methods. On the other hand, the exponential sinusoidal method is not applicative for curves with non-dominant first harmonics. It should be emphasized that a real input annual isotope concentration does not follow sinusoidal function.

The monthly precipitation and river water samples were collected at location Meteorological Station of Belgrade (Zeleno Brdo, 44°47'N, 20°32'E, altitude 243.2 m asl) and Vinca (1145 km from the confluence with the Black Sea), respectively during 1992, 1997, 1998 and analyzed on oxygen-18 using IRMS (SIRA 12) mass spectrometer.

The Danube river is characterized near Belgrade (after mouth the Sava river at Ritopek, 1116.2 km) by a hydrological regime with two maximum flow rates in April-May (6100 m^3/s) and November-December (6200 m^3/s) and a minimum in August-September (3200 m^3/s) for the observed period. The seasonal trend of $\delta^{18}O$ in precipitation fluctuated between –12 ‰ in winter (December-January) and –4‰ in summer (June-July) and it was less pronounced for Danube water from –8‰ (March-April) to -10‰ (August-September).

The $\delta^{18}O$ values in precipitation have been weighted with respect to monthly amount of precipitation in mathematical techniques employed in this work. Obtained values for MRT are between 10 and 12 months for the Danube near Belgrade that is in a good agreement with findings from comparison of $\delta^{18}O$ trend curves for precipitation and Danube water at Vienna (MRT=12 months) [5].

The significance of proposed method is an ability for determination of MTR in the case when sinusoidal fitting of raw data is not possible. In addition, this rapid method requires less data than it is used in sinusoidal function exponential models and can be applied as input for more complex non-exponential models for estimation of MRT.

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IDENTIFICATION OF 3-DIMENSIONAL FLOW PATTERN IN A LOCAL QUATERNARY GRAVEL AQUIFER SYSTEM USING ENVIRONMENTAL ISOTOPE STUDIES

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The study area is situated in the Rhine - Graben about 15 km north of Karlsruhe (Germany). The river Rhine forms the western boundary of the area of investigation, which extends to about 25 km^2. The in situ quaternary porous aquifer is used as reservoir for gravel extraction. On the other hand this aquifer represents important potable water resource for the whole region, which implies serious conflicts [1]. Isotope hydrological investigations (stable isotope ^{2}H, ^{18}O and ^{3}H) essentially contribute to a better insight into this complex hydrological system.

The approximately 30 to 40 m deep quaternary gravel aquifer is partly subdivided in an upper and a lower part by fine grained layer like sandy and silty lenses (quaternary aquiclude) [2]. Hydrochemically the water of the upper part of the aquifer hardly differs from that of the lower one. But in respect to their environmental isotope contents the two parts of the aquifer are clearly different. Different hydraulic pressure conditions exist between the two parts of the aquifer with a spatial distribution over the investigation area, which induces exchange processes within the aquifer. With the help of isotope analyses these local situations can clearly be demonstrated and the in situ interactions monitored.

The complex interaction (FIG.1.) within the aquifer and between surface water and ground water can be described by interpreting the environmental isotope data in connection with the hydrochemical investigations. The study shows that in the area under investigation along the river Rhine water infiltrates in both the upper and the lower part of the aquifer up to an amount of almost 100 %. The different surface waters (small creeks and artificial lakes) take over the drainage function of the ground water in the area. The general flow pattern is essentially disturbed by active gravel pits and in addition by pumping wells of local water supply. The lake water, marked by a typical isotope signature [3], could be clearly indicated in several observation wells. These results give a distinct picture of the three-dimensional flow pattern. Besides the exchange rate of lake water to ground water, in one special case the ground water velocity could be estimated.

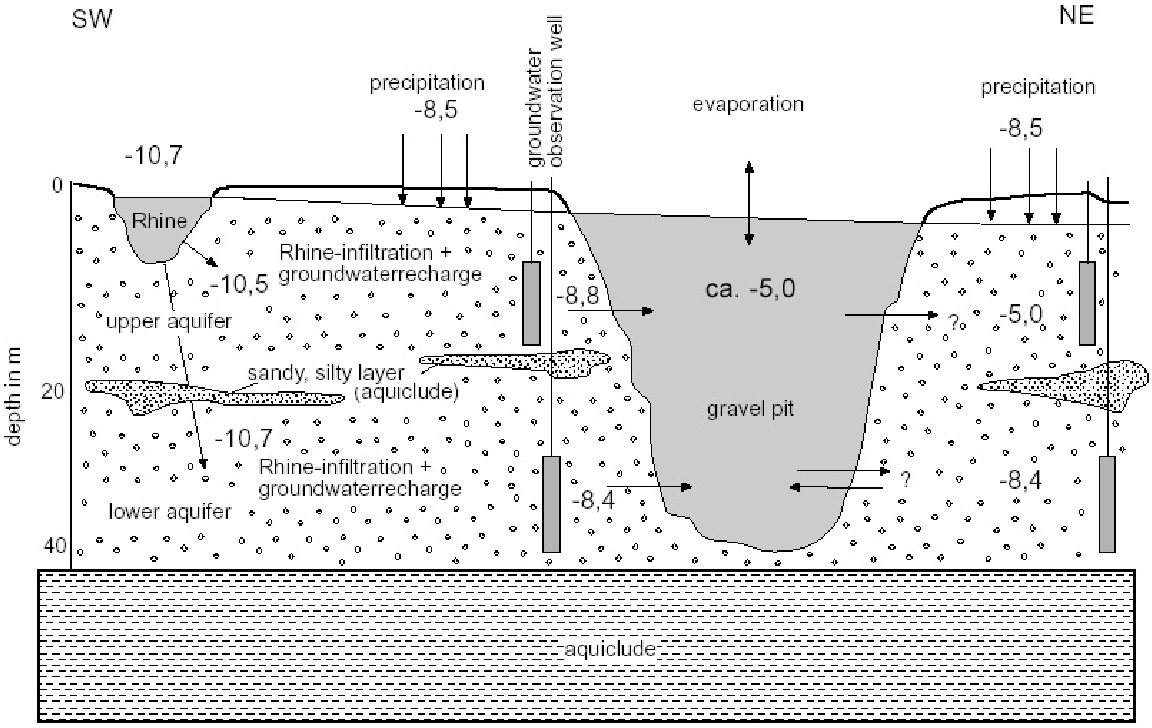

FIG. 1. Average $\delta^{18}O$ - values (‰) of precipitation, ground water and surface water in the investigation area.

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CALIBRATION OF A GROUND WATER CONTAMINATION TRANSPORT MODEL USING TRITIUM-^{3}HELIUM AGES

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Dow Terneuzen is the largest US chemical industrial site in Europe. Situated in the southern part of The Netherlands at the southern shore of the Westershelde, the site occupies an area of roughly 2km times 3km. Several contaminant plumes are known in the ground water below the industrial area. They originate from accidents in the fifties until seventies and are transported with the ground water flow towards the borders of the site. Detailed hydrogeological investigations lead to a three-dimensional numerical model of ground water flow and transport. Although this model was carefully calibrated using the hydraulic heads, unrealistic travel times and ground water ages were obtained.

In a case study one of the contaminant plumes was investigated for ground water age and distance velocity. Out of three multilevel wells along the plume a total of 13 samples for T/^{3}He were obtained. All samples contained tritium, indicating a component of ground water younger than 40 years, whereas the numerical model gave travel times between 40 and 160 years. The Tritium data are further confirmed by SF_6 which was present in concentrations well above the present day atmospheric equilibrium in two out of three samples. Two facts hamper the interpretation of the noble gas data as T/^{3}He ages: i) Degradation of the organic contaminant (benzene) results in CO_2 and CH_4 production causing loss of noble gases in the aquifer by a stripping process. This also caused problems during the sampling and made the interpretation of the data as ages impossible for 5 of the 13 samples. ii) Ground water infiltration temperatures are unknown but elevated due to process heat released from the industrial environment. Accuracy of the derived ages is limited mainly by this unknown infiltration temperature.

Despite these difficulties the derived T/^{3}He ages give clear hints for the improvement of the numerical model. Most probably ground water infiltration does not take place on the whole area as assumed in the model, but is enhanced along channels transporting surface runoff water out of the site. The enhanced infiltration within these channels results in a higher ground water throughput of the system and in shorter travel times.

DETERMINATION OF TRANSBONDARY GROUNDWATER FLOW BY ISOTOPIC TRACING

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In evaluating groundwater resources, it is fundamental to define a precisely delimited spatial framework. This framework which represents the aquifer, is defined by its geometry, its internal characteristics, its boundary conditions and its dynamics. These informations are difficult to aquire by conventional methods (drilling, geophysics) essentially due to economical resources (G. Castany et al. 1976).

The understanding of groundwater flow in large scale African sedimentary basin is confronted to the absence of reliable piezometric data. Yet this knowledge is necessary for better management of groundwater resources.

The lack of data is largely due to the poor quality of topographic levelling. The only topographic maps used for drawing piezometric contours are of a 1/200000 scale with elevation contours of 40 meters. Such precisions do not allow the characterization of flow on a large scale (> 1° square) in the case of vast transbondary basins (Dakoure et al., 2002). The Taoudeni sedimentary basin is an example of this type of aquifer in the southwestern Burkina Faso and the southern Mali.

The isotopic studies provides independent informations whose interpretations, combined with hydrogeological models, can contribute to the knowledge of:

- the structure of the aquifer system (mono or multi layer);
- the type of recharge and renewal of the reserves;
- boundary conditions.

Carbon-14 measurements which allow determination of water residence time, can be used to calculate the Darcy velocity when the effective porosities are known. Isotopic investigations were undertaken in the two countries.

The measurements available permit a detailed interpretation of the groundwater behaviour in a large scale.

CALIBRATION OF A GROUNDWATER FLOW MODEL WITH DIFFERENT TRACER TECHNOLOGIES

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The objective of the present study was to estimate quantitatively groundwater fluxes and velocities in the semi-arid Independence basin by combination of a groundwater flow model with tracer technologies for modern and old groundwater.

The chloride mass balance (CMB) method was applied for estimation of magnitude and distribution of recharge from precipitation. The mean residence times (MRT) of groundwater were estimated by using radiocarbon in groundwater, chlorofluorocarbons (CFCs), Sulfur hexafluoride (SF_6) and tritium (^3H). Radiocarbon data was first corrected for geochemical interaction with the aquifer material by using carbon-13 in combination with mass balance models (PHREEQC [1]). After geochemical correction of radiocarbon data, dating is applied by using the decay equation.

The MRT according to CFCs, SF_6 and ^3H was interpreted by using lumped-parameter models (LUMPED [2]) where the results coincide best with observed data. The used atmospheric input function for CFCs and SF_6 was obtained from NOAA Nivot Ridge station, Colorado [3]), and for ^3H the IAEA station Chihuahua. Henry´s Law constant K_H for CFC-11, CFC-12, CFC-113 was calculated by [4], and for SF_6 by [5]. A barometric correction was applied for both CFCs and SF_6, because the input function is for a different altitude than the observed concentrations.

A numerical saturated flow model was developed and constraint with the recharge rate distribution according to the CMB method and the MRT of the different tracer technologies. The 3-D steady-state model MODFLOW-2000 [6] is linked to the particle tracking model MODPATH [7] to simulate the transport of the different tracers. The calibration process consisted in adjusting the hydraulic conductivity and its anysotropy values until (a) the calculated head distribution matched the observed water level measurements, and (b) the flow balance is satisfied in the whole flow domain (mass balance) and in parts of the flow domain (zone budget), (c) the MRT values of carbon-14, tritium, and CFCs matched the time of travel of corresponding particles in the flow domain. Due to the low time resolution, the tracers for young groundwater (tritium, CFCs) could be applied in the flow simulation only to indicate if the groundwater is younger or older than 40 to 50 years. This calibration approach was not only useful to quantitatively describe the flow regime of an aquifer system, but also to make some observations on its vulnerability and renewability. Comments on the experience of the used tracer technologies in combination with flow simulations are made in this context.

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ORIGIN, RECHARGE AND SUSTAINABILITY OF GROUNDWATER

APPLICATION OF ENVIRONMENTAL ISOTPES ON GROUNDWATER IN KUWAIT

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The tertiary aquifer system is the most significant system in Kuwait,. This aquifer system contains a compatible quality of brackish water with a TDS value of less than 7500 mg/l. Two small locally shallow aquifers of the Neogene, with fresh water (having a TDS value of less than 1500 mg/l), also exist in this aquifer system in the north of the country [1].

The early studies during the 1970's and 1980's, which were based on drilling data, geophysical logs and chemical analysis, showed the importance of the upper clastic sediment (Kuwait Group) and the lower Dammam Limestone of the Tertiary aquifer system, in developing the ground water resources in Kuwait state. Consequently, the activities of ground water exploration and exploitation in Kuwait have been limited to these aquifers.

The flow direction has been recognized since the 1950's to be from the main recharge area in south west Saudi Arabia to the main discharge area in the Arabian Gulf and Shatt Al-Arab in a north easterly direction, in all aquifer systems.

The recharge areas of the aquifer systems in Kuwait are located at the outcrop of the aquifer formations in Saudi Arabia in the south and southwest of Kuwait. These recharge areas provide the aquifers in Kuwait by lateral flow from areas receiving infiltrating rainwater. The quantity of this lateral flow depends on the hydraulic properties of these aquifers

Environmental isotope studies are important tools in the investigations of the complex aquifer systems in different areas of the world. The isotopic characteristics of different groundwater in any system, has often provided powerful evidence for the resolution of hydrological problems, such as groundwater aging, sources of recharge water to the system, and estimated time of recharge.

In the current study the environmental isotope investigations were applied to confirm the recharge area of the aquifer system in Kuwait.

[2] carried out environmental isotopic studies including oxygen-18 ($\delta^{18}O$), deuterium (δD), and carbon (^{13}C and ^{14}C), at the recharge areas of the Kuwait main groundwater aquifers in Saudi Arabia. The results of these studies can be summarised as follows:

1. All the isotopes confirm that effective recharge is currently taking place, though the rate and conditions are highly variable.
2. The rainfall and near surface aquifer data indicate that moisture derived from the Arabian Gulf is less likely to produce recharge than moisture derived from the eastern Mediterranean or the Indian Ocean.

3. The carbon , $\delta^{18}O$, and δD isotopes indicate that a large proportion of the groundwater in the system was probably recharged during a more humid, cool climatic period, 20,000 to 30,000 years ago.
4. Most of the water in the Tertiary aquifer system near the outcrop is a mixture, both in terms of age and origin, due to the vertical flow between the aquifers where the separating layers are discrete or relatively thin.

However, in the present study several samples were collected from the observation sites representing the Kuwait Group and Dammam Limestone aquifers in Kuwait, in order to determine the $\delta^{18}O$ and δD values. The results reflect almost the same range of values as in the recharge area (recharge area $\delta^{18}O$ is range from -4.4 to -2.47^{o}/oo and δD range from -18 to -30 ^{o}/oo). This suggests that the study area has the same stable isotopic properties, and subsequently, they have the same origin and source of recharge under the same conditions. However in the northern part of Kuwait the environmental isotope investigations indicate that the fresh groundwater lenses belong to different regime, which confirm the occurrence of the local recharge in this area only.

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CHEMICAL AND ISOTOPIC COMPOSITIONS OF WATERS FROM SPRINGS AND WELLS IN THE DAMOUR RIVER BASIN AND COASTAL PLAIN OF LEBANON

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A hydro chemical and isotopic study was achieved on groundwater of the Damour River basin and on wells in the coastal Mediterranean plain in Lebanon. The aim of this study was to determine the origin, the age and the quality of groundwater resources in the limestone aquifer of the Damour river basin. The results showed that most of the groundwater in the coastal plain and pumped from wells for irrigation and drinking water supply is directly recharged in this area. It contains up to 30% of groundwater recharged in the high mountains. The pumped groundwater is not polluted by seawater intrusion. The elevated solute content of the ground waters in the coastal plain compared to that of the spring waters is due to the different intensive agricultural activities. The relatively long mean residence time of the spring waters of around 10 years contradicts the assumption that the low Mg^{++}/Ca^{++} ratio is due to a non-established hydro chemical equilibrium.

The results of this combined hydrochemical and isotopic study in the Damour River basin and the coastal plain yielded new hydrological insights:

- Most of the groundwater in the coastal plain and pumped from wells for irrigation and drinking water supply is directly recharged in this area. It contains up to 30% of groundwater recharged in the high mountains. The pumped groundwater from shallow wells contains such water only during the summer season.
- The pumped groundwater is not polluted by seawater intrusion.
- The elevated solute content of the groundwaters in the coastal plain compared to that of the spring waters is due to the different intensive agricultural activities. There is no relationship to the MRT of the water.
- The temperature of the spring waters is related to the altitude of the recharge area. The temperature of the groundwater decreases with depth and reflects the admixture of groundwater recharged in higher elevations. The thermal gradient does not play any role.
- The relatively long mean residence time of the spring waters of around 10 years contradicts the assumption that the low Mg^{++}/Ca^{++} ratio is due to a non-established hydrochemical equilibrium. The reason may be the less CO_2 in the top soil of the mountainous region compared to that in the coastal plain.

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TRITIUM AND RADIOCARBON IN ENVIRONMENTAL COMPONENTS OF THE IGNALINA NPP REGION, LITHUANIA

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The globally distributed beta-emitters tritium (^3H) and radiocarbon (^{14}C) in the Ignalina NPP (INPP) region and in the background regions have been studied in precipitation, annually growing terrestrial and aquatic plants, tree radial rings, surface water, in unconfined and, at smaller scale, in confined groundwater.

The biota samples for ^3H and ^{14}C measurements were collected in co-operation with Dendrochronology Laboratory of the Vytautas Magnus University. The scintillation forms were prepared using chemical methods [1]: the biota samples for ^3H analysis – separating hydrogen from organic matter by oxidation with MnO_2 in high temperature and obtaining chemically bound biota water for measurements of ^3H activity; for ^{14}C determination – by preparation benzene form from organic carbon. Conventional LSC methods have been used for ^3H and ^{14}C determinations.

The annual ^3H variations in precipitation were studied more in detail in 1997-1998 collecting monthly-integrated samples (Fig. 1a). The annual average activity of ^3H in precipitation of the INPP region in 1997 was 16.6 TU, when in winter season it was 11.7 TU and in summer season – 20.2 TU. The ^3H activity in precipitation of the background region in 1993 was the following: annual average – 15.5, in winter season – 11.7 and in summer season – 21.3 TU [2]. The influence of the INPP on the ^3H activity in precipitation, according to the data of monthly-integrated samples of precipitation, was not observed.

Terrestrial plants assimilate ^3H and ^{14}C: the ^3H – in processes of moisture transfer; and ^{14}C – from atmosphere using CO_2 in processes of photosynthesis by plants. For the evaluation of the ^3H and ^{14}C variations in the atmosphere under the influence of the INPP, the activities of these isotopes in annual rings of pine tree (*Pinus sylvestris*), annual terrestrial plants (*Artemisia L.*) and tree leafs (*Alnus*) were studied. Three pine model trees were selected for background area. The maximum and minimum of ring increment coincide in these models very well up to 1961.

The maximum of ^3H activity falls to 1963 for the background tree model and makes up 1665 TU (1 TU=118 Bq/m^3 of biota water), the maximum of ^{14}C activity falls to 1964 and makes up 199.2 pmC (1 pmC=2.27 Bq/kg of carbon). The ^3H activity in the ring of 1995 makes up 25 TU and within the limit of errors coincides with the ^3H activity in precipitation of warm season. In the rings of 1987, 1989, 1991 and 1993 of the pine, which grew near the INPP, the ^3H activity somewhat exceeded that caused by global factors (Fig. 1b). Both, in the case of ^3H and ^{14}C, the maximum of radionuclides, generated by nuclear tests in the atmosphere (1963 and 1964), is observed, however the influence of the Chernobyl NPP remains unrevealed because high activities of above mentioned radionuclides accumulated only near the accident location [1].

The ^{3}H activity in annual terrestrial plants here and there exceeded the level, caused by global factors. Such environs were related to INPP release tracks. The ^{14}C activity in many studied biotic objects (tree rings, annual plants) did not differ from levels caused by global factors, except those located in direction of the prevailing wind from the INPP.

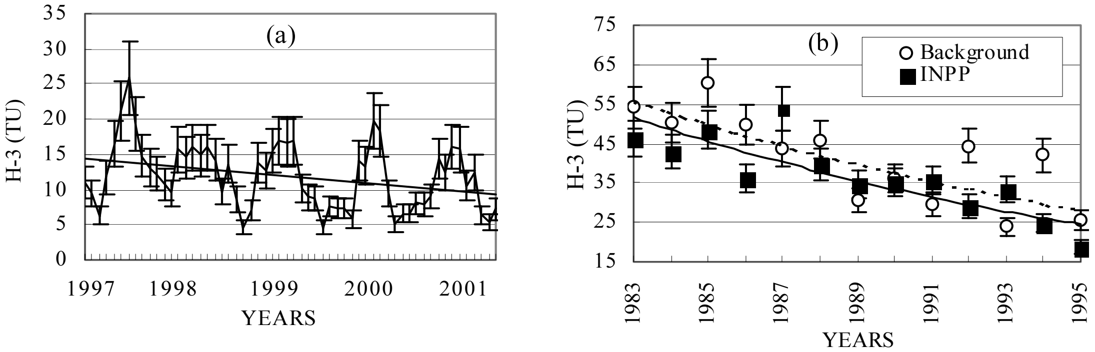

FIG. 1. ^{3}H activity changes in monthly integrated precipitation from the INPP region (a) and in annual rings of tree from INPP and background regions (b).

^{3}H entering the atmosphere from the INPP is observed in biota and exceeds the global level up to 2-3 times in areas located close to the INPP. ^{14}C releases to the atmosphere from the INPP in the form of CO_2 gives a very inconsiderable increase as compared with the global ^{14}C level in atmosphere of the region.

Peculiarities of ^{3}H and ^{14}C distribution in aquatic systems are determined mostly by global factors and the rate of water exchange. An extra ^{3}H and ^{14}C source is peculiar only to cooling basin and other water bodies directly related to INPP. ^{3}H in water of cooling basin has been systematically studied since 1980. The highest activity of this isotope in water of cooling basin (120 TU) was observed in 1988 and 1989. During the last decade the average of ^{3}H activity in water of cooling basin makes up 54 TU, when a maximum of ^{3}H activity in water plants reaches 1245 TU. A background level of ^{3}H in lakes (10-15 TU) was observed in background lake and month precipitation. There was not observed considerably increased ^{14}C activity either in water, or in water plants, except one case, when the ^{14}C activity in *Myriophyllum spicatum* was 133 pmC. It slightly exceeds the level caused by global factors (110-118 pmC).

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SUSTAINABILITY OF GROUNDWATER UNDER CLIMATE CHANGE

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One of the key commitments from the plan of implementation of the *World Summit on Sustainable Development* Johannesburg 2002 was to 'develop integrated water resources management and water efficiency plans by 2005'. In this communication, the potential role for stable isotope (SI) ratios for assessing the sustainability of groundwater in warm arid areas challenged by climate change will be illustrated with data from Alice Springs (Figure 1).

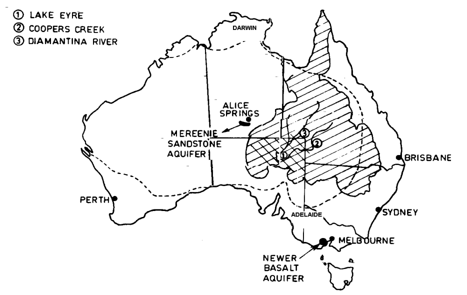


Figure 1: Location of Alice Springs, Melbourne and associated aquifers

Surface water infiltration into an aquifer is dependent on total rainfall within the groundwater intake areas, the seasonal distribution of rainfall, the rainfall intensity, the hydraulic characteristics of the outcropping or sub-cropping aquifer and the antecedent landscape conditions. For sustainable use, infiltration is balanced by a groundwater extraction regime, measured over a specified planning timeframe.

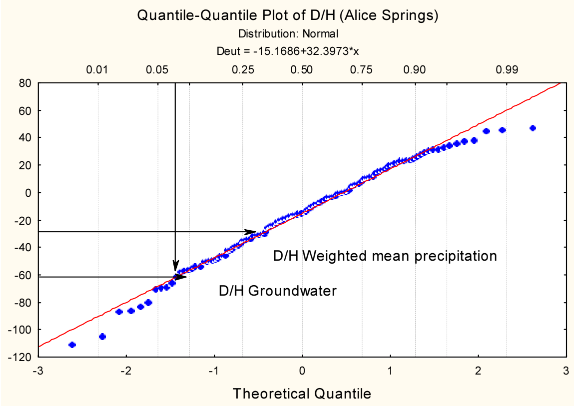
The SI ratios in groundwater reflect processes leading to isotopic fractionation under climatic conditions prevailing at the time of recharge. In low rainfall areas, they are generally depleted with respect to local precipitation in all but shallow groundwaters (eg Airey *et al* 1980; Dray *et al* 1983). The latter authors showed that in Saharan Africa, the effect tends to increase with increasing aridity.

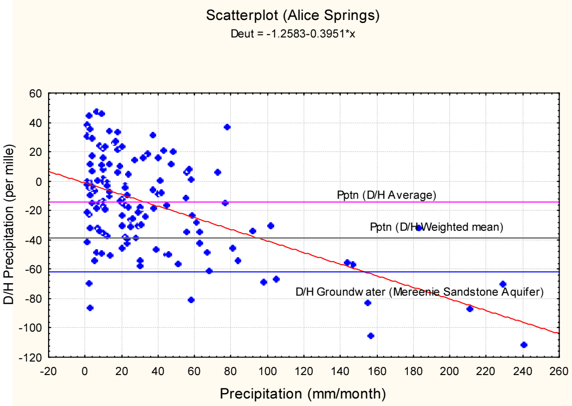
The variation in total rainfall under various climate change scenarios may be predicted using General Circulation Models (GCMs) without recourse to isotope data. It will be argued that SI ratios can be used to separate parameters such as i) temperature at recharge, and ii) threshold intensities (mm/month) for effective recharge. This could lead to a more robust basis for predicting the impact of climate change on groundwater sustainability. GCMs have been used to simulate the stable isotope ratios in global precipitation (Jouel *et al* 1998) in

Greenland ice cores (Hoffman *et al* 1998, Werner *et al* (1998). Outputs from four GCMs were critically evaluated with isotope data from the Amazon Basin (Henderson-Sellers *et al* 2002).

A scatter plot of the D/H ratios for Alice Springs precipitation from the IAEA/GNIP database is shown in Figure 2. Values for the mean rainfall and groundwater from the Mereenie Sandstone aquifer are also shown. Assuming that processes leading to isotopic modification at recharge dominate over those associated with climate change, the scatterplot suggests that isotopic composition of the groundwater largely reflects that of the heavier than average rainfall. The cumulative probability plot (Figure 3) suggests that effective recharge occurs in about the 7 per cent most intense months, corresponding to a threshold of about 80 mm/month. A similar analysis of the D/H excess data in the GNIP database leads to a similar conclusion.

The analysis has been extended to a number of Australian stations. For instance, there is evidence for little if any threshold effect for recharge to the Newer Basalt aquifer near Melbourne.





Space does not permit a detailed analysis of the concept. Based on the cumulative probability plot (Figure 3) and an analogous plot for rainfall intensity, it can be estimated that a depletion of 1 per mille in the groundwater D/H near Alice Springs could be caused by climate change leading to an increase of about 0.9 mm/month in the threshold intensity for recharge (or an equivalent change in the rainfall distribution). The corresponding value for Melbourne is 2.2 mm/month. Moreover, the sensitivity of SI ratios to temperature change generally increases with latitude. Hence changes in the D/H of groundwater near Alice Springs will be relatively more sensitive to threshold intensity effects than groundwater near Melbourne (where temperature effects are likely to be relatively more important). This is consistent with the widely reported correlations of groundwater SI ratio variations with paleo-temperature changes in temperate zones.

The importance of threshold effects appears valid not only at the GNIP monthly time scale. For instance, the effect has been demonstrated at Williams Creek (NSW) where rainfall samples were monitored on a daily basis and shallow groundwater studied (Bradd, 1996). There is also some evidence for selection effects at carbon-14 time scales.

The study is being evaluated by extension to a number of stations worldwide. The ability to use SI ratios to separate threshold effects from temperature parameters at recharge will add to the usefulness of climate change models in assessing groundwater sustainability in the long term.

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COMPARISON OF ENVIRONMENTAL ISOTOPES FOR TRACING GROUNDWATER-SURFACE WATER INTERACTIONS IN A SAND-BED STREAM

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Groundwater discharge to streams is important for delivering essential solutes to maintain ecosystem health and flow throughout dry seasons. However, managing the groundwater components of stream flow is difficult because several sources of water can contribute, including delayed drainage from bank storage and regional groundwater. In this study we assessed the potential for a variety of environmental tracers to discriminate between different sources of water to stream flow.

Chloride (Cl^-), stable isotopes of water ($^{18}O/^{16}O$, $^{2}H/^{1}H$), radon (^{222}Rn) and strontium isotopes (^{87}Sr & ^{86}Sr) were selected to investigate groundwater - surface water exchange, in particular groundwater discharges to stream flow in a sand-bed stream in SE Australia. These different environmental tracers each provide complementary information on such processes. Since chloride concentrations in groundwaters are generally much higher than atmospheric inputs to stream systems, elevated chloride concentrations in stream water can indicate points of groundwater contribution to stream flow. However, such conclusions are often ambiguous because evaporative processes also cause chloride ions to become concentrated in surface water systems. Because evaporated waters have predictable ratios of 'heavy' to 'light' water molecules, the isotopic composition of $\delta^{18}O$ and $\delta^{2}H$, can be used to distinguish whether elevated chloride concentrations in stream water are associated with evaporative or groundwater discharge conditions.

It is also beneficial to use additional tracers that specifically target a single process or water pathway, for example ^{222}Rn and $^{87}Sr/^{86}Sr$. The presence of elevated ^{222}Rn in stream water can only be produced by discharge of groundwater. Because ^{222}Rn has a short half-life (3.8 days) and rapidly outgasses to the atmosphere, it does not persist in stream systems for long. Therefore ^{222}Rn does not become concentrated in stream water as it flows downstream, allowing for more precisely locating groundwater discharge to stream flow. Since chloride, water isotopes and radon signatures may all be rapidly altered after reaching the surface (i.e. via evapo-concentration or decay) they are not always useful for distinguishing between multiple groundwater reservoirs discharging to stream flow. On the other hand, groundwaters develop distinctive $^{87}Sr/^{86}Sr$ ratios depending on their mineralogical characteristics and these ratios are not altered by evaporative processes, and persist on time scales commensurate with stream - groundwater interaction.

A case study comparing Cl^-, $\delta^{18}O$, $\delta^{2}H$, ^{222}Rn and $^{87}Sr/^{86}Sr$ to investigate the spatial and temporal variability of groundwater inputs to stream flow was conducted in the Wollombi Brook Catchment (SE Australia). The objectives were to characterise the three potential sources of water to stream flow (surface water, groundwater from the near-stream sandy alluvial aquifer system, and groundwater from the regional sandstone aquifer system) and estimate their relative contributions to stream discharge at flood recession and baseflow. Surface water was sampled at various locations along the Wollombi Brook and from its tributaries during flood recession (Mar-01) and under baseflow conditions (Oct-01). Alluvial groundwater was sampled from a piezometer network and regional groundwater from deeper bores in the lower to mid-catchment biannually over two years to characterise these potential sources of water to stream flow.

Each of the environmental tracers had distinctive signatures for at least one of the water reservoirs (Fig.1) and their combined assessment facilitated the delineation of water sources to stream flow in different parts of the catchment during flood recession and under baseflow conditions. Chloride identified specific reaches of the catchment that were either subjected to evaporation or received regional groundwater contributions to stream flow. The water isotopes verified which of these reaches were dominated by evaporation versus groundwater contributions. They also revealed that the predominant sources of water to stream flow during flood recession were either rainfall and storm runoff or regional groundwater, and that during baseflow the predominant source of water to stream flow was alluvial groundwater. Radon showed that there was a greater proportion of groundwater contributing to stream flow in the upper part of the catchment than the lower catchment during both flood recession and baseflow. Strontium isotopes showed that regional groundwater contributed less than 10% to stream flow in all parts of the catchment under baseflow conditions.

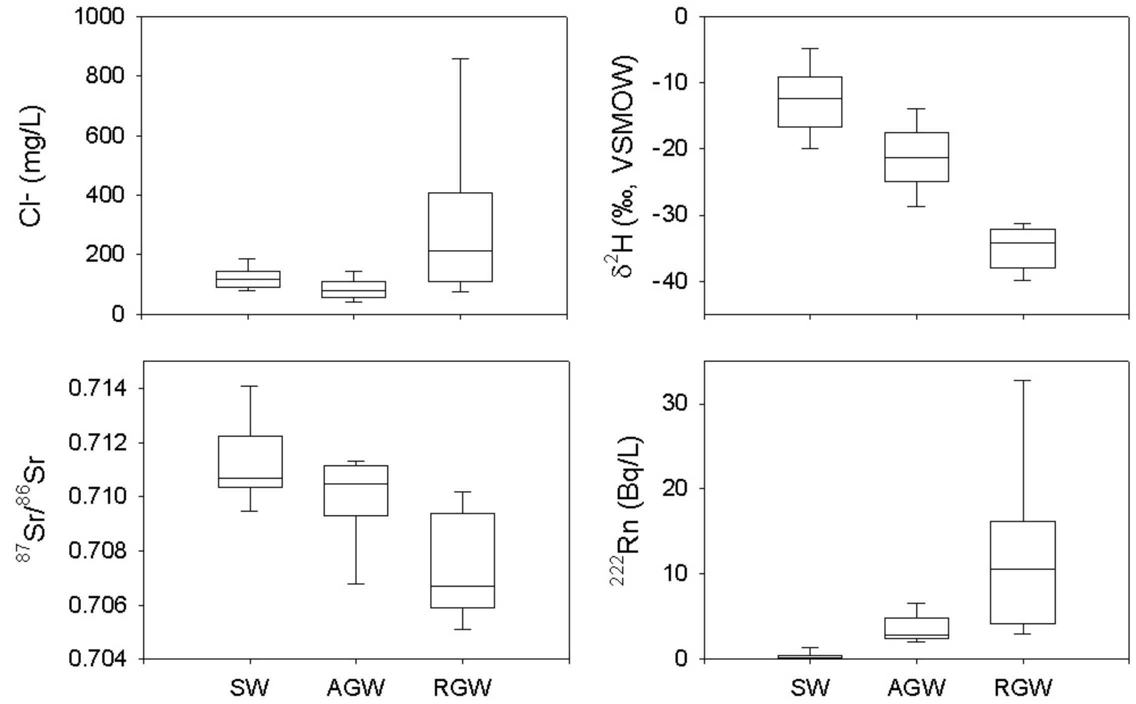

FIG. 3. The 10th, 25th, 75th and 90th percentiles represent the variation throughout the two-year sampling period (2000-01) of chloride (Cl^-), deuterium (δ^2H), strontium isotopes ($^{87}Sr/^{86}Sr$) and radon (^{222}Rn) measured in surface water (SW), alluvial groundwater (AGW) and regional groundwater (RGW), sampled across the Wollombi Catchment.

ISOTOPIC AND HYDROCHEMICAL INVESTIGATION OF GROUND-SURFACE-ATMOSPHERIC WATER-SYSTEM RELATIONS, CORK, IRELAND

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A research project, to assess groundwater resources and groundwater quality within the Cork Harbour area, will be completed in 2003. This paper deals with the applied methodology of the isotopic and hydrochemical investigations within the project, together with the evaluation of water cycle parameter relationships and groundwater origin and quality, respectively.

The Cork Harbour area of SW Ireland lies within the Late Carboniferous Variscan Orogenic Belt. The area is characterised by a series of E-W anticlines and synclines, the former cored by U. Devonian sandstone and shale and the latter by massive karstified L. Carboniferous limestones. Overburden deposits of variable thickness overlie bedrock, consisting mostly of glacial till, but also fluvioglacial sand and gravel, particularly infilling deep buried valleys.

Major aquifers occur both in bedrock and overburden. The Cork-Midleton and Cloyne Synclines are cored by intensely karstified limestones, which have significant storage capacity and transmissivity properties. Overlying these bedrock aquifers, are important ribbon aquifers represented by gravel-infilled buried valleys. These aquifers are a major resource, currently providing significant abstractions of groundwater for domestic and commercial usage, so need to be protected.

The main goals of the project were the evaluation of the water cycle balance of the area, assessment of available groundwater resources and groundwater quality, and its suitability for multipurpose use.

In the light of the established methodology, isotopic and hydrochemical investigations were carried-out to determine:

1. Water cycle parameter interrelationships (rainfall-surface-groundwater relations)
2. Groundwater origin
3. Relationship between the different types of aquifers and
4. Tracing of salt-water front movement.

Since isotopic methods have not been used before in Ireland, it was necessary to create, as a first step, a local meteoric line for Cork. Data for the estimated period 1957-2000 from the Valentia meteorological station, SW Ireland, were used (Global network of isotopes in precipitation, GNIP).

In addition, 50 water samples were analysed (20 for $\delta^{18}O$ and $\delta\,^{2}H$ against VSMOW and 30 for chemical composition). The analyses are discussed in the paper.

The results indicate a meteoric origin for groundwater, which is predominantly of the HCO_3-Ca-Mg type, direct hydraulic connection between the gravel aquifers and surface rivers, as well as interconnection between the three different aquifers. Salt-water intrusion can be traced for up to 5 km inland, along both rivers and gravel aquifers.

The research described represents a background for further, larger-scale, detailed hydrogeological investigations, which should start in the near future.

ISOTOPE TECHNIQUES APPLICATION IN UNDERSTANDING THE RECHARGE PROCESS OF THE DAVAO CITY AQUIFERS

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Davao City, one of the Philippines' major cities, is undergoing extensive urban and eco-tourism development. Generally, groundwater is the most important source of freshwater, supplying 97% of the city's water requirements. Davao City is generally mountainous, characterized by extensive mountain ranges, uneven distribution of plateaus and some lowlands. The city's urban and development areas are concentrated along a narrow coastal strip averaging 5 km in width and extending 56 km facing the Davao Gulf. It is in the coastal area where most of the production wells are located and where heavy abstraction is concentrated. Chemical and isotopic characterization of the water sources in Davao City were undertaken to provide an insight into the processes of groundwater occurrence, particularly on the origin and rate of recharge into the groundwater and evaluation of the aquifer's vulnerability to pollution. Field investigations were conducted from October 1998 to February 2002.

The study area, 42km x 33km, is within the Talomo–Lipadas-Sibulan (TLSS) catchment basin. The groundwater aquifer in the TLSS is composed of reworked and redeposited overlapping flows of Quaternary pyroclastics. It has an upper unconfined aquifer composed of sand, gravel and occasional boulders which is tapped by shallow domestic wells. The deeper aquifer which is being tapped by wells of the Davao City Water District at depths ranging from 46 to about 140 meters below ground level is multi-layered aquifer separated by thin, relatively less permeable layers of clay. Three river systems, Lipadas River to the west, and Talomo and Davao Rivers to the east traverse the study area. These flow through the city and empty to the Davao Gulf, south of the city.

Chemical composition of the groundwater shows that most of the waters in the Talomo–Lipadas–Sibulan catchment (TLSS), except for Well #1, are classified as Ca+Mg-HCO_3 waters. The fluid in Well #1 is a mixture of Ca+Mg-HCO_3 and Na+K-Cl waters. The high Cl, about 200 mg/L, is attributed to the presence of connate water in marine sediments at deeper levels. Composition diagrams of the water sources show three groups of water; one, mixed with river end members (Talomo River in the east and Lipadas River in the west); second, mixed with Well #1; and a third group of unmixed waters, found in the deeper aquifer.

The mean isotopic composition of precipitation in Davao City has been established from data obtained for the period December1999 to January 2002 from four stations located at different elevations in the watershed. $\delta^{18}O$ values ranged from –13.51 ‰ to –3.54 ‰ and $\delta^{2}H$ values ranged from –85.28 ‰ to –16.13 ‰. A local meteoric line (LMWL) was established for the region with the equation $\delta^2H = 8*\delta\,^{18}O + 12$. The isotopic composition of groundwater and surface waters in Davao City showed small variations, clustered along the LMWL. Groundwater from production wells with depths ranging from 90 m to 152 m, exhibited isotopic compositions ranging from -49.9‰ to 39.90 ‰ for δ^2H and - 7.64 ‰ to - 6.38 ‰ This suggests a uniform groundwater recharge derived mainly from local precipitation. Differences in recharge altitude and mixing of different water origin could explain the slight variation in isotopic contents.

The isotopic composition of precipitation exhibited an altitude effect. A gradient of -0.23 ‰ /100m was obtained for ^{18}O while a gradient of -1.6 ‰ /100 m resulted for ^2H. From these altitude effect lines, the elevations of recharge for the groundwater in the study area were estimated.

The profile of ‰ ^{18}O in the groundwater from the Talomo-Lipadas catchment area reveals a distinct trend. The trend goes from less negative values inland to more negative values near the coast. As seen from water chemistry, three groups of water are revealed from the isotopic composition trend of the waters. The inland groundwater has isotopic composition similar to that of low altitude rainfall or river fed from low altitude. This has been estimated to be coming from elevations < 250 m. Groundwater with the most negative values is tapped along a 2-km wide region adjacent to the coast. This coastal water is derived from higher altitudes estimated to be at elevations of not greater than 500m. The coastal waters, on the other hand, exhibit isotopic enrichment approaching the Talomo River and Well 1 located on the eastern end of the study area. Isotopic enrichment and a corresponding increase in chloride concentration in adjacent wells indicate connection with Well#1. Isotopic values gradually decrease towards the coast. Mixing between the shallow low altitude groundwater and the deep high altitude groundwater produces this decreasing trend in isotopic composition.

Tritium values from precipitation ranged from 1 TU to 11 TU while values from groundwater ranged from 0 TU to 6. Groundwater along the coast generally showed negligible or very low TU values. Representative samples from inland wells and from shallow wells had measurable tritium. Further investigation using CFCs showed representative wells from the coast yielded water with no detectable CFC indicating waters older than 50 years. Representative waters from inland had detectable CFCs with indication of mixture of old and recent waters, confirming the trend observed from stable isotopes. Recent recharge ages of 27 (55%), 22 (44%), 17(56%), and less than 10 years (8%) have been determined from the binary mixing model.

ORIGIN AND EVOLUTION OF HIGH PH MINERAL WATERS TRACED BY ISOTOPE GEOCHEMISTRY (S-PORTUGAL)

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Cabeço de Vide mineral waters are considered an important natural resource of the region. Isotope geochemistry has greatly contributed to the elaboration of a conceptual hydrogeological model associated with these mineral waters. This conceptual model has been adopted by the local authorities for the re-definition of well-head and aquifer protection areas. In the study area, the topography rises gradually from Cabeço de Vide Spas (≈ 250 m a.s.l.) to Portalegre city (≈ 620 m a.s.l.), after which the gradient becomes steeper, with a maximum elevation at the crest of the S. Mamede Mountain (1027 m a.s.l.) about 25 km NE Cabeço de Vide Spas. The geology of the region is dominated by the Lower Cambrian carbonate sequence that was intruded and metamorphosed by a heterogeneous suite of mafic (gabbros) and ultramafic (dunites) rocks forming an NW-SE cumulate-type structure of Ordovician age. The ultramafic rocks are highly serpentinized.

Groundwater samples for chemical and isotope analysis were collected from springs, dug and drilled wells located either in the surroundings of Cabeço de Vide Spas or along the main NNE-SSW trending fault, towards Portalegre city. Cabeço de Vide mineral waters belong to the Na-Cl/Ca-OH-type (pH ≈ 11.5) and issue from the intrusive contact between the mafic/ultramafic rocks and the carbonate sequence. The local Mg-HCO_3-type waters, typical of waters issuing from serpentinites [1], constitute most of the shallow groundwaters discharging from ultramafic rocks. In fact, the Mg-HCO_3 waters of Cabeço de Vide area are undersaturated with respect to chrysotile, corroborating the idea that water chemistry is strongly dependent of serpentine dissolution. On the other hand, the Cabeço de Vide mineral waters are undersaturated with respect to forsterite but supersaturated with respect to chrysotile, indicating that they could be responsible for the serpentinization process of the ultramafic rocks. The ^{2}H and ^{18}O results were used to estimate the relative importance of recharge by local precipitation *vs* groundwater infiltrated at higher slopes. The long-term mean of $\delta^{18}O$ and $\delta^{12}H$ values of precipitation collected in Portalegre meteorological station (597 m a.s.l. / approximately 15 km NE of Cabeço de Vide) was used in our interpretations [2]. Similar isotopic (^{2}H and ^{18}O) signatures were observed in both mineral and local Mg-

HCO_3 water samples (Fig. 1). Considering the isotopic composition of precipitation at Portalegre meteorological station ($\delta^{12}H$ = -32.2 $^{o}/_{oo}$; $\delta^{118}O$ = -5.44 $^{o}/_{oo}$) we can admit that the Cabeço de Vide mineral waters are apparently recharged at low elevation sites where ultramafic rocks occur. Also, this pattern indicates that the contribution of recharge from precipitation at high altitude sites (e.g. S. Mamede mountain) seems to be unlikely.

