Isotopes in the Water Cycle

Past, Present and Future of a Developing Science

IAEA
International Atomic Energy Agency

Edited by
Pradeep K. Aggarwal,
Joel R. Gat and Klaus F.O. Froehlich

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PREFACE

Improved understanding of the Earth's water cycle is a key element of global efforts to develop policies and practices for the sustainable management of water resources. Isotope and nuclear techniques have provided unmatched insights into the processes governing the water cycle and its variability under past and present climates. The International Atomic Energy Agency (IAEA) convened the first symposium on isotope hydrology in 1963. As isotope hydrology developed as an independent discipline, the IAEA symposia, convened every four years, provided a vehicle to review the state of the science and discuss future developments. Proceedings of these symposia contain classical papers that still form the basis of a number of applications in hydrology and inspire current research.

On the occasion of the 40th anniversary of the first IAEA symposium on isotope hydrology convened in 1963, it was decided to publish a monograph with an historical perspective and new developments in isotope techniques and their applications in hydrology. The various contributions represent reviews of the given subjects, and they contain comprehensive lists of references for further studies by interested readers.

The monograph begins with a history of isotopes in hydrology, in particular the stable oxygen and hydrogen isotopes, and of the role of the Isotope Hydrology Section of the IAEA in promoting this science. The first part of the monograph presents specific isotope and nuclear techniques that found wide applications in hydrology and related fields, complemented conventional hydrologic techniques, and, in some cases, became indispensable in special disciplines such as palaeohydrology and palaeoclimatology. First, historical developments and achievements in the use of artificial tracers for determining hydrologic parameters are reviewed (Moser and Rauert). In the 1960s, this technique was at the forefront of nuclear hydrology, but it has now largely been abandoned because the related health and safety concerns outweigh the advantages. A review of the use of cosmogenic isotopes in hydrology is presented by Lal, together with a detailed discussion of opportunities arising from the application of silicon isotopes. These are followed by applications of rare gases (Loosli), uranium and thorium series radionuclides (Kaufman), nitrogen and sulphur isotopes (Mayer), tritium (Michel) and stable oxygen and hydrogen isotopes (Gourcy, Groening and Aggarwal). Kerstel and Meijer present a detailed discussion of the latest developments in isotope analysis by optical techniques.

The second part of the monograph provides a number of contributions on applications of isotopes to investigate hydrological systems and processes under past and present climatic conditions. Applications for understanding the origin and movement of atmospheric moisture are discussed by Rozanski. Froehlich, Gonfiantini and Rozanski discuss the use of isotopes for understanding lake dynamics and water balance. Vitvar, Aggarwal and McDonnell present developments in the application of isotopes for investigating and modelling rainfall–runoff processes, both in small and large catchments. These are followed by discussions of isotope applications in groundwater (Edmunds), continental ice sheets (Thompson and Davis), geothermal systems (Kharaka and Mariner), saline waters (Horita), palaeolimnology (Gasse), and groundwater archives of palaeoclimate

(Edmunds). Developments in dating of groundwater are presented by Plummer (young waters) and Geyh (old groundwater). The historical evolution of the classical concepts of stable isotope hydrology, such as Rayleigh distillation and the global meteoric water line of Craig, is described by Gat. Finally, a contribution by Hoffman and others provides an analysis of stable isotopes in precipitation with the help of a global circulation model.

The Appendix includes a list of seminal papers in isotope hydrology and references to landmark developments in this field at the IAEA. The list of technical contributions presented at the first IAEA symposium in 1963 is also included.

Some topics notably are not discussed in detail in this monograph as they have been covered in recent reviews. These topics include stable carbon isotopes, biosphere-hydrosphere interactions, paleoclimate studies based on isotopes in plants and tree-rings, oceanic systems, and Arctic and Antarctic ice sheets.

We hope that this monograph will provide the detailed knowledge on isotope hydrology that is required by graduate students and specialists and that it will further strengthen the integration of isotope hydrology in science and applications related to the hydrologic cycle, climate and environment.

The editors are pleased to acknowledge all the contributions provided for this monograph, including those who have worked at the forefront of developments in isotope hydrology. In addition, we thank Mr. Roger Peniston-Bird for assistance with language editing and word processing, and Ms. Ornanette Azucena for secretarial support.

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INTRODUCTION

1. ISOTOPE HYDROLOGY: A HISTORICAL PERSPECTIVE FROM THE IAEA

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1. Introduction

"Isotope Hydrology", namely, the use of isotopic tools and nuclear techniques in the study of the water cycle, was born during the years just after the second world war through the merging, on the one hand, of the experience gathered in environmental monitoring of radionuclide fallout (tritium in particular) and use of radioisotopes as "dating" tools in geology with, on the other hand, the theoretical knowledge gained on the fractionation of isotopic species, as exemplified by the work of H. Urey, J.Bigeleisen and their students. Following up on very elementary information on isotope variations in water bodies gathered during the 1920s and 1930s in the USA, Europe and Japan, centres for the study of "Nuclear Geology" sprung up worldwide as the nuclear chemists and physicists returned to their

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academic environments, matching their newly acquired skills with their colleagues in geology, meteorology and other earth sciences. Examples are the Chicago group of Urey and his students in the USA, the Pisa group in Italy headed by E.Tongiorgi, the Heidelberg group of K.O. Munnich in Germany, and others in Denmark, Sweden, Switzerland, the United Kingdom, Israel, Japan, India, Canada, France and the Benelux countries.

> *"In the late 1950s, France, the Federal Republic of Germany, Israel, Japan, the USA and the United Kingdom began using radioactive isotopes in studies related to water resources. In conformity with its mission to encourage the Peaceful Applications of Atomic Energy, this development encouraged the IAEA to enter the field, which it did in 1958, its first year of operation."* (From "History of the IAEA, the first 40 years" by D. Fisher, IAEA, 1997).

The IAEA group, initially led by Erik Eriksson, was then consolidated into a special Isotope Hydrology Section headed first by Bryan Payne until his retirement in 1987, to be followed in turn by Roberto Gonfiantini (1987–1993), Jean Charles Fontes (1993-1994), Klaus Froehlich (1994-1999) and Pradeep Aggarwal (1999-). This Section served as a catalyst for the maturation of isotope hydrology, by bringing the isotope specialists face to face with the practising field hydrologists, by providing necessary analytical facilities and internationally accepted reference standards, by coordinating regional and worldwide monitoring activities, by training the personnel in developing countries in the nuclear methodology and, finally, by organizing international conferences and workshops as well as serving as a clearing-house and documentation centre for this field.

The IAEA convened two advisory panels in 1961 and 1962 to determine the nature and scope of its programme in isotope hydrology. The panels were chaired by Aaron Wiener, an experienced applied hydrologist, and included both isotope experts and their counterparts from the hydrological community. As stated in the report of the first panel (Appendix I):

> *"The panel considered that there were two possible approaches to the development of isotope techniques aimed at the solution of hydrological problems. The first might be termed an isotope technique development approach having no particular application in mind. The second approach would be to consider particular projects and then to try and find the isotope techniques which could be applied to their solution. The disadvantage of the first approach is that the isotope specialists are not always aware of the real hydrological problems, and on the other hand, consideration of only what might be called the project approach would handicap application owing to the prevailing lack of standard working techniques. The panel strongly recommended that both lines of attack should be simultaneously followed, resulting in mutual incentive to the two main groups of workers".*

This dual role was then further emphasized as the work progressed. The main focus in the fifties and early sixties was the utilization of short-lived radioisotopes (readily then available from the nuclear industry) as tracers in groundwaters and surface streams, in order to obtain local parameters of the systems such as mixing characteristics, transit times, storativity, porosity and transmissivity. The new technology was rather well received by field hydrologists and widely applied in different parts of the world. However, the increasing difficulty of obtaining permission for the introduction of even small amounts of radioactivity into water supply systems, as well as the limited time and space scale in which they could be employed, resulted in the gradual curtailment of the use of artificial tracers and their replacement by so-called "environmental isotopes" of natural or anthropogenic origin.

The first of these isotopes to come into focus was tritium, the radioactive isotope of hydrogen with a half-life of ~12.4 years, which is not only produced naturally in the atmosphere by secondary cosmic radiation, but was also released in large amounts by thermonuclear explosions (see Michel, this volume). Tritium injection by atmospheric thermonuclear tests inadvertently resulted in the largest tracing experiment ever attempted of the whole hydrologic cycle. The introduction and mixing of excess tritium into the surface and groundwater bodies promised hitherto unrealized opportunities for the study of the dynamics of these systems. The global aspect of this "tracer experiment" necessitated as a prerequisite the documentation of tritium distribution in atmospheric and surface waters (oceans, lakes, etc.), focusing attention on the water cycle as a whole. Because monitoring of radioactive fallout from nuclear explosions was always an important task of the International Atomic Energy Agency, it was only natural that the Isotope Hydrology Section was charged with the responsibility of measuring tritium content in the environment. Thus began the global network of isotopes in precipitation (GNIP), initially with tritium but soon thereafter expanded to include the stable oxygen and hydrogen isotopes. An intensive measurement programme of tritium in rivers, lakes and groundwaters, at selected sites representative of different climate zones, was also initiated, yielding invaluable information on the dynamic aspect of the water cycle, such as the residence time of water in the different hydrologic reservoirs, hydrograph separation in streamflow, exchange rate and mechanisms between the stratosphere (where most thermonuclear tritium was injected) and the troposphere, and between the northern and southern hemispheres, etc. Similarly, the stable isotope data on precipitation were an invaluable source of information on the global circulation patterns of atmospheric vapour and on the connection between isotopic composition and meteorological conditions and major climatic characteristics. Questions such as the linkage of surface water to subsurface or groundwater, the geographic and temporal origin of groundwater recharge, the water balance of whole hydrologic systems, especially in wetlands and evaporation-prone areas, could now be addressed. By the very nature of the methodology, the emphasis of isotope hydrology was on larger scale problems, such as that of the watershed and beyond to the continental scale.

Since the stable isotope composition of precipitation was found to be dependent upon climatic parameters and atmospheric circulation patterns, it became evident that changing isotope compositions of precipitation could be sensitive monitors of climatic change. Moreover, the use of proxy materials, namely ice-cores, lake sediments, tree rings, etc., for palaeoclimate studies relied on the stable isotope record of precipitation in these materials. This then projected isotope hydrology into a central role in climate research, which has been competing in recent years with direct applications for water resources research.

Isotope applications for global issues of water resources management are the primary focus of research and development in isotope hydrology at the IAEA. Current estimates of the world's groundwater resources generally are weak, and reliable information on the proportion of renewable or non-renewable groundwater is sketchy, even though more than half of all freshwater used for drinking and irrigation worldwide is groundwater. Isotopes are critical for building an improved understanding of the global distribution and amounts of non-renewable or fossil groundwater. A significant body of isotope data from aquifers worldwide exists today, with most of the data collected as part of IAEA technical cooperation projects, and is being integrated into continental-scale evaluations of water resources.

Estimates of renewable groundwater resources are critically dependent upon determining the presence and age of modern groundwater. As the strong signal of bomb tritium from thermonuclear atmospheric testing is now essentially washed out of the atmosphere, this ideal tool for characterizing the presence of modern groundwater is becoming more difficult or impossible to use. Radioactive decay of tritium produces helium-3, which is being exploited more often for age-dating of modern groundwater. Helium-3 measurements require capital- and labour-intensive mass spectrometry. This has kept these measurement facilities and applications to a limited number of laboratories, despite the fact that hydrologic applications of helium-3 have been recognized for over 20 years. The IAEA recently established a helium-3 laboratory in Vienna to facilitate a wider use of the helium isotope distributions. Corresponding projects for surveying the age of baseflow in large rivers and shallow aquifers also have been initiated. This initiative should lead to a faster pace in building a database of groundwater ages in shallow aquifers and thus improved quantification of groundwater recharge.

The very first panel convened by the IAEA in 1961 recognized that isotope monitoring of river discharge will improve our understanding of climate change and continental-scale hydrological processes (Appendix I). Yet these data have not been available on a continental or global scale. An IAEA-led programme to collect such data was finally initiated in 2002 as a complementary network to the GNIP.

The practice of isotope hydrology requires measurements on a consistent and common scale with high precision. Following H. Craig's definition of a "standard mean ocean water" or SMOW, the IAEA has led the efforts to develop and distribute isotope reference materials (see Gourcy et al., this volume). Inter-laboratory comparisons to evaluate the quality of stable isotope and tritium analysis of water samples are conducted by the IAEA on a regular basis. Stable oxygen and hydrogen isotope measurements performed by 82 laboratories from 31 countries were compared in 2002. Measurements from nearly 70% of the laboratories were found to have acceptable precision and accuracy. Precision of oxygen isotope measurements improved by about 20% between 1999 and 2002. Tritium measurements from 86 laboratories in 44 countries were compared in 2003. Participating laboratories included those using electrolytic enrichment and helium in-growth techniques. Only 40, or less than half, of the laboratories produced results which met the criteria for satisfactory performance in terms of accuracy and precision. Nearly one third of the laboratories may have had systematic errors in their analytical procedures. The range of results from helium in-growth laboratories was as much as the overall range of all measurements. However, an improvement of about 10% could be detected compared with the previous inter-comparison of 1995.

Future trends and new applications in isotope hydrology are largely possible because of the steady advances that are occurring in analytical methods and instrumentation as well as in the availability of global isotope data. Increased access to accelerator mass spectrometry (AMS) for environmental isotope analyses has made it easier to analyse carbon-14 in small samples of groundwater, resulting in a wider use of the carbon-14 method to characterize groundwater dynamics. Viable spectroscopic methods as alternatives to conventional mass-spectrometric systems for stable isotope abundance measurement are coming closer to realization. The spectroscopic methods require much lower operational skills and basic infrastructure for operation compared to mass-spectrometers and are likely greatly to increase access to isotope measuring facilities in the developing countries. In addition, spectroscopic methods allow in-situ measurements of isotopes and such measurements in atmospheric water vapour at a global scale would further extend the role of isotopes in AGCMs and climate change research.

Isotope hydrology today is a recognized discipline of hydrologic sciences in its own right. The extent to which isotopes are being used is indicated by an increasing number of published papers in major scientific journals where isotopes are one of the investigative tools for hydrologic investigations. Isotopes were featured in less than 100 scientific papers on hydrological research and application in the period 1960 to 1965. During 1995-2000, however, more than 7000 such papers were published.

However, the challenge of integrating isotopes into mainstream hydrology, which is dependent upon a closer interaction between isotope hydrologists and the hydrological community at large, was recognized early in the development of isotope hydrology as a discipline. Professor Van T. Chow, a renowned hydrologist of the 20th century, noted in 1967 at the second quadrennial IAEA symposium on isotope hydrology (Chow, 1967)

> *"There is no doubt that nuclear techniques can prove to be extremely useful in solving hydrological problems. The promise their ultimate use in hydrology will, however, depend upon a close collaboration between the nuclear scientist and the hydrologist."*

After nearly forty years, this challenge remains to be fully realized. In some areas, for example, geothermal systems and the hydrology of small basins and hill-slopes (see Kharaka and Mariner, and Vitvar et al., this volume), isotopes are recognized and accepted as an integral part of the methodologies. However, in the general field of hydrology related to groundwater recharge and dynamics, and river–

groundwater interactions, isotope data are relatively less utilized by physical hydrologists and modellers. To some extent, this may result from a lack of sufficient communication and common scientific language between the two communities. The 2003 IAEA symposium on isotope hydrology recognized the continuing gap in the use of isotope data. The symposium addressed the question “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 that lies at the heart of all efforts to integrate isotope techniques in hydrology. The symposium concluded that the answer to the questions generally was “a lot”, but careful study design was necessary to ensure that the results are relevant to the objectives. It was also concluded that the lack of substantial programmes of field data collection during the 1970s and 1980s may also have contributed to apparent stagnation in efforts to integrate isotopes in the hydrological sciences. In this context, the persistent efforts of the IAEA in helping to collect isotope data worldwide, particularly in the developing countries, were fully recognized and the recent initiatives to build additional global data networks and to synthesize and disseminate existing data were considered to be critical for improved integration of isotopes in hydrology.

ISOTOPIC AND NUCLEAR METHODOLOGIES

2. ISOTOPIC TRACERS FOR OBTAINING HYDROLOGIC PARAMETERS

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Germany

1. Introduction

The use of artificially injected isotopic tracers, mostly radioactive, in hydrology can be traced back to the post-war trend of the peaceful application of radionuclides. The advantages of these tracers were mainly seen in the fact that they can be specifically detected in very low amounts and concentrations which do not disturb the hydrologic system under investigation. In hydrology, further advantages were seen compared to the conventional labelling tests with dyes and salts. Radioactive tracers can be adapted to the purpose and the duration of the investigation by choosing suitable chemical compounds and half-lives. In addition, the variety of available tracers can be extended for multi-tracer tests and finally the radioactive decay results in the spontaneous removal of the tracer substance following the end of the test. At first glance radioactive tracers then appeared to be highly effective in the application of tracer techniques.

As early as 1950, Knop reported the measurements of passage times in a sewage treatment plant using sodium chloride solution labelled with ^{24}Na. Figure 1 shows the tracer passage curve in a round clarifier of the plant. The different residence times can be clearly recognized by the secondary peaks. Groundwater labelling was reported by Hours (1955) using ^{82}Br as a tracer and different groundwater tracers were evaluated early on by Kaufmann and Orlob (1956). With the encouragement of the hydrogeologist Ferdinand Neumaier, the use of ^{131}I for groundwater labelling was started at the Institute of Physics of the University of Munich in a drinking water supply area in autumn 1951. Iodine-131 was injected in the form of ethyl iodide in an upstream row of gauges of an underground barrier and attempts were then made to detect the tracer downstream in order to localize leakage points in the barrier. In order to monitor the tracer outflow, the decrease over time of the ^{131}I concentration was measured in the injection borehole. The decrease turned out to be exponential. This observation led to the development of the ”Point Dilution

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Method", which allows the measurement of the groundwater throughflow within a borehole (See Gourcy et al., this volume).

In the late fifties, the use of radioactive tracers led to great advances in a number of other countries as well, such as Austria, France, Great Britain, Israel, the USA and Japan. This led the International Atomic Energy Agency (IAEA) to establish a Section of Isotope Hydrology. One notes that all the early meetings convened were focused on the topic of artificially injected radioactive tracers. Apart from investigations on the suitability of the tracers, the discussion mainly concentrated on measurements of river discharge, studies of the flow through lakes and reservoirs, studies of sediment transport by labelling of sands and gravels, and determination of groundwater flow velocity and flow direction. Twenty-two of the 27 contributions to the IAEA Symposium held in Tokyo in 1963 dealt with hydrologic selection criteria and applications of added radioactive tracers. At the following IAEA Symposium ("Isotopes in Hydrology", IAEA, 1967), the focus had already changed. Only 24 papers of a total of 41 still referred to studies with radioactive tracers, among them ten papers about sediment labelling tests. As many as 17 papers were devoted to investigations with environmental isotopes, which have dominated isotope hydrology until today. This partially resulted from the fact that the injection of radioactive tracers had been increasingly restricted by radiation protection regulations and decreasing acceptance by the public of the use of radioactive materials. As a consequence, increasing difficulties in obtaining a licence, especially for field experiments. This tendency was enhanced by the advancement of other tracer techniques (e.g. Käss, 1992, 1998; Hebert et al., 2002), in particular those using fluorescent dyes.

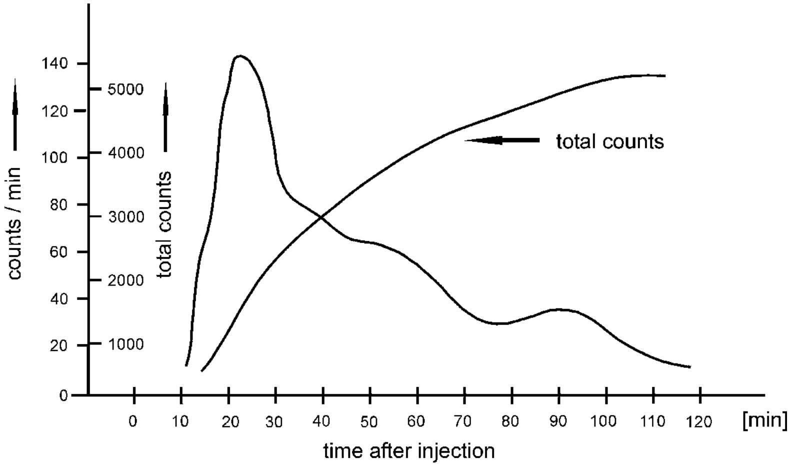

FIG. 1. Tracer passage curve (counts/min) and total counts curve of the tracer ^{24}NaCl in the round clarifier of a sewage treatment plant (after Knop, 1950).

The following is a summary of methods and results of the application of isotopic tracers (for details see e.g. Behrens, 1992, 1998; Evans, 1983; Gaspar, 1987; IAEA, 1983 a,b,c, 1985, 1987, 1991, and Moser and Rauert, 1980).

The hydrologic properties which have been investigated by means of these tracers are:

- in the case of open channels, lakes, reservoirs and treatment plants: flow time, flow rate, flow pattern, mixing processes, re-aeration rates, movements of sediments and suspended matter,
- hydraulic interconnections between surface water and groundwater: seepage flow in the unsaturated zone and in dams,
- groundwater: flow rate, flow direction, flow path, hydraulic interconnection of aquifers.

In the case of groundwater systems, the possible roles of all isotope methods, including artificially injected tracers, were summarized as early as in 1963 by Harpaz et al. (1963).

2. Methods and results

2.1. TRACERS

Table 1 shows a list of nuclides which have frequently been used as tracers for hydrologic investigations, their half-lives, the most commonly used chemical compounds, the radiation type to be measured and their sorption properties. Further, radionuclides such as ^{46}Sc, ^{51}Cr, ^{99m}Tc, ^{182}Ta, ^{192}Ir, ^{198}Au, and ^{140}La were used in studies of sediment transport (see Lal, this volume). In order to avoid problems associated with radiation in the field, non-radioactive tracers which could be detected by activation analysis were used to a limited extent (e.g. bromine, EDTA complexes of Dy, In, La, Mn; see Behrens 1976, 1992).

Despite the optimism prevailing in the sixties, only a relatively small number of isotopic tracers have proved practical for hydrologic investigations. Among those are mostly γ-emitters due to their simple detection. Exceptions are ^{3}H and ^{2}H, which are considered to be "ideal" tracers as they are constituents of the water molecule itself. However, their detection requires significant effort. Besides, in the case of ^{2}H the detection sensitivity and the detection limit are essentially limited by the high natural background and its variations (e.g. Becker and Coplen, 2001). Also, the application of these two nuclides causes changes of the natural isotope distribution in the water of the area under investigation, which can interfere with a subsequent hydrologic evaluation based on the natural environmental isotope contents

Gammma-emitting tracers are measured in the field by scintillation counters which are either immersed in the surface water or (via boreholes) in the groundwater or into a diverted throughflow container located next to the mainstream or the borehole. As an alternative, discrete water samples are taken from the flow to be studied. They are measured directly or after a sample preparation in the laboratory. The detection of ^{3}H (preferably by liquid scintillation counting) and ^{2}H (by mass spectrometry) is only possible in the laboratory,using samples collected in the field.