The very low ^{3}H content (from 0 to 0.32 ± 0.09) found in the Cabeço de Vide mineral waters suggest that groundwater recharge corresponds to an age older than 50 years. On the contrary, the ^{3}H concentrations in most surface and shallow groundwater samples were up to 7 TU.

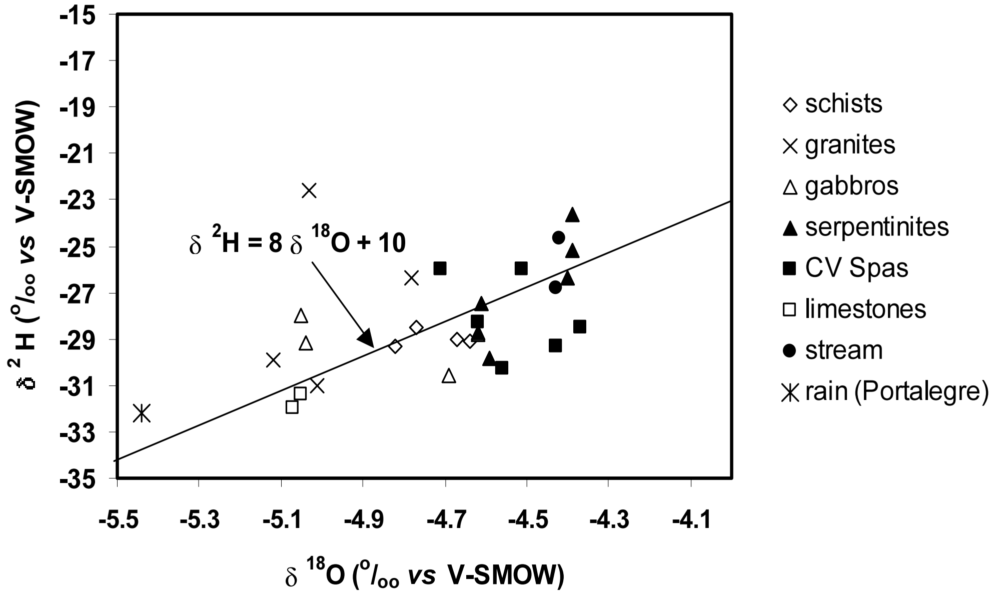

Fig. 1 - $\delta^{2}H$ vs $\delta^{18}O$ relationship in water samples from Cabeço de Vide area. (■) *Cabeço de Vide mineral waters;* (●) *stream waters; waters from:* (x) *granites,* (Δ) *gabbros,* (▲) *serpentinites,* ( ) *limestones and* (◇) *schists.* (✱) *Portalegre precipitation.*

The $\delta^{13}C$ values of -22.9 $^{o}/_{oo}$ and -18 $^{o}/_{oo}$ *vs* PDB (waters from drilled wells AC3 and AC5, respectively) points out for: i) an organic origin for the carbon in the Cabeço de Vide mineral waters, and ii) a negligible contribution of carbon from the Lower Cambrian carbonate rocks (presenting $\delta^{13}C$ values around +1.48 $^{o}/_{oo}$ *vs* PDB) to the isotopic signatures of Cabeço de Vide mineral waters. Two samples for ^{14}C content determinations of Cabeço de Vide mineral waters were collected (AMS determinations - Geochron Laboratories / USA). The values obtained range between 69.12 ± 0.28 and 65.24 ± 0.35 pmc, indicating an apparent groundwater age between 2970 ± 40 and 3430 ± 50 years BP, respectively. Recent research on the progressive evolution from rainwater to neutral Mg-HCO_3 waters and to mature, high-pH, Ca-OH waters indicate that Mg-HCO_3 waters could be generated in the first step, under open CO_2 conditions, whereas Ca-OH waters are produced in the second step, under closed-system conditions [3]. Since, in our case, both Mg-HCO_3 and Cabeço de Vide mineral waters (Na-Cl/Ca-OH type waters) have similar isotopic (^{2}H and ^{18}O) signatures, we can formulate the hypothesis of an evolution from the local Mg-HCO_3 waters towards the mineral waters.

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INVESTIGATING GROUNDWATER PROPERTIES IN HIGH ANNUAL RECHARGE RATE AQUIFERS: EXAMPLE OF THE FONTAINEBLEAU SANDS AQUIFER (PARIS BASIN, FRANCE)

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Aquifers with high annual recharge rates constitute prominent groundwater resource for freshwater supplies. However, they are very sensitive to pollutants. Moreover, in such cases, the establishment of recharge rates based on radiometric age measurements requires specific methodological approaches as in the example of the aquifer of the Fontainebleau Sands, in the Paris Basin, that we investigate here. It constitutes one of the major aquifers exploited for freshwater supply in the area. It is part of the Beauce aquifer that is underlain by the Romainville aquitard (green clays of Lower Sannoisian age) and overlain by millstone clays of Plio-Quaternary age. The Fontainebleau Sands aquifer outcrops principally in valleys, in the southern part of the Paris Basin [1].

Groundwaters from the Fontainebleau Sands aquifer were sampled along a flow-path line in order to determine their geochemical evolution through time. Chemical and stables isotope compositions provide information on mineralisation processes during recharge. They indicate either carbonate dissolution up to saturation during the recharge or addition of recent water along the flow lines. These two possibilities will be discriminated using time tracers.

^{14}C-derived age estimates ($T^{1/2}$ = 5750 years) are not precise enough to assess residence times of recent waters. We will tentatively use ^{226} Ra measurements ($T^{1/2}$ = 1620 years) to add constraints on age-estimates. ^{14}C vs. ^{226}Ra age models already tested in the Astian aquifer from southern France [2], are expected to provide further information on water-rock interactions occurring within the aquifer of the Fontainebleau Sands.

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ORIGIN OF BANK FILTERED GROUNDWATER ON THE CSEPEL ISLAND (BELOW BUDAPEST)

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The drinking water for the Hungarian capitol is mainly covered from bank filter wells of the riparian aquifer system of the River Danube. A part of these wells are located on the Csepel Island (south of Budapest). The aquifer system is highly vulnerable for pollution coming either from the Danube or from the background shallow groundwater. Budapest contaminates continuously the Danube water with communal and industrial wastewater. The contamination can have an effect on the quality of the bank-filtered water on the Csepel Island. The knowledge of the flowing system in the alluvial aquifer is very important for providing high quality drinking water and for protecting the drinking water resources.

The aims of this study are to determine the origin of the exploited water and the shallow groundwater, the ratio Danube water/background water, and the average transit time of the infiltrated Danube water for the observed wells. For reaching of these purposes stable oxygen and radioactive tritium isotope measurements, water chemical and hydraulic data have been applied. These data are compared and built together with the hydraulic data in the modeling process that was made with the 3 dimensional variation of the model program MODFLOW.

The origin of the water from production or observation wells can be determined on the basis of the significant difference between the $\delta^{18}O$ values of the Danube water and the shallow groundwater (recharging from the infiltrating precipitation). The mean $\delta^{18}O$ values in Hungary: -11.0 $[‰]_{VSMOW}$ for the Danube water, -9.3 ± 0.4 $[‰]_{VSMOW}$ for the locally infiltrated phreatic groundwater and -11.8 ± 0.8 $[‰]_{VSMOW}$ for the deep old groundwater [1].

From 1998 till 2002 in every quarter a year water samples were taken from several observation wells in the northern part of the island for stable oxygen isotope measurements. On the basis of the isotopic significance we could separate the middle area of the island, where the measured $\delta^{18}O$ values correspond to the mean of the fresh shallow groundwater, so the Danube water component cannot be detected. From the riverbank towards the middle of the island we could observe the decreasing of the river water component and determine the ratio of the river water.

On the basis of the measured δ^{18}O values we could separate another area where the shallow groundwater (originated from the infiltrated precipitation) mixed with a groundwater characterized with more positive stable oxygen isotope composition. This groundwater has enriched on the surface before the infiltration. Nowadays we can find such water in the "Kavicsos" Lake (Fig. 1).

During the observation period in the case of an observation well (F23 on Fig. 1) the measured δ^{18}O values were always more negative than the mean of the Danube water (-11.0 [‰]). The measured tritium concentrations were always lower (6-12 TU) than that of the Danube water (15-50 TU) and of the phreatic groundwater (15-20 TU). From these data we can infer that in the surroundings of the F23 well the phreatic groundwater and the Danube water have mixed with upwelling old groundwater. This tritiumless old groundwater, based on measurements on wells exploiting deeper groundwater in this area, can be characterized with -12.0 – 13.8 [‰] δ^{18}O values and its radiocarbon age is between 24000 and 31000 years.

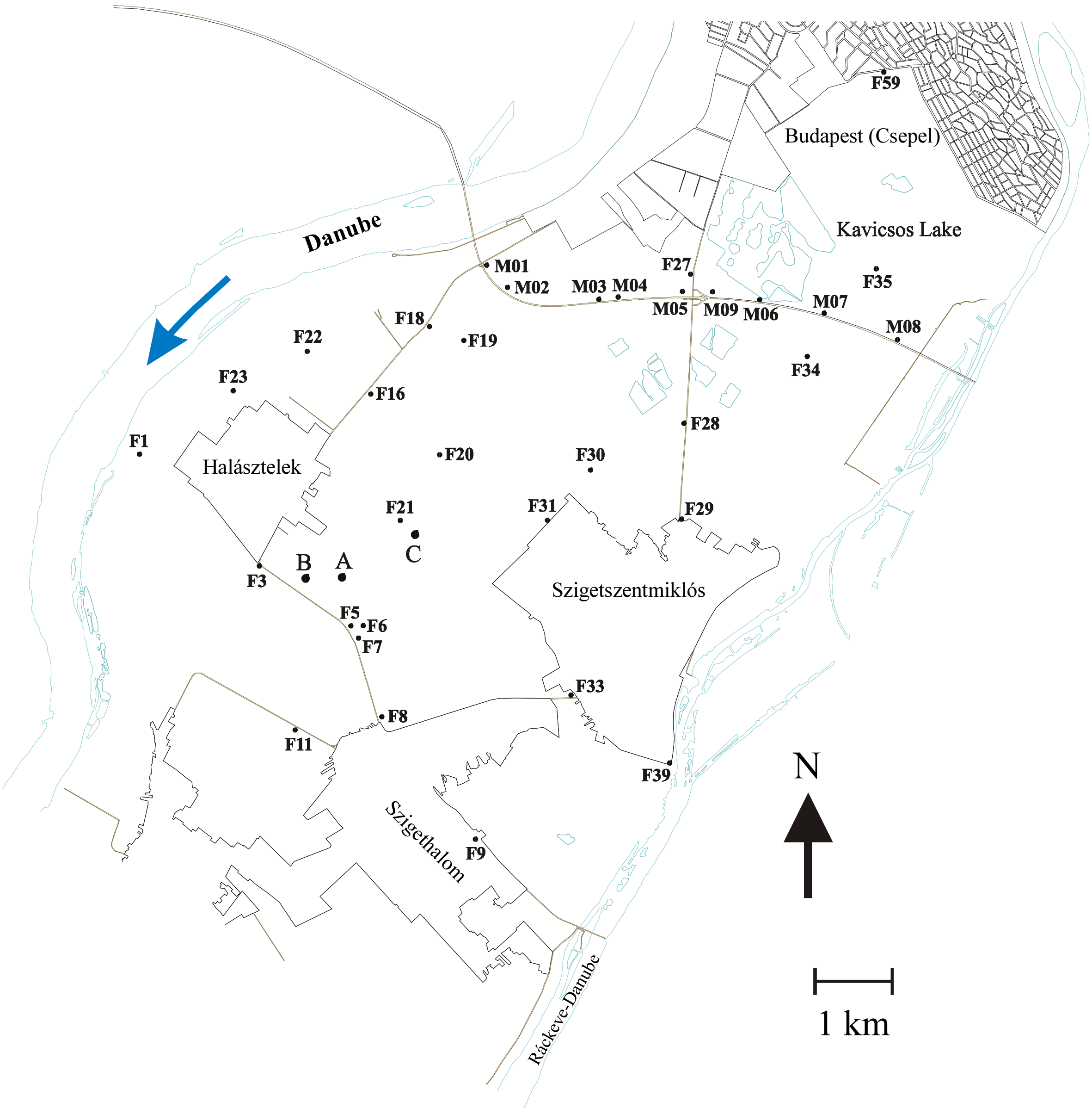

FIG. 1. Sampled observation wells in the northern part of the Csepel Island, Hungary

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EVALUATION OF THE ORIGIN AND RESIDENCE TIME OF THE GROUNDWATER IN A REGIONAL AQUIFER SYSTEM, RIO DE BOGOTA BASIN, COLOMBIA

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The Rio Bogota basin with a surface area of 4,300 km^2, is located in the central part of the Oriental Cordillera in Colombia. This basin is composed of mountains and flat terrains. The mountains areas are elongated chains with an SO-NE orientation and altitude between 2,700 and 4,000 masl. The flat terrains with a surface area of 1,400 km^2 correspond to the Sabana de Bogota located at an altitude between 2,450 and 2,600 masl. The main aquifers are the Guadalupe group composed of fractured sandstones and siltstones from the Cretacic age that outcrop in the mountains areas, overlayered by the Neogeno-Quaternary complex composed of gravels, sands and lacustrine clays located in the flats areas. During the last decade, the demand of groundwater resources in the Sabana de Bogota has increased significantly due to the development and expansion of the horticulture industry and urban areas. This paper will discuss hydrogeological, geochemical and isotope data that was obtained in a study aiming to evaluate the groundwater flow system, the origin and residence time of the groundwater in the regional aquifers. This study was done as part of long-term collaboration between the Instituto de Investigaciones e Información Geocientífica Minero-Ambiental y Nuclear, Bogota, Colombia (INGEOMINAS), the Corporacion Autonoma Regional de Cundinamarca-CAR, and the International Atomic Energy Agency (IAEA).

Isotope data collected from rains and springs sampled between 2,800 and 3,700 masl showed a clear isotope gradient with altitude that varies between -8 and -12.6 ‰ for δ^{18}O and -50 and -85 ‰ for δ^2H (Fig. 1). No significant isotope differences were observed in the groundwater representing the Neogene-Quaternary and Guadalupe aquifers. Most of the groundwater ranges between -9 and -11 ‰ for δ^{18}O and -60 and -79 ‰ for δ^2H. The exceptions are isotopically more enriched groundwater collected in shallow dugwells recharged by local precipitation in the valley. The isotope composition of the groundwater indicated that the recharge areas for the aquifers are located over 2,700 masl, mainly at the foot of the hills for the Neogene-Quaternary aquifer and outcrops in case of the Guadalupe aquifer. There is also the possibility of lateral recharge at the contact areas located at the flanks of the mountains between the unconsolidated aquifer and the Guadalupe formation. The isotope data shown no evidence of recharge to the main aquifers associated to local precipitation and rivers that crossed the Sabana de Bogota.

Tritium was only found in some high altitude springs. Carbon-14 data ranges between 75 pmc close to recharge areas to values as low as 0.5 pmc along the groundwater flow system. These trends in the Neogene-Quaternary aquifer are accompanied by changes in the $\delta^{13}C$ from -17 to + 13 ‰ (Fig. 2), a significant increase in bicarbonate and dissolved organic carbon, and methane production. These data clearly showed a change in redox conditions promoting methanogenesis, associated to the presence peat remains in the aquifers sediments. The peat sediments were deposited during the lacustrine phase (Van der Hammen, 1995). Geochemical modeling using NETPATH was performed to correct the ^{14}C data from the input of old carbon to the dissolved inorganic carbon associated to methanogenesis (2). The geochemical modelling suggested that the main reactions controlling the chemistry of the groundwater along the groundwater flow system are weathering of plagioclasses, dissolution of calcite, Ca/Na exchange and oxidation of organic carbon. Corrected ^{14}C dates produced radiocarbon ages between 7,000 and 25,000 year old in the Neogene-Quaternary aquifer with the oldest groundwater located in the central part of the valley. These are the areas affected by heavy pumping that have shown significant decrease in the water table during the last 10 years. These agreed with the presence of old groundwater in these areas. The Guadalupe aquifer even in wells and springs located at the foot of the mountains showed groundwater older than 5,000 years indicating the existence of a deep groundwater flow system associated to recharge areas located in outcrops of the Guadalupe formation found in the high part of the basin.

The hydrogeological and geochemical study showed the existence of a complex groundwater flow system in the Rio de Bogota Basin. The main areas of recharge for the aquifers are located above 2,600 masl. Rivers and local precipitation in the valley do not play any role in aquifers recharge. Groundwater dating shown most of the groundwater in both aquifers is older than 7,000 years. These findings have significant implication for the long term substaintability of the groundwater resources.

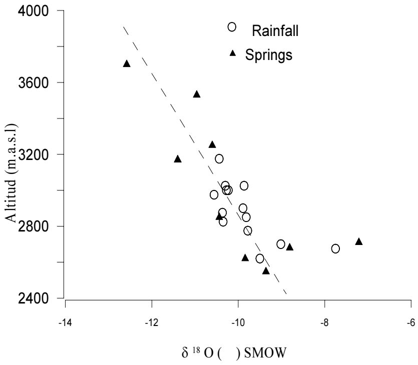

Fig. 1 $\delta^{18}O$ vs Altitude (springs and rains)

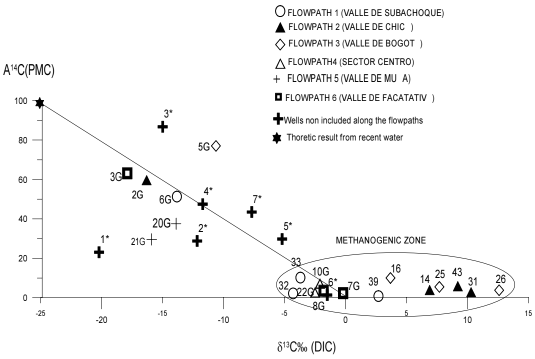

Fig. 2 $\delta^{13}C$ vs Activity ^{14}C (PMC)

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RECENT AGE INDICATORS APPLIED TO GROUNDWATERS IN FRACTURED AQUIFERS IN THE UK

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After early studies using tritium in the 1960s and 70s, the investigation of recent groundwater dynamics in UK aquifers has been largely neglected from the age-indicator standpoint. Now, however, with the ever-increasing stress on water quality issues, attention is once again being focused on this area. In the interim, new and relatively inexpensive dating methods using chlorofluorocarbons (CFCs) and sulphur hexafluoride (SF_6) have arrived to rejuvenate the study of young groundwater components. This study considers preliminary results obtained from fractured aquifers in the UK. Many British aquifers are fractured, resulting in important non-intergranular permeability. Two different lithologies are considered here: a Permian sandstone from southern Scotland, and the Chalk of southern England. The sandstone is sufficiently fractured that the bulk of flow occurs via this ‘secondary’ route. In the Chalk, although it has a porosity twice that of the sandstone (up to 40%), most flow also occurs via the fracture network because pore throat sizes are so small.

The Permian basin of Dumfries, 25 km long and 10 km wide, supplies 11% of Scotland’s groundwater. Farming is widespread in the basin, while industry is locally important. Both activities have potential impacts on groundwater quality. To better understand groundwater quality developments in the basin, a hydrogeochemical sampling campaign was carried out [1]. This resulted in 16 boreholes across the basin being sampled for CFCs and in most cases SF_6. The results were interpreted in terms of mixing between modern (late 1990s) recharge and >50year-old CFC-free groundwater. Fig 1(a) shows modern water percentage calculated from CFC-12 and SF_6 concentrations respectively. In over half the cases the correlation is good. In a few cases CFC-12 percentages exceed 100%, indicating a pollution problem. SF_6 percentages remain below 100% in these cases and so can still be used as age indicators, albeit with caution. In a few other cases SF_6 percentages exceed CFC-12 percentages, but never themselves exceed 100%. Therefore it seems likely that the SF_6 excesses are due to air equilibration during sampling. SF_6 is much less soluble than the CFCs and therefore far more susceptible to the less-than-ideal sampling conditions that were sometimes encountered during the survey.

Fig 1(b) shows a plot of modern water percentage, based on CFCs and/or SF_6 as considered appropriate in the light of Fig 1(a) above, against nitrate concentration. With the exception of one borehole adjacent to a farm, where a point source of nitrate pollution is a likely problem, there is a good correlation. This suggests that the old-new groundwater mixing concept is a valid way of interpreting residence time indicators in this and similar fractured aquifers.

The Chalk is widespread in eastern and southern England and provides a large proportion of the region’s groundwater. High population densities with associated light industrial development mean that the Chalk aquifer is frequently under stress. One aspect of the Chalk that tends to protect the groundwater resource (at least in the short term) is its usually thick unsaturated zone. Judging by the results of tracing experiments either deliberate or environmental [2,3], most recharge will take decades to reach the water table. An important question therefore is whether the CFC or SF_6 'clock' starts ticking at the ground surface or the water table. Early indications based on the major atmospheric gases suggested that the Chalk is more 'open' at depth than might have been anticipated [4]. Recent analyses of CFCs in a 30-m deep borehole in Hampshire with nested gas samplers appear to confirm that present-day atmospheric concentrations are found through most of the unsaturated zone, indicating that CFCs and SF_6 are best regarded as groundwater-only residence time indicators, in contrast to tritium.

Further work on the Chalk aquifer of Hampshire and West Sussex using CFC-12 and SF_6 has shown a higher incidence of CFC pollution (some 40% of sites) than in the Dumfries basin. SF_6 reaches a polluted level in only one case, where it is over twice the modern air-equilibrated water value. In most other cases there is fair agreement between modern water percentages based on CFC-12 and SF_6, though SF_6 percentages are nearly always the lower of the two, suggesting that a small element of CFC pollution could be almost ubiquitous. While there is no clear relationship between nitrate and percent modern water as found for the Dumfries basin (the samples are from a less homogeneous catchment), there is a negative correlation with δ^{13}C-DIC. Since it is unlikely that δ^{13}C-DIC would change via water-rock interaction in just a few decades, the correlation is best explained by simple mixing, justifying the decision to interpret Chalk groundwater age indicators in terms of percent modern water.

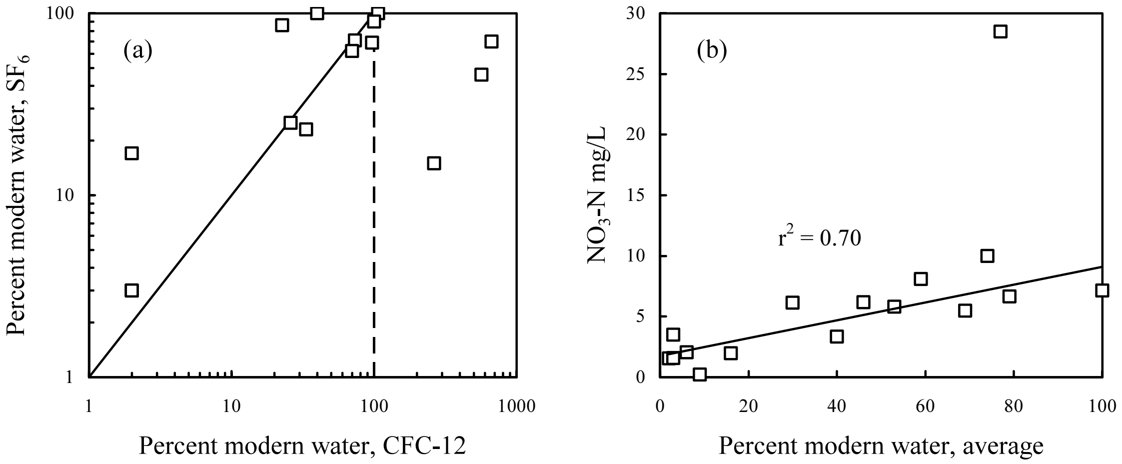

FIG. 1. Samples from the Permian basin of Dumfries: (a) crossplot of modern water percentages calculated from CFC-12 and SF_6 concentrations, (b) crossplot of nitrate vs modern water percentage showing a high degree of correlation except for one polluted site.

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PALAEOWATERS

THE HYDRODYNAMIC FUNCTIONING OF THE DEEP AQUIFER OF THE SENEGALESE BASIN: AN ISOTOPIC APPROACH

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This work represents a synthesis of the main results obtained from the hydrochemical and isotopic study run within the IAEA project framework registered under SEN/8/005 "Hydrogeological study of the deep aquifer of the Maastrichtian". The study has allowed a better understanding of the structure of the aquifer with the help of the new hydrochemical and isotopic data; a good understanding of the motion of ground water inside the aquifers and their impact on the mineralisation which is important for the water quality assessment.

The geographical distribution analysis of the chemical and isotopic concentrations is done from 725 samples collected all over the aquifer through the prpject referenced as followed SGPRE/COWI, 2002; FAYE, 1994; SEN/8/005,2002; this shows a very neat separation of different areas all oriented from the north to the south.

It is noticed, from East to WEST, an increasing of the total dissolved solid (200mg/l to 700mg/l at the meridian line of 15°30'). Then, it is recorded a sudden increase of concentrations reaching maximum values of 1500 to 3000mg/l a long a meridian line centred on a north-south axis through the towns of Louga - Kaolack. At the West, the other side of the so-called " salted central zone", the concentrations decrease again to 350-650mg/l in the area of the Horst de Ndiass.

The spatial distribution analysis of the geochemistry characteristics, has shown 3 main geochemical zones oriented along a meridian line.

1. The "East Zone", at the east of the meridian line of 15°30', characterised by bicarbonate water usually with a very low concentration of dissolved solids; the concentration increases slightly to the west et sometime becoming locally more sulphated.

2. The "salted central zone", characterised by the presence of chlorite of sodium in the water at a very high concentration, from the estuary of the Sine Saloum up to the lake of Guiers, along the North-South line joining the towns of Louga and Kaolack as mentioned above.

3. The " Horst of Ndiass zone": it is situated at the west of the hill of the town of Thiès, within a very narrow band to the shallow Maestrichtian until the Cap Vert peninsula, characterised by bicarbonated water with very low mineralisation.

- This distribution is related to the important structural units defined within the basin (see document on geological structures); the east zone and the “salted central zone” represents the “eastern block” defined previously; it is separated to the other structural unit (“extreme west”- the only part of the maastrchtian aquifer considered as partially shallow) with the help of the geological accidents recorded on the eastern side of the Horst; this type of characterisation by zone has been confirmed by the isotopic geochemistry

- On “the east and south east zone”, the concentration of oxygen 18 show values of δ lower than – 6.2 ‰; in average more negative than the concentrations found in the actual rainfall of the region;

- At the central zone, the concentration of the oxygen–18 are lightly contaminated with heavy isotopes compared to the concentrations found in the eastern and southern area ($-6.4 < \delta^{18}O < -5.5$ ‰), proving the “ paleoclimatic effect” detected in the aquifer;

- In the extreme west zone (Horst of Ndiass), the concentrations of oxygen within the aquifers correspond exactly to the mean values of the concentrations recorded from the local rainfall; this confirms the assumption of a recent recharge in the area.

- The other geo dating elements (^{14}C, ^{36}Cl, Uranium group and the Thorium, ^{4}He) and the Bore 11 have given the opportunity to discuss types and regimes of circulation within the different zones of the aquifer and to design a ground water circulation model.

- The recharge zones located in the Horst de Ndiass, next to the hard rock crystal aquifer, the North east border surrounding the town of Matam and along the Senegal river.

- The directions of groundwater circulation;

- The velocity of water within the aquifer are quite low except in the Casamance region;

- The time variation of the recharge confirms that the ground water circulation does not comply with a permanent regime.

DELINEATION OF PALEOWATER–RECENT WATER INTERFACE IN THE GROUNDWATER TO THE NORTHEAST OF CAIRO

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The present study has been conducted to delineate the interface between paleowater and recent water and to explore the recurrence potential of groundwater in an area to the east of Cairo. The groundwater from Quaternary and Miocene aquifers and the surface water from Ismailia canal were sampled for hydrochemical (major and minor ions) and isotopic (tritium, oxygen-18, deuterium and carbon-14) analyses. The Miocene aquifer which is the major concern of the study is characterized by a high stage of mineralization; avg. TDS equal 6850ppm, water type is Cl-Na, marine genetic salts ($MgCl_2$ and $CaCl_2$) in more than 90% of the samples. Slight hydrochemical variations exist that are controlled by changes in sedimentary facies in the rock/water contact as well as recharge conditions. The aquifer is eutriphied with a relatively high concentration of nitrates, silicates, boron and high hardness level and cannot be used safely for human purposes but suits the livestock and poultry and high salts tolerant plants.

The isotopic composition reflects that Miocene aquifer is less currently recharged than Quaternary one. It is dominated by paleowater from pluvial times meteoric cycle and shows some hydraulic connection with Quaternary aquifer and Nile system in some localities. The samples from Inshass area and some of Heliopolis basin vicinities to the north of the study area mark a zone of mixing and hydraulic connection between present time recharge sources and entrapped paleowater. The aereal distribution of O-18, D, and T isotopes and the hydrogeochemical cross sections confirm the presence of a structural break between Heliopolis basin and the other localities of the study area where structural features resist the reach of recent recharge to the basin while it reaches the northern and eastern boundaries.

CHLORINE-36 AND NOBLE GASES IN DEEP GROUNDWATERS FROM THE NORTHEASTERN SAHARA (ALGERIA)

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The groundwaters occurring in the Northeastern Sahara (Algeria-Tunisia and Libya) constitute huge water reservoirs whose major component is very old (Paleowaters). Water managers are there facing problems related to resource management in terms of estimating budget parameters (recharge, evaporation, leakage, mixing), degradation of the water quality, but also the renewable rate (résidence time).

The Continental Intercalaire from Sahara is one of the largest confined aquifers in the world. The aquifer material is made of complexe layers of sandstone alternating with clayish levels. The depth of the aquifer ranges between 400 and 1800 metres giving rise to temperature up to 70°C and total dissolved salts of 1.5 to 5 g.l-1, in mainly Ci-Na-SO4.

Sampled groundwaters show a quite wide range of ^{36}Cl contents, ranging from 8 to 99 10^{-15} at.at^{-1}, expressed as ^{36}Cl/Cl atomic ratio. The space distribution of ^{36}Cl contents fits fairly well with what is known about the piezometric contours of the aquifer: a decrease is observed from recharge to discharge zones. If this decrease is radioactive decay, it can be interpreted in terms of groundwaters transit time. Maximum time intervals of about 3 half-lives (900 Ka) may be computed using ^{36}Cl specific activities (at.l^{-1}).

In order to evaluate the epigene production, Measurements were performed on chloride extracted by leaching from a soil profile. The results are the same order of magnitude (10^{-15} at.at^{-1}) as for groundwater chloride sampled near recharge areas and could reflect the true value of initial ^{36}Cl input.

However, the values measured on the groundwaters sampled near recharge areas (100 Km) are equivalent (order of magnitude: 10^8 at.l^{-1}) when compared to the calculated values for precipitations in the region. The equivalence between the measured activity in this zone and the expected initial activity could thus be explained by two phenomena: dissolution of Cl^- within the aquifer, and/or radioactive decay of ^{36}Cl .The residence time determined on the main flow line where the radiodecay is observed are expressed in terms of minimum ages (16 to 500 Ka) and maximum ages (25-1200 Ka).

New noble gas data are presented to improve the palaeoclimatic and residence time interpretation for the Continental Intercalaire aquifer system. The groundwater recharge temperatures (RT) were estimated from the averaged amounts of noble gases (Ne, Kr, Xe) corrected for the excess air effect. The RT's for most groundwaters are generally lower than the present day recharge temperatures. Along the main flow direction (south-east from the Atlas mountains), the CI palaeowaters (ages 20 to 40ka BP) have an average RT of 16.9°C which is some 5°C cooler than at the present day. Recharge temperatures calculated in four samples from the CT aquifer (30-150m depth) average 19.7, close to the present day mean annual temperature of 21°C.

POSTER SESSION II

ISOTOPES IN PRECIPITATION

AIR MASS PATTERNS AND TEMPORAL VARIATION OF THE ISOTOPIC COMPOSITION OF ATMOSPHERIC WATER VAPOUR AND PRECIPITATION OVER CENTRAL TURKEY AND GROUNDWATER RECHARGE

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Water vapour and event precipitation have been collected within the program of coordinated research project about isotopic composition of precipitation in the Mediterranean basin in relation to air circulation patterns and climate at Ankara since January 2001. The purpose of this study is the determination of the interaction between climate conditions, chemical composition and isotopic composition ($\delta^{18}O$, $\delta^{2}H$) of precipitation and water vapor in Turkey. For this purpose we have been collecting samples at Ankara station to understand the variation of daily/event and seasonal isotopic values of precipitation and water vapor.

The study focuses on the systematic collection of basic data on isotope content of precipitation and water vapor in Ankara, Turkey to determine temporal variations of environmental isotopes in precipitation and consequently to provide basic isotopic data for the use of environmental isotopes in hydrological investigations within the scope of water resources inventory, planning and development.

Sampling of rain water and water vapor have been carried out in Ankara Turkey, from January 2001 to December 2001, by means of a pluviometer, water vapor sampling system respectively. The relation between the isotopic composition of precipitation and synoptic parameters is examined. The rain samples can be separated into three group based on "deuterium excess" for year 2001 and long term observation of Ankara, Antalya and Adana stations of Turkey. The majority of the samples have a "deuterium excess" between 10 and $22^{o}/_{oo}$ and other has values less than $10^{o}/_{oo}$ and greater than 22. The rains with a "deuterium excess" of more than $22^{o}/_{oo,}$ between 10 and 22 and less than 10 are associated with air masses which comes from East Mediterranean (SW), North Atlantic (N, NW) and Central Atlantic (W, SW) respectively.

Although it is not possible to derive the isotopic composition of the water vapor from isotopic composition of precipitation, a relationship was defined between the isotopic composition of the water vapor and the precipitation for 2001 in Ankara, Turkey. A correlation obtained between the isotopic composition of water vapor data and temperature, which is much better than the precipitation data.

In this study some synoptic parameters are considered with the isotopic composition of event rain. 26 event rains (p>5mm) were recorded in 2001. For synoptic meteorological analyses we are used surface and 500mb synoptic charts and HYSPLIT dispersion model of

NOAA. For each event rain (P>5mm) backward trajectory computed by using Hysplit dispersion model, ground and 500mb synoptic charts.

According to the available meteorological observations 6 main origin of air masses affecting Turkey which are Continental Polar (cP, Russia), Maritime Polar (mP, Europa), Maritime Tropical (mT, Central Atlantic), Continental Tropical (cT, North part of Africa), Mediterranean depression engendered air mass and Asiatic monsoon depression type air masses. The origin and trajectory of air masses are classified. For each group of air masses an approximate local meteoric water lines and percentage frequencies were calculated by using computed trajectories.

The isotopic composition of event rains in relation with cP air masses are varied around MWL, in relation with mP and cT air masses are varied between MWL and EMWL. The isotopic composition of event rains in relation with Mediterranean depression engendered air mass and Asiatic monsoon depression type air masses are varied around EMWL and below MWL respectively. Before reaching to Ankara, the air masses coming to Turkey from all direction, undergo orographic precipitation. This can be one of the reasons why we don't see east Mediterranean sea effect in Ankara. The lower "deuterium excess observed in 2001 may be attributed to the long over sea path and this closer to the equilibrium processes during air sea interaction, mostly with the western part of Mediterranean.

The isotopic composition of water vapor and precipitation examined with meteorological data and precipitation/evaporation ratio average history of air masses precipitating at a given place.

The control mechanism of the isotopic composition of local precipitation is examined by using synoptic meteorological data and back trajectory method and by the average precipitation/evaporation history of air masses precipitating at Ankara. d-excess values in samples from a local spring and well observed. In study area groundwater is recharged predominantly by the Maritime Polar (mP, Europa) originated air masses.

IAEA-CN-104/P-23

ISOTOPE COMPOSITION OF PRECIPITATION ALONG THE ADRIATIC COASTS OF CROATIA AND SLOVENIA

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Monitoring of isotope composition of precipitation includes measurements of radioactive isotope tritium (^{3}H) and stable isotopes (^{2}H, ^{18}O) in monthly precipitation samples. Isotope composition of precipitation at Zagreb (Croatia) and Ljubljana (Slovenia) have been performed for more than 20 years within the Global Network for Isotopes in Precipitation (GNIP) organized jointly by the International Atomic Energy Agency (IAEA) and the World Meteorological Organization (WMO) [1]. Within the IAEA Co-ordinated Research Program "Isotopic composition of precipitation in the Mediterranean Basin in relation to air circulation patterns and climate" the network has been extended since September 2000 to several stations along the Adriatic coast: Malinska on Krk Island, Zadar, Komiža on Vis Island, Dubrovnik, and Zavižan on Mt. Velebit (alt 1594 m) in Croatia, as well as Portorož-Airport and Kozina in Slovenia. The sampling sites are situated in areas characterized with three different types of climate: (i) in the northern part continental climate prevails, (ii) in the mountainous middle part, mostly karst area, colder continental climate dominates, and (iii) the area along the Adriatic coast is controlled by the Mediterranean climate. In this work we present tritium activity and stable isotope content in monthly precipitation samples at the mentioned stations, together with the corresponding meteorological data: precipitation amount and mean monthly temperature.

The results of tritium activity in monthly precipitation are presented in Fig. 1. The results cover the period from September 2000 to September 2001 for marine stations and from January 2000 to December 2001 for continental stations Zagreb and Ljubljana (GNIP stations, Fig. 1d). Seasonal variations are typical for the continental stations of the Northern Hemisphere. The minimal activities in winter approach in the last years the natural, pre-bomb tritium level. Seasonal variations at maritime stations of mid- and south-Adriatic stations (Fig.1a, 1b) are less pronounced (reaching 1.4 Bq/L in summer) than those at the continental and north-Adriatic stations (Fig.1c, 1d), that reach maximum of 2 Bq/L. Tritium concentration at the continental stations Zagreb-Grič and Ljubljana is, on the average, slightly higher than at the maritime stations. No local tritium contamination has been observed.

The stable isotopic composition of precipitation shows different patterns of seasonal variations at different stations. The highest $\delta^{18}O$ and $\delta^{2}H$ values are observed at the coastal stations. The continental stations show larger seasonal variations in the stable isotope content (*e.g.*, seasonal variations equal to 13‰ and 4‰ in $\delta^{18}O$ at stations Zagreb and Dubrovnik, respectively) due to larger temperature variations. The distinct altitude effect is observed at the station Zavižan. At this station the two types of climate, the Mediterranean and the continetal, are mixing and the isotope pattern of precipitation reflects such a mixing: tritium distribution is close to the nearest maritime station Zadar, while the seasonal variations in stable isotopes are close to the continental pattern.

Correlation of δ^{18}O and δ^{2}H with amount of precipitation is poor for all stations, while the correlation with mean monthly temperature is better (Fig. 2). We show the slope and the correlation coefficient of δ^{18}O *vs*. T correlation for each station separately. The long-term slope for the Zagreb station is 0.3‰ δ^{18}O per °C [1]. The correlation between δ^{18}O and δ^{2}H is very good and obtained data fit very well to the Craig's "Global Meteoric Water Line". The observed scattering of the data at individual station can be attributed to short monitoring period.

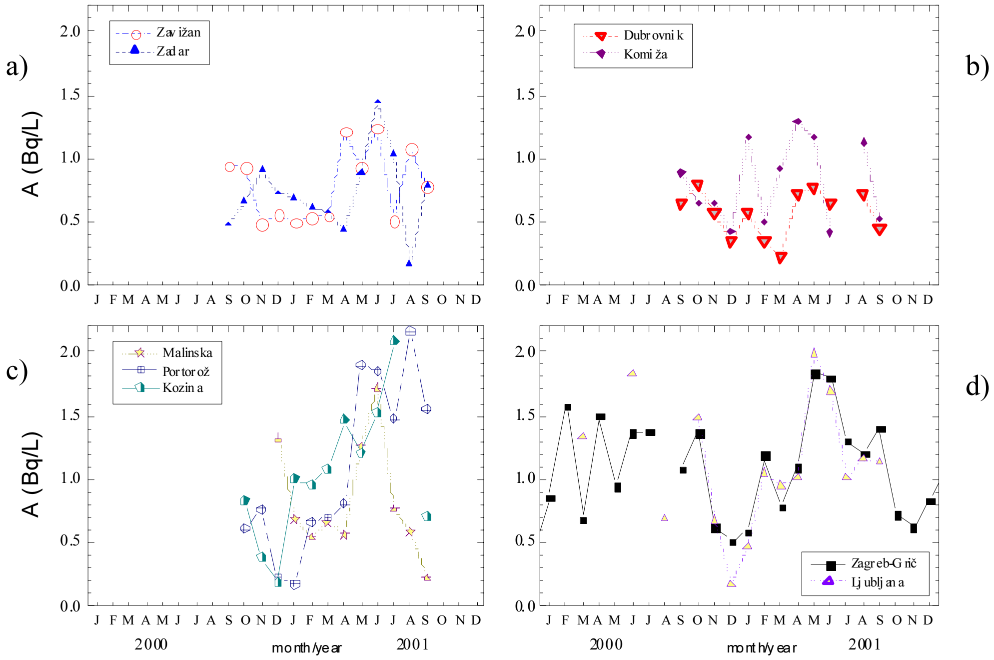

*FIG. 1. Tritium activity in monthly precipitation samples collected at stations along the Adriatic Coast (*a *and* b*: south Adriatic,* c*: north Adriatic) and in Zagreb (Croatia) and Ljubljana (Slovenia) (*d*).*

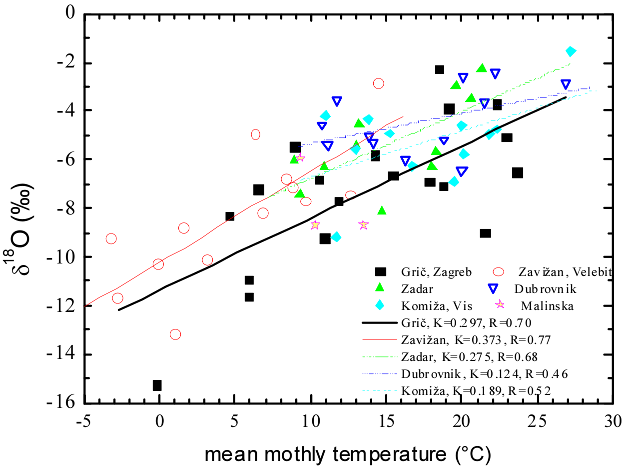

FIG. 2. Correlation between monthly temperature and monthly δ^{18}O content in precipitation. Linear regression lines with the slopes K and correlation coefficients R are obtained.

ACKNOWLEDGEMENT

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RAIN GAUGE WITH INTEGRATED ISOTOPE-SAMPLING DEVICE

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This precipitation station is designed to measure the rainfall and to offer the possibility to take samples for isotopic analyses of the total discharge during one month or any other pre-selected period.

Precipitation measurement: Digital tipping bucket rain gauge with a time resolution from one minute up to some hours (free of scaling) and a quantity resolution (depending on the type of bucket) from 0.1 or 0.2 mm rainfall.

Sampling application: For isotopic analyses it is necessary, that no part of the precipitation can re-evaporate. Therefore in this application the container where the precipitation is stored, can be opened and closed. This procedure is working automatically controlled by the data-logger. When the rainfall starts (=the moment of the first tipping), the container is opened. After the rainfall it is closed again. The time of delay can be chosen individually (for instance 1 till 10 minutes).

To get correct samples of one month, a second valve is changing the flow path between the two containers exactly at the beginning of the month.

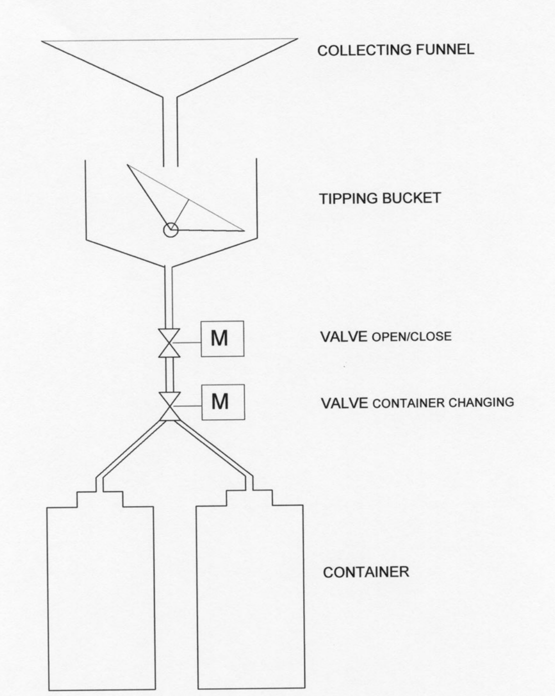

FIG.1. Scheme of the rain gauge with integrated automatic isotope-sampling device.

Apart from precipitation also other parameters like temperature, wind speed, radiation and so on can be stored.

The whole application can be mounted in existing measuring stations, without changing the existing collecting funnel (as shown in the picture). This is important for the continuity of the measurement at an existing station. On the other side, the whole measuring and sampling equipment can be mounted in a new station with any tipping bucket, which allows to gather the measured precipitation.

To avoid large changes of temperature of the sampled water, the containers can be isolated. In cold areas the station must be heated in such a way, that the sample is not freezing. A simple funnel heating is not enough. The heating can be done with gas or electricity regulated by a thermostat. The described station is equipped with two separated electrical heating systems with thermostat control, as the hut is dived off in two parts. In the upper part are the tipping bucket, the data logger and one valve. In the lower part are the other valve and the containers. This allows an exact control of the temperature.

The prototype of this station was erected for the Zentralwasserversorgung Hochschwab Süd, designed and rebuilt with the digital equipment from Joanneum Research, Graz.

Outlook: In stage of development is a temperature controlling system for the collecting funnel. This is necessary during very cold and very hot spaces of time. There are two systems possible: a small cooling plant (perhaps powered with solar energy) or Peltier-elements, both with an electronic control system and an isolated collecting funnel. With Peltier-elements it is possible to heat and cool the funnel according to the temperatures of the surroundings but they need a lot of energy. In our alpine regions especially the cooling of the funnel during summertime will be an important step to optimise the sampling procedure.

Especially the high temperatures before a thunderstorm brings problems with re-evaporation of raindrops at the beginning of a precipitation event. Therefore the cooling of the collecting funnel is a crucial element in the procedure of isotope sampling.

The system (including the temperature controlled liquid gas heating) can be supplied with solar energy and supplemented with remote data transfer systems like LEO-satellites, GSM, dedicated radio or telephone.

ISOTOPIC COMPOSITION OF ETHIOPIAN RAINFALL WATERS: OBSERVATION ON ITS TYPICAL SIGNATURE

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In the eastern Africa the major source of precipitation comes from Indian Ocean, and generally speaking, the isotopic composition is related to the regional circulation patterns; seasonal fluctuations correspond to the seasonal displacement of the Inter Tropical Convergence Zone (ITCZ)[1].

Ethiopia is located on the northern extreme of ITCZ. It is generally believed that, under the present conditions, the Ethiopian region is under the influence of North Indian Ocean in March and April and combined Atlantic and Indian Ocean monsoon in July-August depending of the position of the ITCZ. This generalization has been however subjected to debate but this complex situation probably explains the typical isotopic rainfall signature. As already observed by different authors, using the IAEA Addis Ababa time series, these rainfall regimes have distinct isotope signal. The March-April rainfall is characterized by enriched $\delta^{18}O$ and δD compared to the July-August relatively depleted isotope values. In many part of the country rainfall in months of December, January and February is minimal and isotope signal usually tends to show influence of evaporation. Highly depleted values are also observed in some months of November since the start of the record. Another very important feature of the isotopic composition of the Ethiopian region is that irrespective of high altitude and lower mean annual temperature compared to other East African regions, the isotopic signature is enriched in Ethiopian rain waters. All non-evaporated rains and modern meteoric waters elsewhere in the country plot above the GMWL showing high deuterium excess.

Precipitation isotopic composition ($\delta^{18}O$, δD and ^3H) has been measured at Addis Ababa, a tropical highland IAEA/WMO station, since 1964. This, combined with newly collected rainfall isotope data (short time series) obtained from the Ethiopian rift region under IAEA-TC projects and from the plateaus under the research we are currently conducting; and subsurface groundwater isotopic composition data reported by different investigators from different climate region of the country helped us to grip a better picture on the isotope signal and meteorological processes relationships.

These new data confirm the relative enriched $\delta^{18}O$ values in spring rainfalls and a deuterium excess often higher than 15 in rainy seasons. A closer look at the inter-annual variation of July-August–September rainfall shows that deuterium excess decreases by about 2-3 units since 1961. The highest deuterium excess value, associated with $\delta^{18}O$ enrichment, is observed in September (figure 1), a month characterized by rainfall formed from convective clouds often formed by re-evaporation of regional moisture. Variation of $\delta^{18}O$ with altitude and geographical location is also very weak or lower than the global average if it exists. The existence of altitude effect locally cannot be ruled out. Lack of strong altitude effect may be due to complex derivation of rainfall, superposition of altitude effect over rain-shadow effect, or due to the dominance of rainfall from monsoon or convective systems than from orographic systems.

Based on these observations we draw the following most plausible explanations regarding the signal of isotopes in meteoric waters of Ethiopia. One, moisture coming from the red sea and North Indian ocean seems to play an important role in spring rainfall but may be also during the main July-August rainy season. This has to be verified by closer look at the isotopic composition of vapour produced from north Indian ocean. Continental moisture recycling, mostly from lakes (enriched values in September) seems an important component in summer rainfall, particularly in September.

These conclusions have a wide-ranging application in furthering continental scale moisture recycling studies, in groundwater tracing in the Ethiopian region and in palaeo-hydrology.

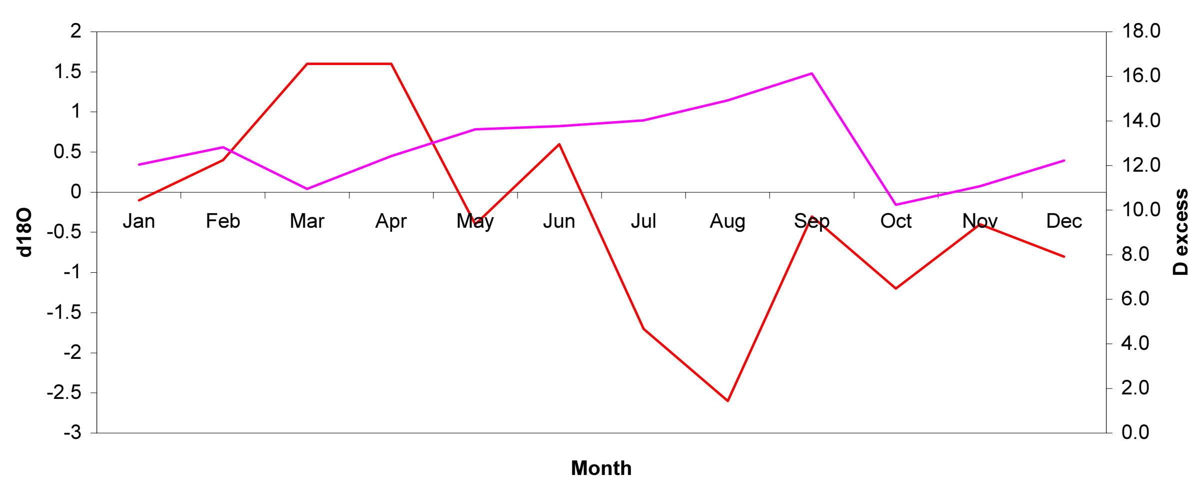

Figure 1. Interannual variation in deuterium excess and d^{18}O in Addis Ababa precipitation

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A 10-YEAR RECORD OF STABLE ISOTOPE RATIOS OF HYDROGEN AND OXYGEN IN PRECIPITATION AT CALGARY, ALBERTA, CANADA

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Global patterns of the stable isotope ratios of hydrogen and oxygen in precipitation have been described by Rozanski et al. (1993) based on the data from stations belonging to the Global Network of Isotopes in Precipitation (GNIP) maintained by the International Atomic Energy Agency (IAEA) in Vienna, Austria. This compilation documents a marked anomaly in Alberta, Canada, displaying significantly lower mean δ^2H and δ^{18}O values in precipitation than in other regions of similar latitude. This has been confirmed by the measurements conducted within the Canadian Network for Isotopes in Precipitation (CNIP). However, the extent of this anomaly is not well constrained, since both the GNIP and the CNIP networks maintain no precipitation stations in southern Alberta, Canada.

Samples of precipitation were collected twice daily from January 1992 to December 2001 in Calgary, Alberta, Canada (51.06N, 114.06W, 1049 m ASL). The stable isotope ratios of hydrogen ($^2\mathrm{H}/^1\mathrm{H}$) and oxygen ($^{18}\mathrm{O}/^{16}\mathrm{O}$) in these samples were determined. The 10-year weighted annual average δ^{18}O and δ^2H values of precipitation were found to be –17.9‰ and –136.1‰, respectively. These comparatively low values are the combined results of continental and altitude effects on atmospheric moisture, which is predominantly derived from the Pacific Ocean.

The following local meteoric water line (LMWL) for Calgary was derived using weighted monthly average δ^2H and δ^{18}O values: $\delta^2\mathrm{H} = 7.68\,\delta^{18}\mathrm{O}$ -0.21 (r^2=0.96; n=104) (Figure 1). Interestingly, the correlation equation using daily (non-weighted) δ^2H and δ^{18}O values was found to be $\delta^2\mathrm{H} = 7.10\,\delta^{18}\mathrm{O}$ -13.64 (r^2=0.95; n=839) (Figure 2), exhibiting significantly lower slope and intercept values compared with the LMWL derived from weighted monthly mean values. On average, approximately 70% of the annual precipitaiton at Calgary (401mm) occurs in the months of May through August (280mm). The hydrogen and oxygen isotope ratios and the d-excess values for daily samples collected in these months were found to be significantly influenced by secondary evaporation effects occurring in the atmosphere. This indicates that the daily collection of precipitation samples provides valuable information on atmospheric processes, which is not readily obtainable from monthly composite records.

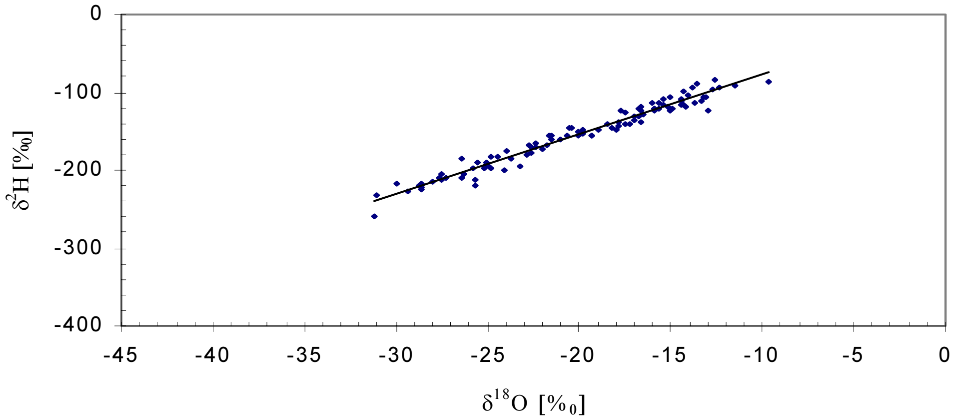

Figure 1 Local Meteoric Water Line for Calgary based on weighted monthly mean δ^2H *and* δ^{18}O *values, using data from samples collected between January 1992 and December 2001:* $\delta^2\text{H} = 7.68\delta^{18}\text{O} - 0.21$ *(*r^2 *=0.96; n =104).*

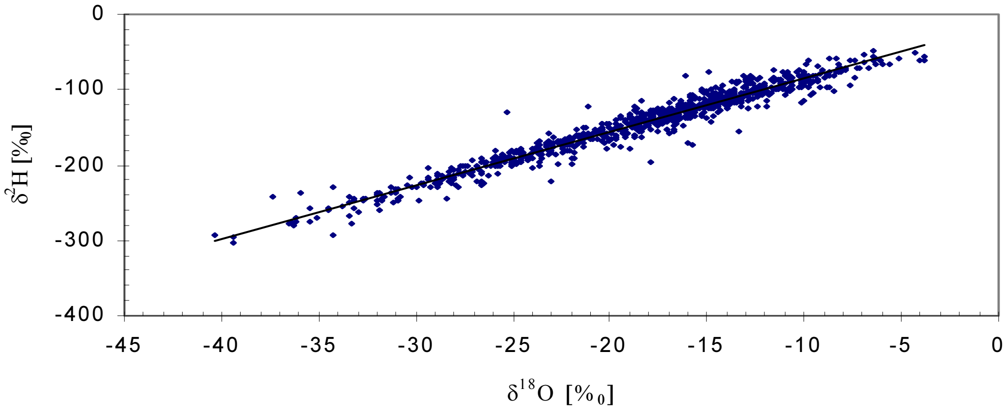

Figure 2 Correlation equation between individual δ^2H *and* δ^{18}O *values for Calgary atmospheric deposition, using data from samples collected between January 1992 and December 2001:* $\delta^2\text{H} = 7.10\delta^{18}\text{O} - 13.64$ *(*r^2 *=0.95; n =839)*

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ISOTOPE CLIMATOLOGY OF CANADA: INSIGHTS FROM THE FIRST FIVE YEARS OF CNIP OPERATION

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The isotopic composition of precipitation is an integrated climate field reflecting temperature, amount of precipitation, air-mass source and history. Previous analysis of Canadian data within the GNIP database has shown that the distribution of long-term weighted isotope fields across Canada clearly reflect differences in the dominant meterological regimes associated with each region [1 and 2]. While these studies were fundamental in providing local hydrological input functions and calibration for paleoclimate archives, there was growing awareness of the significant value of monthly snapshots of the precipitation isotope fields as benchmark maps of the ongoing and dynamic evolution of the global water cycle. Snapshots of the isotope climatology of Canada were limited by the spatial and temporal patchiness of the existing Canadian data.

The Canadian Network for Isotopes in Precipitation (CNIP) was initiated as a joint venture between university and government researchers to provide the spatial and temporal data necessary to examine the sensitivity of isotope fields to changes in circulation patterns, particularly in northern areas where the signal to noise ratio is much lower. The network consists of 18 stations (Figure 1) distributed across Canada (spanning almost 40° of latitude and 70° of longitude) collecting weighted monthly precipitation samples. This marks the first time that both the southern and northern regions of the country have been simultaneously sampled. Sampling of the southern stations was initiated in 1997 to supplement an existing informal arctic network (now formally incorporated in CNIP) resulting in a 5 year dataset for the entire country, including a complete El Niño/Southern Oscillation (ENSO) cycle. The arctic subset of the data includes over a decade of sampling and consequently can be used to evaluate the isotopic expression of the Arctic Oscillation (AO). The data have been reconfigured as an isotope overlay compatible with pressure and flux field data from the NCAR/CDAS Re-analysis Project.

The sensitivity of isotope-climate signals to modes of interannual variability such as ENSO and AO is of interest because they are a primary cause of interannual climate variability. The effects of the ENSO are felt not only near the source in the equatorial Pacific Ocean, but also at higher latitudes [3, 4, 5], however, the strength, location and timing of climate variations in extratropical areas are less predictable since they are the result of oceanic and atmospheric teleconnections.

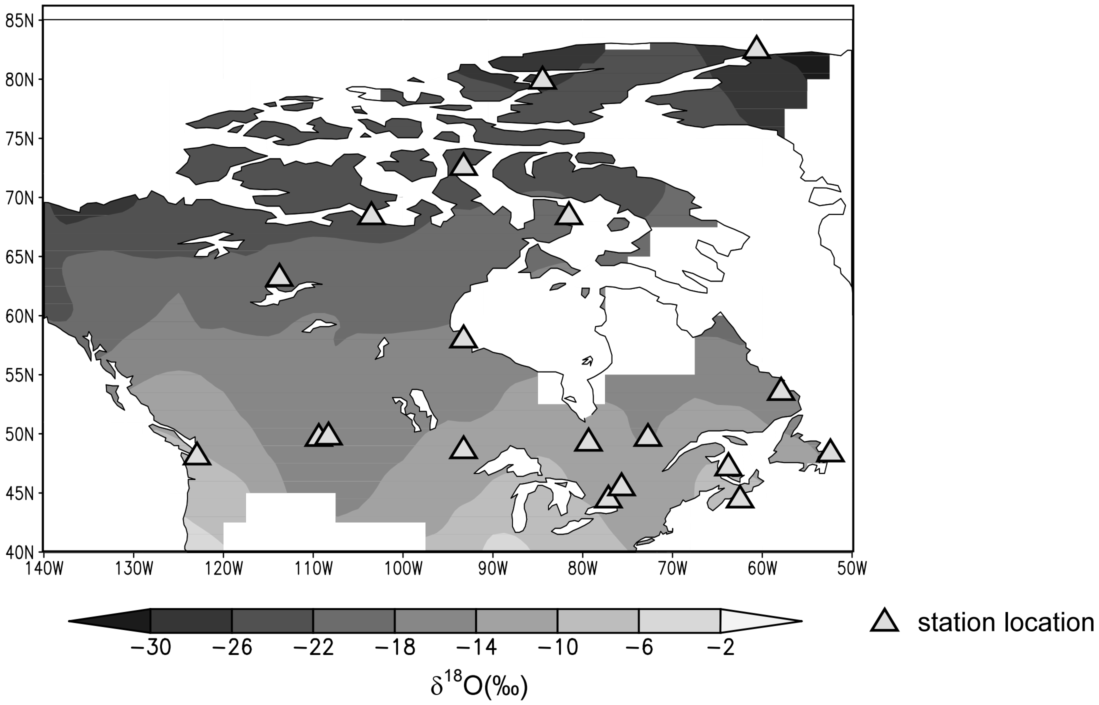

Figure 1: Current CNIP stations are identified above (triangles) on a map of the interpolated distribution of weighted mean annual $\delta^{18}O$ of precipitation derive using all of the existing Canadian data.

Intriguing results have been obtained from preliminary analysis of pressure and flux field data for 1997-2001 and the newly created CNIP isotope overlay. The isotopic fields ($\delta^{18}O$, $\delta^{2}H$ and *d*-excess) generated for individual months between 1997-2001 reveal the complexity and dynamic nature of isotope-climate not apparent in time-series of data from individual stations. The strongest climate anomalies were found during the winter following the 1997 El Niño event consistent with a strengthening of the Pacific North American pattern expected during this period [3, 4, 5, 6].

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IAEA-CN-104/P-86

SULPHUR SOURCES IN RAINWATER AND THROUGHFALL AT A SCOTS PINE (*PINUS SYLVESTRIS,* L.) STAND LOCATED NEAR A COAL-FIRED POWER PLANT IN CATALONIA (NE SPAIN)

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The major ions composition and the stable S isotope ratio of $SO_4^=$ in precipitation and throughfall were analysed at a Scots pine (*Pinus sylvestris*, L.) forest 6.2 km distant from the Cercs power plant (Catalonia, North-eastern Spain) in order to determine the sources of the deposited S at this site. The area around the power plant is heavily forested. The climate is humid Mediterranean, with a mean annual precipitation of 900 mm yr^{-1}.

The Cercs power plant started to work in 1971. In 1985-1986 a trial, the first in Spain for environmental causes, was sued against the plant administration because of the strongly negative impact of the plant emissions on forests downwind of the stack plume. Since then, the plant emissions have been subjected to a closer control: SO_2 emissions have been reduced by 50% and $SO_4^=$ particles have been cut down by 70%. This has been reached through the installation of electrostatic filters and using coal of lower S content (< 2% S). Although the impact of the S emissions has been evaluated in the neighbouring forests through a study of the S contents in Scots pine needles [1], up to now no data existed to document the effects of the coal-burning plant emissions on the hydrological sulphur cycle in the surrounding forests.

Samples of bulk precipitation and throughfall were obtained weekly during 1.5 years (from March 2000 to August 2001). On the 21 June 2001, gas emissions were sampled from the stack of the power plant at a height of 190 m. SO_2 was sampled by means of an isocinetic probe connected to 4 H_2O_2 bubblers to oxidise SO_2 to $SO_4^=$. A Teflon pre-weighed filter was deployed at the inlet of the probe to collect the emitted particles. All solutions were analysed for the major ionic composition and for the $\delta^{34}S$.

The results indicate that the forest canopy exerts an important filtering role as $SO_4^=$ is highly concentrated in throughfall relative to bulk precipitation: e.g. input in bulk deposition was 7.3 kg S ha^{-1} yr^{-1} *vs*. 33.4 kg S ha^{-1} yr^{-1} in throughfall. Sulphur isotope data were used to identify the sources of $SO_4^=$. $\delta^{34}S$ values were highest in bulk precipitation samples when the central was not in operation (mean = 3.6 ‰; s.e. = 0.5), while the values decreased slightly for periods of intense plant operation (mean = 2.6 ‰; s.e. = 0.2), indicating the influence of the SO_2 emissions, of a lower $\delta^{34}S$ signal (–2.8 ‰, n = 2 replicates of stack fumes). The $\delta^{34}S$ values in precipitation during non-operating periods approached those reported for background precipitation in areas of little anthropogenic impact [2], [3], [4]. In consistency with a dry deposition input from the Cercs plant emissions into the canopy, throughfall $\delta^{34}S$ values were lower than those in precipitation ($\delta^{34}S$ = +0.2‰). The large isotopic shift shown in Figure 1, can be explained as a mixing between background values and SO_2 emissions of the power plant.

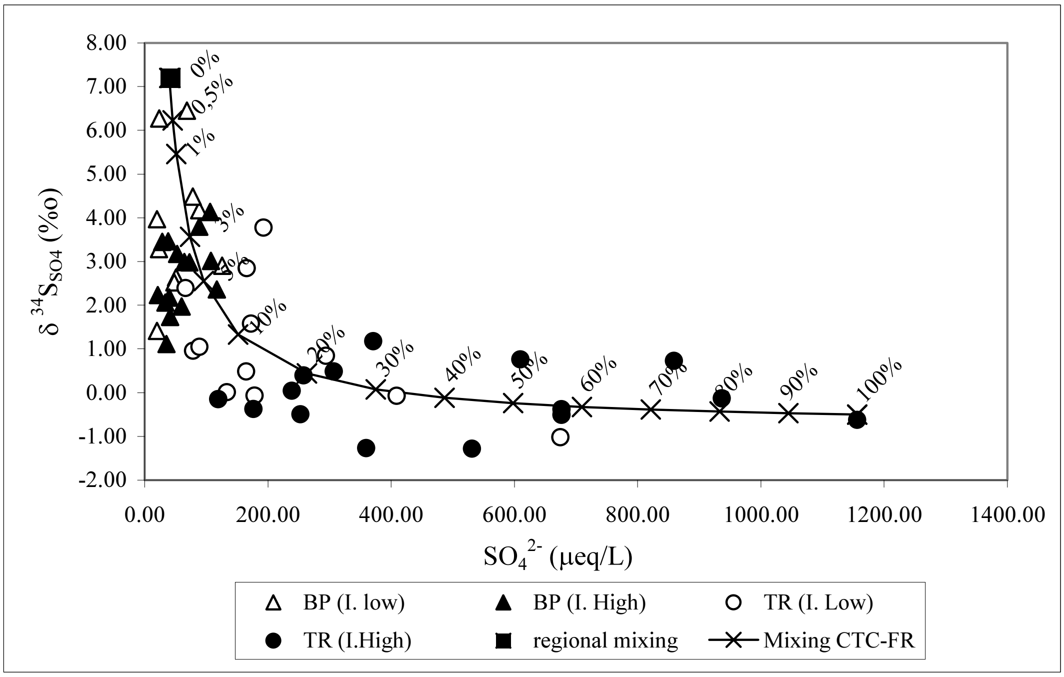

Fig. 1.- Plot of $\delta^{34}S_{SO4}^{=}$ versus $[SO_4^{=}]$ of bulk precipitation (BP) and throughfall (TR) for high and low intensity of plant operation (I). The solid line represents the mixing between the background value ($\delta^{34}S_{SO4=}$ +7,2‰ [3] and 40 µeq /L) and the SO_2 emission of the power plant ($\delta^{34}S_{SO4=}$ -2.7 ‰ and 2670 mg/m^3), according to the considerations described in the text. Numbers indicate the sulphate contribution of the power plant according to the isotopic mixing model.

Considering a scavenging ratio of 1500 [4], that SO_2 is transformed into $SO_4^{=}$ at a rate of 4% h^{-1} [5], a distance between the power-plant and the studied area of 6 km, mean speed wind of 6 km/h^{-1}, an $\alpha SO_4\text{-}SO_2$ =+2.2‰ [4], and that during the study period only 23% of the wind was in the direction of the study site, then, the mixing model indicates that the $SO_4^{=}$ contribution from the emissions of the power plant was up to 6% in bulk precipitation and from 5 to 100% in throughfall (fig. 1).

ACKNOWLEDGEMENTS

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ISOTOPIC COMPOSITION OF PRECIPITATION IN HUNGARY IN 2001 AND 2002

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Abstract

ISOTOPIC COMPOSITION OF PRECIPITATION IN HUNGARY IN 2001 AND 2002

Tritium is one of the most commonly applied environmental isotopes in isotope hydrology. It is suitable for calculation of the age or – more exactly - the mean residence time of young (<50 years) environmental water. Essential input parameter of models used in these calculations is the distribution of the tritium concentration in the precipitation. The aim of this work was to get a time series of the tritium content of precipitation characteristic for Hungary and to identify those factors, which have essential influence on the changes of tritium content. We have found that the tritium content of the precipitation changed between 4.8 and 18 TU in 2001, and between 4.4 and 20.3 TU in 2002 with an average of 10.4 ± 0.3 TU and 10.7 ± 0.3 TU respectively. In addition to the seasonal effect we demonstrate the effect of temperature, meteorological fronts, cyclones on the tritium content. We found that the isotope composition of rain and snow depend on the weather situation.

INTRODUCTION

Knowledge of the isotopic composition of the precipitation is essential for calculation of the age of young environmental waters or their mean residence time. One of the most frequently applied isotopes for this task is the tritium (Top, 1999). Tritium is produced naturally by cosmic ray in nuclear reaction between fast neutrons and nitrogen-14 in the upper atmosphere (Lal and Peters, 1967). Tritium (^{3}H) decays to ^{3}He by β^- emission (E_{max} = 18.6 keV) with a half-life of 12.32 years (Lucas and Unterweger, 2000). After oxidation to water it enters into the hydrological cycle and reaches the surface as precipitation. The concentration of tritium is expressed in the international unit: tritium unit (TU). 1 TU means a tritium to hydrogen ratio of 10^{-18}, in case of water it equals to 0.118 Bq/litre activity concentrations. The precipitation is collected in surface water (as oceans, seas, lakes, rivers, and so on) or infiltrates into the ground (Begemann and Libby, 1957, Beyerle *et al.*, 1999). The time elapsed since the infiltration (the age of the groundwater) can be calculated from the decrease in tritium activity on the basis of decay-law. Important input parameter for these calculations is the tritium content of the infiltrated precipitation. The tritium concentration in the precipitation changes in time due to anthropogenic and natural effects. There are three basic effects, which are responsible for the natural changes of tritium concentration: latitude, seasonal and continental effect. The latitude effect causes an increase in tritium concentration of the rain from Equator to the Poles (Newell, 1963). Its reason is that the cosmic ray, which plays an important role in the tritium production, gets into the atmosphere with a more intensive flux at the poles than at the Equator because of the deflection of the magnetic field of the Earth. As a result more tritium is formed near the poles than lower latitudes. This effect appears in Hungary as the rain or snow from northern fronts includes more tritium than it would come from the South. The tritium concentration of the precipitation depends on the season as well: there is more tritium in the precipitation in summer than in winter. This is the seasonal effect (Newell, 1963, Ehhalt, 1971). The tritium is produced in the stratosphere and the upper troposphere and it gets to the lower troposphere by mixing. The higher the air temperature the more effective the mixing and more tritium get to the troposphere. The continental effect is that the rain inside of the lands has larger tritium content than near the oceans (Gat and Carmi, 1970, Lipps and Helmer, 1990). The vapour from the oceans and seas has relatively low tritium content (2-16 TU) (Bayer *et al.,* 1989, Peeters *et al.,* 2000) so the clouds formed above the oceans are depleted in tritium relative to ones formed above the continents.

In the early sixties a precipitation sampling network was established by the International Atomic Energy Agency (IAEA) in Vienna and the World Meteorological Organisation in Geneva with the view of documenting the isotopic parameters, δD, δ^{18}O and ^{3}H, together with some meteorological parameters of the input into the hydrological systems (GNIP ISOHIS). The network consisted of about 100 sampling sites worldwide, including marine, coastal and inland stations. For our calculations we used to apply the data of the nearest station, Hohe Warte, Vienna. The aim of this work was to get a time series of the tritium content of precipitation characteristic for Hungary, and to find correlation between the changes of tritium content and meteorological data. We intend to continue this work in a long run.

METHODS OF INVESTIGATIONS

The rainwater samples were taken in Debrecen, Hungary in 2001 and 2002 during the precipitation events. Hence, a few samples represented one-day events and others represented multiple day composites of a single event. The collection device consisted of a polyethylene funnel of 20 cm diameter that was attached to a 1.5 l polyethylene bottle. Snow samples were collected from freshly fallen snow by scraping away the upper surface snow. Snow was allowed to melt at room temperature, and the melt water was poured into a sample bottle.

All isotopes were analysed at the Laboratory of Environmental Studies in the Institute of Nuclear Research of the Hungarian Academy of Sciences. The tritium was measured by the helium-3 ingrowth method (Clarke 1976) with a noble gas mass spectrometer (VG 5400). The detection limit of this method is less than 0.01 TU. The accuracy of the measurements is 2-4 % in the range of 1-20 TU. The measurement consists of three steps. The first step is to remove the dissolved gas from the water samples. The second step is the storage of the degassed water in special metal container equipped with valve for one or two months (Palcsu 2002). The helium-3 formed from tritium is measured by the mass spectrometer in the final step. The helium fraction is admitted to the dual collector noble gas mass spectrometer and ^{3}He and ^{4}He are measured simultaneously applying the peak height method. The tritium concentration of a sample can be calculated from the measured tritiogenic helium as follows:

$$c_{trit} = \frac{^3He_{trit}}{C} \cdot \frac{e^{\lambda \cdot t_{se}}}{1 - e^{-\lambda \cdot t_{em}}} \cdot \frac{1}{W - \Delta W} \cdot \left[1 - (\alpha - 1) \cdot \frac{\Delta W}{W} \right]$$

where c_{trit} is the tritium concentration in TU, $^3He_{trit}$ the measured tritiogenic ^{3}He in ccSTP, C the conversion factor from ccSTP to TU ($2.4889 \cdot 10^{-15}$ ccSTP/g/TU), □ the reciprocal of mean lifetime of tritium, t_{se} and t_{em} the time elapsed from sampling to extraction and from extraction to measurement respectively, W and ΔW the weights of sample and the vaporised water during the degassing method in grams, □ the correction for the T/H fractionation due to loss of distilled water during gas extraction: □ = 1.15 (ratio of tritium concentration in the liquid phase to tritium concentration in the water vapour) (Bayer 1989).

Stable isotope ratios ($^2H/^1H$, $^{18}O/^{16}O$) are generally not reported as absolute numbers but as a deviation of the isotope ratio of a sample relative to that of an arbitrary standard. In case of oxygen and hydrogen the standard is VSMOW: Vienna Standard Mean Ocean Water (Gonfiantini, 1984). The accepted unit is the delta-value (δ), given per mil (‰). The δ-value is defined as

$$\delta(‰) = \frac{R_{sample} - R_{standard}}{R_{standard}} \cdot 1000$$

where R represents the isotope ratio (Craig, 1961). The delta-values were measured by a McKinney-Nier-type stable isotope ratio mass spectrometer built in-house (Hertelendi et al., 1987).

AIMS

We tried to find relations among the fluctuations in the isotope data and the actual meteorological situations. Simpkins (Simpkins, 1995) has demonstrated a good correlation between the changes of tritium content and meteorological data. Thirteen macrosynoptic weather situations govern the weather in the Carpathian Basin (Károssy 1994). These weather situations are expressed in macrosynoptic codes (Table 1.). The weather classification rests on the following assumptions: 1) the classification is valid for the Carpathian Basin, 2) the classification takes into account the air pressure calculated to the sea level and recorded at 0 Greenwich Mean Time, 3) the weather situations are defined from 0 a.m. to 0 a.m, 4) to distinguish the pressure systems the threshold pressure value is 1015 hPa. The short characterisation of the weather situations is the following:

1. Cold front from the meridional situation: A situation with meridional direction and northern stream. Hungary belongs to the rear cold front current system of the cyclone located over the Balticum or Ukraine. This situation causes changeable, windy and wet weather. In summer, it is favourable for forming local showers, thunderstorms. In winter, snowstorms are frequent. In summer the temperature is above average, in winter it is below average, in spring the temperature deviation is not significant.

2. Anticyclone over the British Isles: This is a meridionally directed situation with northerly current. Partly because of the Azori cyclone moving to the North, partly because of the anticyclones moving from the arctic basins to the South, high-pressure air masses develop over the British Isles or the North Sea. When this situation is stabilized in summer, the baric gradient is high over Central Europe causing dry, prolonged warm weather in the Carpathian Basin. It is a misty situation in autumn, winter and spring as well. During the greater part of the year it is characterised by colder air masses of arctic origin and average cloudiness, with higher degrees of cloudiness in summer. The temperature-stratification of the air is stabile.

3. Cold front arising from a Mediterranean cyclone: A situation with meridional direction and northern current. It is the current-system of the back-side of the cyclone. The movement of air is in a northern, north-west direction. Especially in summer, precipitation may increase in different amounts at various locations. Snow showers are frequent in winter, storms in spring. Cloudiness is definitely extensive, mostly in the summer half of the year. The temperature is lower in spring and autumn and higher in winter.

4. Warm front arising from a meridional cyclone: This is a situation of meridional direction, with flow toward the south. It is the frontal current system of the cyclone. In autumn it is cooler, in winter and spring milder than the average temperature of the given season. Cloudiness is more extensive, mainly in spring and autumn. Prolonged, slow rains and snowfalls are equally frequent from autumn to spring. The southern air current brings considerable precipitation, especially in the winter half of the year.

5. Anticyclone located east of the Carpathian Basin: A meridional situation with southern current. The weather fronts range west of the Carpathian Basin. This situation is characterised by dry, warm, bright weather in summer. In winter, after snowy days by bitter cold, frequent rime and fog. In autumn and spring, temperature fluctuation is large with a strong rise in temperature. In accordance with the weak, southerly current, the amount of precipitation is small.

6. Warm front arising from a Mediterranean cyclone: This situation has a meridional direction and southerly current. Its warm front passes over the Carpathian Basin causing substantial rains in the winter and spring months, as well as snowfalls in winter. In summer its temperature is lower than the local average temperature.

7. Zonal cyclone: There is a Zonal, westerly flow. Northern Europe is affected by fast moving cyclones. The weather is windy and changeable. The temperature is characteristically cool in autumn, mild in winter, and in summer it is colder than the average for the season. The yield of precipitation is larger at the beginning of autumn and in winter.

8. Anticyclone located west of the Carpathian Basin: It has Zonal current with a western direction. When the Azori cyclone travels to the North (mainly in summer), its protrusion advances as far as the Central-European region. It is characterised by pleasant, warm and bright weather, which, however, is misty in autumn and spring, and mild, misty and foggy in winter. In winter it is colder than the temperature typical for the season. Its cloudiness is average, yet it is overcast in summer.

9. Anticyclone located south of the Carpathian Basin: This situation has a Zonal, western current. The northern fringe of the anticyclone situated over the basin of the Mediterranean Sea protrudes into the Carpathian Basin. In winter, autumn and spring the bright, warm days are followed by mild nights. In winter cloudiness is somewhat stronger, and the frequency of fog is higher. In summer it brings about sultry weather. The airflow is weak, and precipitation is low.

10. Anticyclone located north of the Carpathian Basin: This situation has an eastern, Zonal current. The anticyclone stays north of Hungary over the Balticum or Poland, and forms a high-pressure ridge from the British Isles as far as Eastern Europe. In summer it is warmer than the temperature typical for the season. It causes a strong fall in temperature in autumn and in spring, but after the cold night a rise in temperature follows about midday. It is characterised by clean and northern winds.

11. Anticyclone located over the Scandinavian Peninsula: This situation has a zonal eastern airflow. The characteristic orientation of the longitudinal axis of the anticyclone, which stays in the Fenno-Scandinavian region, has a northeasterly direction. It is characterised by northerly winds, wide fluctuation in temperature, and little precipitation.

12. Anticyclone located over the Carpathian Basin: The whole region of Central Europe is dominated by a centrally situated anticyclone, which rises above the Carpathian Basin. In winter it is accompanied by a strong fall in the temperature and considerable inversions of temperature, and in summer by a great rise in temperature, heat waves and thunderstorms. Precipitation is small, showing large regional variability.

13. Cyclone located above the Carpathian Basin: The centre of the cyclone is located over the Carpathian Basin. The majority of Mediterranean cyclones passing over Hungary belong to this type. In this weather situation the temperature is higher in winter, lower in summer than during the preceding days. This situation is characterised by cold, windy, overcast and rainy weather in autumn and by stormy weather in winter. Precipitation is markedly large.

RESULTS AND DISCUSSION

The fluctuations in the tritium content of precipitation observed in the curve in Fig 1 and 2 may be explained by the weather situations and the temperature data. Comparing the tritium and stable isotope data measured in the same sample we can specify the ruling factors of the local weather situations. Tritium concentrations, δD and δ^{18}O values of precipitation in 2001 water samples were measured (Table 2. and Table 4.). Unfortunately, the stable isotope data of precipitation fallen in 2002 are not available yet, only the tritium concentrations were measured (Fig. 2). Fig. 1 shows the change of the tritium content in the precipitation and the daily mean temperature curve in 2001. The monthly weighted averages of year 2001 are represented in Fig 3. The influence of the seasonal effect can be seen in the annual trend of the tritium concentration represented by a sinus curve (Fig. 3.), with a minimum in winter and a maximum in summer. We can see rather large fluctuations in the tritium content of the individual rainwater samples.

The first local minimum of the tritium curve in Fig 1 was on the 4th of March. During the previous days northern streams were mostly significant (mCc), bringing precipitation with quite negative isotope ratios (δD: -90‰, δ^{18}O: -12.5‰) and rather high tritium content (7.7 TU). After a 3-day southern stream (CMw, mCw) it was a heavy rain (20 mm). In the cloud system carrying water from South the tritium concentration was low (4.8 TU) and the isotope ratios were rather positive (δD: -37 ‰, δ^{18}O: -3.5 ‰) (see Table 1) and that confirms the origin of the rain from a warmer area (Dansgaard, 1964). By the middle of March after a several days of northern stream (mCc) the tritium concentration approached its earlier value (7.8 TU).

We can generally observe a decrease of the tritium content in case of heavy rains (Fig. 1 and 4). Such a local minimum appears in tritium of rain between 28th and 31st December in 2000 when during six days it was 32 mm of precipitation. That time mostly southern (mCw, CMw), partly northern streams (mCc) dominated. The situation was similar at the end of January 2001: after a changeable period a 4-day mediterranean cyclone (CMw) determined the weather conditions and it was 14 mm of rain during three days that decreased the tritium content by 1 TU. Similar processes were responsible for the minimums observed on 25th April, on 4th June and on 6th September in 2001. In April, a southern anticyclone causing a western stream (As) resulted a heavy rainfall (18 mm). A southern and a western anticyclone caused an abundant rainfall (45 mm) at the beginning of June. In early September, the tritium content of the precipitation decreased from 12.9 TU to 8.2 TU due to a heavy rainfall (23 mm) formed by a rather southern stream system (mCw) followed by changeable weather conditions.

There are two significant peaks in the summer period: between 6 and 16 June and between 18 and 29 July 2001. The maximum in June is explained by the sudden heat. As a result of 7 °C mean temperature increase high amount of stratospheric water vapour mixed with the cloud layers coming mostly with western streams (As) causing an increase from 10.1 TU to 17 TU in the tritium concentration of the precipitation. This is supported by the change of stable isotope ratios: both of the δD and the $\delta^{18}O$ became more positive during this warm period (δD: from -63 to -30‰, $\delta^{18}O$: from -9.0 to -4.7‰). The peak of July was produced by other processes. In the second part of July the mean temperature was 27.5 °C and it was little rain mostly coming from the North (mCc, CMc) and resulting an additional increase of the tritium level. The cold northern origin was confirmed by the isotope ratios: the isotope ratio of deuterium decreased from -29 to -56 ‰, the isotope ratio of oxygen lowered from -4.3 to -8.4‰.

At the beginning of the year 2001 the tritium content of the snow was about 10 TU, and it decreased to 8.3 TU only on 28th March. Between 22 and 25 of February the snow arrived with strong northern stream (mCc) and it had rather negative δ-values that confirm its arctic origin. (The δ-values measured in snow samples can be seen as stars in Fig. 5.)

The snow on 28th March had about the same isotope ratios as in February but its tritium content was lower than before by 1.3 TU. This time southern streams were followed by an eastern stream (An), which carried cold air masses above Hungary. The tritium content of the precipitation from a cold eastern cloud system is lower than one from the North therefore the tritium concentration in the snow was this time lower than in February. On 26th November the snow followed a strong northern stream (mCc), on 23rd December it arose from also a northern stream (AB) after an eastern stream (AF). The tritium concentration as low as in the rain in November, it can be explained by the seasonal effect.

The frost formed on 22nd January and 21st March had less negative isotope ratios and contained more tritium than the rain in that period. The isotope fractionation during the condensation of water vapour shifts the isotope ratios to the positive direction (empty rings in Fig. 5). Therefore, the moisture, from which the frost had formed, could possess more negative isotope ratios than the measured δ-values. Similarly, the isotope fractionation could produce the relatively high tritium content of the frost.

We have calculated the local meteoric water line (LMWL) from the δ-values measured in 2001 (Fig. 5.). The equation of the regression line is: $\delta D = 7.17 \times \delta^{18}O + 0.59$. It differs from the Global Meteoric Water Line (GMWL, $\delta D = 8 \times \delta^{18}O + 10$) but it is in a good agreement with LMWL measured at Hohe Warte station, Vienna: $\delta D = 7.2078 \times \delta^{18}O - 0.3353$ (UNESCO/IAEA, 2000). A local best fit for the ($\delta^{18}O$, δD) line is in most cases not a real meteoric water line produced by varying degrees of rainout from an air mass of prescribed isotopic character. A regression line with slope less than 8 indicates the genetic and synoptic history of the rain events and reflects the local conditions at the time precipitation occurs. The similarity of the two LMWLs of above mirrors the similar conditions forming the local water source of both regions.

We have found linear correlations between the monthly mean isotope ratios and the monthly temperature data (Table 3.). The equations are: $\delta D_{monthly} = 2.16 \cdot T_{monthly} + 82.8‰$ and $\delta^{18}O_{monthly} = 0.28 \cdot T_{monthly} + 11.6‰$. The results are in good agreement with those measured in the Black Forest in Switzerland: $\delta D_{monthly} = 2.13 \cdot T_{monthly} + 85.7‰$, $\delta^{18}O_{monthly} = 0.38 \cdot T_{monthly} + 12.6‰$ (Clark, 1997).

The tritium content of the precipitation varied between 4.8 and 18 TU in 2001, and between 4.4 and 20.3 TU in 2002. The monthly weighted average tritium concentration was between 6.4 and 15.6 TU in 2001 and between 5.2 and 16.4 TU in 2002 (Fig. 3). The maximum peak was observed in July in both years and the minimum was in January 2001 and in December 2002. The annual mean tritium concentration of the precipitation was 10.4 ± 0.3 TU in 2001, and 10.7 ± 0.3 TU in 2002. Fluctuations in the tritium content can be explained by the weather situations and the temperature data. A decrease of the tritium content can be generally observed in case of heavy rains. Fast changes in tritium content might be correlated with sudden changes in movement of air masses, for instance with cold or warm fronts. The slope of the ($\delta^{18}O$, δD) regression line is less than 8 indicating that it is not a real meteoric water line but it is formed by the genetic and synoptic history of the rain events and reflects the local conditions at the time precipitation occurs. The analysis of the tritium data may help us to identify those meteorological processes, which are characteristic for a given area.