Table 1. Isotopic tracers for hydrologic tracer tests

Nuclide	Half-life	Chemical compound	Major radiation	Properties important for hydrologic applications (after Behrens, 1972)
^{2}H	stable	$^{2}H^{1}HO$	–	chemically identical with the marked water
^{3}H	12.4 a	^{3}HHO	ß	chemically identical with the marked water
^{24}Na	15.0 h	Na^{+}	γ	high sorption, applicable in sewage plants
^{51}Cr	27.7 d	EDTA complex	γ	low sorption
^{58}Co	70.8 d	$(Co(CN)_{6})^{3-}$ complex	γ	low sorption
^{60}Co	5.3 a	$(Co(CN)_{6})^{3-}$ complex	γ	low sorption
^{82}Br	35.3 h	Br^{-}	γ	very low sorption, chemically very stable
^{99m}Tc	6 h	EDTA complex	γ	low sorption
^{125}I	60 d	I	γ	chemically unstable, sometimes sorption
^{131}I	8.04 d	I^{-}	γ	chemically unstable, sometimes sorption
^{114m}In	50 d	EDTA complex	γ	low sorption
^{198}Au	2.7 d	Au^{3+}	γ	high sorption, used as “reactive” tracer

2.2. ISOTOPIC LABELLING IN SURFACE WATER

Isotopic labelling tests in open channels for determining the flow rate and flow time belong to the first successful applications of radionuclide techniques in hydrology (e.g. Moser and Neumaier, 1957; Guizerix et al., 1963).

Worldwide, the tracers ^{131}I, ^{82}Br, ^{51}Cr, ^{60}Co, ^{99m}Tc were mainly used for measurements in canals and rivers with flow rates from a few L/s up to some 1000 m^{3}/s. For the measurement of high flow rates ^{3}H was mostly used. In addition to the measurement of discharge rates and transit time measurements, methodical investigations on suitable methods for tracer injection, on the mixing of the tracer in open channels and on the accuracy of different measurement and evaluation techniques were carried out. This was also done in comparison with measurements using non-radioactive tracers and rotating current meters. The results are reported by, among others, Behrens (1980, 1992, 1998), Guizerix and Florkowski (1983), Florkowski (1991), Borroto et al. (1999), Pascu et al. (1999). They show that carefully performed discharge measurements with tracers are as accurate as conventional hydraulic measurements and even superior to the latter under turbulent flow conditions and also in the presence of a high transport rate of contaminants, suspended matter or sediment. In the case of high discharges, the ^{3}H tracer is preferred due to its high detection sensitivity and the low health risk associated with it in the field. Outstanding examples are the flow rate measurements with ^{3}H on the rivers Tana (Kenya) by Florkowski et al. (1969) and Rufiji (Tanzania) by Dinçer et al. (1984). Under the given conditions (550 up to 2000 m^3/s, highly turbulent flow, partially high sediment load and variable flow profiles) only tracer methods provided reliable results. In general, the experience gained with radioactive tracers applies to other tracers as well and especially fluorescent and salt tracers.

The radioactive labelling of the suspended matter, the sediment and sludge in rivers, reservoirs, and estuaries soon made it possible to observe directly and measure quantitatively the movement of the sediments . To this end, γ-emitting tracers (Section 2.1.) are either being adsorbed at the surface of the natural sediments to be studied or mechanically fixed on pebbles, or added to the water in the form of radioactive glass grains or powder. After the addition to the water course to be studied, the labelled material is detected by radiation detectors immersed in the water. Comprehensive descriptions of the very different methods of measurement and evaluation which have been applied in such investigations (for example in the mouth of Gironde river, France, and in the lower Elbe river, Germany) are reported, for example, by Pahlke (1980) and Caillot (1983). More recently the sediment transport in the Yangtse estuary, China, has been studied (Zhangsu Li et al., 1994) and in the Paraopeba river, Brazil (Vianna Bandera et al., 1999).

Further investigations wth radioactive tracers deal with flow and mixing patterns in settling-basins of sewage treatment plants, lakes and reservoirs and in individual cases also with their water balance as well as the dispersion of waste water in coastal regions (e.g. Quay et al., 1979; White, 1983; Gilath and Gonfiantini, 1983; Gilath 1983). Along with the measurements of Knop (1950) in settling-basins already mentioned in Section 1, early examples are the measurements in the Lingese reservoir in Germany (Sauerwein, 1967) which had been carried out in 1952 and 1957 using ^{82}Br, ^{46}Sc and ^{140}La as tracers, the discharge analyses by measurements with ^{82}Br at the Eshkol reservoir in Israel (Gilath and Stuhl, 1971) and the study of the water balance with ^{3}H in Lake Chala, Kenya (Payne, 1970). Labelling tests of reservoir water are often used to detect hydraulic connections between the surface water, springs and groundwater, i.e. leakage into the bottom of the reservoir (see Michel, this volume).

Tsivoglu et al. (e.g. 1976) described a radionuclide technique to determine directly the re-aeration rate in rivers, which is important for the decomposition of noxious substances. In this procedure, the gaseous, volatile tracer ^{85}Kr is added to the river water simultaneously with a conservative tracer. At the end of the test section, the change of the concentration ratio of both tracers is determined and thus the re-aeration rate can be calculated. To date the method has been used successfully only for flow rates of less than 20 m^3/s because of the high tracer activities required (Roldao, 1991).

2.3. ISOTOPIC LABELLING IN THE TRANSITION ZONE BETWEEN SURFACE WATER AND GROUNDWATER

Seepage measurements in a canal using injected ^{3}H tracer were reported early on by Kaufmann and Todd (1962). Nuclide labelling found relatively widespread application for tests for leaks of dams and reservoirs (e.g. Drost and Moser, 1983; Plata Bedmar 1991). Labelling of the total reservoir water was attempted up to volumes of 107 m^{3} (e.g. Guizerix et al., 1967), but mostly failed due to inadequate mixing and the large amount of tracer required. However, localized additions of tracers such as ^{82}Br, ^{51}Cr and ^{3}H at suspected infiltration zones of leak water succeeded in many cases (e.g. Makowski, 1970; Molinari, 1976; Guizerix, 1983). An example for the successful application of non-conservative tracers which are fixed at the leakage points is the investigation carried out by Molinari et al. (1970) on the Rhine-Marne Canal (France). In this case bitumen labelled by ^{131}I was used as tracer. Single-well techniques for measuring the groundwater flow (Section 2.4.) were also successfully applied to localize and measure the seepage flow in dams (e.g. Drost, 1989).

In order to investigate the seepage flow in the unsaturated zone of an aquifer and the determination of the groundwater recharge rate, nuclide tracers, preferably ^{3}H, but also ^{2}H, have also been used with success, even though on a smaller scale than measurements of the environmental nuclides ^{3}H and ^{2}H. Both methods allow for a direct measurement of the water movement in the unsaturated zone and thereby of the groundwater recharge rate. Thus they provide basic data for model calculations, for example in the context of pollution and irrigation studies. The method with tracer addition to the unsaturated soil zone was essentially developed at the Institute for Environmental Physics of the University of Heidelberg (Germany). There it was applied in loess and sand soils (e.g. Zimmermann et al., 1967; Blume et al., 1967; Jakubick, 1972) and has since been used worldwide in various climatic conditions (e.g. Dharmasi and Dharmawardena, 1980; Rao, 1983, Sharma and Gupta, 1985; Issar et al., 1985; Sukhija et al., 1994). On the scale of laboratory and lysimeter tests, radionuclides have also been employed as reference tracers in studies of water movement and dispersion in unsaturated soils (e.g. Eichinger et al., 1984; Baker et al., 1985; Seiler, 1998).

2.4. ISOTOPIC LABELLING IN GROUNDWATER

Referring to the spread of contaminants in groundwater and other applications, Mandel (1991) summarized the possibilities of tracer tests to determine parameters of the groundwater flow and the aquifer, i.e. filtration (or Darcy) velocity, distance (or flow) velocity, flow direction, longitudinal and transversal dispersion, dispersivity and effective porosity. In practice, those investigations contribute to the solution of problems of groundwater production, waste and waste water disposal, environment protection, foundation and hydraulic engineering. The use of nuclear tracers can also be helpful for investigations connected with radioactive waste disposal (e.g. IAEA, 1983 a,b). As for the choice of tracers and their amounts, “single-well methods” have to be distinguished from “multi-well methods”. In the former case, the tracer is injected and detected in the same borehole, whereas with multi-well methods the labelled groundwater is detected only after a certain passage through the aquifer, in boreholes located downstream from the injection point. In this context, the sorption of the tracers naturally plays an important role (Table 1). Radioactive tracers have proved useful in both cases. In comparison with fluorescent and salt tracers, the low tracer concentrations (avoiding density currents), a relatively simple detection in the borehole, short half-lives, and, in the case of ^{3}H and ^{2}H, no sorption are the main advantages.

2.4.1. Single-well methods

Single-well methods using radioactive tracers had already been described in the early years of isotope hydrology (e.g. Moser et al., 1957, Mairhofer, 1963, Halevy et al., 1967). Since then, they have developed into accepted methods of groundwater measuring techniques (e.g. Drost, 1983, 1989). The preferred tracers are ^{82}Br and ^{99m}Tc. The necessary concentration is so low that neither interference with the physical or chemical nature of the groundwater, nor essential problems of radiation protection, occur. As for the tracer dilution log, used for the determination of the filtration (or Darcy) velocity vf, the water column in the measuring section of the filter tube of a groundwater measuring point is labelled (Fig.2).

Then v_f can be derived from the decrease in tracer concentration due to the throughflow rate of groundwater. Figure 2 shows also that, in addition, the flow direction is determined with the direction-sensitive radiation detector of the measuring probe displayed. In Fig. 2 the measuring volume has been sealed by packers in order to avoid disturbing vertical flow in the filter tube. If vertical flows are admitted, it is possible to determine quantitatively the flow rate in the filter tube and thereby the water exchange in the vertical profile of the borehole by measurement of the vertical flow velocity of the tracer cloud (tracer flow meter).

These single-well methods have been successfully used for about 30 years, e.g. in over 200 investigation areas by the GSF Institute of Hydrology, Neuherberg/München (Germany). The measurements were mainly carried out in porous aquifers, yet it was also possible in fractured aquifers to localize flow paths and to determine local flow directions. The investigations were mainly connected with the groundwater development for water supply (e.g. estimation of the available water reserve and the influence of bank filtration, delineation of protection zones), with measures against groundwater contamination (e.g. determination of the range of contaminations and their disturbing influence on the natural hydraulic conditions), and with engineering (e.g. measurements of groundwater regimes for planning, during execution of, and securing of evidence for, underground engineering measures). Examples for such case studies can be found in the reports of the GSF Institute as well as in Moser and Rauert (1980), Plata Bedmar et al. (1980), Plata Bedmar (1983), Drost (1989), and the IAEA (1983 a,b,c, 1991).