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TABLE 1**:** Macrosynoptic codes

	MERIDIONAL, NORTHERLY ORIENTED SITUATIONS	
1.	Cold front from the meridional situation	mCc
2.	Anticyclone over the British Isles	AB
3.	Cold front arising from a Mediterranean cyclone	CMc
	MERIDIONAL SITUATIONS WITH A SOUTHERN DIRECTION	
4.	Warm front arising from a meridional cyclone	mCw
5.	Anticyclone located east of the Carpathian Basin	Ae
6.	Warm front arising from a Mediterranean cyclone	CMw
	ZONAL SITUATIONS WITH WESTERN DIRECTION	
7.	Zonal cyclone	zC
8.	Anticyclone located west of the Carpathian Basin	Aw
9.	Anticyclone located south of the Carpathian Basin	As
	ZONAL SITUATIONS WITH EASTERN DIRECTION	
10.	Anticyclone located north of the Carpathian Basin	An
11.	Anticyclone located over the Scandinavian peninsula	AF
	CENTRAL SITUATIONS	
12.	Anticyclone located over the Carpathian Basin	A
13.	Cyclone located above the Carpathian Basin	C

TABLE 2: Isotope data of the precipitation in 2001 and the type of the daily macrosynoptic codes (the codes are denominated in the Table 1)

Date of sampling	Precipitation (mm)	Type of macrosynoptic codes*	Isotopic data		
			δD_{VSMOW} (‰)	$\delta^{18}O_{VSMOW}$ (‰)	Tritium content (TU)
23-28 12 2000	27.6	5-12-4-4-6-6	-48.8	-6.8	5.5 ± 0.2
28-31 12 2000	5.7	6-1-6-1	-65.7	-9.1	4.4 ± 0.2
01-07 01 2001	1.4	12- 5-6-9-6-1-3	-57.0	-7.1	6.1 ± 0.5
08-15 01 2001	3.2	13-6-9-9-2-2-2	-89.4	-11.7	6.1 ± 0.5
22 01 2001	frost	10	-66.9	-10.5	10.0 ± 0.4
22-29 01 2001	17.0	10-5-5-4-5-1-1-6	-33.5	-5.3	7.2 ± 0.2
29-31 01 2001	12.0	6-6-6	-66.3	-10.0	6.0 ± 0.2
01-04 02 2001	1.0	11-11-8-4	-44.0	-6.7	7.7 ± 0.2
05-12 02 2001	6.8	4-7-9-5-5-8-10-12	-40.5	-4.9	7.7 ± 0.2
22-25 02 2001	4.2 (snow)	1-1-1-4	-136.9	-17.5	10.0 ± 0.2
22 02 - 03 03 2001	26.8	1-1-1-4-6-3-5-6-6-4	-89.9	-12.5	7.7 ± 0.2
04-05 03 2001	10.4	1-4	-36.7	-3.5	4.8 ± 0.2
09 03 2001	3.8	1	-32.7	-4.3	6.3 ± 0.7
12-18 03 2001	21.8	9-1-1-1-1-4-13	-49.6	-6.5	7.8 ± 0.3
21 03 2001	frost	9	-48.9	-7.8	9.9± 0.2
18-25 03 2001	12.2	13-4-1-9-4-1-4-4	-56.6	-7.8	8.5 ± 0.3
28 03 2001	1.5 (snow)	10	-137.5	-17.1	8.3 ± 0.3
25 03 - 02 04 2001	2.5	4-13-10-10-10-5-6-5-5	-91.4	-11.5	9.7 ± 0.4
17-22 04 2001	33.7	6-13-11-1-13-13	-26.1	-3.9	-
22-25 04 2001	13.7	13-6-6-9	-76.5	-10.0	11.6 ± 0.3
25 04 2001	9.4	9	-53.7	-6.9	10.5 ± 0.3
19 05 - 04 06 2001	24.8	2-2-2-2-10-5-2-10-12-9-8-1-4-13-8-13-13	-43.1	-7.7	11.9 ± 0.2
04-06 06 2001	19.6	13-8-9	-63.6	-9.0	10.1 ± 0.3
06-16 06 2001	18.4	9-9-9-9-10-13-8-12-5-13-9	-29.7	-4.7	17.1 ± 0.3
16-23 06 2001	34.9	9-1-3-6-13-6-1-1	-39.6	-5.2	14.1 ± 0.3
23 06 - 04 07 2001	16.2	1-1-2-2-12-1-8-8-8-8	-57.4	-7.8	14.1 ± 0.4
04-12 07 2001	15.5	10-10-10-12-1-1-8-5-8	-44.1	-5.9	13.7 ± 0.5
12-18 07 2001	8.5	8-12-5-5-5-13-1	-28.9	-4.3	12.6 ± 0.3
18-24 07 2001	14.9	1-1-6-3-8-8-13	-53.8	-8.3	18.1 ± 0.5
24-26 07	8.9	13-1-1	-52.0	-7.9	17.5 ± 0.4

2001					
26-29 07 2001	6.2	1-10-2-10	-62.6	-8.7	18.1 ± 0.4
29 07 - 12 08 2001	31.4	10-8-8-2-2-5-5-5-8-8-9-5-6-13-8	-34.7	-5.2	11.2 ± 0.3
12 08 - 01 09 2001	dew	8-12-12-12-10-5-10-10-11-8-11-11-11-11-11-12-1-1-11-11-1	-22.5	-3.2	11.6 ± 0.3
01-06 09 2001	26.4	1-4-8-12-1-13	-25.2	-4.0	12.9 ± 0.4
06-09 09 2001	31.4	13-4-4-1	-70.1	-10.2	8.2 ± 0.3
09-12 09 2001	6.9	1-6-4-8	-86.9	-11.7	8.2 ± 0.3
12-18 09 2001	20.4	8-12-1-13-13-6-13	-51.9	-7.3	12.0 ± 1.3
18-19 09 2001	16.3	13-12	-69.4	-10.8	12.0 ± 1.3
19-26 09 2001	25.0	12-5-5-5-5-6-1-1	-58.4	-8.7	8.7 ± 0.4
26 09 - 29 10 2001	5.9	1-10-12-9-11-5-9-9-7-6-12-10-4-1-5-8-12-12-12-12-10-5-3-11-11-11-1-8-11-10-5-5-12-12	-35.3	-5.9	9.8 ± 0.3
29 10 - 13 11 2001	16.5	12-9-9-1-2-2-12-12-8-4-4-1-6-8-6-6	-48.9	-7.0	6.0 ± 0.2
15-16 11 2001	6.8	2-2	-59.6	-9.5	6.7 ± 0.2
17-25 11 2001	-	2-12-9-2-2-8-1-1-1	-	-	-
26 11 - 01 12 2001	20 (snow)	13-4-6-8-8-5	-134.3	-19.3	6.7 ± 0.2
15-22 12 2001	-	11-11-11-2-2-9-2-4	-	-	-
23 12 2001	6 (snow)	4	-136.8	-19.1	8.6 ± 0.3

SIGNIFICANCE LEVEL AND REPEATABILITY FOR STABLE ISOTOPE THERMOMETER OF PRECIPITATION IN CHINA

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1. INTRODUCTION

Using δD and $\delta^{18}O$ in precipitation as indicator of palaeoclimatic conditions has mainly derived from their relation to average surface air temperature. The regression line fit to data of them generally is: $\delta D = B_{D\text{-}T} \times Temp + A_D$ and $\delta^{18}O = B_{O\text{-}T} \times Temp + A_O$. The data of Chinese NIP shows that the δ values alone may not always bear relation to temperature. In order to linking present climate to palaeoclimatic conditions, isotope thermometer has yet to be researched further. The first method used is Least-squares method fitting to data of δ values – Temp., and then use the method of both significance level test for the coefficient of determination (R^2) and test of Repeatability for B as isotope thermometer by the error analysis of statistics.

2. SIGNS

α- Significance level for the coefficient of determination (R^2). A – The δ- intercept (‰) in the regression line. B – The isotope thermometer (‰/℃), i.e. the slope of δ- values on Temp. $B_{D\text{-}T}$ – The δD thermometer (‰/℃). $B_{O\text{-}T}$ – The$\delta^{18}O$ thermometer (‰/℃). N - Number of data points used. Q – Residual sun of squares for$\delta^{18}O$ measured. R^2 – The coefficient of determination. S_B - The root mean square error in B. S_{MY}– Residual root mean square for$\delta^{18}O$ measured. S_M – Standard deviation for$\delta^{18}O$ measured. SQR (x) – Square root of x. Temp. - Surface air temperature (℃). Tmean – The mean surface air temperature (℃). U – Regression sum of squares for $\delta^{18}O$ measured.

3. RESULTS

3.1 The relation between yearly isotope in precipitation and surface air temperature (RYIT)

The good linear relationship with α= 0.01 exists between δ-values in precipitation and surface air temperature with multi-year average for 31 stations in Chinese network. The $B_{D\text{-}T}$ = 3.1‰/1℃ with R^2 =0.67 and $B_{O\text{-}T}$ = 0.36 ‰/1℃ with R^2 =0.64. The RYIT belongs to a closer direct correlation, and the yearly average removed the seasonal component and amount effects from the series of monthly average δ values-temperature. And the good linear RYIT is mainly ascribable to that the isotopic fractionation for hydrogen and oxygen during phase transitions (vapour – liquid – solid) is temperature dependent, and the degree of isotopic fractionation are inversely related to temperature. So the isotope thermometer with yearly average can serve as the temperature yearly measure.

TABLE 1. The oxygen isotope thermometer (B_{O-T}) and the coefficient of determination (R^2) for B_{o-T} and the significance level (α) for R^2 in monthly precipitation in China

The zone of China	B_{O-T}	R^2	α	RMIP
The north belt	0.65 — 0.30	0.73 — 0.30	0.01(mostly), 0.05	A closer direct correlation
The middle belt	0 — - 0.30	<< 0.30	Non	A non-correlation
The south belt	- 0.30 — - 0.44	0.50 — 0.30	0.01(mostly), 0.05	A weak negative correlation

3.2 The relation between monthly isotope in precipitation and surface air temperature (RMIT)

As shown in table 1and Fig 1, according to B_{O-T} and R^2 andα, all of China can be zoned the following three belts:

(1) The North Belt located in the inland of the North China. In this area the RMIT belongs to a direct correlation and is closer in 99% probability;

(2) The South Belt located in the south of Daloushan Mountain - Wulingshan Mountain. In this area the RMIT belongs to a weak negative correlation;

(3) The Middle Belt located in the area between the north belt and the south belt with latitude about from 28°N up to 35°N. In this area the RMIP is a non-correlation. And it is shown that the isotope thermometer and its statistical attribution is site-specific.

3.3. The repeatability for B as isotope thermometer

According to error analysis of statistics, the repeatability of the B as the isotope thermometer depends to a large extent on S_B of the standard deviation in B. $S_B = S_{MY} / SQR (\sum (Temp. - Tmean)^2)$, $S_{MY}=S_M \times SQR((N-1)/(N-2)) \times SQR(1-R^2)$, $S_M=SQR((U+Q)/N)$. The smaller S_B value was, the better the repeatability of the slope B was. The isotope thermometer in precipitation depends upon both of its determination coefficient and the deviation in surface air temperature. The larger extent on the range of them was, the better the repeatability of the isotope thermometer was.

4. CONCLUSIONS

The isotope thermometer with yearly average can serve as the temperature yearly measure. The isotope thermometer with monthly average depends to both of its determination coefficient and the deviation in surface air temperature. The larger extent on the range of them was, the better the repeatability of the isotope thermometer was. The repeatability of the isotope thermometer where (or when) the arctic continental cold air masses are stronger is better than where (or when) the cold air masses are weaker. The isotope thermometer and its statistical attribution is site- specific, it may be used to reconstruct past surface air temperatures or to diagnose regional climate models.

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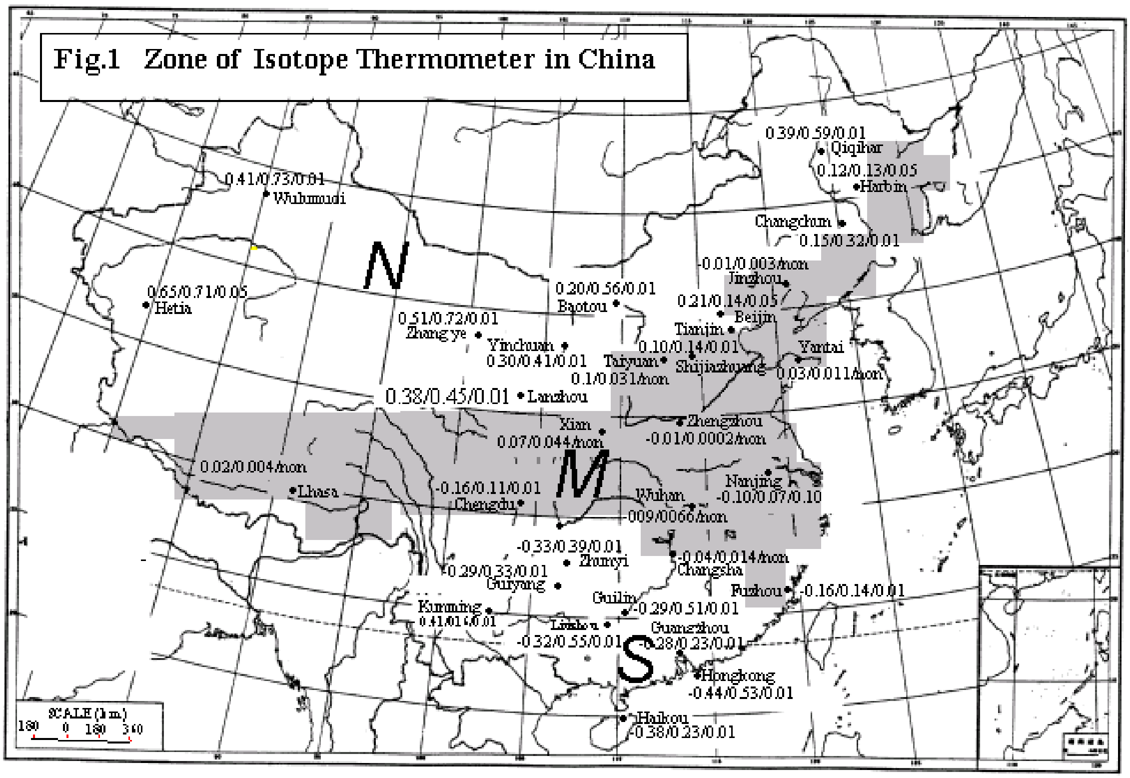

Fig.1 Zone of Isotope Thermometer in China

LEGEND: Number = B / R - sguare / α, N - The North Belt, S - The South Belt, M - The Middle Belt.

THE SWISS NATIONAL NETWORK FOR THE OBSERVATION OF ISOTOPES IN THE WATER CYCLE (NISOT) - 10-YEAR EXPERIENCE OF OPERATION

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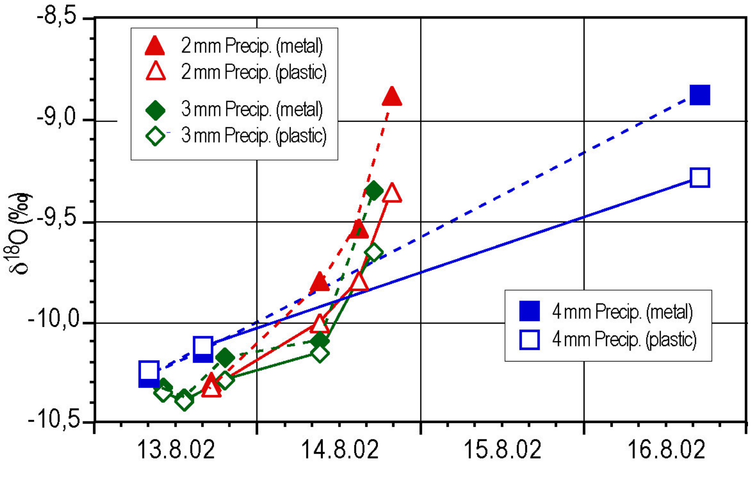
The Swiss National Network for the Observation of Isotopes in the Water Cycle (NISOT) observes since 1992 monthly tritium, deuterium and oxygen-18 in precipitation, surface water and groundwater. The network, operated by the Swiss Geological Survey at the Federal Office for Water and Geology (FOWG), provides specific long-term isotope data series for application and research for the following purposes: hydrological and climatological studies, groundwater management and protection, determination of groundwater origin and age, and calibration of flow and transport modeling. The Swiss Geological Survey operates the isotope network NISOT under the legal framework of the Federal Law on the Protection of Waters and guarantees quality, access and distribution of the isotope data. Financial support is provided to the contributing laboratories. The laboratories participate regularly at the different IAEA inter-laboratory comparison tests. In addition, the Swiss Geological Survey curries out regularly its own inter-laboratory comparison tests. The laboratories carry out tests on their own to improve the data quality and to recommend instructions for water sampling and shipment. An example from the Division of Climate and Environmental Physics of the University of Berne is given below:



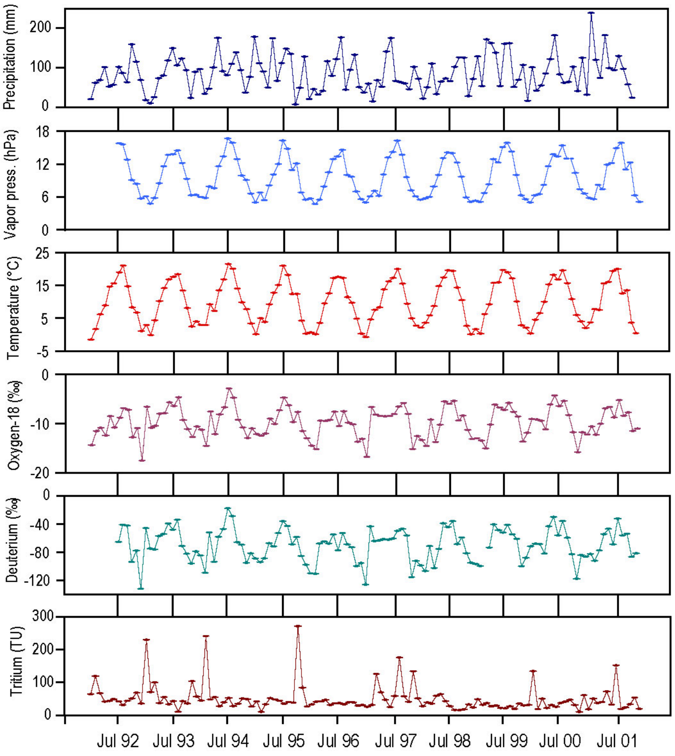
The experiment was carried out to demonstrate the importance of removing a sample immediately after the precipitation event from the standard collector (Hellmann rain gauge). The observed enrichment of stable isotopes depends on exposure time and collector material.

Careful sampling is important because the eleven NISOT precipitation stations are designed to cover regions different in altitudes and climate settings.

The major rivers of Switzerland are sampled at seven stations preferentially at their inflow into major lakes. Climate-induced changes of recharge conditions as indicated by the isotopic composition of shallow groundwater are also part of the NISOT network. One spring is situated within a small catchment and recently two groundwater abstraction wells in characteristic gravel aquifers were added provisionally to the network to observe the fluctuation in isotopic composition.

The NISOT-precipitation stations are located next to rain-gauging stations, which provide specific data for precipitation, water vapor pressure and air temperature. Stations with discharge and water temperature devices were chosen for the monitoring of isotopes in rivers, where isotopes are determined from 28-day, flowrate-proportional composite samples. The Swiss Geological Survey together with a scientific steering committee evaluates once a year the existing stations and also potential candidate stations to operate a close to ideal but minimized long-term network, which allows the characteristic isotope signals in precipitation, surface waters and groundwaters in Switzerland to be observed.

Data sheets are available six months after the end of the year by contacting the Swiss Geological Survey. The isotope data and the associated hydrometeorological data are published by the FOWG as graphs in the Hydrological Yearbook of Switzerland, which can be downloaded as PDF-file from the Internet.



Brief scientific results are illustratively summarized in a 5-year interval in the Swiss “GAS WASSER ABWASSER” Journal. With increasing length of the data series NISOT will be also a valuable contribution to international hydrological and climatological projects. The earlier contribution of selected network stations from the Division of Climate and Environmental Physics of the University of Berne to GNIP, the IAEA/WMO Global Network for Isotopes in Precipitation will be continued and re-established by NISOT. More detailed information about NISOT and links to other isotope and groundwater observation networks can be found under www.bwg.admin.ch/themen/geologie/d/isotope.htm.

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A GLOBAL BALANCE FOR THE STABLE WATER ISOTOPES: A COMPARISON BETWEEN OBSERVATIONS AND GENERAL CIRCULATION MODELS

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Atmospheric general circulation models (AGCMs) equipped with water isotope diagnostics present a major step forward in the understanding of the global cycle of the stable water isotopes, ^{18}O and Deuterium. Several studies published until now focused on a detailed comparison between simulated isotope signals in meteoric water and the IAEA/GNIP network in order to gain further insight into the water cycle as numerically represented by the AGCMs. Another set of studies focused on the application of AGCMs on paleo time scales (from inter-annual to glacial/interglacial cycles). In our contribution here, we discuss the global balance of the water isotopes under varying boundary conditions. We use the ECHAM4 general circulation model which was run under boundary conditions corresponding to different time slices throughout the Holocene until the last glacial (pre-industrial, 6Kyr BP,11 Kyr BP, 11 Kyr BP, 14 Kyr BP,16 Kyr BP,3 different runs for 21 Kyr BP,175 Kyr BP). A further simulation was performed corresponding to the estimated boundary conditions for a possible future doubling of the atmospheric CO_2 concentration. The global balance of the water isotopes is controlled by the isotopic signal emitted in the tropics and subtropics. In these regions, principally sea surface temperatures and the relative humidity in the planetary boundary layer affect the isotopic composition of evaporated vapour. We therefore discuss the influence of this principal water vapour source on extra-tropical precipitation and its isotopic composition. We specifically focus on the possibility of a compensation effect between low and high latitudes in the global balance of the water isotopes. This approach is evaluated by analysing the global water isotope budget for the last 50 years on one hand as simulated by a long-term integration of the ECHAM4 model forced with observed SSTs for the same time period and, on the other hand, as observed by the IAEA/GNIP network.

RIVERS, SURFACE WATER AND SEDIMENTS

APPLICATION OF TRACERS FOR TRANSPORT INVESTIGATIONS IN UNREGULATED RIVERS

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The proper understanding and mathematical description of transport processes mechanism in unregulated rivers is unsatisfactory up to now.

More of previous experience (1-3) have based on solutions of dispersion model for straight channel approximation. Such approach does not take into account the riverbed morphology which is suspected to play a significant role for pollution transport in unregulated rivers. One of the most important phenomena accompanied stream flow in meandering rivers are generating dead or stagnant flow volumes. The factors described that phenomena have been introduced to the one-dimensional dispersion model (4,5). Such approach seems to be very promising, but should be checked in field conditions. The first our results coming from Wkra River - 1998 experiment (6) did not give definite answer if this model is valid or not, because of relative low dead volume (about 10%) at chosen experimental river course.

That was the reason for looking for river with more complex morphology.

We have chosen the upper Narew, the low-land strongly meandered river in the East-Poland region. At 16 km section the five measuring profiles have been located and characterized by hydrometric and hydraulic measurements.

The Br-82 has been used as a test tracer of transverse mixing process.

The results of that test help the decision of proper localization of the first measuring profile which should be localized wider than the transverse mixing distance (between tracer injection cross-section and first measuring profile). It is the fundamental criteria should be fulfilled for one-dimensional dispersion.

The Rhodamine WT has been selected as a fluorescent tracer for main experiment. The time and spatial distribution of the tracer concentration have been measured in all selected cross-sections of the Narew river by means of Turner fluorometers. The dead volume one-dimensional dispersion model with mass exchange between flow and dead zones has been successfully validated on the base of obtained experimental results (table 1).

TABLE 1

Impulse response Nordin model parameters for measured Narew river cross-sections
D - dispersion coefficient; ε - ratio of the dead volume; T - kinetic constant of mass exchange between stream and dead volume; u - mean stream velocity; d - dead volume contribution; QF–quality factor).

Model parameters	Measuring sections					
	[0 - 1]	[1 - 2]	[2 - 4]	[4 - 5]	[5 - 6]	[0 - 6]
D[km^2/h]	0,0027	0,0220	0,0051	0,0338	0,0034	0,0120
ε	0,0920	0,0120	0,7920	0,3690	0,2260	0,1020
T[h]	0,4530	0,6550	11,2570	7,0706	0,9030	1,4440
u[km/h]	0,5200	1,8400	0,4880	1,6200	0,7800	0,9190
d[%]	8,4	1,2	44,2	27,0	18,4	9,3
QF[%]	4,8	2,02	3,21	5,24	9,83	14,3

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PRECIPITATION OF TUFA BARRIERS FROM KRKA RIVER, CROATIA

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The investigated area encompasses a 34 km long section of the Krka river (Central Dalmatia, Croatia) between 15 and 49 km downstream the spring. Ancient and recent tufa barriers form numerous cascades and waterfalls, resulting to an attractive scenery under the protection of the Krka National Park. The aim of the study was to reveal the environmental conditions of deposition or decay of recent and ancient tufa barriers in the area since the various pollutants, nowadays present in the environment, can inhibit deposition of calcite. The main objectives of the study were (1) to demonstrate the utility of dissolved inorganic carbon and Ca^{2+} concentrations in quantifying the CO_2 out-gassing and $CaCO_3$ precipitation, (2) to identify the processes that control the evolution of the stream chemistry and tufa landform formation, and (3) to investigate the isotopic characteristics of the precipitated $CaCO_3$.

Samples of river water were taken during 2 hydrological cycles (November 2000-August 2002)at 4 sampling at Bilušića buk, Miljacka, Roški slap and Skradinski buk 5, 22, 35 and 49 km downstream the spring, respectively, just above the main cascades, except at Miljacka, where the waterfall is not accessible. Total alkalinity, as well as concentrations of Ca^{2+}, Mg^{2+} and Na^{+} were determined, as well as stable isotope composition of DIC and water ($\delta^{18}O$, δD). pH and temperature were measured *in-situ*, while other analyses were performed within 48 hours after sampling. Concentration of dissolved inorganic carbon (DIC) was calculated from total alkalinity and pH using a PHREEQM programme.

Samples of ancient tufa barriers were taken at Bilušića buk, Miljacka and Roški slap, while at Skradinski buk, laminated incrustation was sampled in a tunnel which diverts the river water to the turbines of the power plant (Jaruga). Recent carbonate precipitates were sampled at Roški slap and Skradinski buk on different substrates (wood, glass, copper, plastic foam) submersed into the water between November 2001 and August 2002.

Downstream profiles of δD and $\delta^{18}O$ show a general enrichment in heavy isotopes, however, a steep toward more positive values was observed between the fist two sampling sites (Bilušića buk and Miljacka), followed by a slight decrease. Concentration of dissolved inorganic carbon was much higher at Miljacka compared to all other sampling sites, while the δ^{13}D-DIC here was much more negative. All this indicates that between the first two sampling sites, a considerable amount of water discharges into the stream, although there are no surface tributaries present in this area. Calculation of saturation indices (expressed as log(IAP/K)) revealed that the river water is generally supersaturated with respect to calcite throughout the year, except at Miljacka, where the saturation was reached only in August 2002 at extremely low water level. Saturation indices ranged between 0 and 0.6, which is not necessarily sufficient for precipitation of the mineral phase. However, rapid loss of CO_2 at waterfalls and cascades enhances the precipitation of carbonate.

Precipitation of carbonate collected on various substrates between November 2001 and August 2002 at Roški slap and Skradinski buk took place at temperatures between 9.2 and 22°C. Average δ^{18}O values of carbonate precipitates were 23.23‰ V-SMOW in the period between November and April, 22.63‰ between April and June and 21.94‰ between June and August. Calculation of temperatures of precipitation in equilibrium with water at given temperatures, however, gave much lower values, between 1.7 and 12.4°C. At lower temperatures, precipitation obviously took place closer to the equilibrium than at higher temperatures. δ^{13}C and δ^{18}O of ancient tufa barriers were in the same range than recent precipitates, indicating that the conditions of precipitation were more or less similar. Horvatinčić et al. (2000) determined the age of the barriers by ^{14}C and ^{230}Th/^{234}U; it was found that they derive from early Holocene, i.e. up to 6000 years B.P.

Laminar incrustation from the vicinity of Skradinski buk represents a continuous record of precipitation for last 40 years, as concluded from the number of lamina. The precipitation took place from spray at the ceiling of the tunnel. Although the precipitation could not take place in equilibrium, it is still expected to contain some information on environmental conditions in the period of deposition. The range of δ^{18}O and δ^{13}C values is very similar to those of ancient and recent precipitated collected in the river. From the δ^{18}O record, one could conclude that the precipitation took place in three consecutively warmer periods, the first reaching from 1960-1970, the second between 1970 and 1990, and the last one from 1990 on.

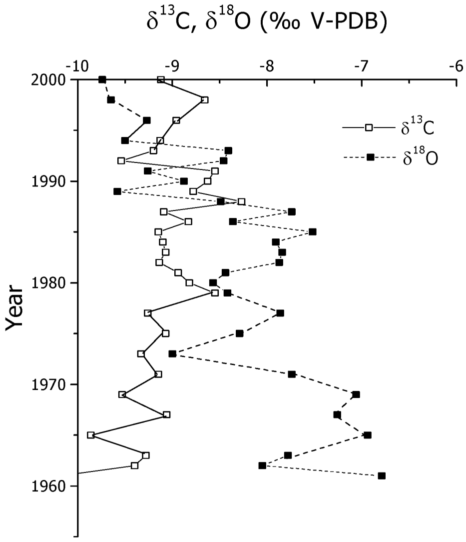

Figure 1: Carbon and oxygen stable isotopic composition of laminated incrustation from the tunnel at Miljacka power plant

From carbon and oxygen isotopic compositions of ancient and recent carbonate precipitates and tufa barriers in the Krka National park we conclude, that the conditions of precipitation were more or less similar since early Holocene. However, the analysis of laminar incrustation precipitated from the spray at a hydroelectric power plant close to Skradinski buk, revealed that in the last 40 year, the average temperature of precipitation is continuously increasing.

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INTEGRATED TRACER HYDROLOGICAL APPROACH AIMING ON TRANSPORT PROCESSES IN SMALL AGRICULTURAL WATERSHEDS IN NEPAL

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Still little is known about environmental risks caused through excessive use of agro-chemicals and pesticides in particular in developing countries. Therefore, a collaborative project was established in the Middle Mountains of Nepal in 1999 funded by the VolkswagenStiftung [1]. The project focuses on environmental hazards and risks caused through the use of pesticides. One main focus was the study for water-bound pesticide transport through the environmental system [4].

The investigations were carried out at two experimental sites at approximately 50 km east of Kathmandu. Due to market-near position and good infrastructure the lands of that area are subject to intensive cultivation of cash crops. The area is characterised through monsoon climate, and loamy soils. In order to match the irrigation and cropping practices of the region with three harvests annually (rice-potato-corn) on irrigated fields and two harvests (corn-tomato) on rain-fed fields experiments were set-up accordingly.

Here, the experiments carried out on *khet*, i.e. irrigated land will be presented. The experimental design was developed on the base of on a conceptual hydrological model and by using the Integrative Catchment Approach (ICA) developed in [2] where the use of environmental and artificial tracers play a major role. In the ICA approach ^{3}H (2 to 50 TU in groundwater), ^{2}H and ^{18}O (+4 to -25 δ^{18}O ‰ in precipitation; -2 to –20 δ^{18}O ‰ in runoff) are used to determine proportions of event and pre-event water for single floods, and to assess origin and pathways of subsurface components. Proper interpretation of isotopic findings on the macro-scale (small watershed of 10 ha) is guaranteed by hydrological, climatic and groundwater data from an appropriate measuring network. Preliminary results are found in [5].

In this context, one of the main issues was the regionalisation of isotope hydrological findings. The local confined/semi-confined perched aquifers were found to vary considerably in size depending on hydrological season and irrigation pattern and have similarly changing soil water saturation conditions in space and time. All isolated, perched aquifers were found to have a specific isotopic signature mirroring evaporation processes [3] (Fig. 1). The isotopic composition of the underlying regional aquifer is quite different and indicates a recharge area of higher elevation (sample site NPGB in Fig. 1).

The unsaturated subsurface system is characterised by distinct preferential flow patterns which were traced on special experimental micro-scale plots of 10 m² [3]. The tracer experiments were performed with D_2O, NaCl, KBr and Vitasin Blue AF 90 (a blue dye). Samples were taken through ceramic candles extracting soil water, and through open pits and Nmin-drillings for the taking out soil. Results show, that the hydraulic short-cuts caused through the preferential flow paths are risky in respect of aquifer contamination by agro-chemicals [4].

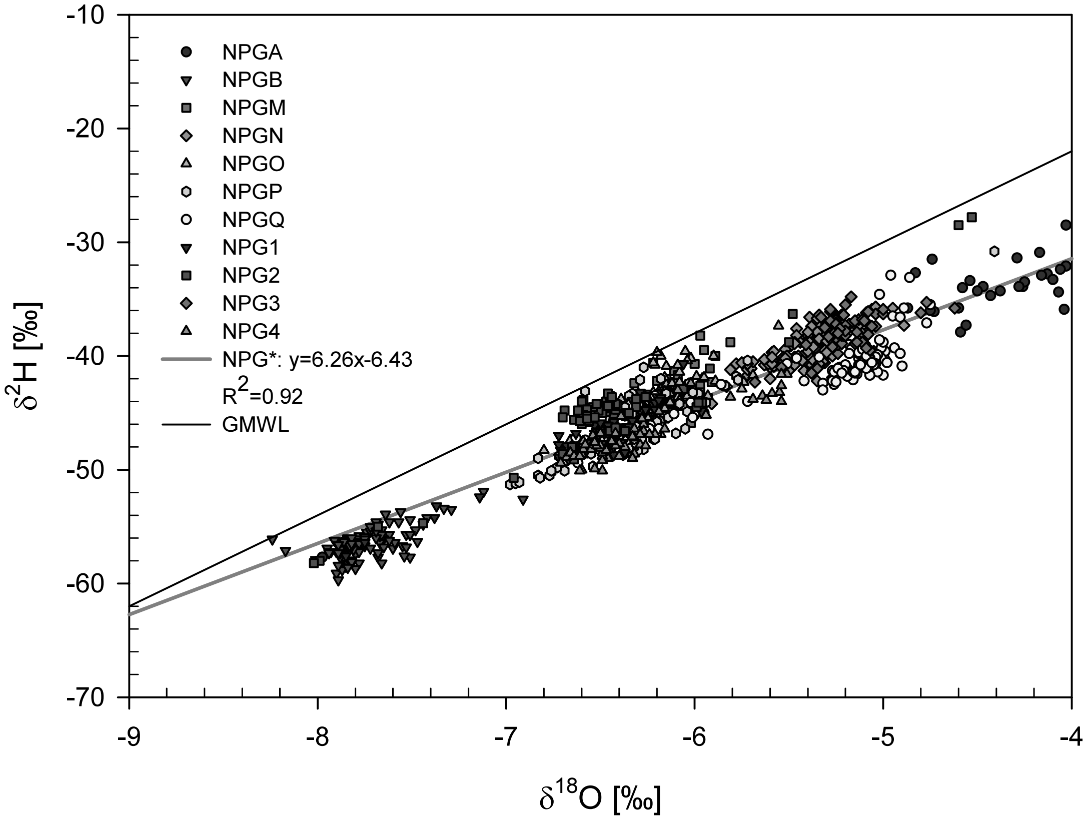

FIG. 1. δ^2H vs. $\delta^{18}O$ from wells of Tamaghat khet land with Global Meteoric Water Line (GMWL), inclination 8 and local NPG water line with inclination 6.26 based on weekly water samples from July 1999-July 2001.

To conclude, environmental tracers contribute to a better understanding of hydrological processes on a small catchment scale in a sub-tropical environment. An important applied outcome from the combined tracer and pesticide experiments on plot scale is, that part of the applied pesticides are transported rapidly to deeper soil layers and towards the uplifted groundwater through preferential flow paths thus creating a considerable risk potential. However, those parts of the pesticides which absorbed to the soil matrix within the upper 15-20 cm of the soil degrade fast due to high soil temperatures and soil moisture and to intensive solar radiation [5].

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SOURCES AND METABOLISM OF CARBON IN A CANADIAN BOREAL HYDROELECTRIC RESERVOIR

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Average emission values of 1 to 2 g of $CO_2 \bullet m^{-2} \bullet d^{-1}$ were observed for hydroelectric reservoirs located in northern Quebec [1]. Here, using isotopic approaches, we try to document the sources and pathways of this CO_2 with special attention to seasonal patterns and to the cycling of organic carbon in the reservoir *Robert-Bourassa* . It is located in the Boreal forest area, south-east of Hudson Bay and is part of a series of 8 reservoirs (including notably LG-2 and LG-3). It has a mean surface area of 2835 km^2 and was flooded in 1979. The isotopic monitoring of the reservoir started in 1998. However, we will essentially refer here to data collected during the summers of 2001 and 2002. Three sampling strategies were retained: i) sampling in surface waters of ~15 sites scattered across the reservoir (e.g., Fig. 1), ii) sampling along three water columns (from shallow to deep sites), and iii) sampling of of inflow and outflow waters of the reservoir, once a month during 1 year. At each sampling site, *in situ* measurements included: water and air temperatures, pH, alkalinity and wind speed. Samples were collected at each site for the measurement of concentrations of dissolved organic carbon (DOC), C/N ratios of dissolved organic matter (DOM) and isotopic compositions of dissolved inorganic carbon (DIC), DOC, air CO_2 and dissolved organic nitrogen (DON). Samples were also collected for the measurements of ^{14}C-concentrations in DOM and of $\delta^{18}O$-values of dissolved oxygen (DO). $\delta^{13}C$-values of DIC vary, throughout the reservoir, from –9‰ to –14‰ *vs* VPDB (i.e., from -13 to -19, for the corresponding dissolved CO_2; Fig. 1) whereas $\delta^{13}C$-values in the overlying air-CO_2 vary from -9 to -11 ‰. Both show a shift towards more depleted values under windy conditions (Fig. 2). $\delta^{13}C$-values in DOC vary little in the reservoir. They average –27.1±0.2‰. C/N ratios of DOM vary between 12 and 38 with a mean of 30. The ^{14}C activity of DOM, at the deepest sampling station vary between 106% (vs. “modern carbon”), at the water-air interface, and 110% at a depth of 70 meters. ^{15}N analysis of DOM are not yet available. The isotopic signature of CO_2 in the reservoir seems to result primarily from exchanges with the isotopically heavy CO_2 from the atmosphere and the production of an isotopically light CO_2 ensuing from the oxidation of dissolved organic matter (DOM), as suggested by the very strongly correlated negative relationship between DOM- and DIC-concentrations that is observed. However, isotopic data do not permit, at this stage of our studies, to weight the relative roles of photolysis and biodegradation-respiration in the production of this CO_2. As shown in Fig. 1, shallow areas depict the minimum $\delta^{13}C$-DIC values, thus the maximum CO_2-production areas. Radio-carbon data suggests that the DOM that is present in the reservoir is essentially derived from very young (post-thermonuclear) organic matter. The high C/N ratios of this young organic matter suggests that it is of terrestrial origin, likely from top soils in the drainage basin. Night vs. daylight pCO_2-values in the water column were compared at a few sites indicate. They suggest that photosynthetic activity may be relatively important during the days also confirmed by the depletion of dissolved oxygen in ^{18}O near the surface during daylight hours.

Photosynthetic activity may thus alter slightly the isotopic composition of DIC, near the surface of the reservoir. Results of the yearly survey at the outlet of the reservoir show that δ^{13}C- values in DIC get more negative whereas pCO$_2$-values increase during the ice cover period. This suggests that part of the CO$_2$ produced by the ^{13}C-depleted organic matter (~ -27 ‰), in winter, is trapped and accumulated under the ice-cover. Upon ice-breakup, δ^{13}C of DIC return to less negative values and pCO$_2$ drops down. Maximum fluxes at the outlet are recorded during this relatively short time interval (Fig. 3).

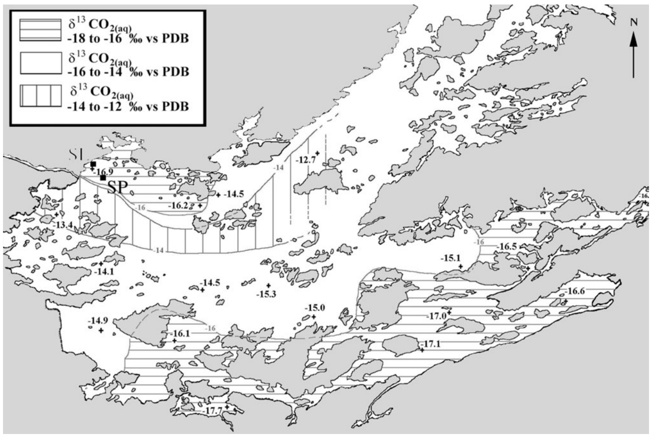

Fig. 1. δ^{13}C-values of CO$_2$ in surface waters during (summer 1999 sampling program)

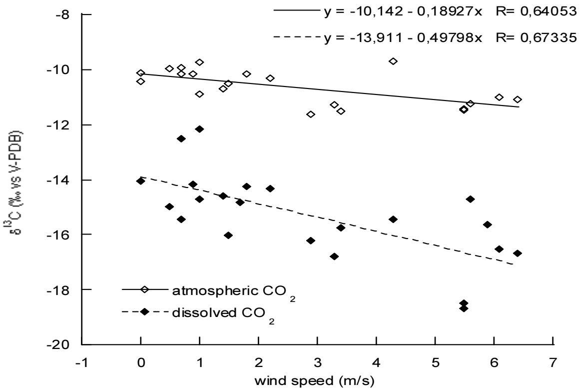

Fig. 2: Relationship between δ^{13}C-values of dissolved and overlying air CO$_2$, vs. wind speed in reservoir Henri-Bourassa (summers 2001 and 2002).

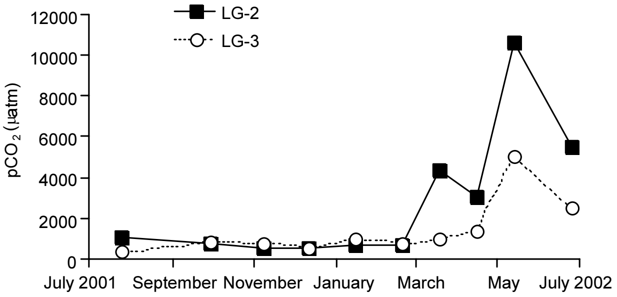

Fig. 3: Seasonal change in pCO2-values at the outlet of the reservoirs LG-2 and LG-3.

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SEPARATION OF HYDROGRAPH COMPONENTS USING STABLE ISOTOPES CASE STUDY: GUVENÇ BASIN, ANKARA

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In this paper, a stable environmental isotope study was carried out from analysis of water samples collected from rainfall, runoff (total discharge), springs (subsurface flows), and wells (groundwater) between 1996-2000. The research site was Güvenç basin located near Yenimahalle-Ankara having a drainage area of about 16.125 km^2. There are many representative hydrologic basins established in Turkey by the General Directorate of Rural Services (GDRS). In these basins, the precipitation and runoff values are recorded continously and relationship between these values are also investigated in the last ten-twenty years. Güvenç basin, the study area, is one of these representative basins. On this basin, a stream gaging, station and five rain gages have been installed to collect and analyze runoff and rainfall data. A small dam was constructed at the outlet of the basin to store and provide water for distribution to agricultural areas.

The characteristics of precipitation data are collected at raingage station, installed near the runoff measuring. To monitor the groundwater isotopic compositon regular samples are also collected from a dug well near runoff station. Spring samples representing the contribution interflow from the unsaturated zone are collected from a location not far from rainfall station. Stream flow samples are collected as well from weir located at the outlet of the basin during each event. The frequent water samplings are performed during the rising limb and the frequency of sampling decreased during the falling limb of hydrographs.

The total number of collected rain samples are 10. Two of five samples produce single peak runoff resulting from rainfall depths greater than 19 mm and the other three are produced from the depths ranging between 9.5 and 11.7 mm. The single storm observed on May 19, 98 is produced from minimum rainfall depth (9.5 mm) with time duration (420 min). The produced runoff results from saturated soil condition due to antecedent rainfalls. The multi-storms show rather large variation in rainfall depths from low to medium (6.8 mm to 28.5 mm).

The analysis of runoff samples collected about a half an hour time interval from runoff station indicates that the single peak hydrographs are mainly produced from pre-event water which may be contributed as subsurface plus groundwater flow to the stream. The instant surface flow is noticed to be dominant in two events (27.5.1998, 24.5.2000) due to high rainfall intensity and depth. Similar findings are also noticed by Sklash, et al. (1979), on hydrographs from short duration and high intensive storm events.

The basic objectives of this study are to investigate the proportion of storm water during distinct hydrological events and also to analyze the hydrograph separation in order to better understand the behavioir of individual precipitation events using isotope techniques and to compare the results with a semi-log graphical method. Because natural variations in stable isotope composition of response of the basin, water balance can be used to idendify the important processes and flow patterns that cause the generation of stream flow in a basin. Recorded total discharge hydrographs are separated to their components using isotopes (Oxygen-18, Deuterium) contents. Among these samples, unit hydrographs from two one-peak storm hydrographs were derived using both isotope and graphical (Barnes Semi-Log) methods and the derived unit hydrographs peaks were compared.

It was found out that, the contribution of subsurface flow originating from various sub layers composed of different geological formations of the basin are important in hydrograph separation using isotope method of approach. The samples for rainfall isotope analysis are also noticed being affected to the separation of hydrographs and composition vary from storm to storm. The hydrograph separation gets more difficult when they became complex with multi peaks. Therefore it is recommended that well logs are needed to clear out some of the questions raised for the contribution of the subsurface flow component.

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HYDROGEOLOGY OF AWASSA LAKE CATCHMENT: ISOTOPIC AND HYDROCHEMICAL APPROACH

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The Main Ethiopian Rift (MER) is a major structural depression where a number of lakes are found; Awassa is one of these lakes. Pervious studies carried out on lake sediments, in the MER, have suggested that lake levels have dropped by about 210 meters from the level they were 10,000 years ago, at the end of Pleistocene[2]. In contrast, recent trends suggest that lake levels in the MER have been increasing, on average, at a rate of 6 cm / year. Similarly, the gauging data of Awassa Lake have indicated that the lake has been rising at a rate of 7.6 cm /year (Fig.1). Flooding caused by the lake has posed a serious development problem on Awassa town, which is located along the eastern shore of the lake.

Environmental isotopes and major ions chemistry were used to define the groundwater flow system and recharge conditions in the study area. Isotope data from four rainfall-sampling stations, gave a Local Meteoric Water Line (LMWL) with slope 7.5 and deuterium excess of 13.3.Three Local Meteoric Water Lines can be proposed for Ethiopia based on sampling carried out at four stations under this project and the GNIP station at Addis Ababa. They are: $\delta^2H= 8\ \delta\ ^{18}O + 14$ for the western high land, $\delta\ ^2H=7.5\ \delta\ ^{18}O+13$ for the rift valley and escarpment areas, and $\delta\ ^2H=8\ \delta\ ^{18}O+16$ for the eastern highland.

The Deuterium versus Oxygen–18 plot of water samples form springs, boreholes and some dug wells show rather closer distribution with mean values of 1.3 and –1.5, respectively. Such a clustered distribution can suggest a homogenous source of groundwater in the study area. The samples from dug wells and lake Awassa fall along evaporation line with slope 5.5 and deuterium excess of 7.6. The evaporation line established by this study is similar to that of evaporation line established for east African lakes [1].

Mean recharge elevation of 2000m was estimated from the dependency of ^{18}O on elevation ($\delta^{18}O = -0.0012*h+0.8718$, $R^2 = 0.94$), which was established from isotopic data of four stations, having different elevation that has continuously been sampled for two years. Correlation of rainfall and evaporation with elevation has given a recharge elevation of 2100m, which is almost similar with isotopically determined recharge elevation.

Groundwater in the MER, in general, and in the study area, in particular, is dominated by one water type: $Na\text{-}HCO_3$, which is also, supported by closer distribution of isotope data. Awassa, being a closed lake, is one of the freshest lakes in the MER with mean EC of 800 µs/cm and pH 8.5. The freshness of the lake is related to shorter turnover time (about 6 years).

The lake has groundwater inflow both from the eastern and southern shore and a subsurface out flow towards north. Thermal springs, discharging into Lake Shalla north of Awassa Lake, are believed to have been recharged by Awassa Lake. Unlike thermal springs in the study area, Chitu- Shalla hot springs, north of Awassa Lake, show positive values of ^{18}O, which can be the result of mixing of enriched Lake Awassa water with depleted paleogroundwater. Contour maps of EC and pH have depicted similar groundwater flow direction as inferred from that of the piezometric map.

The ten-years moving average rainfall, in the study area, has shown a decreasing trend whereas discharge data of Tikurwoha River that flows into Awassa Lake show an increasing trend. Similar trends have also been observed in adjacent areas. The decreasing trend of rainfall is related to the increasing trend of aridity of the region (climatic change) whereas the increasing trend of river discharge is related to change in land use (deforestation). The recent lake level increase of Awassa Lake is, therefore, related to increasing trend of surface water input.

Many remedial measures have been proposed, to mitigate the problem of lake level rise, among which watershed management is believed to be the best solution according to this study.

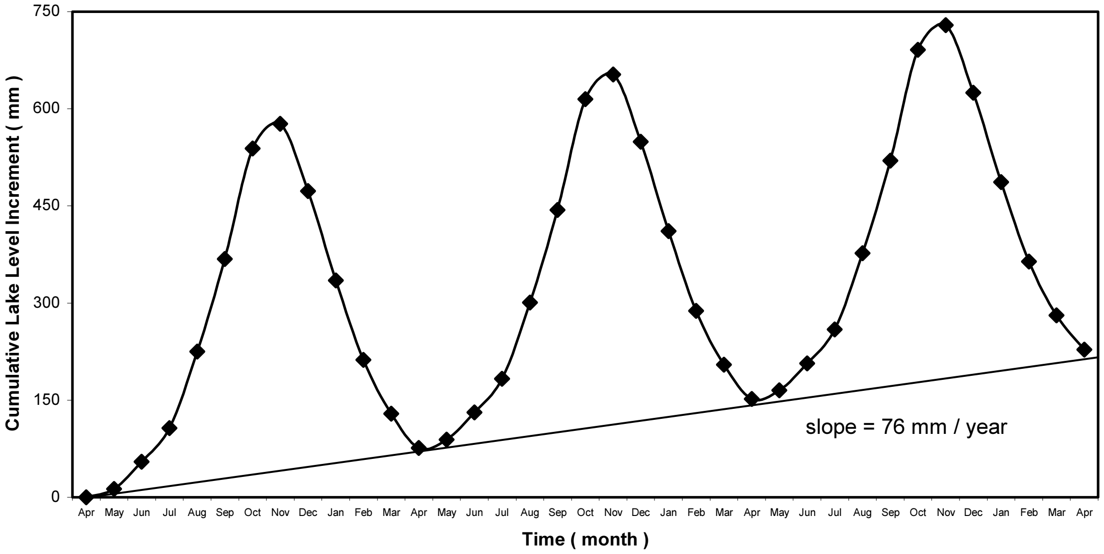

Fig.1. Model of Periodic Oscillation and Trend of Awassa Lake Level (1973-1999)

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COMPARISON OF ISOTOPIC TIME-SERIES PARTITIONING ANALYSIS WITH AN EVAPORATIVE ENRICHMENT MODEL IN LAKE- AND WETLAND-DOMINATED RIVER BASINS, MACKENZIE BASIN, CANADA

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The use of the water isotope tracers oxygen-18 and deuterium to partition the streamflow components into snowmelt, surface water and groundwater can provide fundamental information about the factors that influence water balance and runoff generation in cold regions. Defining the isotopic composition of surface water (lakes and wetlands) is a challenge with the partitioning strategy, since the surface water contribution to streamflow, which is influenced seasonally by inputs of snowpack in spring and evaporative enrichment in summer, is a mixture from different water sources. Furthermore, the isotopic composition of streams in cold climates, particularly in subarctic wetlands, is often skewed because of non-contributing water balance compartments that undergo evaporative enrichment [1]. That is, streams tend to reflect lower isotopic enrichment, especially in wetland-dominated basins.

The streamflow partitioning strategy relies on ‘set points’ of low flow during late winter and fall leading to the development of a conceptual model for the isotopic variations in streamflow, which allow closure of the water balance over complete annual cycles. Fig. 1 shows the isotopic variation in source waters for five subarctic basins near Fort Simpson, Northwest Territories, Canada. The temporal changes in the volume of snowmelt, surface water, and groundwater contributions to streamflow from each river basin are displayed in Fig. 2. Evaporation/inflow (E/I) ratios are obtained from isotope-mass balance calculations and the results are presented in the table below. Correspondingly, runoff contributions are calculated based on the water balance equation.

Basin	Dominant Characteristic	Partitioning Analysis: Surface Water (%)	E/I Estimates: Evaporative /Inflow ratio	Surface Runoff (%) (1-E/I)
Birch R.	Wetland	71	0.12	88
Blackstone R.	Wetland	81	0.12	88
Jean-Marie R.	Lake/Wetland	89	0.11	89
Martin R.	Lake	63	0.15	85
Scotty Creek	Lake	74	0.15	85

The lowest level of the drainage hierarchy collects the maximum surface water accumulation, representing the corresponding isotopic signal (a value close to summer low-flow signal) integrated over the catchment area, and reflects the total water loss by evaporation. Hence, the evaporative enrichment model for E/I can be used to predict the net surface water contributions for comparison with the results from the partitioning analysis (surface water contribution). Notably, lake- and wetland-dominated basins systematically differ in surface water contribution and water losses by evaporation. Wetland-dominated basins have higher runoff contributions, which suggests that these basins are hydraulically better connected than lake-dominated basins.

The discrepancy in the surface water component obtained from the different methods may imply that E/I estimates are too low, leading to higher surface runoff, or the partitioned component of surface water may be too low. However, the lower values of the partitioned surface water component may be attributed to transpiration losses. The estimate of E/I is only dependent on the isotopic enrichment and climate parameters, and is not affected by potential errors related to catchment morphological characteristics, precipitation amounts, or differences in vegetation coverage. On the other hand, the surface water component of streamflow may be controlled by hydrological mechanisms. Furthermore, the streamflow partitioning method uses the groundwater end-member specific for each basin, whereas water balance estimates use the same MWL intersection value (flux-weighted precipitation) for $\delta^{18}O$ and δ^2H, which is more depleted than the groundwater isotopic value.

Isotopic tracing of source waters and catchment-weighted evaporation losses may be combined in future studies to gain complementary understanding of the hydrological processes and water balance at a larger scale, and aid in the improvement of hydrological modelling.

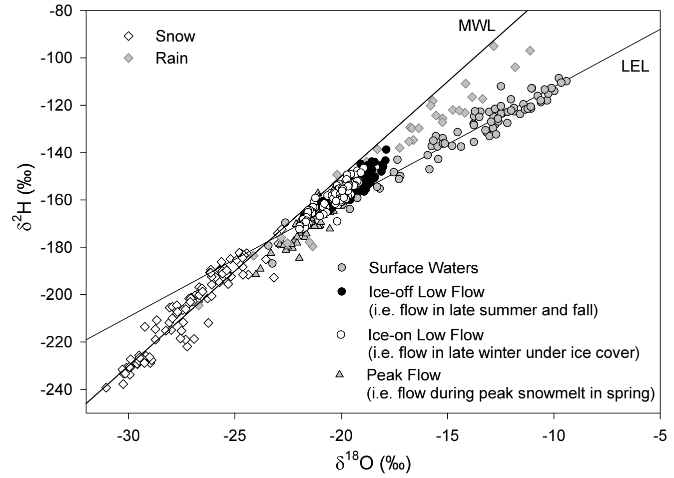

FIG. 1. $\delta^{18}O$-δ^2H crossplot showing the isotopic composition of source waters of Birch, Blackstone, Jean-Marie, and Scotty Creek river basins. Three main sources of water in streamflow are depicted, namely snowmelt, groundwater (ice-on low flow), and surface water (ice-off low flow). The isotopic signal of these source waters reflect changes in the seasonal cycle.

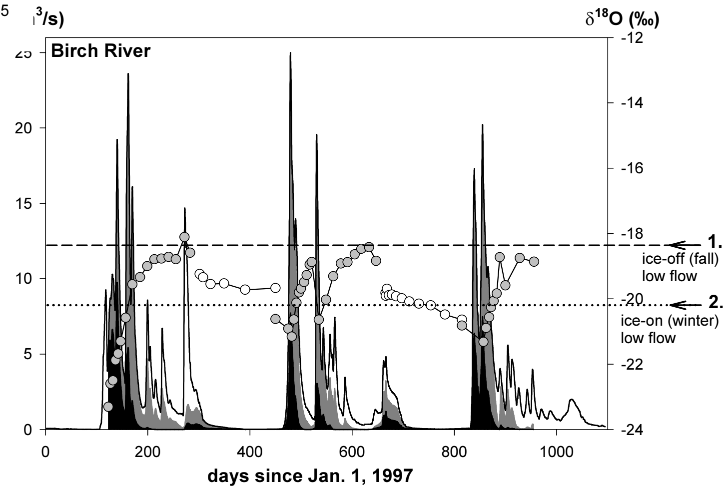

FIG. 2. Time-series of discharge (Q) and $\delta^{18}O$ for Birch River, exemplifying the partitioning end-components of streamflow. Black-shaded areas under the total discharge curve represent the total amount of snowpack contributing to streamflow; gray-shaded areas represent snowpack and groundwater amounts, and; white areas depict surface water contributions. The isotopic composition of streamflow is shown by the series of circles: gray-filled circles represent ice-off streamflow; empty circles represent ice-on streamflow. Markers 1. and 2. indicate the average isotopic limit for ice-off low flow (fall) and ice-on low flow (winter), respectively.

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EVOLUTION OF THE ISOTOPIC COMPOSITION OF DISSOLVED SULPHATE IN CALDERS STREAM (LLOBREGAT BASIN, NE SPAIN)

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The Calders stream is a tributary of the Llobregat River characterised by negative values of $\delta^{34}S$ of dissolved sulphate, whereas in the Llobregat basin most of the reported values are positive [1]. Stream waters were sampled monthly between 1997 and 1998 and quarterly in 1999. Data show an overall increase in $\delta^{34}S$ from–10‰ to 0‰, coupled with an increase in Na and Cl concentrations. This trend has a break on May 1998, with a maximum $\delta^{34}S$ of +2‰. The oxygen isotopic composition of dissolved sulphate, $\delta^{18}O$, displays an opposite trend with a slightly decrease from +9‰ to +6‰. The aim of the present study is to elucidate the origin of these negative values and to understand their evolution.

Pristine stream water from a tributary has a $\delta^{34}S$ = –18‰ and $\delta^{18}O$ = +2.5‰ (site 8 in Fig. 1), in accordance with the reported values for the sulphate produced by pyrite oxidation in this area [2]. Moreover, these values fall in the field of sulphate produced by sulphide oxidation in a $\delta^{18}O_{SO4}$ vs $^{18}O_{H2O}$ plot. Therefore, negative $\delta^{34}S$ values of Calders stream are interpreted as natural values obtained by leaching of bedrock, pyrite-bearing marls and limestones.

In order to determine which processes caused the isotopic evolution described above, a detailed sampling up stream was performed on November 2000. Is interesting to notice the significant variation in major ions observed in Fig. 1, with an increase of Cl and Na content in sample 6, which is progressively diluted downwaters. This change is recorded by a drastic $\delta^{34}S$ enrichment from +0.3‰ in site 7, to +21‰ in site 6, and back to lower values downstream.

Water chemistry and isotopic values of sample 3 can be explained by a mix between natural sources and fertilisers. Sample 7 has the same inputs that sample 3, with the contribution of pig manure, which is increasingly spread onto the field as a fertiliser (one sample of pig manure analysed has a $\delta^{34}S$ = 0‰ and a $\delta^{18}O$ = +5.6‰). Sewage effluents in the Calders Basin flow directly into the stream and only a small volume is plant-treated since April 1999, and hence their contribution cannot be discarded. Therefore, the $\delta^{34}S$ of sample 7 could be interpreted as a three end-member mix, natural, agricultural and sewage sources.

Wastewater collected from a dye industry located near sample 6 is sodium-chlorine type with a $\delta^{34}S$ = -0.8‰ and four times more sulphate than sample 7. The increase in Na and Cl detected in sample 6 (with values up to 110 and 175 ppm, respectively) is interpreted as a contribution of 10% in volume of water coming from this industry. However, this balance cannot account for the ^{34}S-rich value found and its low sulphate concentration, even lower than in sample 7. It is important to point that occasionally oil spillage from this dye industry into the stream has been reported. The last one took place in spring 1998, and during the November 2000 sampling, part of the oil was still visible. The δ^{34}S of the stream water at this site has a value of +21‰, sulphate reduction mechanism accounts for such increase of the isotopic signature coupled with a lowering of sulphate concentration.

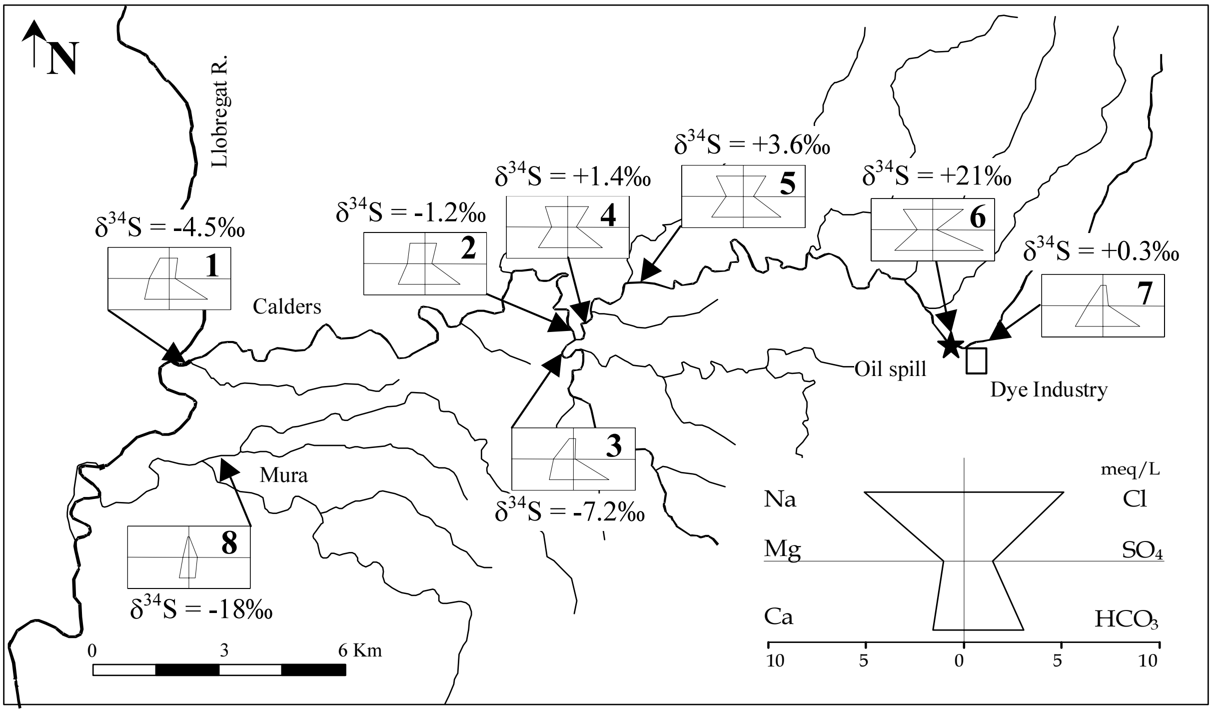

Fig. 1 Calders Basin showing Stiff diagrams and $\delta^{34}S_{SO4}$ of November 2000 sampling.

Downwaters of site 6, stream waters show a decrease in the δ^{34}S, [Na] and [Cl], with values down to -4.5‰, 30 and 50ppm, respectively at the last sampling site (Fig. 1). This evolution is interpreted as a dilution with waters similar to sample 3, a mix between pristine waters and fertilisers.

This detailed sampling indicates that the negative isotopic composition of dissolved sulphate in the area has a natural origin. Regardless to most of the surficial waters of the Llobregat basin, with a $\delta^{34}S_{SO4}$ mainly controlled by evaporites, in the Calders stream sulphate is derived from pyrite oxidation. Moreover δ^{34}S-rich sulphate effluents from anthropogenic sources, mainly, agricultural sources, dye industry effluent, sewage and oil spills, controls the δ^{34}S of the stream waters. Sudden increases of δ^{34}S of dissolved sulphate in stream waters are believed to be caused by oil spillage. The long-term enrichment (from Jan-97 to Aug-99) in the area is interpreted as a progressive increase in the agricultural and industrial activities.

ACKNOWLEDGEMENTS

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THE OXYGEN AND HYDROGEN ISOTOPE RATIOS IN WATERS FROM THE LARGEST RIVER SYSTEMS OF THE UNITED STATES

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The objective of the U. S. Geological Survey's (USGS) National Stream Quality Accounting Network (NASQAN) program is to characterize water quality in large river systems of the United States. [1] In concert with NASQAN's ongoing activities, we have obtained river water samples from the Mississippi, Missouri, Rio Grande, Upper and Lower Colorado, Columbia, and Yukon systems, and analyzed them for oxygen and stable hydrogen isotopic composition. Recent water samples have been obtained for the period 1997 through 2003, but isotopic data for the period 1984 through 1987 are also available for several stations [2]. This work represents our initial investigation of this new data set.

The global relationship between δ^{18}O and δ^{2}H in precipitation, referred to as the Global Meteoric Water Line (GMWL), has been determined [3] to be:

$$\delta^{2}\text{H (in ‰)} = 8.13 * \delta^{18}\text{O} + 10.8$$

Despite the fact that the isotopic composition of river waters reflects the full complex history of surface channel water (including influences by recent precipitation, seasonal temperature variations, groundwater of different ages, and even direct upstream contributions from reservoir releases), the relationship between δ^{18}O and δ^{2}H in U.S. river water samples has been shown to be generally consistent with the GMWL collectively (on a continental scale) if not locally [4]. We computed the regression line of δ^{2}H versus δ^{18}O for the full sample set (N=2325) called herein the River Water Line (RWL), as well as regression lines for each of the seven river systems (N = 882, 448, 315, 194, 78, 327, and 81 samples, respectively) called Local River Water Lines (LRWLs). RWL has a slope of 8.08 consistent with GMWL, but its intercept is $\sim 7 < \sim 10$: RWL parallels but is lower in δ^{2}H than GMWL. Consistent with earlier studies [4], LRWLs are more variable.

We examined the data for seasonal variation with respect to deuterium excess defined [5] as:

$$\text{d-excess (in ‰)} = \delta^{2}\text{H} - 8 * \delta^{18}\text{O}$$

Four consecutive three-month seasons were defined for October through December, January through March, April through June and July through September (with N=331, 512, 852 and 630 samples, respectively). Seasonal median d-excess values fall below the reference value of 10. (Values << 10 can indicate strong evaporative effects.) Mean d-excess for the January through March season was not statistically significantly different (t-test with $p \leq 0.05$) than that for the April through June season, but each differs significantly from both the October through December season and the July through September season, and the latter two seasons differ significantly from each other. Within each river system, the range in d-excess also displays seasonality.

El Nino - Southern Oscillation (ENSO) phenomenon influences the interannual variability of climate conditions in the United States. We examined the question as to whether an ENSO signal can be discerned in these terrestrial hydrologic systems by examining the d-excess values. Data were subdivided into three categories: (1) that arising during a warm ENSO phase or El Nino, (2) that arising during a cool ENSO phase or La Nina, and (3) that arising during a Neutral year. We adopted the Japanese Meteorological Agency (JMA) definition [6] for the annual ENSO condition, but labeled the year according to its USGS "water year" designation; that is, a year spanning October 1 through September 30 is designated by the ending year. Data were available for El Nino years 1987,1998, and 2003 (N=565); La Nina years 1999 and 2000 (N=748); and Neutral years 1984, 1985, 1986, 1997, 2001, and 2002 (N=1012). Treated collectively, all La Nina samples yield a mean d-excess value that is significantly (t-test with $p \leq 0.05$) different than the mean d-excess in El Nino as well as Neutral years; this observation also holds for the mean values of $\delta^{18}O$ and $\delta^{2}H$. This relationship was significant particularly in the Mississippi and Missouri systems.

The conclusions of this study are: (1) The collective average value of d-excess in NASQAN river waters differs significantly between seasons, where relevant seasonal groupings appear to be October through December, January through June, and July through September. (2) The range of d-excess values in individual river systems differs by season and between each river system. (3) During the La Nina years, not only was the collective mean value for d-excess significantly lower than that in El Nino or Neutral years, but also the mean values of $\delta^{18}O$ and $\delta^{2}H$ were different. This relationship was also statistically significant in the Mississippi and Missouri systems. Further investigation is required to determine (1) if these results are unduly influenced by the small sample sizes available to us for some systems, in particular during El Nino or La Nina years, and (2) if these results reflect some other effects, such as homogenization of waters in highly dammed systems.

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ISOTOPIC AND CHEMICAL INVESTIGATION OF WATER SAMPLES FROM ARNO AND TIBER RIVERS (CENTRAL ITALY)

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The δ^{18}O and $\delta\ ^{2}$H isotope signature in the main rivers Tiber and Arno and principal tributaries, in Central Italy, were investigated along with major ion chemistry in order to evaluate the relative impact of natural processes and pollution on superficial water quality of related catchments.

The Tiber Basin extends over an area of about 17156 km^2 between the Apennine and Anti-Apennine Ridges to the Tyrrhenian Sea, in the Umbria and Latium regions. The main direction of fluid flow is NE-SW. Along its 402 km lenght, the Tiber River undergoes a vertical fall of about 1300 meters and crosses the town of Rome.

With a surface area of about 8228 km^2, northwest to Tiber Basin, the Arno Basin is located in Tuscany between the Apennine Ridge and the Tyrrhenian Sea. The Arno River flows westward crossing the tows of Florence and Pise. Along its 241 km length, the Arno River undergoes a vertical fall of about 1360 meters.

Repeated surveys were carried out from 1996 to 2001 as to obtain water samples representative of high and low flow hydrologic conditions. The chemical and isotopic compositions of waters from both the systems were compared in order to assess the impact of local environmental factors on surface chemistry.

Despite very similar climatic conditions, i.e. monthly precipitation amounts, average ambient temperature, temporal duration of dry, wet and intermediate seasons, the geochemical signature of surface waters results in different patterns in the two catchments.

The Arno River shows a fairly homogeneous geochemical behaviour, characterised by a progressive enrichment of solute contents and ^{18}O and ^{2}H concentrations moving away from source to mouth, essentially due to the evaporation processes of the surface/soil waters. Both the chemical and isotopic data suggest that runoff control the chemical behaviour of river waters, according with the low average permeability of outcropping formations.

In contrast, the Tiber River is characterised by a more impulsive behaviour, with sudden variations in chemical and isotopic composition in correspondence of the confluence with major tributaries. This is a consequence of a different geomorphologic structure of the basin, where important regional carbonate-karstic and volcanics-hosted aquifers feed the main tributaries, locally controlling also the hydrology of the main river. Stable isotopes suggest that a significant contribution occur from meteoric precipitations falling at higher altitudes than as they occur in the Arno Basin, and that evaporation processes play a minor role on the isotope variations of the Tiber waters.

THE STABLE ISOTOPE SIGNATURE OF CONTINENTAL RUNOFF

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Recent international programmes such as the IAEA coordinated research project on "Isotope tracing of hydrological processes in large river basins" have increased scientific awareness of the potential value of incorporating isotope tracers in large-scale water cycling studies to trace water origin and residence times, snowmelt processes, surface-groundwater exchange, evaporation-transpiration partitioning, precipitation variability, and climate/land use changes [1]. Although isotope techniques have been widely tested and are operationally applied at the small catchment-scale, theoretical development and testing of isotope-mass balance approaches at the continental scale are still in progress. This paper proposes a theoretical basis for predicting the long-term (interannual) signatures of oxygen-18 and deuterium in continental runoff applicable for describing global isotope variability in the mean flux-weighted discharge of large rivers.

For long time periods, the mass and isotope balances for the oceans and continents, respectively are given by

(1) $P_o = E_O - P_C$

(2) $\delta_{Po} P_o = \delta_{Eo} E_o - \delta_{Pc} P_C$ and

(3) $P_C = R_C + E_C + T_C$

(4) $\delta_{Pc} P_C = \delta_{Rc} R_C + \delta_{Ec} E_C + \delta_{Tc} T_C$

where P_o and E_o is oceanic precipitation and evaporation, and $P_C, R_{C,} E_C$ and T_C are continental precipitation, runoff, evaporation, and transpiration (Fig 1a). Changes in atmospheric moisture are expected due to admixture of evaporated and transpired moisture to air masses over the continents. Oceanic moisture in coastal areas is shown as A_o which becomes subsequently modified as it moves across the continent to inland areas (ranging from A_1 to A_2). The approximate isotope compositions (δ) of components are shown in Fig 1b. Long-term differences in precipitation arise from Rayleigh-type fractionation of atmospheric moisture and precipitation during rainout over the continents. Transpired moisture is expected to be similar to precipitation or groundwater recharge for a given location, whereas evaporated moisture will be isotopically depleted (plotting on or above the MWL) and river discharge will tend to be isotopically enriched (plotting on or below the MWL). Fig. 1c shows specific hydroclimate forcings on the ^{2}H-^{18}O isotopic composition including those related to long-term precipitation input signals (temperature, latitude, altitude, distance from ocean source), seasonal signals (temperature, monsoon cycles, moisture sources, glacial melt), bias in recharge due to selection of high-precipitation or thaw-season events, and seasonal oscillations in evaporative enrichment from the river or contributing sources (soil water, lakes, reservoirs, wetlands, etc.). In addition to monitoring of volumetric fluxes, the characterization of long-term and seasonal isotope signals is expected to provide additional insight into hydroclimatic changes in each hydrologic regime.

In some cases the primary water balance signals in precipitation may be more preserved in river discharge whereas in arid or seasonally arid zones the selection and evaporation signals may make the differences more pronounced. While systematic surveys of flux-weighted isotope signatures of discharge have not been widely collected, the anticipated long-term separation can be postulated based on the isotope and mass balance shown in Fig. 1b and depicted in eq. (3) and eq.(4). The isotope separation between flux-weighted continental runoff and continental precipitation $\left(\delta_{Rc}-\delta_{Pc}\right)$ is expected to depend on

$$(5)\quad \delta_{Rc}-\delta_{Pc}=\frac{E_c\left(\delta_{Rc}-\delta_{Ec}\right)+T_c\left(\delta_{Rc}-\delta_{Tc}\right)}{P_c}$$

which is obtained by rearranging eq. (4) with substitution of $R_c=P_c-E_c-T_c$ from eq. (3). If it is also assumed that continental transpiration is similar to continental precipitation, i.e. $\delta_{Tc}\approx\delta_{Pc}$ then this further simplifies to

$$(6)\quad \delta_{Rc}-\delta_{Pc}=\frac{E_c\left(\delta_{Rc}-\delta_{Ec}\right)}{P_c-T_c}$$

Eq. (6) demonstrates that the long-term isotope separation between runoff and precipitation will approach zero only as $E_c\to 0$ or as $\delta_{Rc}\to\delta_{Ec}$. While very low (free-surface) evaporation may be characteristic of some humid areas dominated by vegetation, the latter condition where

$$(7)\ \delta_{Rc}\approx\delta_{Ec}$$

is not expected to occur due to the well documented evaporative enrichment effects. This can be shown by substitution of the Craig and Gordon model [2]:

$$(8)\ \delta_{Ec}\approx\frac{\alpha*\delta_{Rc}-h\delta_{Ac}-\varepsilon}{1-h+10^{-3}\varepsilon_K}$$

into eq. (7) assuming $\alpha*\approx 1$,which shows that $\delta_{Rc}\to\delta_{Ec}$ only as $\delta_{Rc}\to\frac{h\delta_{Ac}+\varepsilon}{h-10^{-3}\varepsilon_K}$ which is the limiting isotope enrichment under prevailing atmospheric conditions. Note that in this case δ_{Ac} is the average isotope composition of continental atmospheric moisture comprised of a mixture of δ_{Ao},δ_{A1}, and δ_{A2}. Limiting enrichment is only expected to occur under conditions where waters evaporate to dryness and is therefore unlikely for the case of sustained discharge. Variations in evaporative enrichment of continental discharge is therefore expected to depend mainly on the fraction of water loss by (free-surface) evaporation in the river basin, as well as on the atmospheric humidity, its isotope composition and the ambient temperature. This conceptual model provides an example at the global scale for development of quantitative approaches to examining river discharge signals. Specifically, it provides an initial basis for understanding and quantifying the hydrological significance of the long-term precipitation-runoff isotope separation which is expected to vary with the ratio of E_c/T_c .

Such information is not available via conventional hydrometric monitoring. One key assumption of this derivation is that the isotopic composition of continental groundwater is similar to that of precipitation, although due to selective recharge and storage effects this may not be an appropriate representation for some large river basins. Other long-term storages such as glaciers need to be explicitly included in some areas. This and similar models need to be developed and tested to account for seasonal variations in the hydrological processes and specific influences of long-term storage reservoirs such as groundwater and glacier melt.

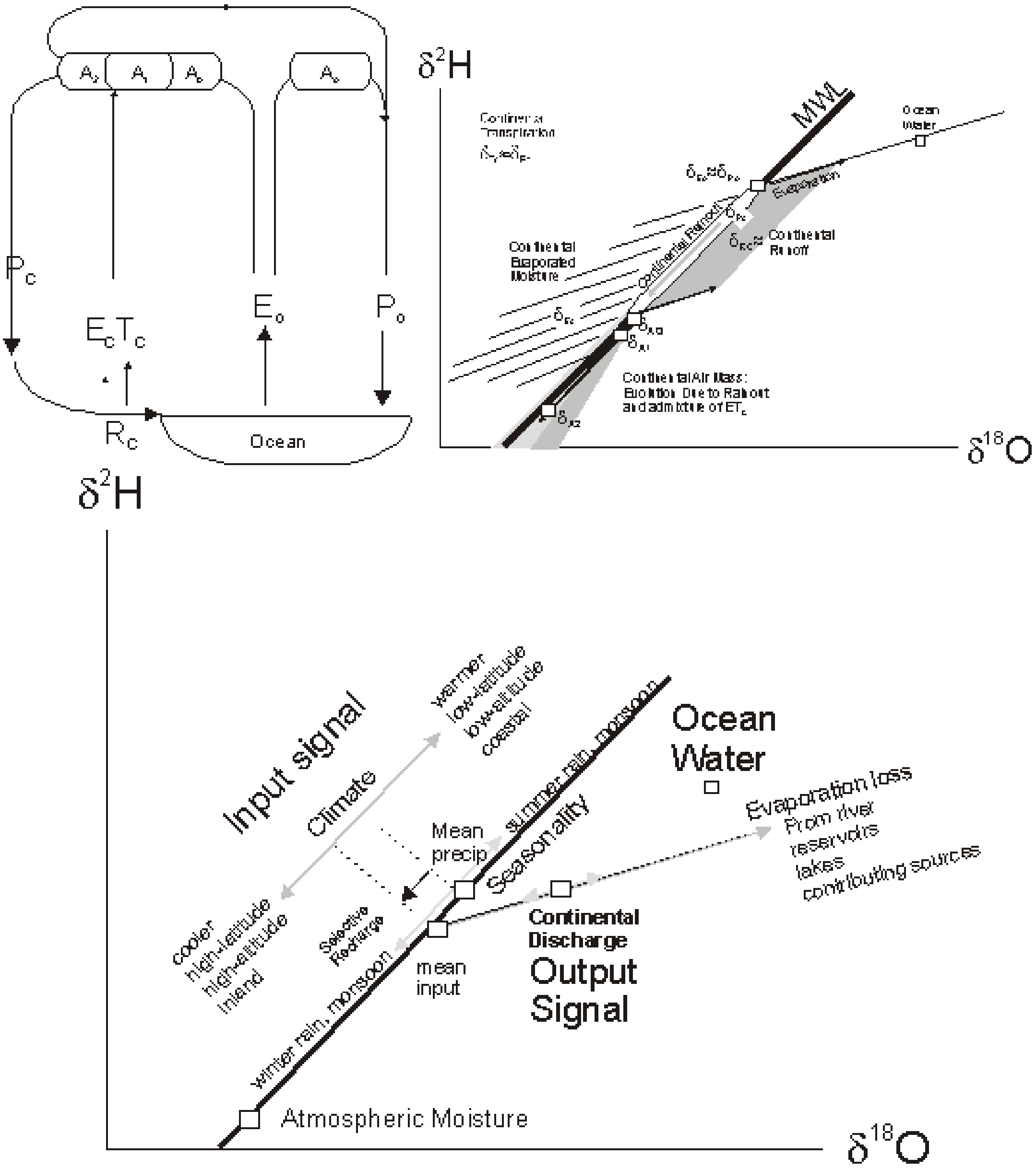

Fig. 1. Conceptual model of the ocean-continent water cycle. (a) Upper left: Schematic of the global water cycle fluxes. (E_o and P_o are the oceanic evaporation and precipitation, E_c, T_c, R_c and P_c are the continental evaporation, transpiration, runoff and precipitation, A_o, is water vapour transport over the oceans, and A_1 to A_2 denotes water vapour transition over continental areas as modified by evaporation and transpiration feedback and moisture recycling. (b)Upper right: Isotope signatures (δ values) for the ocean-continent system, where subscripts denote signature of components shown in (a); (c) Bottom: Primary forcings on isotope composition of hydrological inputs and outputs from large river basins.

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HYDROGRAPH SEPARATION USING ^{222}RN AND STABLE ISOTOPES ESTIMATIONS IN FOUR SUB-CATCHMENTS OF THE ATTERT BASIN (LUXEMBOURG)

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In order to get informations about the hydrologic signature of small rivers during and after heavy rain events, four small catchments were selected as experimental sites. Hydrograph separations based on environmental tracers were performed. Natural isotopic tracers such as ^{18}O, ^{2}H and particularly ^{222}Rn may help to distinguish the components dominating the outflow, particularly of ‘pre-event waters’, ‘event waters’ and ‘post-event waters’. Even with moderate concentrations in groundwater, radon can be a very sensitive indicator of groundwater input into rivers.

The selected sub-catchments under investigation are situated in the western part of Luxembourg and belong to the Attert basin, the latter being integrated in the European Network of Experimental Research Basins (ERB). Radon gas detectors were adapted to measure continuously the radon activity in water. These detectors are installed at chosen points at the basins outflows together with high precision thermometers, conductivity meters, flow meters and automatic water samplers for chemical analysis. Besides the continuous measurements, grab water samples were taken for radon measurements at different locations along a stream, most of them during periods of heavy rain events. A limited number of samples was also analysed for their content of radium and uranium and of the stable isotopes ^{18}O and ^{2}H.

Presented are results over a one year measurement campaign. During the dry season i.e. during more or less continuous discharge conditions, the observed values did not show substantial variations and could be used as reference values. The high fluctuations of the measured data during heavy rain events are discussed and the interplay of the different parameters analysed.

The research is part of the national project “CYCLEAU” based on the study of the interactions between different parameters in the water cycle, at several scales. The project CYCLEAU is supported by the FNR (National Research Fund - Luxembourg).

DEEP SOURCES OF SALINISATION OF LAKE KINNERET, ISRAEL–AN ISOTOPE AND RARE EARTH APPROACH

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Salinisation of fresh groundwater reservoirs is a widespread problem, especially in arid regions. As a first step for protection it is crucial to identify its sources and mechanisms. The Jordan Rift Valley between Israel and Jordan is the deepest land depression on earth with the Dead Sea with -410 m below sea level, functioning as a receiving reservoir for the surrounding highlands. Groundwater quality changes drastically within sharp boundaries indicating an admixture of saline groundwater components of different origins. Lake Kinneret (Sea of Galilee), situated in the northern part of the Jordan Rift Graben, serves as an important drinking water reservoir for Israel and by treaty also for Jordan. The water quality is affected by an influx of saline groundwater by salty springs located at the lake shore but also within the lake and by an up welling seepage via the lake floor.

More or less two main groups of theories exist about the primary origin of the salinity. One is that the salinisation derives by dilution of an ancient, intensively evaporated brine developed in a lake formed in the Rift Valley following seawater intrusion during late Miocene [1]. The other is that the salinisation derives from dissolved evaporative sediments in a depth of 2000 meters or more. The existence of these sediments is not proven but strong hints exists [2]. Based on isotope, Rare Earth elements and chemical data at least three different water types can be distinguished which all can be explained by mixing of more or less one original brine with recent young groundwater.

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NEW DATA ON STABLE ISOTOPE COMPOSITIONS OF LAKE MALAWI WATER: PROPOSITION FOR A NEW INTERPRETATION OF THE RELATIVE ENRICHMENT OF THE HYPOLIMNION WATER

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Within the framework of the Project CASIMIR [1], a field campaign was organized in October 1993 (end of the dry season) in the northern part of Lake Malawi (Tanzania). River water samples were collected nearby the lake northern shore, as well as lake water columns, for stable isotope measurements ($\delta^{18}O/\delta^{2}H$) and tritium contents. The results obtained on two of these profiles (P1: 9°43'S-34°01E, 197 m deep, and P3: 9°40'S-34°04E, 240 m deep) are very similar, and mark both the spatial homogeneity of the vertical distribution, and the representativity of the profiles, at the timescale considered.

With respect to the analytical uncertainties, the stable isotope compositions are relatively constant with depth, and of about +2.0 ‰ and +12 ‰ *vs* SMOW for $\delta^{18}O$ and $\delta^{2}H$ respectively. However, a slight depletion is observed between the lake surface and the -100 m level, while an increase of the isotopic compositions seems to caracterise the bottom part of the water columns. This evolution could be linked to the thermo-haline structure of the lake northern sub-basin. Indeed, the thermocline (located at around -80/-90 m deep) corresponds to the inversion of the isotopic gradients.

On the basis of the lake thermo-haline structure, three water bodies can be distinguished: (1) Zone I, from the surface to 45 m deep ($\delta^{18}O$ = +2.0 ‰ and $\delta^{2}H$ = +12 ‰), (2) Zone II, between 45 and 100 m deep, and corresponding to diluted waters (lower isotopic values: $\delta^{18}O$ = +1.9 ‰ and $\delta^{2}H$ = +10 ‰), and (3) Zone III, from 100 m deep to the bottom, caracterised by a progessive enrichment of the water ($\delta^{18}O$ = +2.0 ‰ and $\delta^{2}H$ = +13 ‰).

The isotopic enrichment of the lake surface water is due to the evaporation of the epilimnion. The bottom of the epilimnion (-50 to -100 m deep) gathers diluted water, as already observed on the salinity profiles [2]: marked by depleted isotopic values, this section thus receives surface runoff from the Livingstone escarpment.

Compared to data obtained on samples taken along a water column at the lake centre in June 1976 (end of rainfalls-beginning of the dry season), our results give stable isotope compositions very similar to those of hypolimnic waters at that time ($\delta^{18}O$ = +2.08 ‰ and $\delta^{2}H$ = +13.5 ‰; [3]).

In agreement with available data (i) on the lake hydrological balance [4], (ii) on isotopic compositions of rainfalls, and (iii) on the lake water circulation and composition knowledge, the isotopic contents of the hypoliminic water would be influenced by the lake surface water during the turn-over at the end of the dry season, while, during the wet season (phase of the lake stratification), the epilimnic water would be diluted by direct rainfall over the lake surface and by runoff over the catchment. So, the observed hypolimnion enrichment can be interpreted as reflecting the evaporated signature of the epilimnion water during the dry season, which also corresponds to the major mixing period.

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STREAMFLOW GAUGING OF MPIOKA USING DILUTION METHOD (BAS-CONGO/DRC)

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The Mpioka stream is a small affluent on the left bank of The Congo river which is localized in the Bas – Congo region. This stream knew its first hydrological studies thanks to the dam project planned on this one.

Water level had been registered at stream gauging station which was equipped of River stage recorder.

Due to the torrential characteristic of the stream, interrupted by several rapids and small falls greatly stratified and the characteristics of bed bottom which is covered of rounded shapes; the classical methods of measuring of discharges (current meter gauging) was difficult to apply. To palliate this difficulty, the method of gauging using a dilution tracer has been applied.

The sodium chloride (NaCl) was used, because it offering multiple advantages (no expensive, available and no toxic). A volume of 200 liters excessively concentred is injected upstream in the stream by the process of the integration (instantaneously). The registration of the phenomenon in situ (fig.1) has been achieved by a conductivimeter WTW to probe immersed in water downstream at the stream gauging station to a distance of 1100 m of the point of injection of the tracer; distance qualified of "good mixing length" considering the hydraulic features of the stream that permit a good brewing of the tracer.

Taking sample to constitute the middle sample are done downstream at the stream gauging station and are executed to intervals regularly distributed in the period of time of the passage of he saline cloud (on average all minutes).

The total of 49 gaugings have been achieved during the years 1994 and 1995 along different seasons in order to establish the level – discharge rating curve Q(H). This gotten curve (fig.2) served to transform gauge heights from River stage recorder in discharges. A more detailed description of the method and results will be published (1).