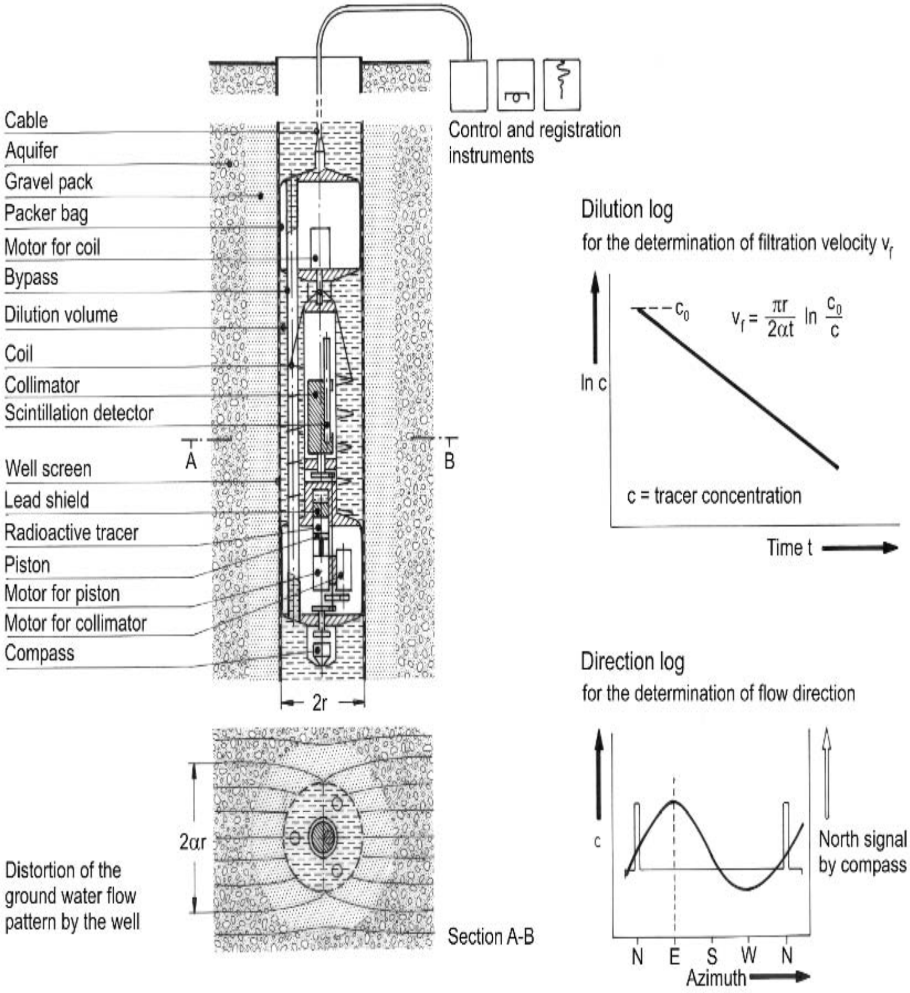

FIG. 2. Tracer borehole probe for the depth-depending determination of the filtration (Darcy) velocity and flow direction of groundwater (from Drost, 1983).

It is evident that single-well measurements require a sufficient number of groundwater measuring points in order to provide hydrologic results which are geostatistically significant. The number of measuring points depends substantially on the structure and texture properties of the aquifer. These are reflected in the generally correlated variances of the measured values of the groundwater filtration velocity and flow direction. Comparative measurements in different aquifers show that the value of the hydraulic conductivity, which results from single-well measurements of filtration velocity in the investigated range between 10–4 and 10–1 m/s, correlates well with the values obtained from pumping tests (Drost, 1984).

Another single-well method is the single-well pulse technique, which was developed in Israel early on (Mandel, 1960, 1991). With this technique, the radioactive tracer solution initially injected into a well is allowed to drain into the aquifer. In the course of repeated injection tests, the labelled water is pumped back again. From each of the pumped volumes and the respective time of the recovery of the tracer, it is possible in principle to determine the groundwater flow velocity and dispersion parameters. The technique was applied in Israel and in the Viennese basin, Austria (e.g. Sternau et al., 1967, Borowczyk et al., 1967). However, it was apparently not further developed, presumably due to technical and interpretation problems.

2.4.2. Multi-well methods

The numerous multi-well tracer techniques which have been reported in the literature (e.g. Käss, 1992, 1998; Mandel, 1991; Moser and Rauert, 1980) serve to determine the flow of groundwater, the longitudinal and transversal dispersion in the aquifer and the effective porosity and transmissivity. In addition, it is possible to determine water paths and the boundary of catchment areas. The injected tracer is detected in boreholes or springs located in the known or assumed flow direction, under natural hydraulic conditions or under stressed conditions, i.e. pumping. The hydraulic parameters mentioned above can be deduced from the concentration–time distribution of the tracer. With regard to radiation protection, radioactive tracers should be used in multi-well tests only to a small extent because the amount of tracer needed is considerably higher than in the single-well methods. The use is justified, however, in the case of model tests in the laboratory (e.g. Klotz, 1971,1973; Wolf et al., 1998) or of pumping tests in the field on a small scale (e.g. Sternau et al., 1967; Landström et al., 1978). Under certain conditions, the application of radioactive tracers is also justified if ^{3}H is needed as a reference tracer almost free of sorption (Claassen and Cordes, 1975; Webster et al., 1970) or with a multi-tracer experiment for extending the number of available tracers. This was the case for instance, with hydrologic investigations in karst regions, where the radioactive tracers ^{3}H, ^{51}Cr, and ^{131}I were successfully used in addition to Mn, La, and In as tracers detected by activation analysis (e.g. Bourdon et al., 1963; Batsche et al., 1967, 1970; Bauer et al., 1976, 1981; Behrens et al., 1981, 1992).

In fractured rock, radioactive tracers as well as ^{2}H – the latter only on a small scale – were successfully applied to establish hydraulic interconnections, for example in view of the feasibility as a final underground repository for radioactive wastes (Keppler et al., 1994; Himmelsbach et al, 1998; Becker and Shapiro 2000). Such measurements are also suitable for determining water exchange between fractures and the porous rock matrix, thus providing data for modelling of the diffusion processes in fractured rock aquifers which are important for water movement and therefore, contaminant transport (e.g. Małoszewski and Zuber, 1993).

2.5. ISOTOPIC LABELLING TESTS IN THERMAL WATERS

Isotopic tracers for the determination of hydrologic parameters during the exploration and operation of geothermal fields are primarily used in order to solve economic and environmental problems caused by the re-injection of thermal water

(McCabe, 1991). Due to their smaller volume, radioactive tracer solutions are technically easier to handle during injection than conventional tracers. In addition, short-lived radionuclides allow for a prompt repetition of the labelling tests, as is often necessary. Further, the choice of tracers is limited, in view of the required thermal stability, which, in general, is not achieved by organic and metal–organic compounds. McCabe (1991) concludes that ^{82}Br and ^{131}I generally fulfil these requirements. The same applies, of course, to water labelled with ^{3}H, which has been used successfully (e.g. Abidin et al.,1999). It may, however, disturb the hydrologic evaluation of measurements of the environmental ^{3}H content in the area under investigation.

3. Summary and outlook

Isotopic labelling tests in hydrologic systems were among the earliest peaceful applications of nuclear techniques. Above, an attempt has been made to give a summary of the historical development of such methods and their applications up to the present. In this context, it has only been possible to deal with the principles of the various methods for solving hydrologic problems related to surface water, groundwater and their interaction. For details and special applications, the reader is referred to the technical literature and in particular to the relevant publications of the IAEA.

The application of proven methods, using added radioactive tracers in hydrologic field tests declined sharply after 1980. This was essentially due to stringent radiation protection regulations and the waning public acceptance of artificial radioactive substances in the environment. Therefore, it is likely that in the future probably only special measurement techniques will remain in use, such as the application of ^{3}H as a tracer for the determination of high discharges in surface waters as well as its use as a reference tracer in multi-tracer experiments. This equally applies to the use of short-lived radionuclides (^{82}Br, ^{99m}Tc), e.g. in geothermal fields or in connection with single-well techniques for the investigation of groundwater flow. Measurements with tracers often provide detailed hydrologic information which, even though confined as to locality and time, can be a valuable supplement to the interpretation of environmental isotope measurements, which is often possible on a regional scale only. This also applies for the collection of data necessary for the development and verification of adequate mathematical models. In laboratory model experiments with added nuclide tracers will also have their place in the future, for instance, to further develop the general tracer method.

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3. HYDROLOGIC PROCESS STUDIES USING RADIONUCLIDES PRODUCED BY COSMIC RAYS

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1. Introduction

The global hydrologic cycle is the vastly complex dynamic process which transfers all phases of “water” molecules, gas, liquid and solid, through the atmosphere, land and the oceans. Its complexity in part ultimately results from the properties of the phase diagram of water, and in part from 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 and the operation of the hydrologic cycle is closely related to the climate controls on the hydrologic cycle. The cycle evolves with strong feedbacks which regulate the climate in an important manner (Peixoto and Oort, 1992; Pierrehumbert, 2002). An example of a possible extreme climate, resulting from changes in the manner of coupling between the atmosphere and the water reservoirs, is the concept of a ‘Snowball Earth’, put forward by Hoffman et al. (1998).

The discipline of hydrology, earlier directed principally for aiding in better water utilization and conservation, is now under great pressure from several academic directions (cf. Allen and Ingram, 2002) to resolve important questions: for example, how small changes in solar insolation (Lean et al., 1995, Pang and Yau, 2002) are possibly amplified by the hydrological cycle to produce the well-documented paleo-climates recorded by a great varieties of climate proxies.

Tracers provide a convenient way of obtaining space-time integrals of motion of “water” molecules over both large and small ranges of space and time. It is now well recognized that several stable, as well as naturally and artificially produced radioactive isotopes can be used to study the hydrologic cycles, which is a subset of their wider applications in all dynamic reservoirs of the geosphere (Craig, 1961; Lal and Peters, 1967; Stuiver and Braziunas, 1989; IAEA, 1992; Phillips, 1994; 1995;

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Clark and Fritz, 1997; Lal, 1999). The great attraction of tracers of different half-lives and chemical properties in geophysical/geochemical studies lies in the fact that they allow integration of complex fluid motion over very different space and time scales. To illustrate the power of tracers, one can cite the example of the great advance which occurred in our understanding of the atmospheric processes in the fifties, when artificial radionuclides were introduced in the atmosphere as a result of nuclear weapons tests. The 1954 spring Castle thermonuclear test introduced a large amount of artificial ^{3}H (tritium: half-life = 12.3 years) in the atmosphere. Studies of its concentrations in rains clearly showed that it was removed from the atmosphere in periods as short as weeks, and provided insight into many hydrologic processes and their time scales (Begemann and Libby, 1957).

In this paper, the main emphasis will be on the applications of cosmogenic nuclides, i.e. those produced on the Earth, with a brief review of their applications as tracers in the past and of recent advances. It must of course be realized that for a complete understanding of hydrologic processes, one has to use multiple tracers to characterize the state of the system as it evolves with climate; it is a well-nested problem involving the Sun, the atmosphere and the hydrosphere. Cosmogenic tracer studies must therefore be integrated with other tracers, and all supplementary information, to characterize the system's state in the past.

2. Cosmogenic nuclides produced in the atmosphere and the hydrosphere

Cosmic rays produce nuclear reactions in the Earth's atmosphere, and in surficial materials, resulting in formation of new nuclides (Lal and Peters, 1967). Table 1 lists 15 cosmogenic nuclides with half-lives exceeding two weeks, and the target elements from which they can be produced in the earth's atmosphere and in the ocean water. We are concerned here with nuclides useful as tracers in hydrology, and have therefore excluded shorter-lived nuclides. Cosmic ray intensity is appreciably reduced at sea level due to nuclear interactions in the atmosphere (Lal and Peters, 1967), and consequently isotope production rates in surficial materials are appreciably smaller than in the atmosphere (on a per gram target element/s basis). Therefore, nuclides which can be produced in nuclear interactions with the major elements present in the atmosphere, N and O, have their principal source in the atmosphere. The next most abundant element, Ar, occurs at an abundance of only 0.93% (v/v) in the atmosphere. Nuclear interactions with surficial materials can therefore be an important source of some of the nuclides produced from Ar.

Isotopes produced in the earth's atmosphere, (Table 1), are introduced in the upper ocean:

(i) in wet precipitation, in the case of isotopes which are removed directly (^{3}H), or attached to aerosols (^{7}Be, ^{10}Be, ^{22}Na, ^{26}Al, ^{32,33}P, ^{32}Si, ^{35}S, ^{36}Cl), and
(ii) by air–sea exchange of ^{14}C (as ^{14}CO2), and of isotopes of rare gases (^{3}He, ^{37}Ar, ^{39}Ar and ^{81}Kr).

Besides direct in situ production of isotopes in the ocean waters (Table 1), some isotopes are also introduced to the oceans with river runoff as a result of weathering of the crustal materials in which they are produced, e.g. ^{10}Be, ^{26}Al, ^{41}Ca, and ^{53}Mn

(Lal, 1988,1991). To date, the latter, i.e. those introduced by weathering of crustal materials, have not been either studied or identified as important, and therefore we are not presenting estimates of the strength of this source.

The source strengths of nuclei in the oceans produced by cosmic rays, due to their injection from the atmosphere and due to direct production in the ocean water, are shown separately in Table 1. The in situ production rates of nuclides in fresh waters are expected to be much lower than in the oceans because of the much lower abundances of S, Cl, Ca and K, the principal elements that contribute to their production. The rates of injection of cosmogenic nuclides from the atmosphere to the hydrosphere have been estimated from the atmospheric production rates (Lal et al., 1988), and are also given in Table 1. Generally, atmospheric production is the dominant source of all nuclides, except for ^{36}Cl, whose in-situ oceanic production exceeds the atmospheric production by about 50%, and in the case of ^{37}Ar where it is comparable. In the cases of ^{32}P and ^{33}P it is an order of magnitude lower.

Historically, the cosmogenic radionuclides, ^{14}C (half-life = 5730 a) and ^{3}H had been discovered before the first Castle test in the atmosphere, in 1947 and 1951 respectively. Soon thereafter, in the mid-fifties, the long-lived radionuclide, ^{10}Be (half-life = 1.5 Ma), and several short-lived cosmogenic radionuclides, ^{22}Na, ^{35}S, ^{7}Be, ^{33}P and ^{32}P with half-lives in the range of weeks to years were discovered (see Lal and Peters, 1967). Studies of their distribution in the atmosphere, in wet precipitations, in ocean waters and in marine sediments clearly showed the power of these nuclides as tracers for studying wide-ranging problems in meteorology, hydrology, groundwaters, soil dynamics, and oceanography (Lal and Peters, 1967; Lal et al., 1970; 1988; Froehlich et al., 1987; Stuiver and Braziunas, 1989; Stuiver et al. 1998; Lal, 1999). Fortunately, tracers with different half-lives and chemical properties are available to answer a host of diverse questions in hydrologic cycles in the atmosphere and the hydrosphere (see Fig. 19 in Lal and Peters, 1967). The greatest virtue of tracers produced by cosmic rays lies in the fact that they are naturally injected in the atmosphere continuously at a rate which can be determined fairly accurately.

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 (Lal, 1999). In Table 2, we present a broad brush description of the utility of the cosmogenic nuclides as tracers in diverse geophysical studies, including hydrologic processes, based primarily on the chemical properties and half-lives of different nuclides.

3. Stable and radioactive nuclides as tracers in hydrology

The usefulness of stable and radioactive nuclides as tracers in hydrology has repeatedly 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

Table 1. Rates of production of cosmogenic nuclides, with half-lives >10 days, in the atmosphere and directly in the ocean waters (from Lal and Peters, 1967; Lal et al., 1988)

		Principal target element(s)		Global average production rates in the atmosphere[a] (atoms·cm^{-2}·min^{-1})	Integrated in-situ production rate in the oceans (atoms·cm^{-2}·min^{-1})
Nuclide	Half-life	Atmosphere	Oceans		
^{32}P	14.3 d	Ar	S, Cl, K	4.86×10^{-2} (5.82×10^{-3})	7.6×10^{-4}
^{33}P	25.3 d	Ar	S, Cl, K	4.08×10^{-2} (6.93×10^{-3})	2.9×10^{-4}
^{37}Ar	35.0 d	Ar	K, Ca	4.98×10^{-2} (9.10×10^{-6})	8.1×10^{-6}
^{7}Be	53.3 d	N, O	O	4.86 (1.27)	6.0×10^{-3}
^{35}S	87.4 d	Ar	Cl, Ca, K	8.40×10^{-2} (2.84×10^{-2})	5.1×10^{-4}
^{22}Na	2.6 a	Ar	Na	5.16×10^{-3} (3.75×10^{-3})	3.9×10^{-4}
^{3}H	12.3 a	N, O	O, D (^{2}H)	15.0 (13.9)	1.2×10^{-2}
^{32}Si	~150 a	Ar	S, Ca	9.60×10^{-3} (9.60×10^{-3})	2.5×10^{-5}
^{39}Ar	269 a	Ar	K, Ca	7.80×10^{-1} (2.00×10^{-1})	1.2×10^{-5}
^{14}C	5,730 a	N, O	O	1.50×10^{2}(1.20×10^{2})	

Table 1. continued

		Principal target element(s)		Global average production rates in the atmosphere[a] (atoms·cm^{-2}·min^{-1})	Integrated in-situ producttion rate in the oceans (atoms·cm^{-2}·min^{-1})
Nuclide	Half-life	Atmosphere	Oceans		
^{41}Ca‡	1.0x10^{5} a	—	Ca	—	2.4 x 10^{-5} ***(n)****
^{81}Kr	2.1x10^{5} a	Kr	Sr	7.20 x 10^{-5} (2.30 x 10^{-5})	1.9 x 10^{-8} ***(n)****
^{36}Cl§	3.0x10^{5} a	Ar	Cl	6.60 x 10^{-2}(6.60 x 10^{-2})	^{1}.06 x 10^{-1} ***(n)****
^{26}Al	7.0x10^{5} a	Ar	S, K, Ca	8.40 x 10^{-3}(8.40 x 10^{-3})	6.8 x 10^{-6}
^{10}Be	1.6x10^{6} a	N, O	O	2.70 (2.70)	1.8 x 10^{-3}

a) The figures within parenthesis give the estimated injection rate of isotopes in the hydrosphere from the atmosphere, either by air–sea gas exchange (^{37}Ar, ^{39}Ar and ^{81}Kr), or by fall-out with precipitation (other nuclides in the table).

‡) Flux to oceans from rivers should be included to take into account production in rocks and soil by ^{40}Ca(n,γ) ^{41}Ca reaction; this estimate is not given here because of large uncertainties in these calculations.

§) As in the case of ^{41}Ca, due to ^{35}Cl(n,γ) ^{36}Cl reaction.

(n)* The in-situ production of ^{41}Ca, ^{81}Kr and ^{36}Cl in the oceans is primarily due to the relevant thermal neutron capture reaction. Note the 50% greater in situ production of ^{36}Cl in the oceans compared to its atmospheric source.

of the hydrologic cycles (Craig, 1961). The relationship discovered by Craig, 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 (IAEA, 1992; Clark and Fritz, 1997). Subsequently both naturally and artificially produced radionuclides have been extensively applied to study processes and time scales in hydrologic cycles. Besides the cosmogenic radionuclides, two other categories of radionuclides have been extensively studied: (i) those produced naturally in radiogenic and nucleogenic nuclear processes associated with the ^{238,235}U and ^{232}Th decay series, and (ii) artificially produced radionuclides released in the environment 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 hydrologic cycle in its operation through different scales of space and time, it becomes necessary to study two or more tracers simultaneously. 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 hydrologic cycles.

Artificially produced tracers serve as transient tracers since they are sporadically injected in the atmosphere-hydrosphere system. Cosmogenic nuclides on the other hand are continuously produced and injected in the environments. Their concentrations reach a quasi-steady state. A perfect state of equilibrium can not be expected because (i) cosmogenic isotope production rates are not constant, changing with time due to changes in solar activity and earth's geomagnetic field, and (ii) changes in the rates of transport/mixing between the principal reservoirs of interest.

Several of the cosmogenic tracers are currently behaving as transient tracers, because they have been added in appreciable amounts from anthropogenic sources. Thus, the natural inventory of several nuclides ^{3}H, tritiugenic ^{3}He, ^{14}C and ^{36}Cl and ^{129}I has been appreciably altered due to nuclear weapons tests and also due to operation of nuclear power plants. Currently, the latter is an important contributor of ^{129}I.

An important consideration in the use of any tracer is knowledge of its source strength. Whereas the source functions are fairly well known in the case of cosmogenic nuclides (Lal and Peters, 1967), this is clearly not the case for artificially produced tracers. The nearly constant source function makes ^{14}C the most powerful tracer for varied applications in earth sciences. However transient tracers are also extremely useful since they can in some cases provide valuable information beyond that which can be obtained from naturally produced tracers. We have already discussed the information obtained from the large amount of ^{3}H introduced by the 1954 spring Castle thermonuclear test primarily in the troposphere (Begemann and Libby, 1957). Jenkins and Clarke (1976) demonstrated that one can measure both the artificially introduced ^{3}H and tritugenic ^{3}He in a water sample, which allows one to define an "age" of the water mass starting from the time that the artificially produced ^{3}H was introduced into it. The painstaking work of Jenkins (Jenkins, 1988) has produced a large database and yielded very useful insight into large-scale ocean circulation in the upper ocean based on this method (Doney and Jenkins, 1988).

Table 2. Important characteristics and principal applications of selected cosmogenic tracers.

Isotope	**Half-life**	**Principal applications**
(i) 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 a	Air–sea exchange; vertical mixing in oceans
^{81}Kr	2.3×10^{5} a	Groundwater ages, and constancy of cosmic radiation
(ii) Isotopes which label constituent molecules in the atmosphere and the hydrosphere		
^{3}H (H_20)	12.3 a	Characterizing water molecules in the atmosphere, hydrosphere and cryosphere
^{14}C (CO_2, CO_3, HCO_3)	5730 a	Characterization of the carbon cycle reservoirs
^{32}Si ($HSiO_3$, SiO_2)	~150 a	Biogeochemical cycle of silicon, ground water infiltration rates
^{33}P,^{32}P (DIP, DOP)	14.3, 25.3 d	Biogeochemical cycle of phosphorus
(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} a	Role of particle scavenging in the coastal and open oceans; dating of sediments and accretions
^{26}Al	7.1×10^{5} a	Role of particle scavenging in the coastal and open oceans; dating of marine sediments and accretions
^{32}Si ($HSiO_3$, SiO_2)	~150 a	Labelling the dissolved oceanic silicon pool; atmospheric circulation
^{33}P, ^{32}P	14.3, 25.3 d	Labelling the dissolved oceanic phosphorus pool; tropospheric circulation

In practice, one has to work with tracers of different properties, and each of its properties can be taken advantage of, as its special attribute. Except for ^{3}H, ^{3}He, ^{37}Ar, ^{39}Ar and ^{81}Kr, other cosmogenic tracers behave as non-conservative tracers in fresh waters and in oceans. This property gives them special attributes, making them useful for diverse geophysical, geochemical and biological studies (Table 2).

4. Recent advances in studies of a variety of geophysical processes

By the end of the seventies, the field of cosmogenic tracers had clearly recognized the usefulness of most of the cosmogenic tracers, with sufficient measurements at hand in each case. The eighties and nineties saw a flowering of the field, with larger scale exploitation of several tracers for answering specific questions. The eighties also marked an era of dramatic advance in the techniques of measurements (Gosse and Phillips, 2001) of long-lived cosmogenic radionuclides ^{14}C, ^{10}Be and ^{26}Al using AMS (accelerator mass spectrometry). This opened up new windows for observing in detail a host of physical, chemical and biological processes. The ease with which these nuclides can be measured allows obtaining long series of measurements in space and time. Examples of this development are: the direct measurements of ^{10}Be and ^{26}Al concentration profiles in the principal oceans (Kusakabe et al., 1982; Measures and Edmond, 1982), and of ^{10}Be and ^{36}Cl in ice cores providing invaluable data on past changes in polar meteorology and hydrology (Baumgartner et al., 1997; Yiou et al., 1997).

In Table 3, we present considerations relevant to the applications of the radionuclides, ^{10}Be, ^{32}Si, ^{14}C, ^{39}Ar and ^{81}Kr in groundwater studies. The non-conservative cosmogenic tracers, ^{10}Be and ^{32}Si should serve as useful tracers for measuring groundwater infiltration rates. The conservative cosmogenic tracers, ^{39}Ar (Loosli, 1983; Schlitzer et al., 1985; Schlosser et al., 1994 , 1995) and ^{81}Kr (Collon et al. 2001, 2003) hold very important promise for dating groundwaters. The former, because of its short half-life (269 a), is an ideal tracer for studying 'ages' and rates of mixing in the oceans. Recently Broecker and Peng (2000) have summarized the present status on studies of ^{39}Ar in the oceans. They conclude that this tracer may prove useful for studying changes in the ventilation of the deep sea during the past ~ 1000 years, and that together with ^{14}C in the same water masses, ^{39}Ar serves as a very useful tracer to constrain models of diffusive mixing in the oceans. To date, ^{39}Ar activity has been measured by counting its emitted β-radiation. Collon et al (2003) have now shown that its natural activity in oceans can be measured using the AMS method.