The application of this method opens ways to the extension of this technique to the other tracers notably the tritium, considering the emergence of a local appraisal capable to promote the development of the used of isotopic tool in the resolution of problems regarding management of water resources.

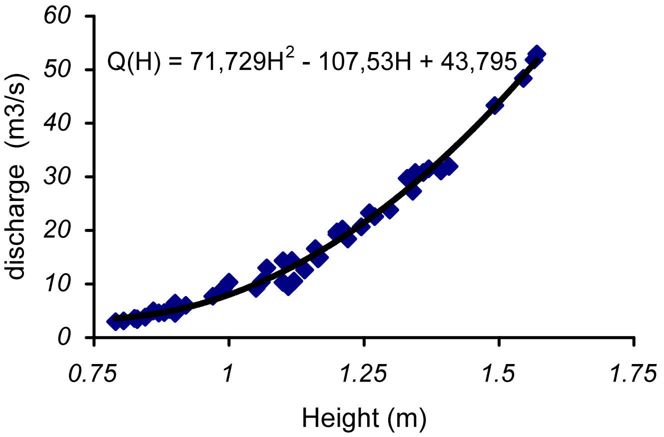

Fig. 1: Restitution curve of NaCl (Variation of electric conductivity in time).

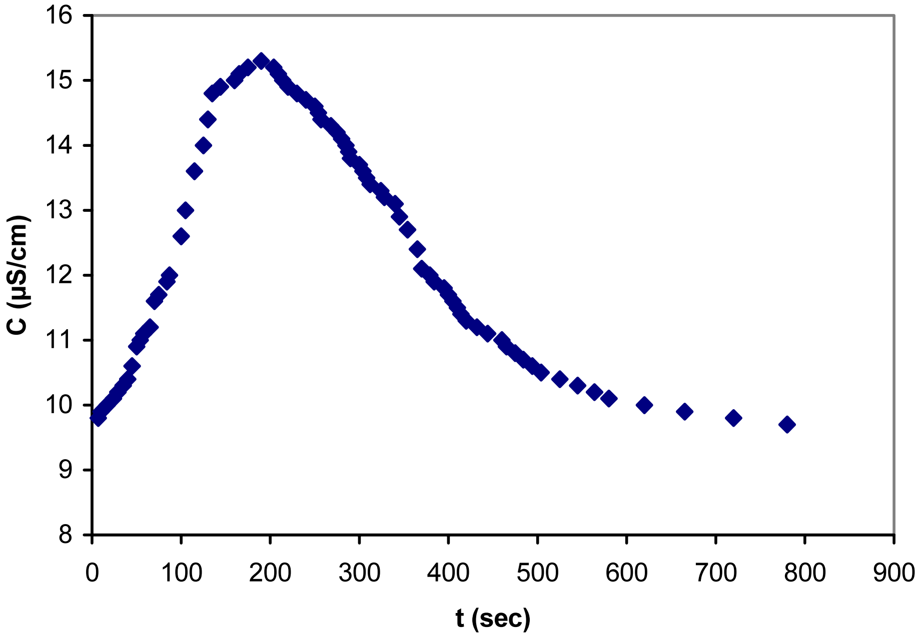

Fig. 2: Level-Discharge rating curve of Mpioka station.

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LOWERED TRITIUM LEVELS IN RIVER WATER INDICATE SIGNIFICANT STORAGE OF WATER IN A LARGE CATCHMENT

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Tritium in the runoff of the Tugela river, in Kwazulu-Natal province on the east coast of South Africa, was monitored for a three year period from 1970 to 1972 (Fig 1). The catchment above the sampling site (Mandini) is 29000 km^2 in extent; the altitude ranges from sea level to 3000 masl, the mean annual rainfall ranges from 700 to 1500 mm (all in summer) and the mean annual runoff ranges between 6 to 49% of the rainfall (46 to 724 mm, average 174 mm). At that time there were no significant reservoirs present within the entire catchment.

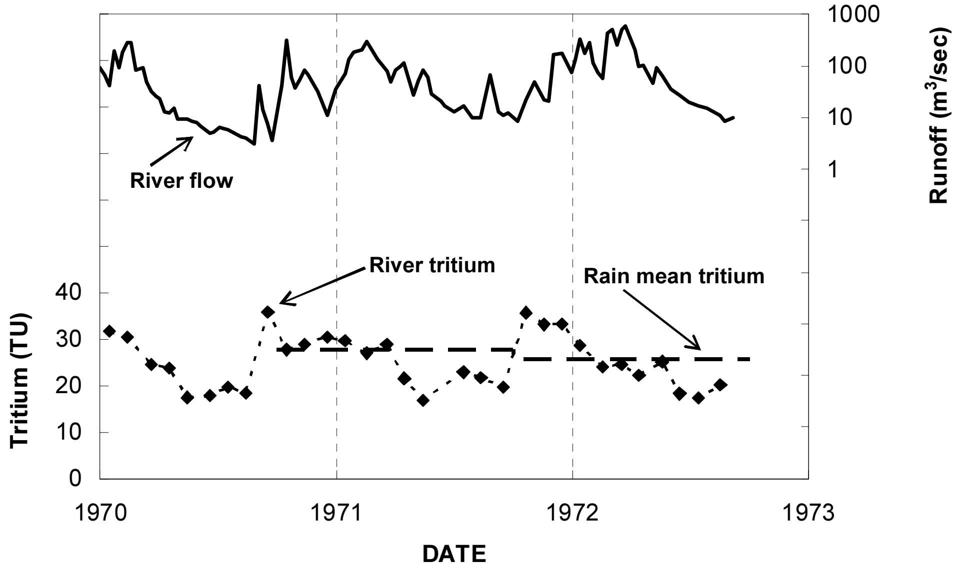

FIG. 1. Tritium variations in Tugela runoff at Mandini compared to mean annual rainfall in the catchemnt. Runoff values at Mandini indicate the high flow variability and low base flow.

Tritium in rainfall was monitored at three sites representing a range of altitudes and distance from the coast. Tritium levels in the river water showed strong seasonal variation with the lowest values during winter base flow. The flow-weighted mean annual tritium content of the river was considerably lower than that of rainfall of the inland stations (Fig 1).

The total tritium input into the catchment was modelled based on a rainfall-runoff model that describes 74 sub-catchments (200 to 1200 km^2 in size) by their characteristic rainfall and runoff [1] from which the relative contribution of each sub-catchment to the total runoff was calculated (Fig 2). Labelling the runoff of each sub-catchment with the tritium level of its rainfall determined by the local continental effect (Fig 2) yielded a weighted mean tritium content of rain input for the entire catchment. For the hydrological years (Oct-Sept) 1970/1 and 1971/2 these are 37 and 30 TU respectively. The measured flow-weighted mean tritium level of the runoff was 26 and 27 TU for the same two years. Lower tritium in runoff than in rainfall indicates that a significant source of low-tritium water contributed to the runoff. This was unexpected in an arid area since the sampling period was six years after the bomb peak of tritium in the southern hemisphere [2]. Any carry-over water in the river from a previous year should actually increase the tritium content in the river.

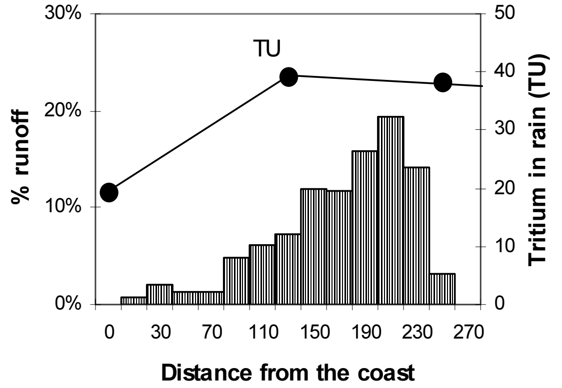

FIG. 2. Distribution of runoff generating areas (histogramme) and of rainfall tritium content as function of distance from the sea. This was used to calculate the weighted tritium input into the catchment

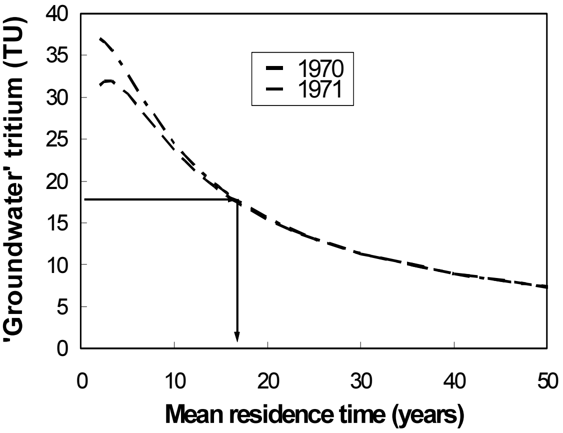

FIG. 3. Tritium content of a well-mixed reservoir (exponential mixing model) as function of the mean residence time based on local rian input. Curves for the two years differ only for low residence times.

The tritium level of the runoff was interpreted as a mixture of rainfall from the same year and water from a reservoir of low-tritium content [3]. The consistently low 17.5 TU of the base flow indicates that this is likely to represent reservoir water. Mixing calculation then shows that the runoff on a monthly basis contains a fraction of 34 to 50% of reservoir water; the remainder being rainfall of the same season.

A 17.5 TU tritium content for the catchment reservoir water can be calculated from the local rainfall tritium values as input into a well-mixed reservoir with a mean residence time of 16 years [3]. Given the runoff quantities for the two years involved, this implies a potential water storage of some 570 to 670 mm throughout the entire catchment.

On the other hand, the rapid flow response in this catchment to rainfall and the low base flow during the dry season (10% of the annual mean flow) suggest that there should be little storage available. If this model seems feasible, it would require investigation of the location of this large reservoir. The experiment cannot be repetead since the bomb-tritium peak has now passed.

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LATE MIOCENE MONSOONAL RECORD FROM OXYGEN ISOTOPE RATIO OF SIWALIK SOIL CARBONATE

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A seasonally reversing wind system with moist oceanic air from southwest during summer and cold, dry continental air from northeast during winter characterizes the Asian Monsoon climate. This system is responsible for heavy rains during June, July, August and September in the Indian sub-continent. It is believed that the Monsoon system got initiated relatively recently in the geological past (about 20 my ago) due to uplift of Himalayas beyond a critical height which established a summer-time high altitude low-pressure zone (Tibetan Plateau). But how the Monsoon evolved with time and if there were times of major changes are still not clear.

The Siwalik sediments of Himalayan foothills were deposited in an associated foreland basin, which developed in response to the Himalayan orogeny. An interesting feature of these sediments is the presence of large number of palaeosols in the mudstone beds, which formed in flood plains during pauses in sedimentation. Many of the palaeosols contain soil carbonates which are sensitive recorder of past rainfall regime. The oxygen isotope ratio ($\delta^{18}O$) of soil carbonates depends on the isotopic composition of soil water, which is derived from local precipitation with minor modification due to evaporative enrichment (~ 1 ‰). Therefore, analysis of $\delta\,^{18}O$ of soil carbonates from different horizons can be used to derive information about rainfall and monsoon performance. For the present study, three Siwalik sections, two from Kangra valley (Ranital and Kotla) and one from Haripur Khol, Himachal Pradesh, India (together spanning the last ~12 my. Sangode et al., 1996) were selected.

The $\delta\,^{18}O$ values (in ‰ with respect to PDB) show interesting variations with depth. In a composite profile (Fig.1.a) the isotope data show three evolutionary phases. Around 10.5 Ma, the $\delta\,^{18}O$ values are highly negative ranging from –10.3‰ to –8.7 ‰. The data tend towards positive values with decrease in age, reaching –6.6 ‰ at around 6.5 Ma. Subsequently, the isotope ratio is characterized by a sharp depletion with value up to –9 ‰ and then a second phase of enrichment reaching –6.5‰. Overall there were two broad phases of depletion at about 10.5 Ma and 5 Ma and one short phase of enrichment at 6 Ma.

Assuming isotopic equilibrium during precipitation one can calculate the oxygen isotopic composition of water from which the soil carbonate precipitated if temperature of precipitation is available. Assuming that soil carbonate formed during the warm season we estimate a soil temperature of 25 °C from the available meteorological data in nearby low altitude stations. Since the latitude of this region was not significantly different from today and the altitude was near sea level (floodplain of the basin) this estimate seems to be reasonable. A confirmation for temperature estimate is provided by the derived $\delta\,^{18}O_{\text{soil-water}}$ (–5.3 ‰ w.r.t. SMOW) based on average $\delta\,^{18}O$ (–7.3 ‰ w.r.t P.D.B) of recent carbonates.

Correcting for evaporative enrichment of 1 ‰ the mean isotopic composition of precipitation in Kangra valley would be about –6.3 ‰. This value is close to that expected from available isotope data pertaining to New Delhi (mean annual value –5.8 ‰ and mean summer season value –6.5 ‰, IAEA, 1992).

The two episodes of 2 to 3 ‰ depletion in the oxygen isotopic composition of carbonate and by inference that of rainfall are intriguing and point out that the evolution of Monsoon was not smooth. Since a temperature change of large magnitude can be ruled out these two periods probably indicate phases of intensification of Monsoon. An intensified monsoonal wind system would generate more intense and frequent depressions (storms) and probably result in depleted ^{18}O in rainwater. This inference is supported by a marine proxy. Abundance of G. bulloides in the Arabian Sea cores (Kroon et al., 1991) shows dramatic increase (Fig.1.b) at about the same periods (~ 9 and 5.5 Ma). This species is an indicator of upwelling intensity and its abundance increase suggests enhanced wind stress during these periods. Small difference in timing could be due to dating problems in either of the methods.

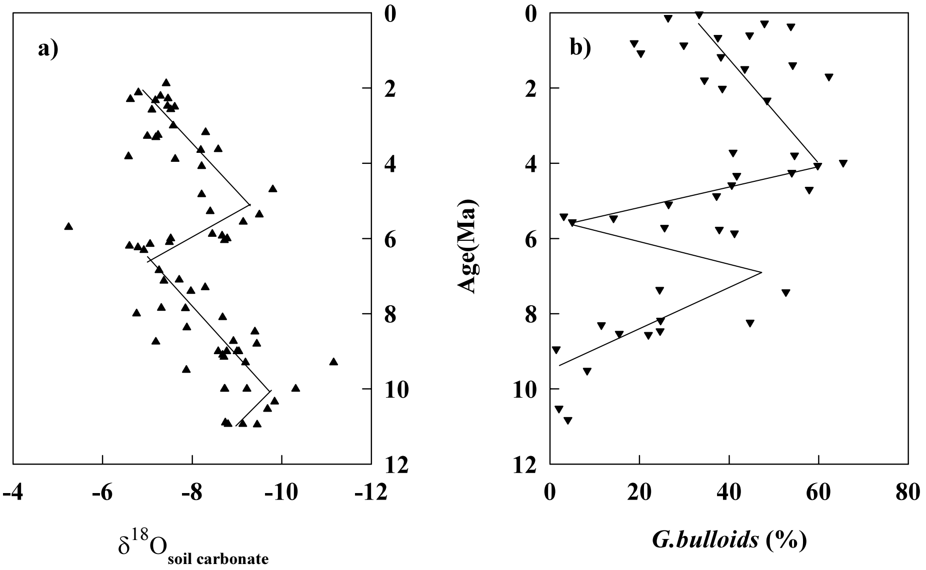

Fig.1. a) Variation of oxygen isotope ratio in soil carbonate from northern India showing changes in Asian Monsoon intensity in the past (~10 and 5 Ma). b) The Monsoon variation correlates well with record of upwelling intensity in the Arabian sea as revealed by abundance of *G.bulloides*. The lines are drawn to guide the eye.

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GROUNDWATER RESOURCES FOR EMERGENCY CASES IN THE LOWER REACHES OF THE LABE (ELBE) RIVER (CZECH REPUBLIC)

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Floods in the Czech Republic and elsewhere in the world during past years contaminated a large number of wells. The conventional water supply from individual wells and public water supply systems collapsed and had to be interrupted to prevent epidemic diseases. The substitution of water supply by import of drinking water in bottles and tanks became one of most topical tasks of the emergency activities right after rescuing of human lives endangered by floods. Similar cases repeated during transportation of liquid fuels and toxic chemicals and during accidents in chemical plants and elsewhere.

The valley of the Labe (Elbe) River in Northern Bohemia in the Czech Republic is an industrial region with a frequent risk of endangering drinking water resources. The potential accidents in water supply have to be considered and measures of prevention have to be at hand to attenuate the consequences and to make sure supplementary water resources for the period until the consequences of accidents are removed.

The water supply systems of numerous towns along the Labe (Elbe) River use groundwater resources of the fluviatile sediments and are exposed to a similar danger as the water supply in Moravia in 1997 and 1998. This has been proved again during the floods in the Labe and Vltava (a tributary of Labe) watershed in summer 2002. Because of this, the aquifers in the Cretaceous formation beyond the alluvial plain, which were considered safe and protected from the surface pollution, were investigated in the first step. They include a confined aquifer in the Cenomanian sandstone at the base and an unconfined aquifer in the Coniacian sandstone at the top of the Cretaceous strata. Between the aquifers, there is an about 350 m thick aquiclude of the Turonian strata consisting mainly of marlstones.

Radiocarbon ground-water dating, together with analyses of tritium and stable isotopes, was used. The aim was to determine the time of ground-water origin in the geological past, to evaluate the degree of its vulnerability due to external interference and to assess the methodology of investigation and development on the examples of some developed ground-water resources.

It was found that the ground water of the deep confined Cenomanian aquifer at the base of the Cretaceous formation is of Pleistocene origin and safe from interference while the ground water of the shallow Coniacian aquifer is of modern origin and might be endangered by pollution from the surface.

The investigation has been a part of a research project of the Charles University which since 2003 will be included into the VI phase of the UNESCO IHP as Theme 2: Integrated Watershed and Aquifer Dynamics, Focal area 2.1: Extreme events in land and water resources management.

ISOTOPIC EVIDENCE FOR GROUND WATER CONTRIBUTIONS TO RARE FLOODS IN ARID ZONE EPHEMERAL RIVERS

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Isotope data has shown that the ground water component ("old" water) feeding rivers during rainfall events can be more important than surface runoff (Sklash et al. 1976). This has been established for rivers in temperate climates with perennial base flow. We report here on possibly unique isotopic and chemical evidence of ground water contributions to flood periods in major ephemeral water courses in the arid/semi-arid western Kalahari of Namibia.

In the framework of a major ground water resource investigation in the area numerous samples were analysed for their isotope and chemical content. It was established that especially the shallow aquifer in the largely unconsolidated Kalahari formation which blankets the area shows clear evidence of kinetic evaporation. This evaporation signal is observed also in parts of the deeper sedimentary aquifers.

During the period of this project the exceptional rainfall of the 1999-2000 season, experienced by many southern African countries, produced rare flood events in the ephemeral river system of the area of study. Flow rates in the rivers could only be estimated from water depth measurements. However, in some cases daily river water samples were collected for isotope analysis.

Stable isotope, tritium and certain chemical parameters measured on these samples are presented and placed in context of available ground water data. The results suggest that a substantial proportion of the flow in the river was derived from perched ground water. This conclusion is strengthened by the fact that the river again flooded during the more normal 2000-2001 rainy period.

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TWO-YEAR D, ^{18}O, T OBSERVATIONS IN THE WATER OF THE VOLGA RIVER AND PRECIPITATION AT THE ASTRAKHAN HMS (46.25 N, 48.03 E, - 18 MSL)

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The Volga River is the greatest river of the European continent. Its length is almost 3690 km and watershed basin area equals about 30 % of the total Russian Plane territory, widening from the Valday Highland and Middle Russian Hills on the west up to the Ural Mountains on the east. The watershed area exceeds 1,3 million square km. The averaged multi-year water discharge is estimated to be 8100 m^3 c^{-1}. The annual run-off by Volga River is recorded as ≈ 250 km^3y^{-1}. This is (on the average) about 80 % of the total water inflow to the Caspian Sea [1].

Thus, the Volga River with its tributaries form a drainage system collecting ground waters discharged from a large territory, and, in this way, contributing to the river's run-off.

In order to estimate the mean residence time of those ground waters that provide the permanent river flow at the Astrakhan Hydrometeorological Station, the observations of isotope composition in the river water and local precipitation were carried out (see Table and Figs) during two years – from January 1997 to December 1998. The Table also includes some additional records on temperature of the river water and atmosphere, air humidity, river water pH, precipitation (all monthly averaged). As it was expected, the well remarkable seasonality (almost quasi sinusoidal) with absolute differences (of 65 and 8 ‰) has been revealed in δD and δ^{18}O values respectively for atmospheric precipitation. At the same time, the same seasonal differences have been also noted but with less differences for these value (29 and 2.5 ‰ respectively) in the Volga River water. This was caused by macro dispersion effects, as well as proper residence times of the water drained by the river. The tritium content in the river water is slightly less than that in the precipitation, which indicates to approaching a quasi stationary status (with respect to tritium content) of groundwater discharge, as well as to its relatively small residence time in the drainage system. A direct and independent evaluation of residence time values has been undertaken using amplitudes and a phase shift of the seasonal variation of δD and δ^{18}O as it is prescribed in [2]. It is noteworthy that, firstly, the residence time values calculated on the basis of the amplitudes are estimated to be from 4 to 6 months, whereas on the basis of the phase shift - as 4 months; secondly, comparing the tritium content in the Volga water and in precipitation, it can be concluded that in the run-off observed it is caused by a fast and slow discharge (balance) component of both surface and ground water simultaneously. The same behavior of ^{18}O in the river water was reported for the Danube [3].

It should be taken in mind that there are seven artificial reservoirs with hydroelectric power plants on the Volga River which soundly disturb the natural river water run-off, and in this connection the study should be continued by setting up a sampling station at each artificial reservoir.

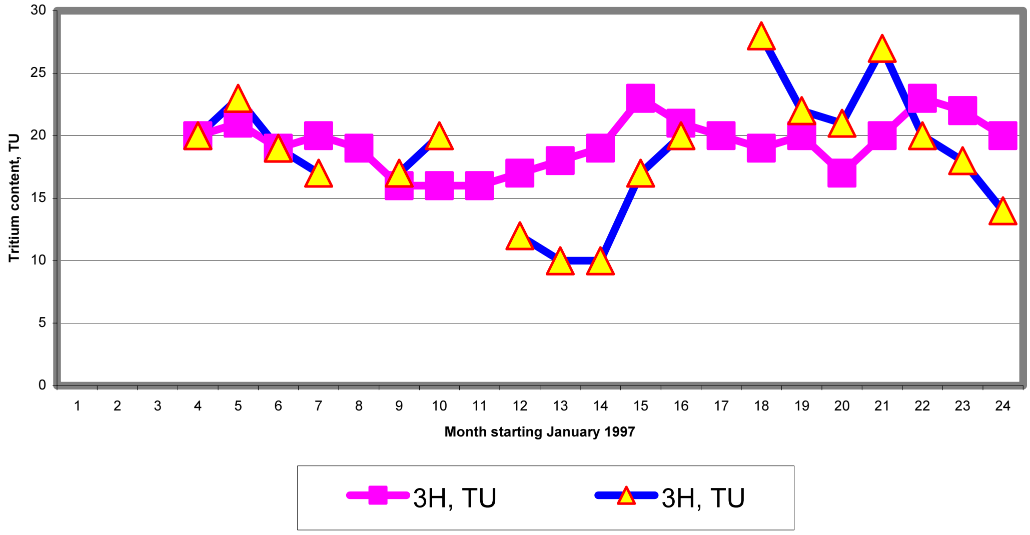
TABLE

Deuterium and Oxygen-18 (vs. SMOW) and Tritium (TU) in Volga River Water & Local Precipitation

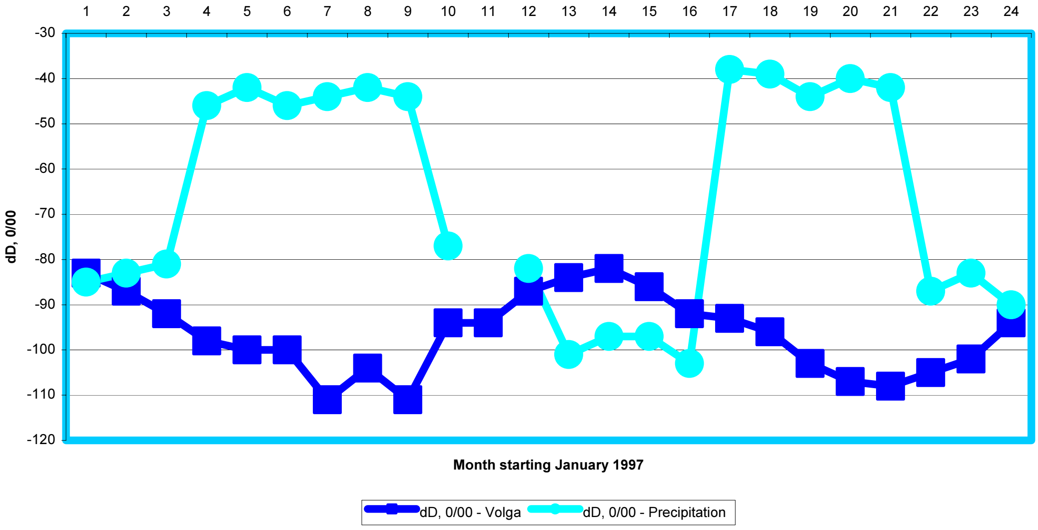
(Astrakhan hydrometeorological station, 46.25 N, 48.03 E, - 18 msl altitude)

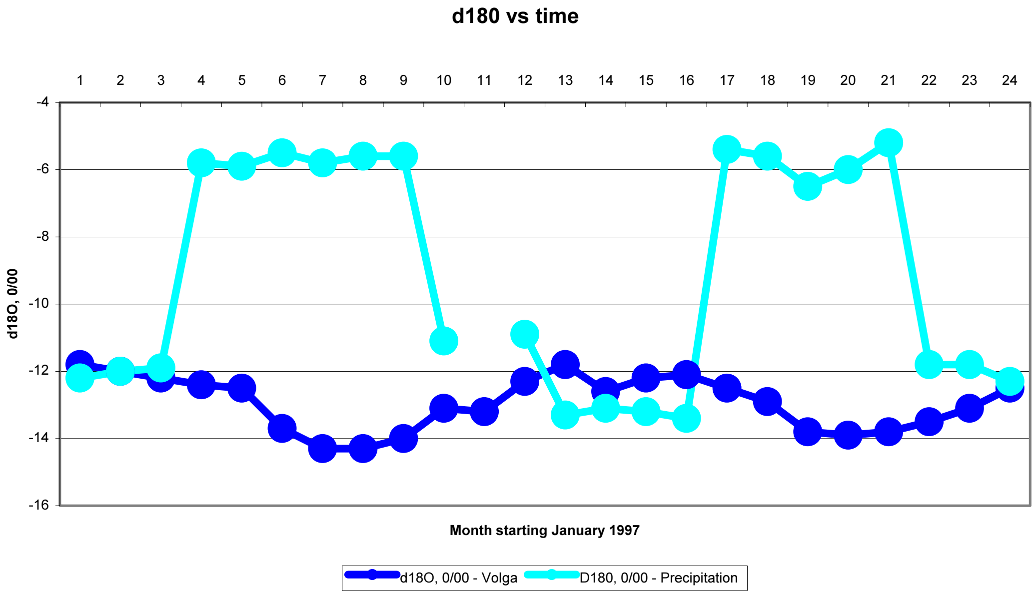
Year	Month	t^0C, water	δ^2H	$\delta^{18}O$,	^3H,	pH	t^0C	δ^2H	$\delta^{18}O$	^3H	Prec.,	Humid.
			‰	‰	TU			‰	‰	TU	mm	%
1997	1	0,2	-83	-11,8		7,79	-6,6	-85	-12,2		21,1	82
1997	2	0	-87	-12		8,32	-4,2	-83	-12		11	82
1997	3	4	-92	-12,2		7,67	2,9	-81	-11,9		18	75
1997	4	6,8	-98	-12,4	20	8,2	10,5	-46	-5,8	20	18,2	67
1997	5	9,4	-100	-12,5	21	7,99	18,8	-42	-5,9	23	11,8	59
1997	6	19	-100	-13,7	19	7,85	23,7	-46	-5,5	19	41,7	65
1997	7	23,8	-111	-14,3	20	8,2	24,5	-44	-5,8	17	80,9	67
1997	8	25	-104	-14,3	19	8,16	23,7	-42	-5,6		4,1	60
1997	9	18,3	-111	-14	16	8,12	14,8	-44	-5,6	17	8,9	67
1997	10	14,5	-94	-13,1	16	7,91	12	-77	-11,1	20	28,1	79
1997	11	6,4	-94	-13,2	16	8,08	2,6				0	81
1997	12	2,4	-87	-12,3	17	7,98	-4,2	-82	-10,9	12	14	83
1998	13	-0,4	-84	-11,8	18	8,15	-6,3	-101	-13,3	10	14,1	86
1998	14	0	-82	-12,6	19	8,08	-4,9	-97	-13,1	10	29,8	81
1998	15	-0,2	-86	-12,2	23	8	1,2	-97	-13,2	17	42,9	80
1998	16	0,5	-92	-12,1	21	8,05	11,4	-103	-13,4	20	68	66
1998	17	13	-93	-12,5	20	7,8	17,5	-38	-5,4		6,7	56
1998	18	19	-96	-12,9	19	7,94	26,6	-39	-5,6	28	12,9	56
1998	19	25,1	-103	-13,8	20	7,82	26,7	-44	-6,5	22	16,1	57
1998	20	28	-107	-13,9	17	8,1	24,1	-40	-6	21	37,4	59
1998	21	22,6	-108	-13,8	20	8,36	17,2	-42	-5,2	27	11,1	60
1998	22	12	-105	-13,5	23	8,58	10,6	-87	-11,8	20	1,4	71
1998	23	9,3	-102	-13,1	22	8,55	13	-83	-11,8	18	33,7	78
1998	24	0	-94	-12,5	20	8,1	-2,3	-90	-12,3	14	11,3	86
min			*-111*	*-14,3*				*-103*	*-13*			
max			*-82*	*-11,8*				*-38*	*-5*			
|2A|			29	2,5				*65*	*8*			
Ξ=								*2,24*	*3,2*			

Tritium records in Volga water & precipitation (Astrachan station)



Deuterium vs Time





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STABLE ISOTOPES AND MAJOR ION CHEMISTRY OF CONTINENTAL SALT LAKES FROM SOUTHERN, SPAIN

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In several lakes from Southern of Spain, the parameters geochemical and isotopic ($\delta^{18}O$ and $\delta^{2}H$) have been studied. The main objective was establish the hydrological regimen by analysing the relationship between surface and groundwater in the different lakes using both isotopic and the hydrochemical characteristics of their waters and to quantify the degree of correlation between these variables.

Lakes are systems that, although complex as is every natural system, are well fitted to the study of environmental isotopes. The origin and subsequent evaporative process of natural waters can be determined by the investigation of the relationship between the oxygen and hydrogen isotopes [1].

A total of four lakes have been selected and according to the results obtained, the hydrological dynamics and the relation between salinity and isotopic content within the lakes studied could be determined [2]. Two main hydrologic models have been established:

a) Lakes with a mainly epigenetic hydrologic regime, in which very high isotopic contents are not found, seeing as, they have not had continuous evaporite processes, but instead have frequently dried up in summer (temporary lakes). In such systems a “reflux brine” appears under the lake basin, and the brine magnitude is in proportion to the extension of the lake. It may be added that, even though the surface runoff is the main recharge component in the hydrologic cycle, these systems have some groundwater recharge when the piezometric levels are above the free water level and, so, they can store water even in low or zero precipitation periods in which, otherwise, they would dry up. In this way, an accurate classification would be epigenetic-mixed.

b) Lakes in which the water shows several evaporite cycles. These kind of lakes do not have a very high salt content, but a very high isotopic content. They are permanent lakes in which the principal water balance component is groundwater. The classification is hypogenic, according to the hydrologic regime.

There was no clear correlation between the isotopic content and the water salinity when all the data were analysed, due to the different water dynamics, but there were some trends observed in the separate analysis of the different wetlands. The dissolved salt effect, in this kind of salt lakes, decreases the thermodynamic activity of the water, and compensates or has an influence of the same magnitude as the heavy isotope increment of submitted to intense evaporation water.

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IAEA-CN-104/P-166

STABLE ISOTOPE COMPOSITION OF THE RIO DE LA PLATA ESTUARY: A CONSEQUENCE OF ITCZ MOVEMENT AND ENSO RELATED PHENOMENA

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The Río de la Plata estuary is the collector of a vast drainage basin of about 3.1 x 10^6km^2. Their major tributaries are the Paraná, Paraguay and Uruguay rivers. The main course of the Paraná river starts at the "Planalto do Brasil", located at the central east Brazil. Pilcomayo and Bermejo rivers contribute to Paraná water from the high Andes range. Paraguay river release water coming from the Mato Grosso. The Uruguay river, directly and the Iguazú river through the Paraná, also contribute water from braziliam east coastal hills to the estuary. Less significant are other rivers like the Salado, Negro, etc.

The objective of this work is to study the variations in isotopic composition of the Río de la Plata estuary and its correlation with the ITCZ, ENSO-related, and other meteorological phenomena. The methodoly consists in the monthly collection of a 2 liter sample in the estuary and the measurement of ^{18}O and ^{2}H concentration. An aliquot is reserved for further tritium analysis, mainly related to nuclear plants on the Paraná river.

In this report, we present 40 isotope analyses for the Río de la Plata estuary. Cyclical variations of oxygen isotopes, with minima in winter and maxima in summer has been observed, ^{2}H concentrations also change cyclicaly.

Figure 1 shows the ^{18}O variation that is influenced by the austral summer ITCZ that migrates to higher southern latitudes leading to an increased pluviosity and thus to an amount effect.

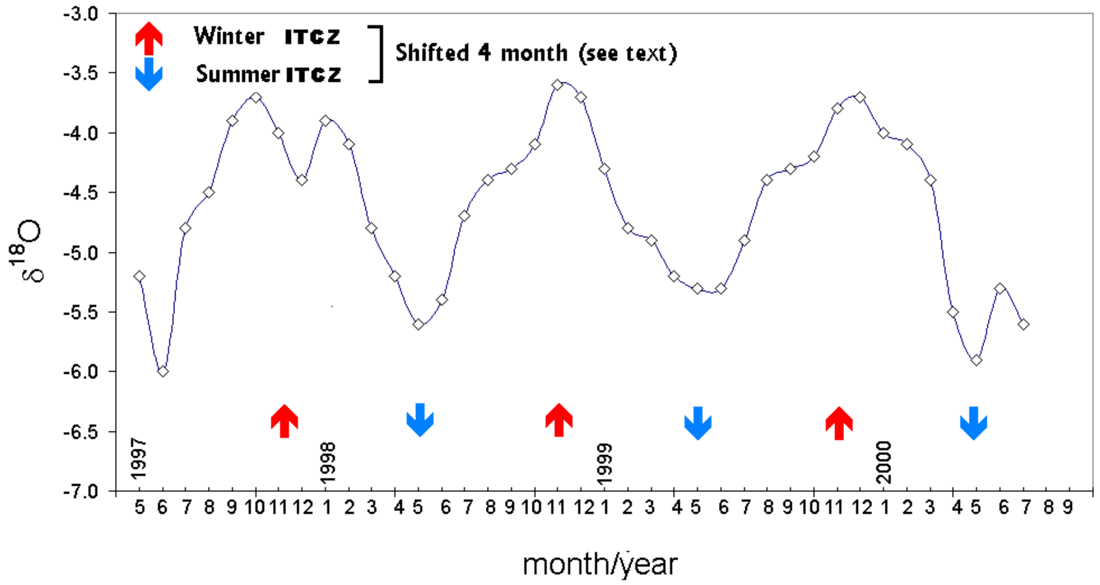

Figure 1 Cyclical variation of the oxygen isotope composition related to the ITCZ excursions.

(Albero and Panarello, 1982; Rozansky and Araguás Araguás (1995). The signal in the estuary is delayed in about 4 months due to the average transit time of water from the catching areas. The deuterium composition follows also a cyclical pattern but is strongly influenced by ENSO-related phenomema, "El Niño", which increases the ocean surface temperature, leading to an enhanced kinetic effect, that increase the "d" value and "La Niña" (cold episode) making the evaporation process occurs more close to isotopic equilibrium, resulting in a smaller deuterium excess (Figure 2).

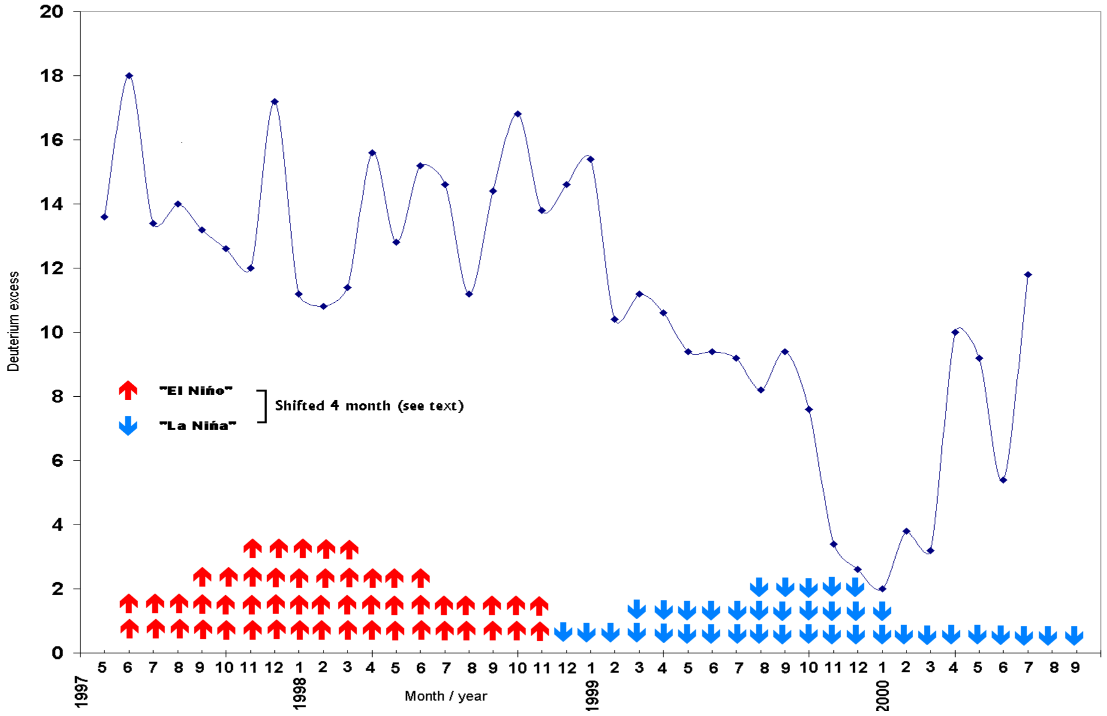

Figure 2. Variation of the deuterium excess and a semicuantititative approach to the El Niño, La Niña clycles. (The Southern Oscillation Index (SOI), 2000)

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STABLE ISOTOPE STUDIES OF INDIAN RIVERS

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To understand the surface water characteristics in India, the nine most important rivers have been sampled around the sub-continent. Both Oxygen 18 and Deuterium have been measured to determine the origin of the water and the possible evaporation process. Also the main ions have been analyzed to obtain complementary information. Where some basins have been previously studies, mainly in the North [1], this is a first attempt at a wider investigation of Indian rivers.

If we compare our results (see Figure 1) with the mean isotopic variation of rainfall over Indian as seen from the GNIP data set, a general NW/ SE isotopic gradient is revealed. The west coast and the south part of Dekkan are the least depleted in heavy isotopes, with a $\delta^{18}O$ values of between 0 and –2 ‰, and this relate to the Kaveri, Nethvrati and Krishna rivers. The area below the Thar desert displays a $\delta^{18}O$ value of around –3 ‰, as in the Narmada and Tapti rivers. The central part of the Dekkan and the east coast are characterised by $\delta^{18}O$ values of around –5 ‰, like for the Godavari and Mahanadi rivers. The North India big plains present $\delta\ ^{18}O$ value of between –6 and –12 ‰, like for the Ganga and Brahmaputra rivers.

For the Ganga and the Brahmaputra rivers, the seasonal effect is stronger due to significant variations in different water sources i.e.: i) perennial tributaries coming from the inland hills, or the ground water discharge, which contributes water moderatly depleted in ^{18}O (winter and spring), ii) Himalayan tributaries fed by snow and glacier melt which are very depleted in heavy isotopes (sommer and fall), and iii) the heavy monsoon rainfall (early summer) which can travel deep inland more lighter water.

As seen from the slope of the $\delta^{18}O$ and $\delta^{2}H$ regression and the calculation of the deuterium excess, the water of these rivers evaporates only slightly during the wet monsoon season (June-Septembre). Evaporation could be more intense before in the hot and dry season (April-May), as seen from sampling on the Yamuna River, the main tributary of the Ganga [2].

Better understanding the characteristics and water origin of these rivers will help to improve the management of the substantial water needs (potable water, irrigation, industry) of this expanding country. But also it can contribute to our understanding of means of flood control, drought prevention, hydroelectric power generation, and improvements in environmental quality

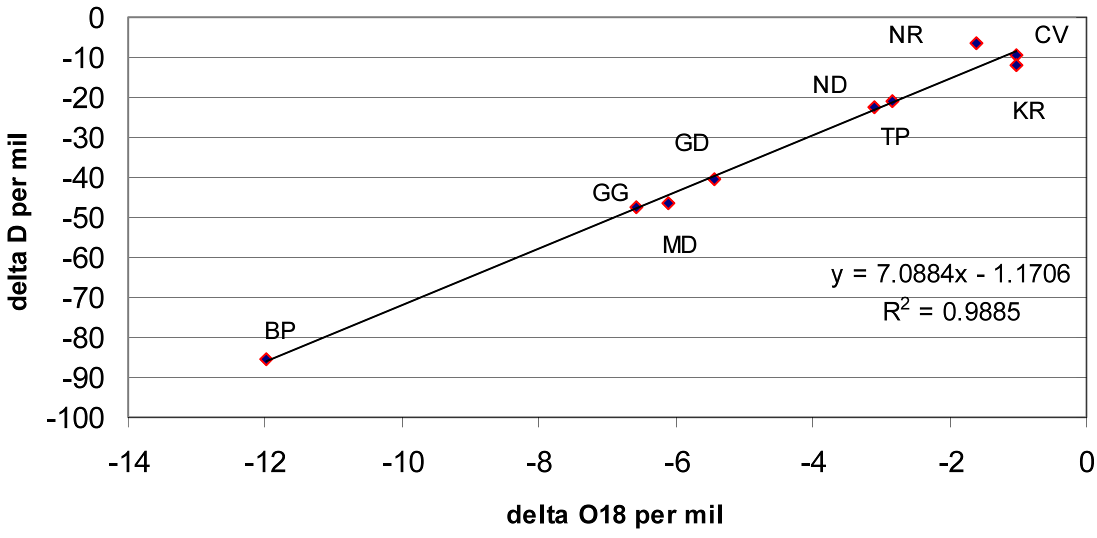

FIG. 4. Relation between $\delta\ ^{18}O$ and $\delta\ ^{2}H$ for the June 2002 sampling of the Indian rivers. (Brahmaputra: BP, Ganga: GG, Mahanadi: MD, Godavari: GD, Krishna: KR, Kaveri: C, Nethvrati: NR, Tapti: TP and Narmada: ND).

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δ^{13}C TRACING OF DISSOLVED INORGANIC CARBON IN THE PATAGONIAN RIVERS

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Dissolved Inorganic Carbon (DIC) transported by rivers originates from three main sources: (1) the dissolution of carbonate rocks (with a δ^{13}C close to 0‰); (2) the atmospheric CO_2, with a δ^{13}C of –8‰; (3) the soil CO_2 derived from the degradation of organic matter and root respiration (its δ^{13}C depends on the vegetation type: around –26‰ for C3 plants and –12‰ in for C4 plants). The soil CO_2 participates, after forming carbonic acid in presence of water, to the weathering of carbonate and silicate minerals.

Within the framework of the European project PARAT (INCO/DC), the main Patagonian rivers (Colorado, Negro, Chubut, Deseado, Coyle, Chico, Santa Cruz and Gallegos) have been sampled (eight sampling trips) between September 1995 and November 1998 to determine their chemical and isotopic composition, the origin of the suspended and dissolved river loads and their inputs to the South Atlantic Ocean. The Patgonian river waters are mainly suppied by the Andean Cordillera (lakes, glaciers, rain fall and snow melt). They cross the Patagon plateau (a semi-arid region) to reach the South Atlantic Ocean. The vegetation of these river basins is of C3 type (forests in the Andes and steppes in the plateau). The geological substratum is dominated by volcanic rocks, continental and marine sedimentary rocks with very few carbonates.