A new field, the study of P-biodynamics in surface waters using cosmogenic ^{32}P and ^{33}P (Lal et al., 1988), surfaced in the late eighties. This tracer application was not, however, advanced sufficiently because in this case it was not realized that these short-lived nuclides (half-lives:14.3 and 25.3 days respectively) in fact had about the appropriate half-lives for studying time scales of exchange of phosphorus between dissolved inorganic P, organic P and plankton processes.

Recently innovative applications have been made of cosmogenic tracers for studying soil dynamics and groundwater recharge (Lal et al., 1996; Barg et al., 1997; Lal, 2001). Since soils are primarily "open systems", containing a suite of chemical

Table 3. Comments on behaviours of different tracers of half-lives exceeding 100 years in groundwaters

	Cosmogenic nuclide				
COMMENTS	**^{10}Be**	**^{32}Si**	**^{14}C**	**^{39}Ar**	**^{81}Kr**
Tracer losses on exchange with *soil-matrix*	yes	yes	yes	no	no
Tracer losses on exchange with *rock-matrix*	yes	yes	yes	no	no
Underground sources of tracer	no	no	yes	yes	yes
Decrease of dissolved tracer concentrations due to non-radioactive processes	yes	yes	yes	no	no
Suitability as a tracer					
(i) for dating groundwaters	no	no	yes	yes	yes
(ii) for groundwater *infiltration rates*	yes	yes	yes	no	no

compounds, which are labile and freely exchange elements and isotopes with the environment, studies of soil dynamics cannot be carried out with the conventional nuclear methods. Consequently soils have resisted most attempts to study their dynamics, even using the most widely applied methods, and have continually challenged the imagination of physicists and chemists. But it now appears that there is a good hope of overcoming this problem, based on studies of cosmogenic ^{10}Be (Lal, 2001). Similarly new approaches now seem very promising for measuring groundwater infiltration rates using cosmogenic ^{32}Si (Lal and Einloth, 2003), based on pioneering studies of Nijampurkar et al.(1966), Lal et al (1970) and Froehlich et al (1987). Very sensitive measurements of ^{32}Si activities are now being made by Morgenstern et al (2001), using the liquid scintillation counting method.

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Because of the long half-life of ^{81}Kr (2.1x10^{5} a), this isotope should be useful for dating old groundwaters. The central problem in its application has been the difficulty in detecting its low concentration in groundwaters. Significant advance in its measurement by Collon et al. (2003) now makes it possible to measure its activity in groundwaters, but not so conveniently as yet for it to be adopted as a routine method.

5. Concluding remarks

Cosmic rays produce six radionuclides of half-lives ranging between 2 weeks and 3 years, and nine between 10 years and 1.5 my (Lal and Peters, 1967); see Table 1. Radionuclides are also produced by cosmic rays directly in the oceans by cosmic ray interactions (Lal et al., 1988). In Table 2, a broad overview of the wide ranging applications of atmospheric cosmogenic nuclides is presented. 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}·s. The incident energy flux is ~ 5 x 10^{-3} cal/cm^{2}/a, 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 it is for this reason that even the weak cosmic ray source is able to make a significant contribution to several problems in earth sciences, in addition to meteorology, hydrology and oceanography (Lal, 1991).

Thus we see that a large number of cosmogenic tracers are available for studies of the water cycles between different water reservoirs, and the use of these tracers has steadily increased to date. *But of course, tracers are not the complete answer to the mysteries of the hydrosphere: they are not a panacea! We have to learn how to* *use tracers, how to model them, how to combine them with other tracers, singly and multiply, etc., etc.* The usefulness and application of a tracer cannot be discussed on an absolute basis, because such an approach would result in a largely academic discussion. A tracer may have the appropriate physical and chemical attributes, but its source strength may be too weak, or else its source function may not be known at the present time. The tracer suitability has therefore to be evaluated periodically as our frontiers of knowledge expand. With the freedom in thinking about what type of tracer measurements can be made, one can probably expect to derive a great deal of valuable information from it; however, one has to think about applying it within practical constraints. An important constraint is the number of measurements which one can make within a reasonable period, and within available financial resources. Today, the principal constraint is indeed the inadequacy of spatial and temporal coverage of the tracer data. With more synoptic data, one would be able to refine tracer modelling also!

The availability of the AMS method has already made a tremendous advance in the extensive applications of ^{10}Be, ^{14}C, ^{26}Al and ^{36}Cl in a great variety of hydrologic problems. It is quite apparent that with continued developments in methods of sensitive (and convenient) measurement of other cosmogenic nuclides, e.g. ^{32}Si, ^{39}Ar and ^{81}Kr, cosmogenic isotopes will play a much greater role as tracers in hydrologic studies, providing important clues to the roles of water and vapour in regulating the Earth's climate.

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4. STABLE OXYGEN AND HYDROGEN ISOTOPES IN PRECIPITATION

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1. Introduction

The fact that water on earth moves in a cycle, from oceans to clouds to rivers to oceans, has been known since ancient civilizations existed on different parts of the globe. However, the quantification of fluxes between various parts of the cycle, particularly the atmospheric and surface parts, has been difficult to achieve even today. Understanding of climatic processes controlling these fluxes and, therefore, the ability to predict variability and changes in the hydrologic cycle, also depends upon the quantification of moisture fluxes between atmospheric and surface reservoirs.

Soon after the discovery of the heavy isotopes of oxygen and hydrogen in the 1920s and early 1930s, significant differences were observed in the isotopic contents of seawater, freshwater, and snow (Gilfillan, 1934; and review by Rankama, 1954). By the early 1950s, as a result of the availability of better measurement techniques, the dependence of isotope content of rain on a variety of climatic factors such as surface air temperature, amount of rain, and the altitude and latitude of precipitation, were also observed (Friedman, 1953; Dansgaard, 1953; Epstein, 1956). Together with the known temperature dependence of isotope ratios (Urey, 1947), the observed relationship between isotopes and climate also provided a means to study past climates by using isotope distributions in continental and marine archives (Emiliani, 1955).

The foundations for the use of isotopes to help quantify fluxes in the hydrologic cycle were firmly established by the 1950s, albeit with a limited scope and limited records of measurements (Craig, 1961; Dansgaard, 1964). Atmospheric nuclear testing of the 1950s and consequent requirements to monitor the tritium fallout resulted in an exponential increase in the number and geographic distribution of stable isotope measurements in the hydrologic cycle (Dansgaard, 1964; Ericsson, 1965; Froehlich et al., this volume). In this summary review, we discuss the developments in stable oxygen and hydrogen isotope measurement techniques, the nomenclature of isotope measurements, the structure of the IAEA/WMO global

P.K. Aggarwal, J.R. Gat and K.F.O. Froehlich (eds), Isotopes in the Water Cycle: Past, Present and Future of a Developing Science, 39-51.

network of isotopes in precipitation (GNIP), and an analysis of GNIP data from 1961 to 2000.

2. Analytical Methods

2.1. MEASUREMENT TECHNIQUES

Stable isotope compositions in natural waters are typically measured using double-focusing magnetic sector field mass spectrometers, as originally designed in 1947 (Nier, 1947). Due to the low abundance of isotope species of interest (e.g., ^{18}O - 0.2%) and the very small deviations of isotope ratios (in most cases few per mil only), the precision of such measurements is limited by the stability of mass spectrometers in the time span when multiple samples are analysed. To overcome these limitations, McKinney et al. (1950) designed a dual sample inlet system where a sample and a reference standard were measured in rapid succession. This allowed the measurement of sample isotope ratios with respect to a reference material, resulting in precise measurement of isotope ratios in natural materials. Excellent reviews of mass spectrometric measurement of isotope ratios are given in Gonfiantini (1981) and Platzner (1997).

The basic design of instruments as described above is still used for mass spectrometric measurements today. Continuous flow techniques are now being used by an increasing number of laboratories where tiny sample aliquots are introduced in sample preparation lines (e.g. high temperature pyrolysis oven for oxygen isotope analysis) and flushing the reaction product (e.g. CO gas) with a continuous stream of helium carrier gas for mass spectrometric analysis. These continuous flow techniques permit a very fast measurement cycle and the possibility of using very small samples. Details on the measurements are given in a number of publications; see e.g. articles in IAEA (2001), Werner and Brand (2001), Gehre and Strauch (2003), Werner (2003).

By measuring isotope ratios in a sample with respect to a common standard, it is not necessary to know all corrections for instrumental effects and interferences in a mass spectrometric measurement. Most of the influences on a sample also affect the reference standard and, therefore, cancel out. As a result, it is more convenient not to report the $^{18}O/^{16}O$ ratio (R) of a sample directly, but to report the deviation δ of this ratio from that of the reference standard. Due to the small values of the δ-value commonly all data are multiplied with thousand and reported as per mil deviation:

$$\delta = \frac{R_{sample} - R_{reference}}{R_{reference}} \times 1000 \text{ ‰} \tag{1}$$

A detailed and comprehensive review of all aspects of the δ notation and the realization of a conventional reporting scale is given in Gonfiantini (1981).

2.2. ISOTOPE STANDARDS

The primary criterion for a reference standard is that it should represent a major pool of the element under consideration. By 1953 "average ocean water" was suggested and used as a reference point for isotope-ratio measurements. Because no "average ocean water" existed, Craig (1961) refined this concept by defining the hypothetical Standard Mean Ocean Water (SMOW) as zero-point of that conventional scale in terms of real reference water. The isotope ratios of SMOW were compiled by taking a weighted average of the isotope ratio measurements of different seawater compartments available at that time (Horibe and Kobayakawa, 1960). But because SMOW was just the concept of hypothetical water and never existed as a real water sample, it could not be used directly for calibration of laboratory measurements. Its isotopic composition was defined in terms of an isotopic difference from an existing water sample (NBS 1) distributed by the US National Bureau of Standards (Mohler, 1960). During an IAEA interlaboratory comparison in 1965, serious doubts were raised concerning the preservation of the NBS-1 water standard and about possible changes of its isotopic composition over time. For this reason, it was unsuitable to be used as a standard any more.

An IAEA panel of experts recommended in 1966 that two new primary water reference materials should be established - one being as close as possible to the defined SMOW and the other with an abundance of the heavier isotopes close to the lowest limits observed in natural waters. The new "SMOW" was subsequently prepared by R. Weiss and H. Craig at the Scripps Institution of Oceanography, La Jolla, USA, by mixing distilled ocean water with small amounts of other waters. The second water reference material was obtained by E. Picciotto, Université Libre de Bruxelles, Belgium, from melting a firn sample at Plateau Station, Antarctica. This material was named Standard Light Antarctic Precipitation (SLAP). Control analyses performed by H. Craig indicated that the new "SMOW" had the same $^{18}O/^{16}O$ ratio as the defined SMOW, but a slightly lower $^{2}H/^{1}H$ ratio or $\delta^{2}H$ value (-0.2‰) relative to SMOW. This difference, however, is about a factor of four to five lower than the measurement uncertainty of most laboratories and for practical purposes, the two standards had identical isotope ratios. Absolute isotope ratios ($^{18}O/^{16}O$, for $^{17}O/^{16}O$ as well as for $^{2}H/^{1}H$) in the standard prepared by Weiss and Craig have recently been determined and are listed in Groening (2004).

Unfortunately the same term, SMOW, was used for reporting isotope measurements using the synthetic water standard. The IAEA then decided to rename the water prepared by Weiss and Craig to VSMOW (Vienna-SMOW) in order to distinguish between the hypothetical SMOW of Craig (1961) and the synthetically prepared standard. An IAEA Consultants' Meeting in 1976 recommended that all future results for hydrogen and oxygen isotope ratios should be reported as δ values relative to VSMOW. To increase coherence and consistency between reported δ values, the meeting also recommended that a fixed δ value for the second water reference material, SLAP, should be adopted for both the $^{18}O/^{16}O$ and $^{2}H/^{1}H$ δ and that these values should be normalized relative to VSMOW water, the primary reference material.

The definition of VSMOW as zero-point for the oxygen and hydrogen δ scales and the adoption of fixed δ values for SLAP is therefore a slight modification of the original definition of the δ scale (Coplen et al. 1996):

$$\delta = \frac{R_{\mathrm{SAMPLE}} - R_{\mathrm{VSMOW}}}{R_{\mathrm{VSMOW}}} \cdot \left(\delta_{\mathrm{SLAP}} \Big/ \frac{R_{\mathrm{SLAP}} - R_{\mathrm{VSMOW}}}{R_{\mathrm{VSMOW}}} \right) \times 1000 \ ‰ \tag{2}$$

Due to the limited amount of VSMOW and SLAP produced in the sixties, their stock will be exhausted by about 2010. The IAEA has therefore taken steps to produce replacements for both reference materials. A large quantity (~300 litres) of replacement material has been prepared for VSMOW. The new material has an isotopic composition very close to the existing VSMOW and calibration tests reveal deviations in the order of less than 0.01 ‰ for $\delta^{18}O$ and of about 0.1 ‰ for $\delta^{2}H$. Work is in progress to prepare a similar replacement for SLAP.

3. Global Network of Isotopes in Precipitation (GNIP)

3.1. NETWORK STRUCTURE

A panel of experts convened by the IAEA in 1959 recommended a set of network stations to monitor the isotope contents in precipitation. These stations were to form the global network of isotopes in precipitation (GNIP). It was also recommended that monthly composite samples of precipitation would be the basis for isotope monitoring. The network began with 151 precipitation stations at the onset of its operation in 1961, and quickly reached a maximum of about 220 stations in 1963-1964. After a review of the 1961-1975 data, primarily based on the decay of the bomb-derived tritium peak in precipitation, a number of GNIP stations was discontinued in the late 1970s and resulted in a significant loss of global coverage for both tritium and stable isotopes. Following the recognition of the role of precipitation stable isotopes in better simulating the hydrologic cycle in climate models (Jouzel et al., 1984), there was a renewed interest in GNIP data. This led to the re-activation of some of the GNIP stations that had been inactive since the 1970s. A growing water resources programme of the IAEA in the 1980s and 1990s also made it possible to establish or strengthen national networks of isotopes in precipitation and bring them into GNIP. Today, 183 stations are contributing monthly and/or daily samples from 53 countries (Fig. 1).

At the very beginning of GNIP, a few laboratories in the United States of America and Europe (primarily Dansgaard's laboratory in Denmark) analysed most of the GNIP samples. Presently, about 30% of the GNIP samples are analysed at the IAEA laboratory in Vienna (from stations listed as IAEA stations in Fig. 1) and the rest by other laboratories in various countries. These laboratories report the results to IAEA once a year for their incorporation into the GNIP database. To date, a total of 70 laboratories from 38 countries have contributed to the GNIP database. National laboratories providing GNIP data participate in inter-laboratory comparisons organized by the IAEA on a regular basis, thus maintaining the quality of analytical data reported as a part of GNIP.

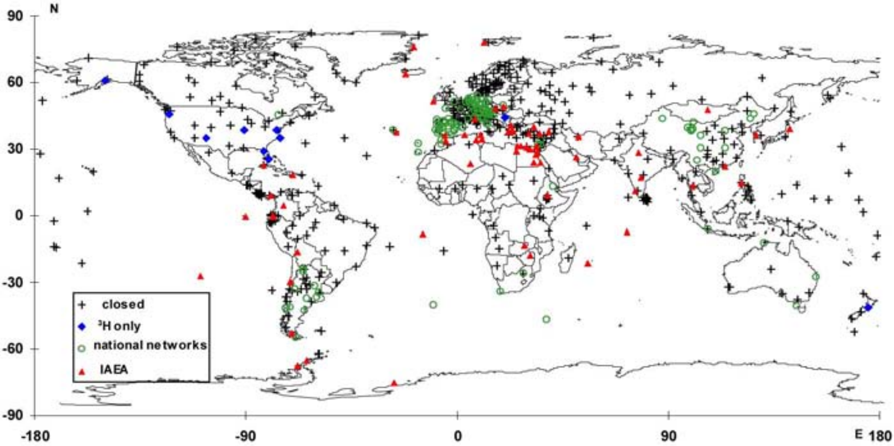

FIG. 1. Global Network of Isotopes in Precipitation in 2003.

3.2. DATABASE

The GNIP database is located at the IAEA Headquarters in Vienna (http://isohis.iaea.org) and allows easy access to data through numerous selection criteria. More than 88,000 records are available and can be downloaded freely. The longest isotope record is available for the station in Ottawa, Canada, where tritium in precipitation has been measured since 1954. For 79 stations, less than 12 months of isotope and meteorological data are available in the database. For a majority of stations, the length of isotope records varies between 4 and 8 years (Fig.2).

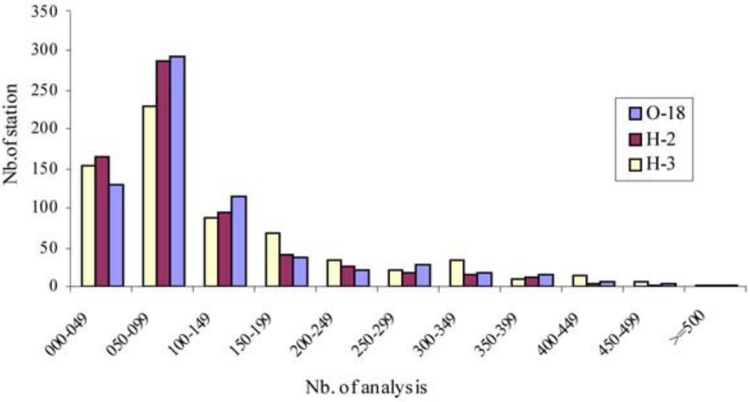

FIG. 2. Numbers of ^{18}O, ^{2}H, ^{3}H records in the GNIP database.

The spatial distribution of data accumulated in the GNIP database is far from homogeneous owing to difficulties in maintaining stations at high altitudes, high latitudes and/or isolated locations such as small islands. As can be seen in Fig.3, 52% of GNIP stations are located within the 30° - 60° N latitude band, and 72% of the stations are located at altitudes between 0 and 500 m.

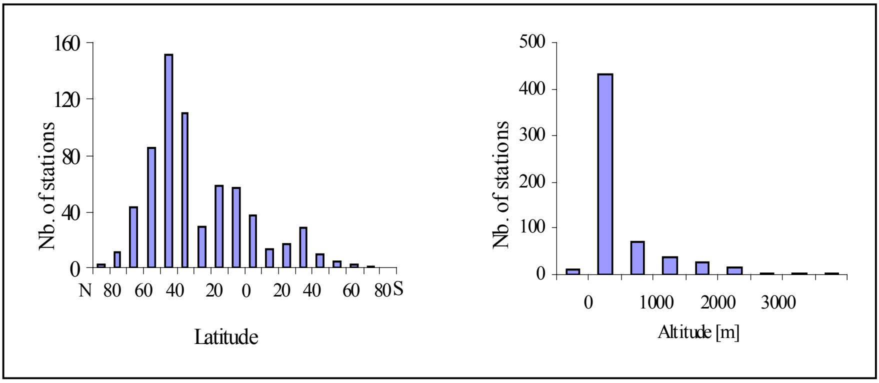

FIG. 3. Latitude and altitude distribution of the GNIP stations.

The records for each station include the stable isotope compositions δ^2H and δ^{18}O) and tritium contents with the analytical uncertainties stated by the reporting laboratory. In addition to the isotope data, basic meteorological variables as recorded by the stations such as type and amount of precipitation, surface air temperature and vapour pressure, are also stored in the database.

4. Analysis of GNIP data

4.1. THE METEORIC WATER LINE

The very first analyses of a few meteoric water samples from non-marine environments (Epstein and Mayeda, 1953; Friedman, 1953) indicated that their oxygen and hydrogen isotope values were linearly correlated. Craig (1961) analysed about 400 samples river and lake water, rain, and snow from diverse geographic locations. He found that all of the data, except for those from the lakes, plotted along a line defined by the equation

$$\delta^2\text{H} = 8\ \delta^{18}\text{O} + 10 \tag{3}$$

Although Craig did not call it as such in 1961, the above equation became known as the “global meteoric water line (GMWL)” which traced the isotopic compositions of natural waters originating from atmospheric precipitation and not subjected to surface evaporation. The physical basis for this correlation lies in the fractionation of isotopes during evaporation-condensation processes and is discussed in more detail by Gat (this volume).

Dansgaard (1964), using precipitation data from the early phase of GNIP, found that isotopes in precipitation from northern hemisphere continental stations followed the GWML of Craig, but that significant deviations existed in precipitation data from other continents and from island stations. These deviations from GMWL were attributed to differences in meteorological conditions and processes responsible for precipitation (see also Gat, this volume).

Statistical analyses of GNIP data for the periods 1960-1978 and 1960-1987, respectively, were reported by Yurtsever and Gat (1981) and Rozanski et al. (1993; IAEA, 1992). Using the same methodology described in the above reports, data from 1961-2000 have now been analysed. The arithmetic (unweighted) means of isotope ratios in precipitation from nearly 410 stations are described by the following equation:

$$\delta^2H = 8.07(\pm 0.02)\,\delta^{18}O + 9.9(\pm 0.1) \qquad (R^2=0.98) \qquad (4)$$

Long term means weighted by the amount of precipitation were calculated considering only the years for which more than 70% of precipitation was analysed for a given isotope and at least one year of observation was available. The correlation between the weighted means is:

$$\delta^2H_{(\mathrm{weighted})} = 8.14(\pm 0.02)\,\delta^{18}O + 10.9(\pm 0.2) \qquad (R^2=0.98) \qquad (5)$$

The unweighted best-fit line is remarkably close to the line derived by Craig in 1961 from a very small number of observations. This indicates that the basic processes controlling the isotope distributions in precipitation are well understood (see Gat, this volume).

With the relatively large temporal record now available, it is possible to compare decadal datasets for systematic changes in isotope compositions. Thirty-one GNIP stations have reported data throughout the 1961-2000 period. Linear regressions of weighted annual means of δ values from these stations for the periods 1960-1978, 1960-1987, and 1960-2000 are shown in Fig. 4. Although the weighted means for these stations are slightly different than the global relationship discussed above, there is no clear trend of isotope variations from 1961 to 2000. The deuterium excess is about 1 per mil lower for 1960-2000 compared to the 1960-1978 data, but this is most likely due to improvements in measurement techniques and precision rather than changes in climatic conditions.

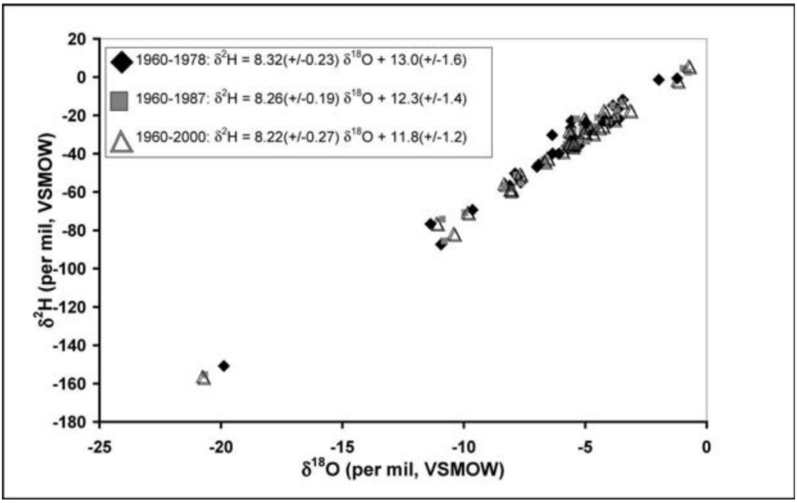

FIG. 4. Weighted annual means of δ^2H and $\delta^{18}O$ in precipitation at 31 GNIP stations with a continuous record from 1960 to 2000. The data do not show a discernible pattern of temporal change in isotope values.