The $\delta^{13}C_{DIC}$ signatures measured at the mouth of these rivers varies between –12.8‰ and –1.8‰. So high values indicate first that the $\delta^{13}C_{DIC}$ is partially controlled by the atmospheric CO_2 according to the rivers and depending on the water residence time in the main channel. However, one can distinguish two groups of rivers: (1) rivers with high $\delta^{13}C_{DIC}$ values and very low seasonal variations (Santa Cruz, Colorado, Negro and Chubut) and (2) rivers with lower $\delta^{13}C_{DIC}$ and high seasonal variations (Deseado, Coyle, Chico and Gallegos). For the first group, $\delta^{13}C_{DIC}$ is mainly controlled by important exchanges with the atmospheric CO_2 due to lakes and dams which increase the water residence time and allow a better isotopic equilibrium with the atmospheric CO_2. A similar pattern could be observed for the St. Lawrence River [1]. It is important to note that these rivers supply 94 % of the total Patagonian river discharge to the South Atlantic Ocean. For the second group of rivers, the

$\delta^{13}C_{DIC}$ variations cannot be related to the discharge variations because few discharge data are available. But $\delta^{13}C_{DIC}$ values appear to be a mixing of two main sources: atmospheric CO_2 which tends to increase the $\delta^{13}C_{DIC}$ and organic carbon oxidation which decreases the $\delta^{13}C_{DIC}$ signature. Going from the Andes to the river mouths, the $\delta^{13}C_{DIC}$ tends to increase as a result of progressive equilibrium with atmospheric CO_2 for all rivers, excepted for the Coyle. For this river, the upstream-downstream $\delta^{13}C_{DIC}$ decrease exhibits the role of the organic carbon oxidation in the main channel. Indeed, the plot of the DIC isotopic signature versus DOC content shows that the less negative values of $\delta^{13}C_{DIC}$ correspond to the highest DOC concentrations (fig. 1). For low DOC content (corresponding to the Colorado, Negro, Santa Cruz), there is no relationship with $\delta^{13}C_{DIC}$, indicating that DIC is controlled by atmospheric CO_2 (fig. 1). When DOC content is more important (more than 2 ppm) we observed a decreasing trend for the $\delta^{13}C_{DIC}$ (Fig. 1). This relationship shows that, in the river, organic carbon oxidation or respiration contribute to increase the pool of DIC (eq.1: $CH_2O + O_2 \leftrightarrow CO_2 + H_2O$) and to lower its isotopic signature. C:N ratios measured in the river sediments average 4 and could indicate that in these rivers (except Gallegos) the organic matter is mainly supplied by phytoplankton production rather than by the soil erosion.

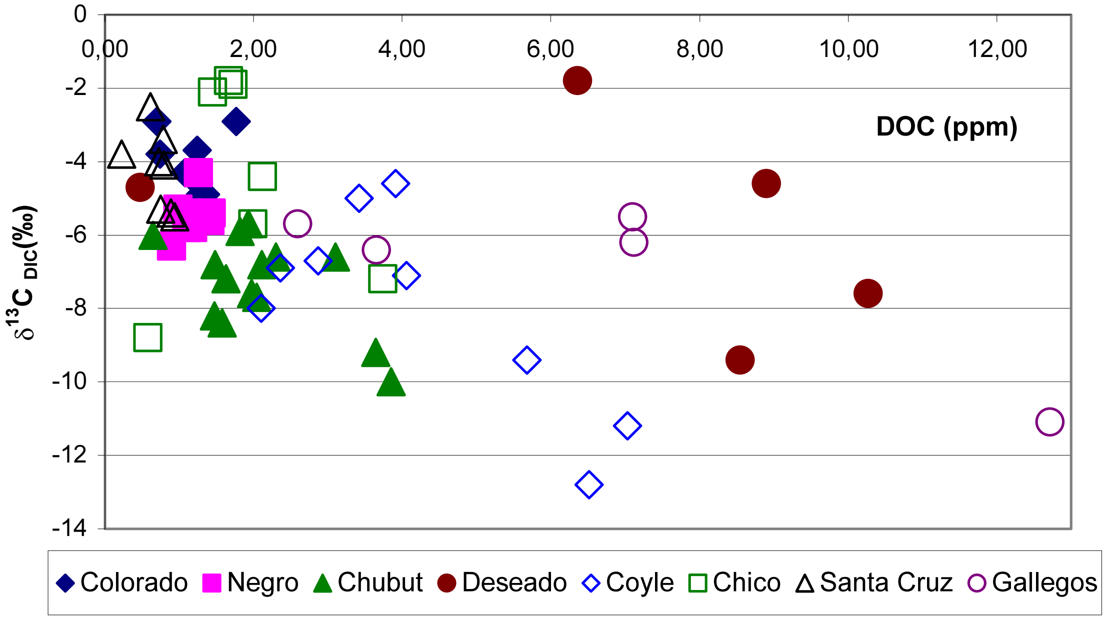

Figure 1: Relationship between $\delta^{13}C_{DIC}$ and DOC content.

In terms of DIC budget exported by the Patagonian Rivers to the South Atlantic Ocean, one can estimate a flux of 603.10^3 T/year of inorganic carbon. This result is comparable to the estimation of Ludwig *et al* (1996). The contribution of the Patagonian rivers represents 3.6 % of the total DIC flux exported by rivers to the South Atlantic Ocean. Average $\delta^{13}C$ value is estimated to –4.9‰. In spite of the low contribution at a global scale, the high value of the DIC isotopic signature of the Patagonian rivers must be taken into account for the carbon cycle modelling in this confluence zone of the South Atlantic Ocean.

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INTERACTION BETWEEN GROUNDWATER AND SURFACE WATER IN A COASTAL WETLANDS SYSTEM IN SOUTH WESTERN AUSTRALIA

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The Lake Warden wetlands system is located in Esperance, in South Western Australia and is formed within a basement rock depression. The wetlands system is connected to a certain extent to local and regional groundwater flow systems. As part of a larger investigation into the hydraulics of the wetlands system, temporal and spatial variations of the isotopic and chemical composition of water bodies within the system were investigated.

Lake Warden is the largest surface water feature in the system, and is hypersaline with chloride concentrations ranging from 26,000 to 46,000 mgL^{-1} (Fig.1). The chloride concentrations of groundwater taken from within the boundaries of the wetland system range widely from 7000 to 139000 mgL^{-1}. Creeks feeding into the wetlands range from brakish to saline (4600-19,600 mgL^{-1}) while groundwater taken from inland of the system is fresh to brakish (129-5500 mgL^{-1}). The coastal aquifer is the freshest water body in the region with chloride concentrations ranging from 96 to 538 mgL^{-1}.

Groundwater samples from inland and from the coastal plain are depleted in heavy isotopes, ranging from -31$^{0}/_{00}$ to -22$^{0}/_{00}$ (VSMOW) and -6.8$^{0}/_{00}$ to -5.3$^{0}/_{00}$ for δ^{2}H and δ^{18}O respectively. In contrast, samples from Lake Warden itself are the most enriched in heavy isotopes with values ranging from +17.4$^{0}/_{00}$ to +29.40$^{0}/_{00}$ and +0.65$^{0}/_{00}$ to +3.35$^{0}/_{00}$ for δ^{2}H and δ^{18}O, respectively. The values of the isotopic composition of deuterium (δ^{2}H) and oxygen-18 (δ^{18}O) reported for all samples have been corrected for salt effect [1].

The activity-corrected stable isotopic data (corrected for salt effect) are plotted in Figure 2. The isotopic composition of the weekly precipitation for the Esperance region (from April 2002 to September 2002) ranges from -54 $^{0}/_{00}$ to -5 $^{0}/_{00}$ and -9.7 $^{0}/_{00}$ to –2.8 $^{0}/_{00}$ for δ^{2}H and δ^{18}O respectively, defining the Local Meteoric Water Line, (LMWL): $\delta^{2}H = 6.7\delta^{18}O + 17.1$.

Most of the data points plot below the LMWL following a general evaporation/mixing line (line $\delta^{2}H = 5.2\delta^{18}O + 4.0$), which intersects the LMWL at δ^{2}H -36$^{0}/_{00}$ and δ^{18}O -8.1$^{0}/_{00}$. The data points representing the coastal plain and the inland groundwaters are close to the mean composition of the winter depleted precipitation and lie slightly below the LMWL. This may indicate that the groundwater is recharged by depleted winter precipitation which has been modified by some degree of evaporation during or prior to recharge. Seepage and creek water compositions show some enrichment with respect to inland groundwater, suggesting groundwater discharge into the creeks followed by evaporation. Winter lake samples evidence the highest degree of evaporation, with Lake Warden being the most enriched. The weekly isotopic results show that the enrichment in Lake Warden approaches a δ^2H value of $+31^0/_{00}$ before reversing as the salinity increases in the lake. The evaporation trend observed in the creeks and lakes is confirmed by the deuterium versus chloride relationship depicted in Figure 1. The isotopic composition of groundwater beneath the wetland system has an intermediate composition between the inland and coastal groundwaters, lake and precipitation end members while the salinity is much higher (Fig.1). This suggests mixing between all end-members accompanied with dissolution of salts.

The preliminary findings demonstrate that the lakes in the wetland system are connected in some manner and dominated by groundwater discharge. These data also form the basis of a hydrologic budget of Lake Warden wetlands system performed using the stable isotope mass balance method [2].

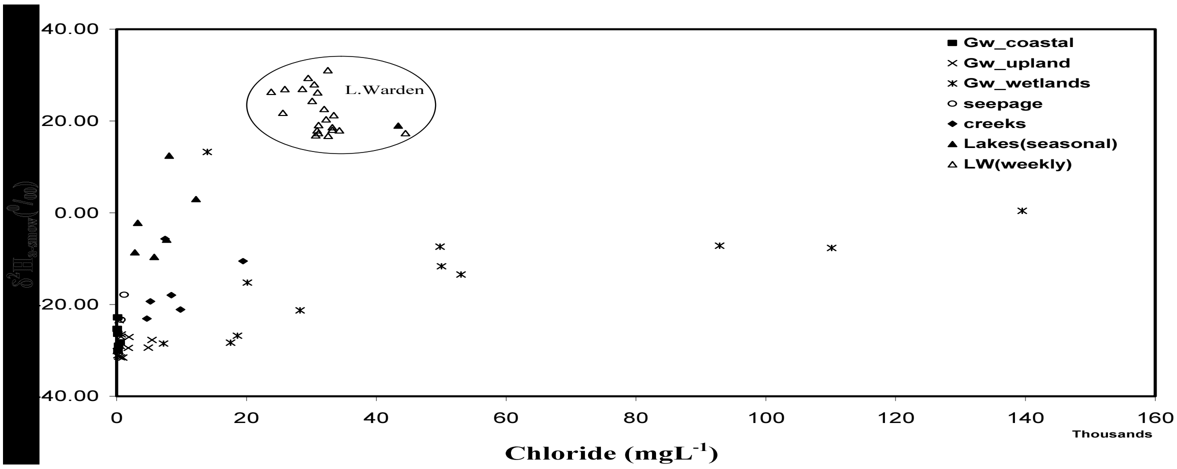

FIG. 5. δ^2H vs Chloride for Lake Warden wetlands system. LW denotes weekly samples for Lake Warden (8/5-24/9/02) and others denote winter (2002) samples

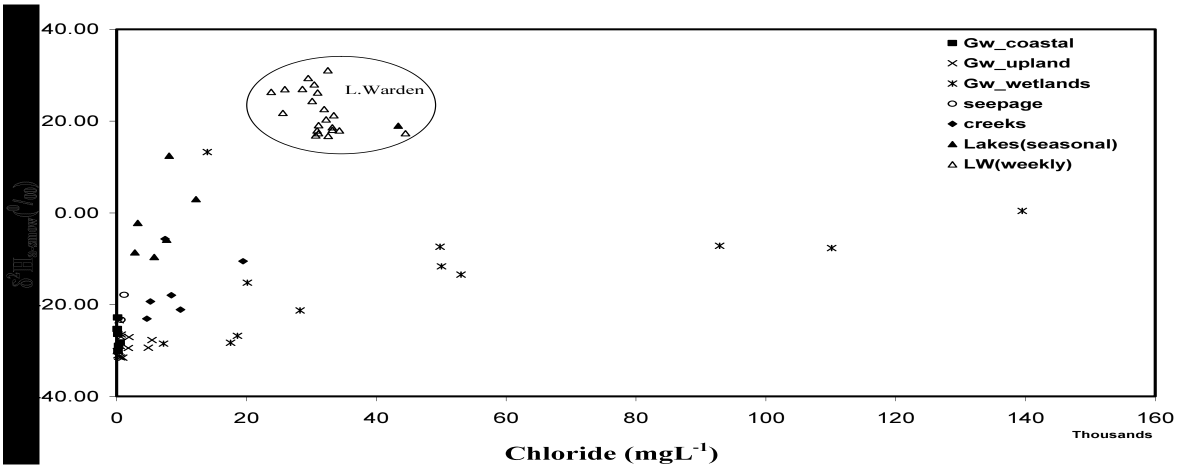

FIG. 6. A plot of $\delta^{18}O_a$ vs δ^2H_a (a- isotope activity ratios) for Lake Warden wetlands system. LW denotes weekly samples for Lake Warden (8/5-24/9/02) and others denote winter (2002) samples

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STABLE ISOTOPE RATIOS AND SULPHATE/METHANE INTERACTION IN LAKES

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This study concern sulphate ion and methane from about 50 freshwater aquifers from Poland. Samples have been collected dominantly in the late August and early September 1993. Eutrophic lakes show high $\delta^{34}S(SO_4^{2-})$ and $\delta^{18}O(SO_4^{2-})$ values as compared to clean oligotrophic or mesotrophic lakes. All lake sulphates fall into a restricted field (Fig. 1) and evolve along a positive $\delta^{34}S(SO_4^{2-})$ and $\delta^{18}O(SO_4^{2-})$ correlation line (R^2 = is 0.4, n = 147). The points behind the field represent rain from Wrocław downtown (SW Poland) or surficial lakewater collected during or just after heavy rains (Jędrysek 2000). In general, increase both in sulphur and oxygen isotope ratios results from: (i) bacterial reduction of the dissolved sulphate; or/and (ii) presence of oceanic origin sulphate - when $\delta^{18}O(SO_4^{2-})$ value do not exceed much more than 10 ‰.

Lakes and rivers from NE and SE Poland represent mesotrophic conditions and receive the lowermost in Poland acid rain impact. Consequently, they show lowermost $\delta^{34}S$ and $\delta^{18}O$ values. However, relatively high concentration of sulphate as compared to the low $\delta^{34}S$ value suggest that the sulphur, in these systems, comes mostly from acid rain or forms due to oxidation of some reduced forms of sulphur. The low $\delta^{18}O$ value evidences the second scenario. Thus, one can believe that the sulphate in the clean lakes is dominantly of natural origin (see e.g. [5]). The relatively high isotope signatures in some of NE Poland lakes result, most probably, from advanced reduction of the sulphate. On the other hand, low $\delta^{18}O$ as compared to sulphate concentration may suggest sulphide oxidation. The advanced reduction may result from the fact that the lake is very deep and narrow (width/depth ratio is about 0.1). Thus, the reduction in the bottom zone may proceed simultaneously to an active oxidation in shallower zone.

Mountainous lakes (SW and SE Poland) are expected to show strictly oligotrophic parameters. However, all of them show relatively high isotope values, especially as compared to the corresponding low sulphate concentration. This may suggest that the sulphate concentration violated individual biological abilities of lakes to buffer the anthropogenic sulphate. In the SE Poland, where the anthropogenic impact is limited, one may believe also that a significant portion of sulphate in mountainous lakes is of oceanic origin (^{34}S-enriched oceanic spray). This could be especially valid for Czarny Staw lake (1650 m asl), which is highly oligotrophic, without any signs of ongoing reduction, and negligible photosynthetic processes in the high mountains area above the lake (no source of organic matter).

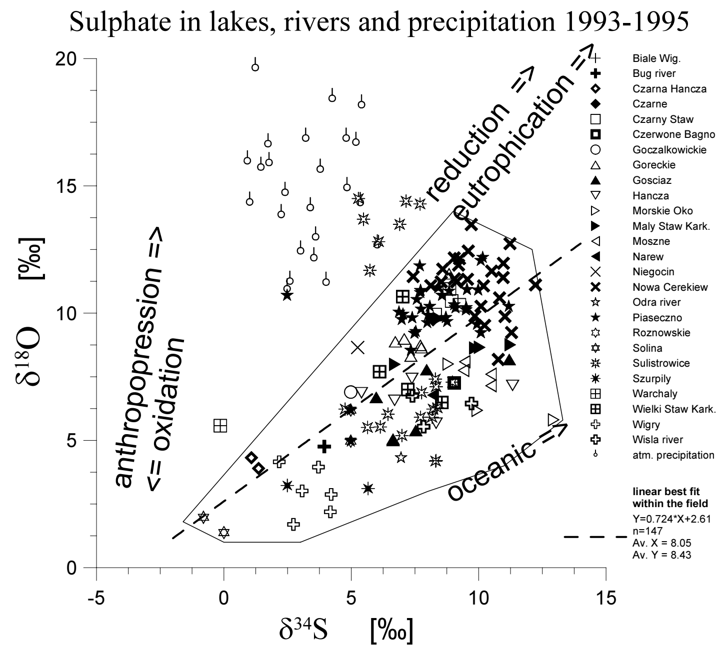

Fig. 1 Sulphur and oxygen isotope ratios in sulphate dissolved in lake water. Sulphur and oxygen isotope variations in lake water may results from some ongoing processes. The points behind the field represents rain from Wrocław downtown (SW Poland, see Jedrysek 2000) or surficial lakewater collected during/after heavy rains

On the other hand, reoxidation of S^{2-}-bearing compounds, in the presence of ^{18}O depleted mountainous water can be expected. This process could be important in SW Poland lakes, where anthropogenic SO_2 impact is extremely high [4]. The importance of red-ox processes in these lakes may be supported by isotope study of bubble methane (n = c.a. 400). Mechanisms of methanogenesis and potential oxidation of methane are main factors controlling concentration and isotope ratio in methane [e.g. ,1 ,2, 3, 6]. Likewise, sulphate is the main oxidant of methane and the methane precursors. In contrast to the other lakes, the observed negative correlation in the system $\delta^{13}C(CH_4)$ - depth of the water column, may be the result of the strong contamination by the SO_4^{2-}, exceeding the biological buffering abilities of the lake.

CONCLUSIONS:

1. Most lakes show an individual $\delta^{34}S$ and $\delta^{18}O$ signal and relatively little variations. It reflects trophy, red-ox and individual buffering potential for acid rain contamination
2. In contrast to not contaminated lakes, a higher carbon isotope ratios in methane at depths may result from strong contamination with sulphate ion

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UNSATURATED ZONE

ENVIRONMENTAL ISOTOPES AND EVAPORATION IN SHALLOW WATER TABLES SOILS

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An estimated 0.66 of a billion cubic meters of water is lost each year from the Nile Delta fallow soils using a physical model based on environmental isotopes profile data. Three times this amount is supplied to the root zone during the crop growing seasons through capillary rise. A modified water strategy should take into account this upward flow in order to optimize water management on the regional scale. The evaporation rate estimation and its extrapolation of capillary rise evaluation presented are subject to the working assumption. Some factors lead to certain difficulties, namely: the presence of secondary evaporation planes, highly developed structure cracking at the soil surface, clay dispersion in the lower layers, sporadic winter rains, micro climate fluctuations, slight depletion in the inner water molecules compared to bulk pore water due to the history of soil material humidification and, finally bulk density errors shrinking and swelling of soils.

Three sites been chosen covering the triangular shape of Delta; their characteristic features are described bellow:

1. Mansouryya profile site: It is located in Mansouryya experimental irrigation station near Giza City (about 15 km west of Cairo), i.e near the southern end of the Delta. The soil is moderately saline clayey loam.
2. Hoch Issa – Hararah profile site: It is located near Damanhour City, about 150 Km to the NW of Cairo, and west from Rossetta Branch of Nile by 45 km. The soil is saline clayey loam with the clay getting richer in the bottom layers.
3. Om El- Sienne profile site: It is located at Om El-Sienne site, Kafer El-Sheike Governorate, in the middle north saline belt of Nile Delta, about 120 km to the north of Cairo, and due to west of Domeitta branch of the Nile by 40 km. The soil is highly saline clayey.

Soil moisture was quantitatively recovered from each sample under vacuum by the first freezing of the sample by liquid nitrogen (-180 ^{0}C), then releasing the water vapour by heating the sample to 80 ^{0}C under vacuum. The isotopic composition of the collected moisture was then measured as δ^{18}O and δ D relative to SMOW on a double inlet isotope ratio mass spectrometer MAT 230 at Heidelberg in Germany. The δ^{18}O was measured after equilibrium with CO_2 and δ D after reduction of water over heated zinc ($\simeq$ 430 ^{0}C) with a precision $\pm$ 1% $_0$ (Sonntag, et al , 1985).

To estimate the evaporation rate at each site, the isotopic data obtained for the extracted soil moisture were treated using the isothermal steady state isotope profile modelling (Allison et al 1983 a, 1983 b) as explained above.

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SOIL 13C-CO$_2$ PROFILES UNDER A CORN CULTIVATED SITE: IMPACT OF A RAINFALL EVENT

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A 7 months experiment (from October 2001 to May 2002) was undertaken in a bare field after corn harvesting, situated at Velleron, in the south of France (43°91' N, 5°06' E). Velleron is located in an area labelled "zone vulnerable" with regard to major groundwater NO_3^- pollution due to agriculture practices (EEC 91-676 directive). The soil studied is a fluvic hypercalcaric cambisol (FAO classification) and was cultivated with corn during two years. Water table fluctuations allowed the existence of temporary anaerobiosis (reduction-oxidation stains). The objective of this experiment was to follow C and N elements behaviour in the unsaturated soil zone (2.5 m thick), thanks to corn residue decomposition and leaching in the soil profile. We put several apparatus in the soil profile to follow soil water content, gas and temperature.

These probes were:

- Temperature sensors, installed at 5, 20, 60, 100 and 170 cm depth
- Tensiometers, installed each 20 cm from 20 to 220 cm depth
- Capacitive probes, installed each 20 cm from 20 to 160 cm depth
- Gas probes, installed each 20 cm from 20 to 200 cm depth
- A piezometer reaching 300 cm depth
- A pluviograph

Temperature sensors, tensiometers and capacitive probes are electronic probes connected to a data collecting apparatus. With gas probes, we followed CO_2, O_2, N_2 and N_2O concentrations.

One of the objectives was to determine the ^{13}C gas profile and also to evaluate rainfall effect on soil CO_2 production and $^{13}CO_2$ isotope.

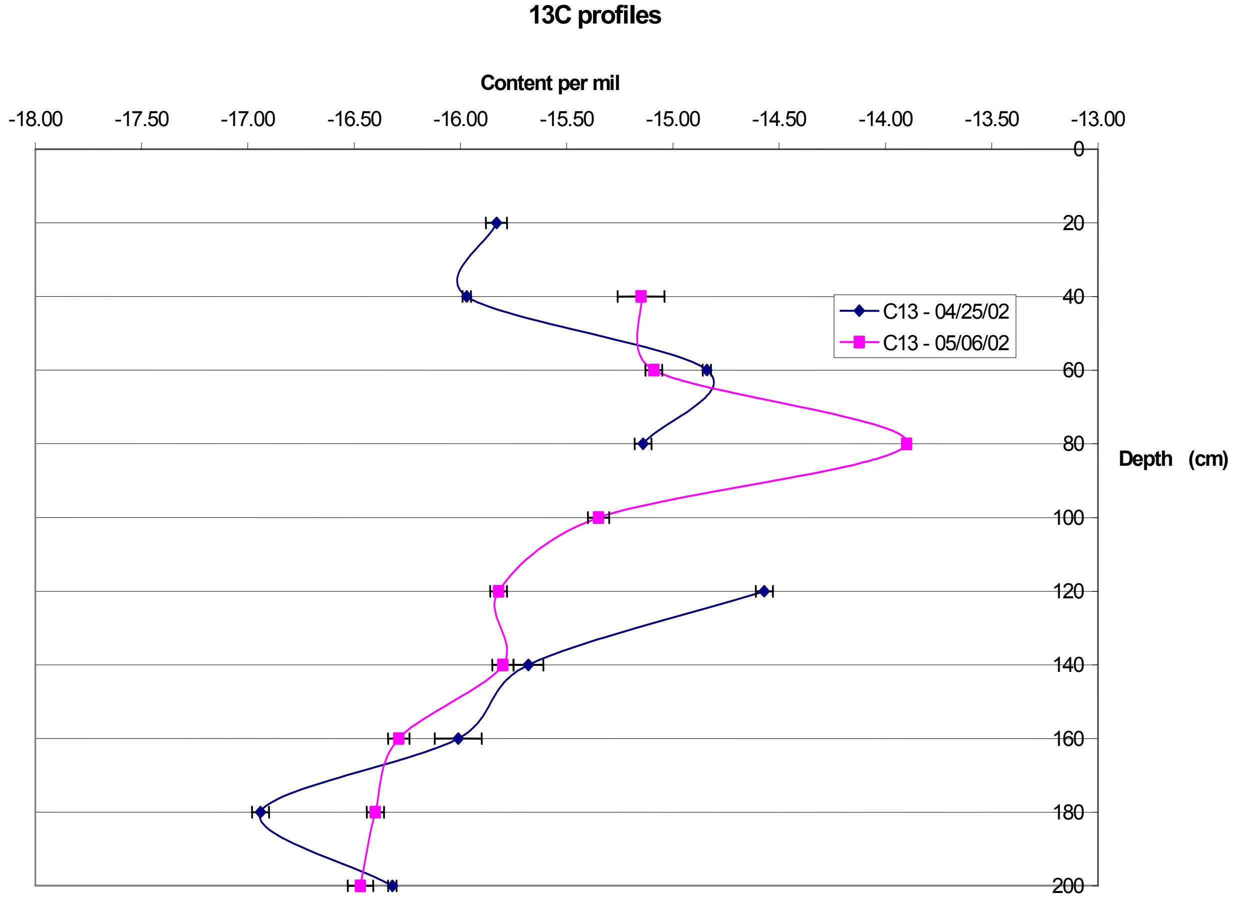
Then, two soil $^{13}CO_2$ profiles (figure) were established before and after a rainfall event (55 mm), at the beginning of May 2002, and discussed relative to CO_2 gas diffusion, soil texture and composition (organic carbon content), soil water content and microbial respiration measurements. The last has been carried out by O_2 consumption measurements on soil samples re-wetted and equilibrated at a 0,001Mpa water suction for 48h at 20°C.

As expected for a soil cultivated with C_4 plant, isotopic ^{13}C content varies from – 16,94‰ to – 13,90‰ with a mean of – 15,70‰ becoming more depleted with increasing depth. These relatively depleted values are in agreement with those usually observed at the end of vegetal cycle [1].

Compared to theoretical models which show $^{13}C-CO_2$ variations related to depth and CO_2 diffusion [2], we observed some discrepancies along the profile, such as:

i) relatively depleted values near the ground surface
ii) continuous depletion but irregular under 100cm
iii) some levels with enriched values. This highlights the high biological activity near the surface and influence of mineral sources.

After raining, CO_2 gas and water contents significantly increased up to more than 100 cm depth. 13C values variation give evidence of increased microbial activity, and in low permeability levels, a CO2 diffusion significantly limited by water content.



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GEOTHERMAL

A PRELIMINARY CONCEPTUAL GEOTHERMAL MODEL OF THE GEOTHERMAL SYSTEM OF KIBIRO, UGANDA

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Abstract

Kibiro hot springs discharge water of Na-Cl type, and of neutral pH with 5 g/L of total dissolved solids [1]. In order to provide hydrological information for the assessment of fluid origin and geothermal energy potential of hot springs in the geothermal prospect, water and rock samples from 39 sampling sites (30 cold water, 4 hot water and 5 rocks) (Figure 1) including Lake Albert, rivers, boreholes, dug wells and a rainfall sample as well as hot springs were collected for chemical, isotopic ($\delta^{18}O$ and $\delta^{2}H$), Tritium, $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$ and $^{87}Sr/^{86}Sr$ isotope analyses from 1999 to 2002.

METHODS

Standard sampling procedures of the IAEA were employed for water sample collection. Grab rock samples were taken of the country rock, and intrusives in the surrounding areas to the geothermal prospect. Agency's Isotope Hydrology Laboratory performed water chemistry analysis. Stable isotope and tritium analyses were sponsored by the IAEA but performed by the Isotope Hydrology Laboratory at GSF Munich, Germany and $^{87}Sr/^{86}Sr$ by IGG, Pisa, Italy.

RESULTS

The water samples were analyzed for stable isotopes of ^{18}O and ^{2}H with respect to VSMOW. The water compositions are restricted in the ranges $\delta^{18}O = -0.73‰$ to $-3.58‰$ and $\delta^{2}H = -0.4‰$ to $-15.2‰$, suggesting that the waters are all related to each other. Lake water compositions are strongly enriched (with $\delta^{18}O = +5.23‰$ and $\delta^{2}H = +37.2‰$) due to strong evaporation effects. Hot spring water samples lie on the Local Meteoric Water Line of Entebbe expressed as follows: $\delta^{2}H = 8*\delta^{18}O + 12.3$, which is slightly different from the Global Meteoric Water Line (GMWL) expressed as follows: $\delta^{2}H = 8*\delta^{18}O + 10$. This suggests a similar origin of the geothermal water and the local groundwater. The hot spring waters show a $\delta^{18}O$ enrichment of about 1‰, which implies water-rock interactions either due to high-temperature (>200°C) at depth or low water/rock ratio as a result of low permeability (Figure 2). Tritium values range from 0.13 to 3.5 TU, suggesting that the residence time of the waters is greater than 50 years. Strontium isotope ratio of the rocks in the region shows two major categories of signatures, a higher one between 0.7800 to 0.8000 for gypsum and feldspathic gneiss, and a lower one below 0.7300 Thermal waters generally have high Sr concentration and the $^{87}Sr/^{86}Sr$ ratio falls in the lower range as compared that of the rocks.

Deep temperature based on direct calculation of quartz geothermometer is 150°C. Cation geothermometers such as Na/K give a higher temperature of 220 to 240°C Two hot spring samples were analyzed for aqueous sulphate and the Oxygen-18 geothermometer [2] indicates temperatures of 120 and 150°C, respectively, which is in agreement to that by quartz geothermometer.

CONCLUSIONS**:**

1. The chemical composition of the geothermal discharges at the Kibiro hot springs of Uganda is characterized by slightly high salinity and neutral pH suitable for most geothermal utilizations.
2. Stable isotopes of the thermal waters point meteoric recharge but affected by water-rock interactions, implying a relatively longer residence time, confirmed by Tritium data, low water-rock ratio and probably low permeability.
3. Chemical and isotopic geothermometers yield a reservoir temperature of 150°C, but a deeper reservoir may also exist with temperatures in the range of 220 to 240°C.

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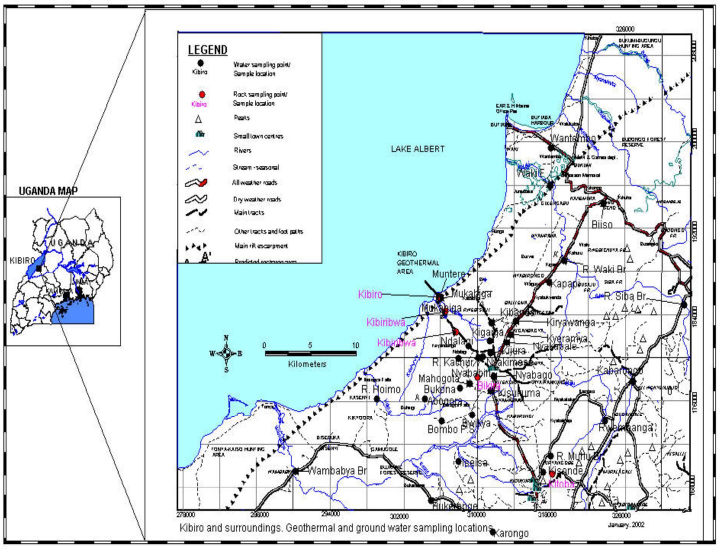

Figure 1: Kibiro and surrounding. Geothermal, surface and ground water sampling points

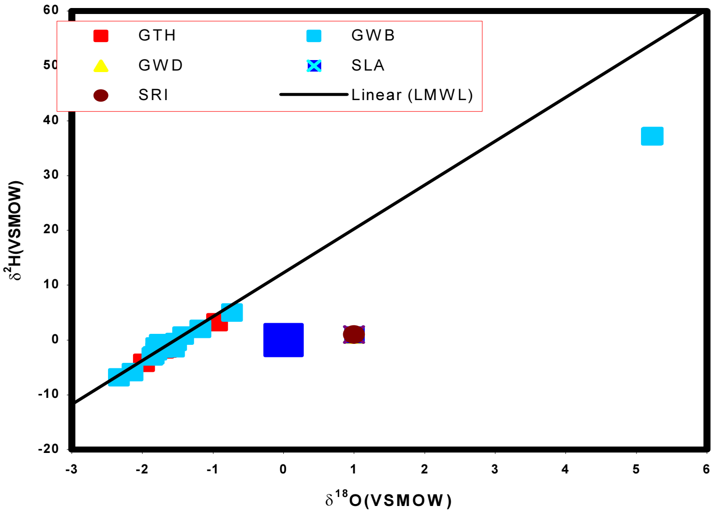

Figure 2. Isotopic composition of natural water samples from Kibiro geothermal area, Uganda

THE GEOCHEMISTRY OF THE STABLE ISOTOPE COMPOSITION OF THE THERMAL FLUIDS IN CENTRAL JORDAN

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Chemical analysis of 38 wells discharge thermal fluids in central Jordan near (Khan Ezabeeb area), and chemical characteristics of the thermal fluids were studied. 6 samples from cold water and 6 samples of thermal water were sampled from all over the Jordan for comparison purposes, 22 and 7 samples were reviewed and studied for stable and radioactive isotope respectively.

The data was interpreted by the use of WATCH program for speciation and construction of mineral equilibrium diagrams and other graphical presentation and classification. The maximum reservoir temperature for the wells predicted by calculation of various geothermometers exceeds 80°C.

There is an evidence of mixing with cold water, for plot of O18 versus Cl and a linear relationship between Cl versus Br and B. The calculated Quartz and Chalcedony, for the geothermometers values of the geothermal well waters indicate that reservoir temperature about 60°C - 80°C, and the Na-K-Ca geothermometers give mostly higher values for the wells, however, the calculation of mineral saturation indicates that the geothermal water shows fluid from some of the wells which is about to be close to the equilibrium at 115?C, and some degree of under saturation with anhydrite, fluorite and chalcedony.

The chemical composition of the waters in the studied area is governed by water rock interaction in area concerned and the ($Cl-SO_4-HCO_3$), (Na - K - Mg) triangular diagrams and stable isotopes were used to classify the geothermal and cold waters and to study some processes in the geothermal system, the geothermal waters are bicarbonate type with some samples of chloride and sulfite type, indicating reactions with sedimentary rocks (sandstone), the origin of the fluids are of meteoric water and the age extends 20,000 up to 38,000 years.

GEOCHEMISTRY OF THE GEOTHERMAL SYSTEM OF PAIPA, COLOMBIA

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The geothermal system of Paipa is located in the Eastern Cordillera of Colombia in a sedimentary geological environment, where volcanic bodies of acidic composition occurr on the surface. About 25 km SE from Paipa, in a similar geological setting, the geothermal area of Iza is found. In order to study the water origin and energy potential of Paipa and Iza geothermal prospects of Colombia, water samples from 40 sampling sites including rainfall stations, rivers, springs and dug wells were collected for chemical, stable isotopic ($\delta\,^{18}O$ and δ^2H) and Tritium analyses in 2001. Preliminary interpretation of results is presented here.

The chemical composition of the hot springs at Paipa geothermal area is dominated by a sodium sulfate source, which also characterizes the water chemical composition of shallow groundwater. A mixing relation between low and high temperature springs is inferred, in first place, from the relative Na-K-Mg composition, illustrated in Figure 1, in which the warm shallow water from a dug well (PP-21), is the concentrated end-member. Likely, the mineral source is very rich in mirabilite ($Na_2SO_4.10H_2O$), a non-marine evaporite which was identified by X-ray Diffraction as well as on the earth surface in its anhydrous form (thenardite). On the other hand, Paipa springs show high $\delta\,^{18}O$ and δ^2H enrichement following the mixing line illustrated in Figure 2, which again shows that sample PP-21 is the most enriched end of this mixing process.

Based on the surface temperature, salinity, and isotopic enrichment of the sample PP-21, it is postulated that such an enrichment is not originated by fluid-rock interaction occurring in the geothermal reservoir and that probably the source of salinity and heavy isotopes is the same, that is the dissolution of the mineral mirabilite. Hydrated minerals such a gypsum originated by deposition of sulphate in equilibrium conditions with the saturated mother brine show an isotopic enrichment following evaporation lines (Sofer, Z., 1978). However in the case of Paipa's springs, the slope of 1.38 does not fit to an evaporation line. This could be due to other possible isotopic exchange processes, promoted by the low melting point (32°C) of the mirabilite, which would prevent the mineral to keep the isotopic composition of formation.

Geothermal conservative species (Cl, B) do not follow a correlation with temperature, but seem to be controlled by the contribution of the inferred saline source for both cold and hot waters.

Quartz geothermometer gives 120°C in the reservoir. However from the Enthalpy-silica mixing model, which corrects the dilution effect of the silica, a much higher temperature (160-230°) is projected.

The three hot springs from Iza area are low in salinity (<2 g/L). They are chloride-bicarbonate waters typical of water dominated geothermal systems. Assuming the existence of feldspars at depth, the calculated Na/K temperature of the reservoir is between 240 and 290°C. These springs are very much affected by dilution with cold shallow water, as the quartz geothermometer indicates 110-120°C. However, after correcting the dilution effect by applying the Enthalpy – silica model, points out a temperature of 260°C, which agrees with the Na/K temperature.

In conclusion, both Iza and Paipa are high temperature geothermal systems. Hot springs from Paipa lose the deep geothermal water chemical and isotopic signatures because of the influence of a concentrated saline source. Paipa system can be better characterized if exploratory wells are drilled.

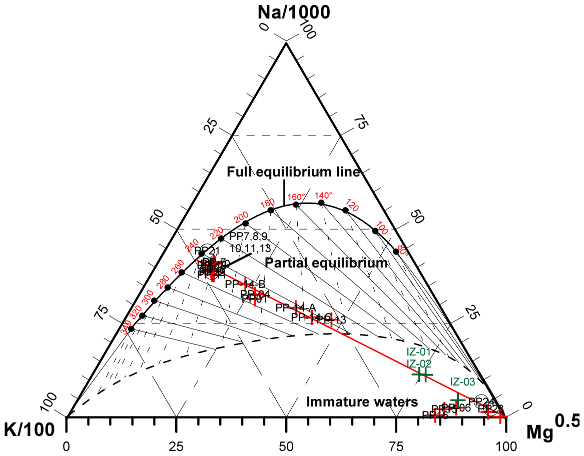

***Figure 1**. Relative Na-K-Mg composition for water samples from Paipa Geothermal area. A linear trend suggests the existence of a mixing process, in which PP-21 a shallow high salinity water at 21°C, is the sodium concentrated end-member. The composition of the springs do not reflects the equilibrium at the reservoir and from this Na/K and K/Mg geothermometers are not reliable. The low salinity samples from Iza (IZ) show a high dilution. Their Na/K geothermometer are higher than 240°C.*

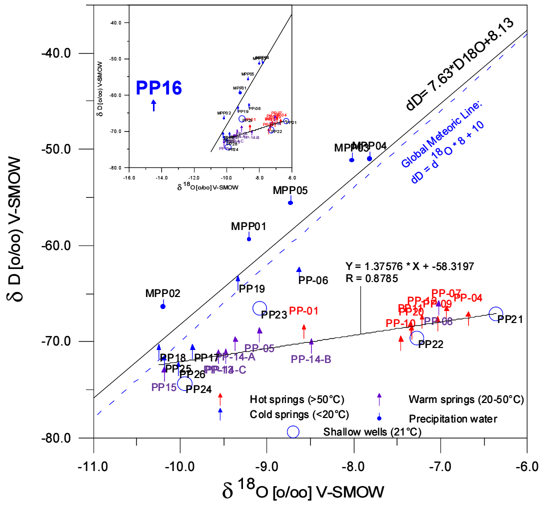

***Figure 2**. Stable isotopic composition of hot, warm and cold water samples from Paipa geothermal area. Hot and warm ground water show $\delta^{18}O$ and δD enrichment. The warm spring El Hervidero (PP16) exhibits a significant $\delta^{18}O$ decay, which has been explained by Bertrami et al. (1992), as the high oxygen-18 exchange with CO_2, which discharges abundantly and permanently in that spring.*

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ISOTOPE AND GEOCHEMICAL STUDY OF THE GEOTHERMAL FIELDS OF CHIOS ISLAND, GREECE

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The study area is located in the west part of Aegean sea, in the Chios Island. Chios is characterised by a strong geothermal activity especially in the area of Aghia Eleni and Agiasmata where the temperature ranges from 26 - 54°C. In the framework of a 1998-2001 bilateral research programme between Italy and Greece, geochemical and isotope investigations were conducted on spring and water wells of Chios in order to improve the knowledge on the geothermal potential of the island.

A number of hydrothermal manifestations were found in the northern and southeastern parts of the island, namely in the areas of Nenita-Thimiana, Patrika, Aghia Eleni and Aghiasmata. In the plain of Nenita the outcropping formation is entirely constituted of neogene fluvio-lacustrine deposits which act as the impervious cover of the underlying hydrothermal acquifer. The springs of Aghiasmata issue from the lower-middle Miocene volcanic formations.

Groundwater samples from boreholes and springs were collecteand analysed for major cations and anions (Cl^-, NO_3^-, SO_4^{2-}, Na^+, K^+, Ca^{2+} and Mg^{2+}), for stable isotopes of water (^{18}O and D), and aqueous sulphate [$^{18}O(SO_4^{2-})$ and ^{34}S]. Moreover temperature, conductivity and pH are measured in the field. A study of ionic and isotopic contents shows that thermal springs (Aghia Eleni and Aghiasmata) of Chios Island are fed by seawater. In the case of Aghia Eleni the big marine contribution (89%) disturbs the chemical and isotopic geothermometers. In the case of Aghiasmata the geothermometers suggested equilibrium temperature near 200°C. For the boreholes of the southern part of the island the initial temperature is estimated in the order of 80-90°C.

CHEMICAL AND ISOTOPIC ($\delta^{18}O$, δD) BEHAVIOR OF THE LOS HUMEROS (MEXICO) GEOTHERMAL FLUIDS

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Chemical and isotopic ($\delta^{18}O$, δD) data of fluids from the Los Humeros geothermal field wells collected before exploitation, were used to obtain the total discharge and the reservoir liquid phase compositions to obtain reference values which are useful to investigate reservoir processes during exploitation. Gas equilibria (FT-HSH2 method) [1], was used to estimate both, the reservoir temperature and the reservoir excess steam. The reservoir temperature ranged from 280°C for the upper liquid-dominated reservoir to 330°C for the deeper, low-liquid saturation reservoir. Excess steam values were lower for the upper reservoir while for deeper, mostly steam wells (H-23 and H-18) such values were almost 100 % [2]. Reservoir data interpretation indicated that a multi-steam separation process with condensate counter-flows occurs in the Colapso Central zone, this process is schematically shown in Fig. 1 where the elevation of production zone vs δ^{18} O values were plotted. This process explains the wide range of isotopic composition of the fluids, which was found to be from –1.2 (well H-18) to –6.7 (well H-16R) for δ^{18} O; and from –52.2 (well H-18) to –80.4 (well H-16R) for δD. The multi-separated steam is produced by wells H-10 at an elevation of 742 m. a. s. l.; H-16 at an elevation of 790 m. a. s. l. and subsequently by the well H-16R (H-16 after repaired) at an elevation of 1400 m. a. s. l.

The convective process transports non-volatile specia to the shallower levels of the reservoir where higher CO_2 concentrations in the reservoir liquid were obtained, (Fig. 2). The convective process can be the responsible for the HCl presence in well H-16 as well as in other wells in the Colapso Central zone. Exploitation of the upper reservoir in the Colapso Central, has caused the ascent of hotter fluids through fractures and a heating process for this zone was also inferred.

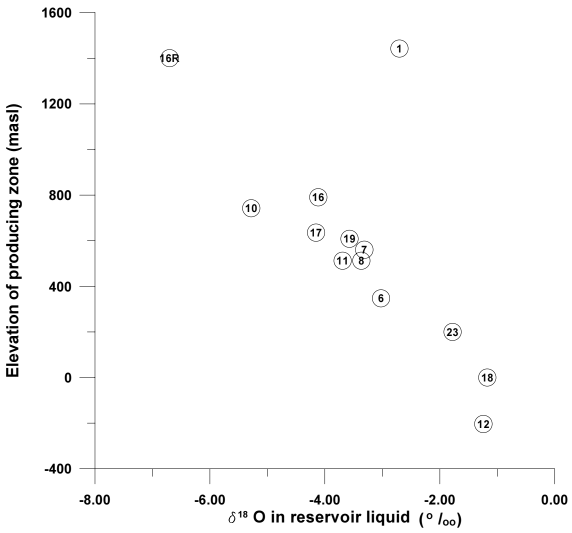

FIG. 1 Elevation of production zones of wells vs δ^{18} O in reservoir liquid.

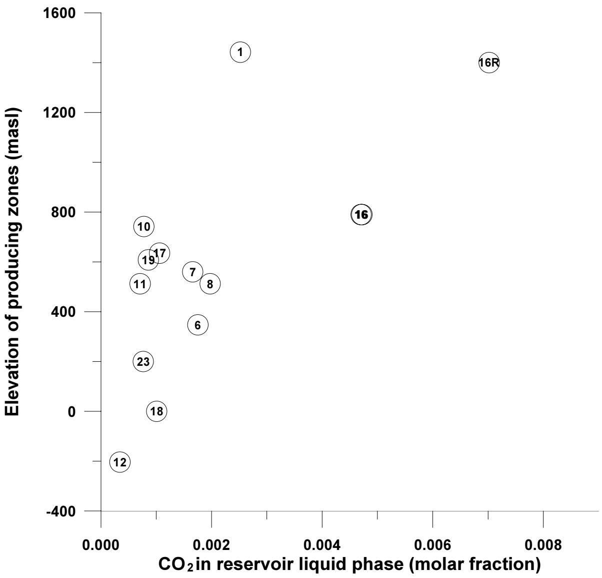

FIG. 2 Elevation of producing zones of wells vs CO_2 in the reservoir liquid phase.

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ORIGIN AND BEHAVIOUR OF NOBLE GASES IN THE GEOTHERMAL FLUID OF PALINPINON (THE PHILIPPINES) AS TRACED FROM THE CONCENTRATION AND ISOTOPIC COMPOSITION

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The use of noble gas isotopes to study geothermal fluids as an aid in reservoir management is a relatively new and unexplored field. Most of the work done on noble gas geochemistry deal with origins and composition of mantle noble gases or monitors and interprets changes in volcanic areas and natural gas fields. Few studies are actually tackling the effects of field exploitation on noble gases composition and isotopic ratios. The noble gases, due to their peculiar characteristics such as chemical inertness, low solubility in water and well-known and relatively invariant composition in natural reservoirs (mantle, crust and atmosphere), are in principle useful for detecting and monitoring processes affecting the geothermal reservoir. One process currently investigated is re-injected water returns, for which noble gases complement, and in some cases are more sensitive than, other tracers like as chloride and stable isotopes.

We applied the noble gases geochemistry to the Palinpinion geothermal fluids to investigate their origin and the reservoir processes occurring in the field. This study is part of a technical co-operation project funded by the International Atomic Energy Agency (TC PHI/8/023). The isotopic and elemental compositions of noble gases in geothermal fluids were measured in eleven wells of Palinpinion geothermal field (Philippines), carefully selected to obtain a representative spectrum of the fluids.

Most of the isotopic ratios of noble gases of Palinpinon samples are close to those of air. The only exception is helium, which is in large excess in all the samples and exhibits a clear mantle isotopic signature. In fact, the R/Ra range of helium is 6.5-8 and falls in the widely accepted range of 6-8 typical of mantle in the Pacific subduction setting.

The concentration of noble gases is expressed as $F(^{a}X)$ (where $F(^{a}X) = (^{a}X/^{36}Ar)_{sample} / (^{a}X/^{36}Ar)_{air}$ and ^{a}X is a specific isotope such as ^{20}Ne), i.e. is normalised through ^{36}Ar (which derives solely from air dissolution). It appears that there is a systematic depletion in Ne accompanied by enrichment in Kr and Xe.

Using simple boiling models, the bulk concentrations of the samples were evaluated in relation to possible sources and effects of reservoir processes. We assumed that the meteoric water recharging the geothermal reservoir is equilibrated with air at 20°C and then heated at 300°C. These conditions are believed to likely approximate those of Palinpinon.

Steam dominated wells almost exactly fit the line representing the steam separated from deep fluids by a single step boiling process, while most liquid dominated wells fit that of steam separated by a multi-step boiling in a temperature range of 285 –290°C. These processes well explain the observed depletion in light noble gases (Ne and Ar) and increases in heavy (Kr and Xe) noble gases.

The temperature estimation for the recharge meteoric fluids is higher than 20°C for all the samples and falls in the range 40-120°C. This indicates that the steam is originated by a fluid which is the result of mixing between a meteoric recharge water and probably the re-injected fluids. In fact the lowest temperature (<40°C) is showed by the only well strongly affected by re-injection fluids return.

In conclusion noble gases are sensitive tracers of origins and processes occurring in the reservoir of geothermal fields. In the case of Palinpinion, the high R/Ra ratios of helium points to mantle derived magmas as heating source of the geothermal system. Noble gases isotopic and elemental composition indicates that in Palinpinion geothermal fluids are mainly derived from a multi-step boiling of water equilibrated with air mixed with re-injected residual fluids. The rapid decline to very low content of noble gases in fluids is due to their low solubility, which makes these elements well suited to investigate boiling processes.

IAEA-CN-104/P-116

CHARACTERIZATION OF THE KHOY GEOTHERMAL AREA /NW IRAN BASED ON ISOTOPE AND CHEMICAL INVESTIGATIONS

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The Khoy geothermal system is located in the extreme northwest of Iran, about 30 to 40 km from the Turkish border and about 30 km southwest of the city of Khoy (Fig. 1). They main thermal and mineral springs are observed along an approximately 2 km long segment of the north bank of the Qotur Chay (Qotur River).

Figure 1. Geothermal prospects in northwestern Iran.

The study area is also situated within a zone with active tectonic features in which different geological formations are set close together. A granitic batholith is detected at the depth of 200 meters below the riverbed, using drilling and gravity investigations [1], [2].

The oldest formations are metamorphic rocks of Mesozoic or older. The Cenozoic formations are clastic sediments and limestones. In this area several horst and graben systems parallel to this valley exist. The Qotur valley itself coincides with a fault zone and is filled with clastic sediments. The Quaternary formations consist of old sediments of Qotur River bed and travertine sediments of thermal and cold springs, forming lowland around the river.The hot water outflows are most probably related to the occurrence of this Qotur fault system.

Based on the data of the analysed samples of the July 2002 survey of normal low mineralized cold, mineral and hot thermal water spring outflows, including also an artesian borehole and the water of the Qotur river upstream and downstream of the investigated thermal area the following chemical characterisation results

- Cold Groundwater are of Ca-Mg-HCO_3 type as represented by spring of the Avri mountain area (K7) and the cold water spring at the Almalu Oasis (K8) with water temperatures of 5 - 12 °C,

- River Water corrsponds to a Ca-Mg-HCO_3 type similar to the cold groundwater (originating from upstream and downstream the zone with outflows of thermal water) which yield a water temperature of 20 °C at the sampling date of 21. July 2002)

- Mineral Water are of Na-Mg-HCO_3-Cl type like to hot thermal waters and are showing water temperatures of 17-19 °C These highly mineralalized waters (electrical conductivity in the range of 3000 to 5000 μS/cm) as also cooled thermal waters contain big amounts of (gaseous) CO_2, largely in excess of the atmospheric equilibrium conditions.

- Thermal waters are of Na-HCO_3 type and are naturally out flowing with temperatures between 50 -60 °C.

For the stable isotopes of δ^2H and $\delta^{18}O$ according to the data of a previous sampling campaign of the waters of the Khoy area [1] it can be recognised that:

- Cold groundwaters and the analysed samples of rain and snow and river water are situated in vicinity of a local meteoric water line with a deuterium excess d of 22 ‰ or in between this line and the global meteoric waterline with d = 10 ‰.

- Thermal Waters are showing an enrichment of the heavy oxygen-18 isotope which probaply reveale the effect of high Temperature isotope exchange with oxygen containing minerals of the host rock.

- Mineral Waters show a much bigger effect of oxygen isotope exchange probably caused by contact with CO2 gas of thermo- metamorphic origin [3], [4].

From the now presented data the conclusion results that two water systems are interacting, i) a first one being represented by the cold low mineralized waters with actual recharge in the high mountain areas as the Almalu Spring K8, and the avri Spring K7 and ii) a second one representing the deep thermal and mineral waters originating from a deep aquifer upwelling along tectonic fault zones (as the Qutur fault). This deep water component is contains high amounts of CO^2 which is characteristic for thermal systemes which are dominated by a high influx of CO2 of deep thermo – metamorphic or mantle origin. This hypothesis is shown by the conceptual model on Fig. 2 (modified from [1]). The deep waters are recharged by the cold low mineralized waters. The thermal and mineral waters arrise along the tectonic fault zones as the one coinciding with the valley of the Qutur River and are ouflowing at the observed springs. The chemical composition reveals that individual mixing processes with cold shallow waters of short residence time and the uprising gaseous CO2 of thermometamorphic origin occur.

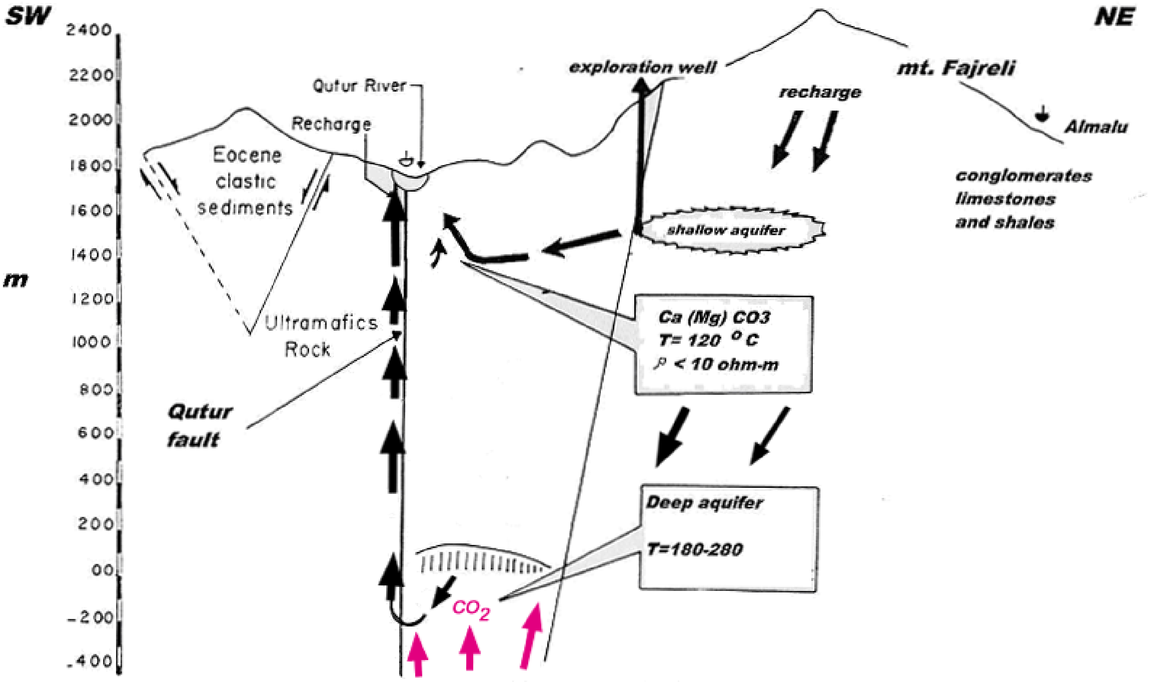

Fig. 2 Conceptual model of the Khoy geothermal system (modified after [1])

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MIRAVALLES GEOTHERMAL FIELD EVOLUTION: ISOTOPIC, CHEMICAL AND THERMAL STUDIES

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Commercial generation in the Miravalles geothermal field began in 1994 with the installation of 55 MW condensing power plant and at present the total generation is about 142.5 MW. The main reservoir fluids have a sodium-chloride composition with a TDS of 5500-6000 ppm, a neutral to slightly alkaline pH, and temperatures around 230-240 C. In the North East zone, there is an occurrence of acidic reservoir with pH around 2.5 and similar chemical composition of the main reservoir. All production wells (neutral and acid) require deep chemical treatment. The totality of the waste fluids is injected. According to isotopic measurements the recharge zone is located in the northern part of the Miravalles area. After eight years of exploitation, most of the production wells have shown isotopic and chemical changes with time. The spring waters all over the area present almost constant chemical and isotopic composition through time, indicating that no contamination has been detected due to the exploitation of the field. Most of the fluids are injected in the south, slightly affecting the nearby production wells. There is a steam cap from North to central area that is spreading.

According to the thermal-chemical and isotopic data and also numerical simulation runs done with Tough 2, was possible to modify the injection policies, reducing 300 kg/s of injectate in the south and shift it to the west to increase pressure support for most of the wells and reduce thermal breakthrough coming from south.

STRONTIUM ISOTOPE AS AN INDICATOR OF FLUID RESIDENCE FROM SELECTED GEOTHERMAL FIELDS IN CHINA

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The purpose of this study is to develop a new indicator of fluid residence in complex geothermal systems. The method is based on a serious of assumptions in geothermal systems. Firstly, the Yangbajain geothermal field of Tibet is chosen to study the behaviors of strontium isotope and verify these assumptions when a deeper thermal fluid ascends.

In the past years, two reservoirs have been identified at different depths in the Yangbajain field. A shallow reservoir is found at depths less than 450m, with temperature varying from 150°C to 170°C and decreasing toward the southeast. Parent rock in the shallow reservoir is altered Himalayan granite in the northwest part of the field and Quaternary alluvium in the southeast part. A deep reservoir is found at depths in the range from 750m to 1400m, with temperature higher than 250°C. Parent rock in the deep reservoir is fractured Himalayan granite. Both thermal fluids from the shallow and deep reservoir and cold groundwater are collected for the analysis of chamical compositions and strontium isotope. Rock samples are also collected at different depths in wells for strontium isotope measurement.

The results show there is a linear relation between chloride and boron concentration in the thermal fluids. It implies both reservoirs are hydraulical connected in the region. The shallow fluid is a mixture of the deep thermal fluid and cold groundwater. The Na/K ratios of the shallow and deep fluid do not keep a constant due to water-rock interaction at shallow. The rock samples are quite distinct in $^{87}Sr/^{86}Sr$ values, which indicates the granites are multiple intrusitions in the field. However, $^{87}Sr/^{86}Sr$ values are quite accordant to both the shallow and deep thermal fluid and can be identified easily from the cold groundwater. So it is reasonable to assure strontium component in both thermal fluids are dissolved from a particular granite at depth. The dilution/mixing process seems not to affect significantly the $^{87}Sr/^{86}Sr$ values because the cold groundwater is low concentration of strontium. In addition, when the deep thermal fluid approaches the surface, the pressure in the fracture zone decreases so that the thermal fluid can boil CO_2-rich steam escaping from the residual along its ascent channel. This process lead strontium carbonate in the condition of over-saturation. At this stage, it is dominant of precipitation but not dissolution in the fluid. It is clear that the $^{87}Sr/^{86}Sr$ value can preserve evidence of fluid residence at depth, where water-rock interaction occures intensivly and most of strontium is dissolved from the rock. The mixing/dilution can not affect the initial $^{87}Sr/^{86}Sr$ value apparently.

Secondly, this method is applied to the Rehai geothermal field to confirm whether there is hydraulic connection between two hydrothermal areas in the field. The Rehai field is unique high-temperature geothermal system related to the magma chamber of mantle-derived. It is a un-exploitated geothermal field in Yunnan Province, with a great potential for electricity generation. Previous researches demonstrate the thermal fluids in the region have similar hydrogen and oxygen composition. These thermal fluids are depletd in boron component. Although two hydromal areas can be easily distinguished on the basis of Na/K and Cl/SO_4 ratios, the ratios are easily changeable by water-rock interaction and oxidation-reduction reactions when the thermal fluid flows up. These two hydrothermal areas of the Rehai are located in different N-S striking faults, but most of people previously believe they are hydraulic connected through E-W striking faults. However, the thermal fluids of these two parts show obviously different in $^{87}Sr/^{86}Sr$ values. So it is reasonable to assure they are two independent hydrothermal systems in the field even they have a common heat source and the same meteoric origin. This conclusion will be of great benefit to geothermal exploration and assessment of resources in the future.

OXYGEN STABLE ISOTOPE GEOCHEMISTRY OF CHRYSOPRASE FROM WIRY AND SZKLARY MINES (SE POLAND)

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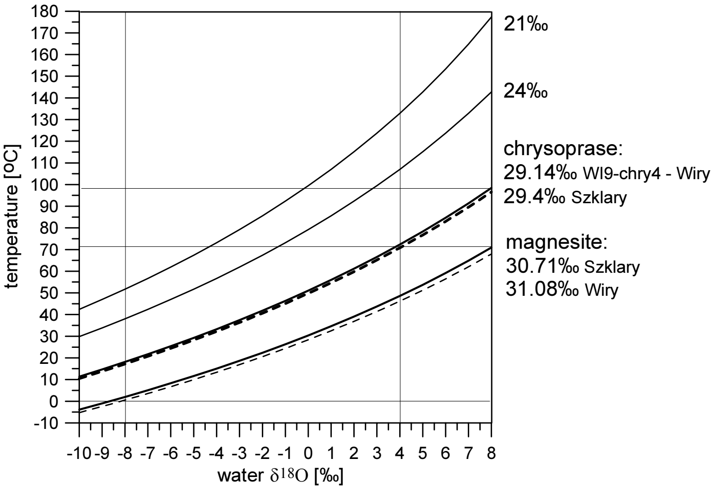
Poland

Three chrysoprase deposits, significant in the world, are known in Poland, Kazakhstan and Australia. This paper reports mineralogical (microscope, raman spectroscopy , X-ray, DTA) and oxygen isotope ($\delta^{18}O$) results from two locations in SW Poland (90 samples from Szklary and Wiry mine), and one lacation from Sarykul Boldy (3 sample, Kazakhstan) and Marlborough Creek (5 samples, Queensland, Australia). The chrsoprases anayzed form veins and have been associated by apparently somewhat younger vein magnesite [1]. Three mineralogical phases of chrysoprases have been specified in Szklary: a) opal phase – the opal matrix contain the chalcedony or quartz crystals; b) chalcedony phase – microcrystal or fine-crystal structure, c) chalcedony–opal phase (continuous structural transition from chalcedony crystals up to quartz crystals). The chrysoprase from the magnesite mine of Wiry are relatively homogeneous (mostly chalcedony phase up to 95%, grain 0,1 to 0,25mm). The chrysoprases from Sarykul Boldy are very similar to the Szklary type (opal-chalcedony 1:1 up to 2:1 or chalcedony chrysoprase phase). The chrysoprase form Marlborough Creek are represented by two different groups: a) the microcrystal quartz and fibrous chalcedony – the dominant one, b) second type: the crystals of chalcedony and quartz surrounded by opal matrix. The homogenisation temperatures of fluid inclusion in chrysoprase from Szklary are in the range from 40 to 120ºC. [1, 2, 3].

The $\delta^{18}O_{(SMOW)}$ value of all chrysoprase samples analysed ranges from 22,03 to 32,74‰ (with mean average 26,03‰). Remarkably, the $\delta^{18}O_{(SMOW)}$ value does not correspond to mineralogical variability observed (*e.g.* chalcedony/opal ratio) nor geological position of the chrysoprase analysed. This suggests that the mechanism of chrysoprases formation is uniform wit respect to temperature, origin of water and water-to-rock ratio. High oxygen isotope ratios suggests that the chrysoprase precipitated from mixed solution of meteoric at pneumo-hydrotermal conditions. This is consistent with fluid inlcusion results [2]. In this study, $\delta^{18}O$-based (oxygen isotope fractionation in chrysoprase-water system) paletermometric etimations can be rather qualitative than quantitaive. Extensive mineralogical and geologisal studies (see [1] and citations there) evidence that chrysoprase-host serpenitinite rocks, were changed (weathered) at warm climate. Thus, we accpeted, to our calculations, that the $\delta^{18}O$ value of water present during formation of chrsoprase, was not lower than –8 ‰ but not higher than 4‰ (0‰ – oceanic water, +4‰ magmatic solutions of meteoric origin). Likewise, the accepted lowermost $\delta^{18}O$ value of chrysoprase was 21‰ (mean 24‰) and the highest $\delta^{18}O$ value was 29,4‰ (29,4‰ in Szklary and 29,14‰ in Wiry). The other isotope pair applied was magnesite-water system [5]. The $\delta^{18}O$ value in magnesite, apparently not syngenetic to chrysoptrase analysed, was 30,71 (Szklary) i 31,08‰ (Wiry) [1].

The $\delta^{18}O_{(SMOW)}$ value in the pure gemmological value chrysporase ranges from 24.88‰ to 32.74‰ (Szklary); from 23.60‰ to 31.04‰ (Wiry), from 27,18 to 28,71‰ (Marlborough

Creek), and 25,17‰ (Sarykul Boldy) – see Fig. 1. These vaules corresponds to following temperatures of cristallisation: from 5-55ºC to 40-115ºC; from 10-60ºC to 40-110ºC; from 20-75ºC to 25-85ºC and 30-95ºC, respectively. Summing up, the estimated isotope temperature of crystallisation of chrysoprases ranges from 5 and 132ºC. Therefore, it is higher than that of vein magnesite (0-47ºC). Diverted cristallisation temperatures and δ^{18}O values of chrysoprase and magnesite, evidence oxygen isotope disequilibrium in th echrysoprase-magnesite system, thus suggest that these minarals are not of syngenetic origin. They probably crystallised independently during subsequent stages in evolution of ultramafic rocks.



Chrysoprase form Poland, Kasakhstan and Australia probably precipitated from warm solutions (5 to 130˚C) of meteoric origin.

ACKNOWLEDGEMENTS

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ORIGIN OF HIGH SULFATE CONTENTS IN THE THERMAL WATERS OF KIZILDERE AND ENVIRONS, WESTERN ANATOLIA, TURKEY

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In thermal waters of Kızıldere and environs, there are sulfate concentrations of up to 1.665 mg/l which differ from other thermal waters in the Menderes Massif extremely. The source of sulfur, which encounters a transformation to sulfate ions by disproportionation and is found in thermal waters of Kızıldere and environs, can be attributed to a magmatic input due to isotope ratios of $\delta^{34}S$ in sulfate and sulfide precipitations of thermal waters. The magmatic origin of sulfur might be corroborated by the isotope ratios of $\delta^{13}C$, $\delta^{11}B$, and $^{3}He/^{4}He$ of the thermal waters in the investigated area. The gypsum occurrences and diagenetic pyrite ore minerals in Pliocene sedimentary rocks form a second source of high sulfate contents in thermal waters of Kızıldere and its environs.

RECENT ANALYTICAL DEVELOPMENTS

IAEA-CN-104/P-43

STUDY OF TRITIUM CONCENTRATIONS IN ENVIRONMENTAL WATER SAMPLES MEASURED BY TWO STANDARD METHODS

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The general trend of environmental tritium concentration is to decrease toward the values present before the early 1960s, when the maximum ^{3}H content was recorded due to nuclear tests. Despite de low toxicity of tritium, monitoring of tritium activity concentrations in the environment is necessary in order to follow its circulation in the hydrosphere and biosphere.

There are two standard recommendations [1,2] that specify a method for determination of tritium concentration in water by liquid scintillation counting. Basically, the principle is the same. There are small differences between the two chemical treatments of water samples, but the goal is to hold back most quenching materials by alkaline distillation, as well as radioiodine and radiocarbon.

In the present work, a low background liquid scintillation system detector Quantulus 1220, is used to determine tritium concentration in different type of water, drinking water, precipitation, surface water and wastewater. It must be specified that the wastewater was taken from chemical plants in the immediate vicinity of our Institute.

The specific conditions used in our laboratory were: 20 ml polyethylene vial, Opti Phase HiSafe 3 scintillation cocktail, 8:12 ml ratio water: scintillant, 1000 minutes counting time (50 min/cycle and sample). The low limit of detection was calculated according to ISO standard method, and that was 8.4 TU, with 0.750 CPM background and efficiency of 24.72 %. After the distillation process, water samples must have pH between 6 and 7 and conductivity between 2 and 10 S/cm. Any other value for these parameters requires another distillation process, or another preparation process. A low-background water sample and a reference sample have been prepared in the same way for each type of water. All samples were measured according to the two studied standards, but we observed at least two parameters that were important for a good scintillation measurement, pH and conductivity. Another parameter, which influences the result, is the time to hold the samples in a dark and cooled place. During the study the holding time has been varied from 3h, recommended by standard, to 48h.

Even if the pH samples are around 7, and the conductivity respects the above-specified conditions there are some interference in the measurement process that lead to different results for the same water sample prepared by the two methods. The most obvious difference is recorded between tritium concentration values for drinking water, but the same situation is observed for wastewater. Tritium content in drinking water is lower than in surface water, which can be explained by the spring type that contains underground water in composition. A mean of 13.06 ± 2.5 TU for a spring with underground component is more appropriate than a mean of 21.53 ± 2.7 TU (march is the month for sampling). The aforementioned reveals that the tritium values obtained by first method have a higher probability to be closer to the real values than the one obtained by second method. Drinking water and wastewater contain dissolved gasses, one from purification method and the other from chemical processes in which it is used. It is well known that distillation process has a poor efficiency in removal of this type of contaminants and we can't give emphasis to this phenomenon, our measure of quenching, SQP(E), being in the same range (accepted uncertainty, 1%). A more detailed description of the results will be found in the poster presentation.

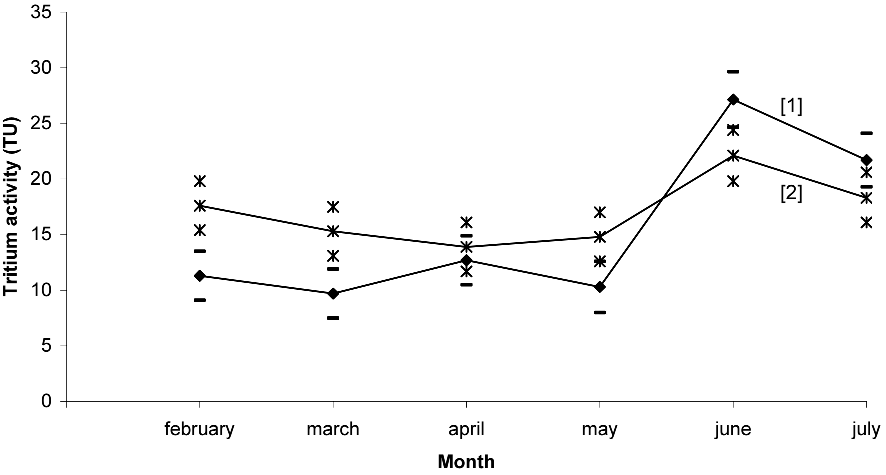

Fig. 1 Tritium concentration variation in precipitation over 2001 year measured by [1] ISO method and [2] APHA-AWA-WEF method (monthly sampling and reported uncertainty ± 1δ).

We continue to monitor tritium activity in precipitation, and Fig. 1 presents the evolution of tritium concentration in precipitation over six months measured by the two mentioned methods. Mean value for the first method over the monitoring period is 13.62 ± 2.5 TU against 20.06 ± 2.6 TU for the second method. Studding the reported values and general trend of tritium decreasing, we believe that the mean of first method is near the reality, known that in studied area is no source of tritium contamination.

There is some interference in the measurement process that leads to different results for the same water sample prepared by the two methods. Even if the differences aren't large, they exceed the uncertainty of the method.

Each laboratory must study their particular conditions. These conditions are related to type of liquid scintillation spectrometer, materials and routine procedures. In our case ISO method will be used for monitoring program in order to establish the baseline of tritium level around our institute, or in hydrological studies.

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NEW REFERENCE MATERIALS FOR OXYGEN ISOTOPES IN NITRATE

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Oxygen isotope analyses of nitrate (NO_3^-) in the atmosphere, hydrosphere, and geosphere can provide important information about sources, transport, and reactions of N in the environment. Despite rapid growth in this area of research, there is evidence that existing data may not be comparable because the calibration of O isotope measurements in NO_3^- is not secure (Casciotti and others, 2002; Michalski and others, 2002; Revesz and Böhlke, 2002). For example, only a few laboratories have reported independent analyses of the international KNO_3 isotopic reference materials IAEA-NO-3 or USGS32, and the $\delta^{18}O_{VSMOW}$ results vary substantially from about +22 to +26 ‰. These variations indicate undocumented uncertainty in the application of "offset" corrections for biases in the mass spectrometry and (or) sample preparation. Furthermore, there are no widely distributed NO_3^- reference materials with $\delta^{18}O$ values far from that of atmospheric O_2 ($\delta^{18}O_{VSMOW}$ = +23.8 ‰) despite the fact that important environmental samples have $\delta^{18}O$ values that vary by at least 80 ‰. Several recent studies indicate that the spread of values obtained from samples with widely varying $\delta^{18}O$ (the $\delta^{18}O$ "scale factor") may vary substantially with the method of sample decomposition and (or) mass spectrometry.

To address these problems, we prepared large quantities of two nitrate salts with contrasting O isotope ratios for distribution as reference materials for O isotope-ratio measurements (Böhlke and others, 2003). USGS34 (KNO_3) was prepared by equilibrating HNO_3 with Antarctic precipitation. USGS34 has a negative value of $\delta^{18}O$, with a normal mass-dependent relation between $\delta^{18}O$ and $\delta^{17}O$. USGS35 ($NaNO_3$) was prepared from natural nitrate ore from the Atacama Desert, Chile. USGS35 has a high positive value of $\delta^{18}O$, with a substantial non-mass-dependent ^{17}O anomaly ($\Delta^{17}O$ = +21.6 ‰) owing to its atmospheric origin (Michalski and others, 2002). These new reference materials, in combination with previously distributed NO_3^- isotopic reference materials (IAEA-NO-3 and USGS32), can be used to determine offset values, scale factors, and mass-independent effects in the complete analysis of ^{15}N ^{14}N and ^{18}O ^{17}O ^{16}O in environmental NO_3^- samples.

Provisional values of $\delta^{15}N$, $\delta^{18}O$, and $\delta^{17}O$ for nitrate isotopic reference materials (Böhlke and Coplen, 1995; Michalski and others, 2002; Böhlke and others, 2003)

Sample	**$\delta^{15}N$ [i/AIR]**	**$\delta^{18}O$ [i/VSMOW]**	**$\delta^{17}O$ [i/VSMOW]**
IAEA-NO-3	+4.7	+25.6	+13.2
USGS32	+180.0	+25.7	not determined
USGS34	-1.8	-27.9	-14.8
USGS35	+2.7	+57.5	+51.5

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IAEA-CN-104/P-81

LABDATA: A DATABASE AND LABORATORY MANAGEMENT SYSTEM FOR ISOTOPE HYDROLOGY, GEOCHRONOLOGY AND GEOCHEMISTRY

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Online measurement and digital storage of data have become a prerequisite not only for isotope hydrology laboratories all over the world. Nearly all commercial devices for chemical, isotope and radiometric analyses include more or less well-designed database software. Nevertheless in a laboratory practicing many preparation steps or combining several techniques per sample, bookkeeping of all subsamples, techniques and results over a time scale of decades remains a non-trivial task. This especially holds true for isotope hydrology, because here usually several techniques are combined for any sample and long time series for a special site are very valuable.

A data model able to map laboratory processes with any number of techniques and parameters and with the possibility to create any number of subsamples from any subsample was published earlier (Suckow & Dumke 2001). Here a MS Windows® compatible graphical user interface (GUI) is described which was developed and adopted for organization of the laboratory workflow, for quality assurance tasks and for the special post-processing problems in isotope hydrology and geochronology.

Features included which are not necessarily found in other laboratory management systems are:

- From any (sub)sample any number of subsamples can be created in order to map subsequent laboratory processes for one sample (sieving, dissolution, dilution, electrolytic tritium enrichment, preparation of counting gas…).
- For any subsample any number of parameters can be measured and stored (chemical parameters, isotopes…).
- For multiple analyses for the same (sub)sample, mean values and statistical characteristics are given automatically (standard deviation, weighted error of the mean, chi-squared…).

Besides that, several post-processing routines are available in the GUI, necessary especially for geochronology and isotope hydrology:

- For U/Th disequilibrium dating, bioturbation coefficients or sedimentation rates are calculated using the csr, cf and cic models.
- Up to two lumped parameter models like the exponential model, piston flow model, dispersion model, exponential piston flow model, linear model and linear piston flow model can be combined in parallel and model parameters for these can be fitted with interactive graphics.

- Input functions for several different tracers like Tritium, ^{85}Kr, CFCs, SF_6 in these models can be fitted simultaneously, and they can be derived from any query of stored data in the database (own time series are directly available as input functions).
- Geochemical correction models for radiocarbon ground water dating are included, following the formulas of Vogel, Tamers, Münnich, Pearson, Mook, Fontes & Garnier and any user defined initial activity.
- Algorithms for the separation of measured helium components are available, including the calculation of $T/^3He$ ages.

The server software of LabData is implemented using Microsoft SQL Server®, but any client-server database software (like Dbase, Oracle…) will work, if it is able to handle SQL procedures and triggers and to communicate via ODBC. The graphical user interface is programmed using Microsoft Access®. Data import and export routines are programmed for Microsoft Excel®. The talk/poster will present the basic concepts and ideas of the database system, a presentation of the software is possible for a smaller audience.

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IAEA INTER-LABORATORY COMPARISON EXERCISE FOR δ^2H AND δ^{18}O ANALYSIS OF WATER SAMPLES

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Isotope Hydrology laboratories routinely use oxygen and hydrogen isotope ratios in water samples to delineate water sources and processes involved in the hydrological cycles, for palaeo-climatic research and other applications. For this purpose it is of importance to maintain stringent precision and accuracy in the isotope ratio analyses since signals of natural variations are not large and conclusions often depend on how accurately one can measure these small signals. In this context, the IAEA Isotope Hydrology Laboratory organised a Inter-laboratory Comparison Exercise for δ^2H and δ^{18}O of water samples (WICO2002) recently to help laboratories evaluate their analytical capability. This exercise was carried out in the framework of the Analytical Quality Control Services Programme of the International Atomic Energy Agency.

95 laboratories expressed their willingness to participate in this exercise. Each of these laboratories was given a code number and received four water samples prepared by IAEA. These were marked as OH-5, OH-6, OH-7, and OH-8 and designed such that they cover the typical natural range of δ^{18}O and δ^2H values. The IAEA Isotope Hydrology Laboratory itself carefully calibrated the stable isotopic composition of these water samples by performing a large number of analyses (about 80 for each sample) spread over a period of 5 months using two mass-spectrometers and associated gas extraction systems. The rounded IAEA reference values are given below for OH-5, OH-6, OH-7 and OH-8: −0.20, −4.16, −10.65, −16.20‰ with average uncertainties of ±0.03‰ for δ^{18}O; and for δ^2H: −1.7, −38.7, −77.6, −121.5‰ with average uncertainties of ±0.6‰. Those mean values obtained are used here as reference values for facilitating the inter-comparison. The laboratories were requested to report the δ-values on the normalised VSMOW-SLAP scale, together with the overall uncertainty at one sigma level. By the end of October 2002, 82 laboratories from 31 countries had submitted the results of analyses back to the IAEA. Also the IAEA Isotope Hydrology Laboratory participated in the exercise by analysing the samples ten times in two mass spectrometers, keeping the data strictly separated and independent from the calibration data set.

The submitted data set were subjected to statistical scrutiny and several interesting features have emerged from this analysis. The first requirement for evaluation is to determine the consistency of the data by identifying the outliers and evaluate consensus values along with acceptable statistical deviations. Two different evaluation procedures were applied. In the first procedure (IC test), the population of submitted results is used to derive mean values after rejection of outliers. Obvious outliers were rejected by InterQuartile Method, which identifies data much above the upper quartile and much below the lower quartile. Next, using this output, any value outside of 2.7 times the standard deviation from the mean was rejected until a consistent set emerged in the exclusive sigma test. In the second procedure (proficiency test), the IAEA reference value was taken as the true value and deviation from this value by more than 2.7 times the typical standard deviations for oxygen and hydrogen isotope analyses (0.1 ‰ for $\delta^{18}O$ and 1 ‰ for $\delta^{2}H$) formed the criterion for rejection. In the internal consistency check about 25% results were outliers for oxygen isotope ratios and the consensus values were: −0.21, −4.17, −10.69, and −16.24 with standard deviations: 0.06, 0.04, 0.07, 0.09 for OH-5, OH-6, OH-7, and OH-8 respectively. For hydrogen isotope ratios the consensus values were: −1.7, −38.8, −77.8, −121.8 with standard deviations: 1.0, 1.0, 0.9, 0.8 for the same series of samples respectively. In the second check with IAEA values as reference, the consensus values obtained were almost the same and the number of rejections was only slightly different validating the robustness of the two methods. The frequency histogram of the accepted results shows a trapezoidal distribution, which can be approximately equated to a normal distribution and therefore, the usual interpretation of standard deviation in terms of probability distribution remains valid.

With the present WICO2002 exercise being the third IAEA water isotope interlaboratory comparison, it is of interest to compare the relative performance of those laboratories, which also participated in the last exercise organised in 1999. 52 labs participated in the oxygen analysis and 46 labs in the hydrogen analysis using the same method in both years. The maximum absolute deviation of the results from the consensus values was calculated for each laboratory for each isotope ratio in the two exercises and a cross-plot (Fig.1) shows that majority of the labs maintained their standard of performance. The statistics of deviations shows that unfortunately a large number of laboratories are not able to perform even at the accuracy level of 0.1 ‰ for $\delta^{18}O$ and 1.0 ‰ for $\delta^{2}H$, which are well accepted performance levels for isotope hydrology laboratories. For $\delta^{2}H$, 60% of the laboratories are not performing well. However, for $\delta^{18}O$ 60% of the 52 laboratories could not perform at that level in 1999, whereas the percentage dropped to 40% in 2002, which shows a considerable improvement in average performance. Since the deviations are mostly consistent among the four samples, it can be ascribed to the problem of calibration in these laboratories. If the internal or external water standards are kept in bottles subject to evaporative loss a sample would be ascribed a lower than true δ-value. With the results of these interlaboratory comparisons available, the laboratories should be able to identify their analytical problems and take steps to rectify.

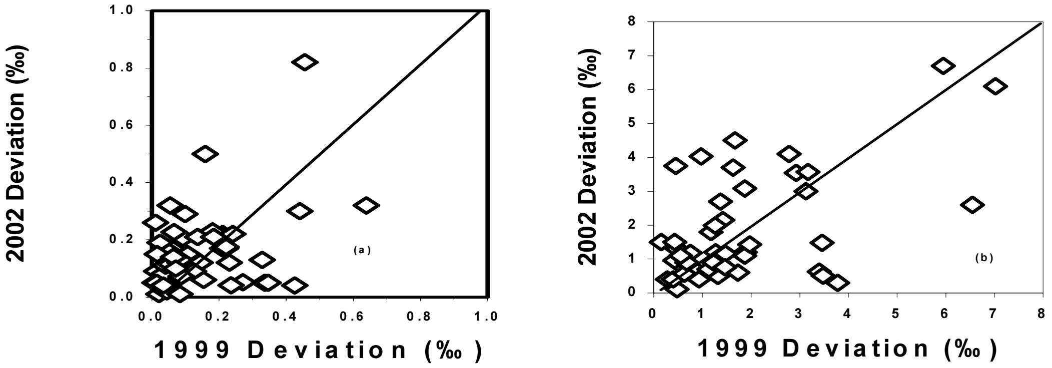

Figure 1. Comparison of 1999 and 2002 laboratory data: Maximum absolute deviation of a given laboratory from reference values for (a) oxygen and (b) hydrogen isotope ratios from data of four samples.

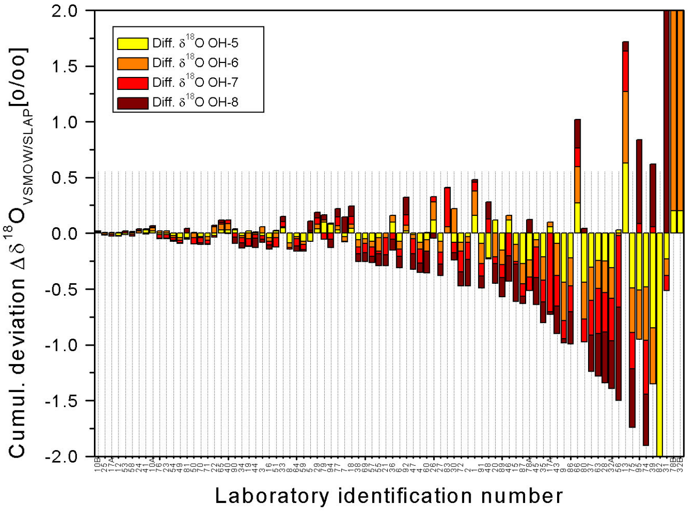

Figure 2: Graphical comparison of $\delta^{18}O$ deviations for all laboratories participating in 2002 isplayed as stack column plot for four samples.

COMPOUND-SPECIFIC δ^{13}C ANALYSIS OF DOC IN GROUNDWATER BY LC–TIC/TOC–CONTINUOUS FLOW IRMS

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The isotopic composition of both dissolved organic carbon (DOC) and dissolved inorganic carbon (DIC) in groundwater can now be routinely analysed by an automated total inorganic and organic carbon (TIC/TOC) instrument interfaced with a continuous flow isotope ratio mass spectrometer (CF-IRMS). The TIC/TOC analyzer uses a helium carrier gas compatible with the CF-IRMS. This allows rapid, automated analysis of concentration and ^{13}C composition for these two important carbon components in groundwaters. Having developed this new method, we now add a preparation step where DOC components are separated by liquid chromatography and fraction collector, allowing the analysis of δ^{13}C in specific DOC compounds. This provides insights into the consumption and production of organic carbon substrates during bacterial degradation of DOC. Applications with leachate-contaminated groundwaters and methanogenic groundwaters are presented.

MEASUREMENT OF δ^{13}C AND δ^{18}O ISOTOPIC RATIOS OF CACO$_3$ BY THERMOQUEST-FINNIGAN GASBENCH II AND DELTA PLUS XL CONTINUOUS FLOW ISOTOPE RATIO MASS SPECTROMETER WITH APPLICATION TO DEVILS HOLE CORE DH-11 CALCITE

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A new method was developed to analyze the stable carbon and oxygen isotope ratios of small samples (0.4mg) of calcium carbonate. This new method streamlines the classical H_3PO_4-$CaCO_3$ reaction method by making use of a Thermoquest-Finnigan GasBench II preparation device and a Delta Plus XL continuous flow isotope ratio mass spectrometer. To obtain reproducible and accurate results, optimal conditions for the phosphoric acid-calcite reaction had to be determined. Using temperature close to that the factory suggested (65 °C) for the acid-carbonate reaction even the shortest reaction time possible using a single arm robot, the precision of oxygen isotope ratio results was unacceptable, probably due to a secondary reaction. When the acid-carbonate reaction temperature was lowered (to 26°C), and the reaction time was increased to 24 hours, and screening rules for sample analysis quality were put in place, the oxygen and carbon isotope ratio precision of duplicate analyses improved to 0.2 and 0.1 per mil, respectively.

The technique was tested by analyzing Devils Hole calcite, which precipitated from ground water onto the walls of a sub-aqueous cavern during the last 500,000 years. Isotope ratio values for Devils Hole core DH-11 had previously been obtained by the classical method and is reported by Landwehr and others (1997). The DH-11 core was resampled and isotope-ratio values were obtained using the new method. The results were comparable to those obtained by the classical method (Figure 1). Indeed, the consistency of the isotopic results is such that an alignment offset could be identified. This cutting error was later independently confirmed. The reproducibility of the isotopic values (correlation, after correcting for alignment offset, is approximately 0.96 for both carbon and oxygen, Figure 2) shows that the new method is a viable alternative to the classical method. In particular, the new method requires less sample material and allows automation of some processes, so it is superior to the classical method when sample amount is limited and/or finer resolution is desirable.

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