4.2. CAUSES OF VARIATIONS IN ISOTOPE COMPOSITIONS

Dansgaard's (1964) comprehensive analysis of global distributions of stable isotopes identified several "effects" on isotope variations resulting from a number of physical and meteorological parameters such as latitude, altitude, distance from the coast, amount of precipitation, and surface air temperature. The reviews that followed (Yurtsever and Gat, 1981; Rozanski et al., 1993; Ingraham, 1998; Gat et al., 2001) substantiated these so-called "effects" which are caused by isotope fractionation associated with phase changes of water in the hydrologic cycle (see also Gat, this volume). Some of these effects are caused by isotope fractionation at the condensation of atmospheric water vapour to precipitation. The air masses lose water as they move along surface temperature gradients from tropical to polar latitudes ("latitudinal effect"), from the sea to inland ("continental effect"), or from lower to higher elevations ("altitude effect").

Figure 5 shows the correlation between weighted means of $\delta^{18}O$ in precipitation and local air temperature for 325 GNIP stations.

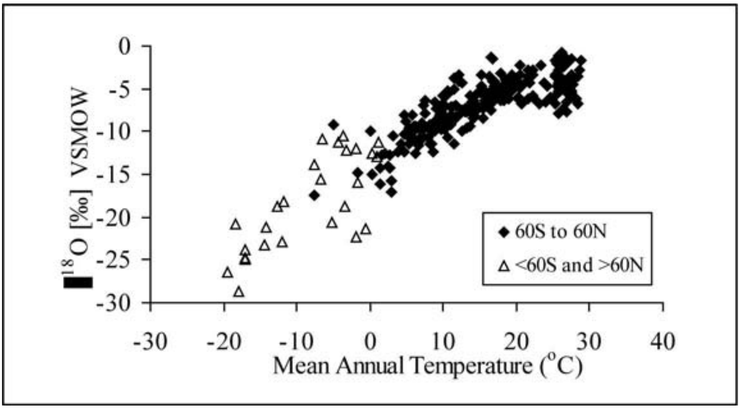

FIG. 5. Correlation between weighted means of $\delta^{18}O$ in precipitation and local air temperature for 325 GNIP stations.

As described in previous reviews, there is a clear dependence of isotope contents on temperature for stations with annual means of air temperature (t) from about –20 ˚C to +20 ˚C.

For polar stations (-20 ˚C to -2 ˚C), the calculated temperature dependence of $\delta^{18}O$ is 0.82‰ per ˚C. Rozanski et al (1993) and Dansgaard (1964), for the same temperature range, reported dependencies of 0.9 and 0.8 ‰ per ˚C. For the temperature range of 0 - 20 ˚C, the temperature dependency is lower (0.53‰ per ˚C). This compares with earlier estimates of 0.69 ‰ per ˚C (Dansgaard, 1964) and 0.58 ‰ per ˚C (Rozanski et al., 1993). It should be noted that Dansgaard's analysis was based on a much smaller dataset compared to the analysis of Rozanski et al. and to this study.

Isotopic compositions of precipitation at stations with a mean annual air temperature higher than about 18°C (mainly tropical stations) do not show a discernible temperature dependence. This lack of temperature dependency in tropical precipitation has been attributed to the more dominant role of the amount of precipitation or the "amount effect" (Dansgaard, 1964; Rozanski et al., 1993; Gat, 1996). Figures 6(a) and 6(b) show the $\delta^{18}O$ – precipitation amount relationships for all stations, including polar and tropical stations. Isotope–amount relationship is better defined for the polar stations, but overall the relationship is rather poor.

The dependencies of isotope compositions on temperature and amount of precipitation are now considered to be more complex (Aggarwal et al., 2004; Alley and Cuffey, 2001; Fricke and O'Neil, 1999; Hendricks et al., 2000; Hoffman et al., this volume; Jouzel et al., 2000), than were suggested in earlier reviews of GNIP data. These complexities arise from the much greater influence of moisture source and transport patterns on isotope composition compared to the influences of temperature and/or precipitation amount alone.

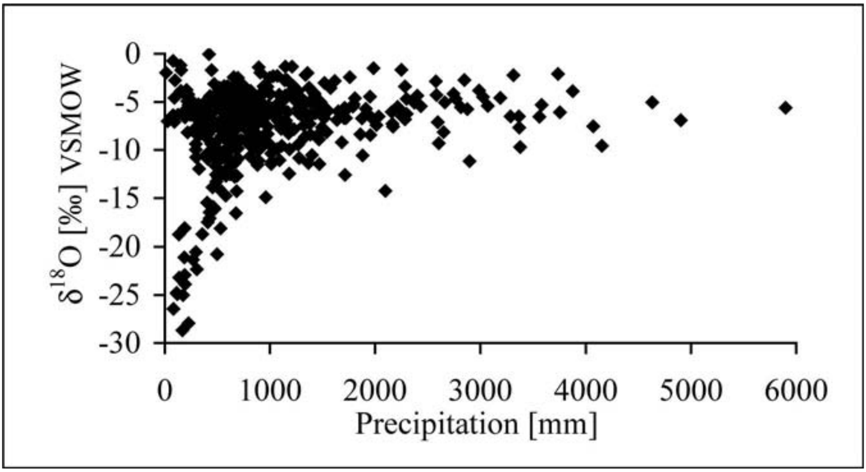

FIG. 6(a). $\delta^{18}O$ vs. precipitation amount for all GNIP stations.

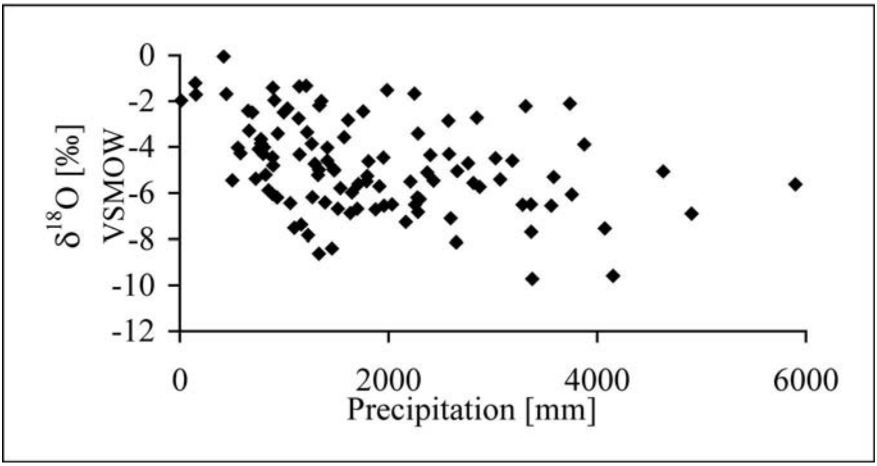

FIG. 6(b). $\delta^{18}O$ vs. precipitation amount for tropical GNIP stations.

5. Future trends

Isotope data from GNIP have provided a basis for global applications of isotopes in hydrology, palaeoclimatology, and climate change research. While the utility of these data has been wide-ranging, some of the limitations of GNIP also should be recognized. Precipitation samples for GNIP are a monthly composite of all precipitation at a station. Therefore, these data cannot be used to investigate the causes of daily or event-based variations in precipitation processes. The relatively limited geographical density of stations also makes it difficult to use GNIP data for investigating inter-annual variability in precipitation. An isotope network designed to study precipitation and climate variability at daily scale would include perhaps thousands of stations across the globe, similar to a terrestrial network for climate monitoring on this scale. However, an isotope network for global monitoring of monthly variations of precipitation may only require about one thousand stations. Such a network can be operated with increased cooperation from the scientific community at large and would contribute substantially to improved applications of isotopes in hydrology and hydro-meteorology. The IAEA has made substantial efforts in this direction and it is likely that a strengthened GNIP with a desirable station density and distribution would become available in the next five years. This global network may then be supplemented with additional stations for more detailed local or regional studies of hydrology and climate. Recent efforts of the IAEA to explore the feasibility of global networks of isotopes in river discharge and in terrestrial moisture would complement a global precipitation network. A strengthened GNIP together with isotope data from rivers and terrestrial moisture should spur additional research related to climate modelling, biosphere–hydrosphere interactions, and local or continental scale hydrology.

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5. TRITIUM IN THE HYDROLOGIC CYCLE

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1. Introduction

Tritium, the radioactive isotope of hydrogen of mass three and a half-life of 12.32 years, is one of the most important transient tracers used in hydrological research. After the discovery of natural carbon-14 in the late 1940s, it was suspected that tritium and other radionuclides might also be produced by cosmic-ray spallation. Early studies of heavy water produced by electrolysis indicated that natural tritium was present in the environment at a level of about $1x10^{-18}$ moles of tritium to 1 mole of hydrogen (Grosse et al., 1951). This led to the designation of this ratio as the now familiar tritium unit (1 tritium atom/10^{18} atoms of hydrogen). Although the major natural source of tritium on the earth is the spallation of atmospheric molecules by cosmic rays, a small amount is also produced by natural fission and reactions with thermal neutrons in the lithosphere (Lehmann et al., 1993). However, this production is rarely of importance in hydrologic studies. The natural production by cosmic rays results in a steady-state inventory on the Earth's surface of about 3.5–4.5 kilograms of tritium (Lal and Peters, 1967; O'Brien et al., 1992), most of which is present as part of the water molecule (HTO). As part of the water molecule, tritium follows the pathway through the hydrologic cycle almost exactly, with only small perturbations due to fractionation effects during phase changes (Bigeleisen, 1962). These fractionation effects are usually small and can be ignored relative to measurement uncertainties and the larger change resulting from radioactive decay. Consequently, information on time scales for hydrologic processes can be obtained from tritium measurements (Buttlar and Libby, 1955).

Tritium is one of the nuclides produced during nuclear weapon testing. Beginning in 1953, the atmospheric testing of fusion weapons dramatically increased the inventory of tritium on the Earth's surface, with the highest increase resulting from the nuclear tests of 1962 (Eriksson, 1965; Carter and Moghissi, 1977). These atmospheric bursts increased the tritium inventory on the Earth's surface by more than two orders of magnitude, with most of the tritium finally ending up in the world oceans (Miskel, 1973; Michel, 1976). Tritium concentrations in rain prior to nuclear testing were of the order of a few tritium units, with highest concentrations occurring in mid-continental areas. Tritium concentrations in

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precipitation peaked in the northern hemisphere during 1963, rising to a few thousand tritium units in most mid-continental locations (IAEA, 1981, 1992). Smaller increases were seen in the tritium concentrations of oceanic and continental surface waters in the mid-1960s (Stewart, 1966; Dockins et al., 1967). After deposition on the continents, tritium entered into the vadose zone, surface water and groundwater. The value of this tritium transient for studying hydrologic processes was quickly recognized (IAEA, 1962; Suess, 1969), and for the past five decades tritium has been widely used to obtain time scales for physical mixing processes in oceanographic and hydrologic systems. In hydrology, tritium has proved useful in studies on the movement of water through the unsaturated zone, on time scales for physical processes occurring in surface waters and groundwaters, and interactions between groundwater and surface water systems. Frequently, tritium has been able to provide information on time scales that are not easily obtained from other methods or to furnish a baseline against which results from other methods could be compared. Below, we discuss some of the approaches that have been used in studies of hydrologic processes with tritium data.

2. Tritium in the atmosphere

Initially, most tritium is produced in the atmosphere, where it enters the hydrologic cycle. Tritiated water within the troposphere can be deposited quickly in the ocean and other surface bodies of water, either by direct precipitation or by molecular exchange across the air–water interface. It is generally thought that molecular exchange is the dominant mechanism for removal of tritium from the atmosphere and deposition into oceans and lakes (Ostlund and Berry, 1970). Pre-bomb tritium concentrations are not well known, although some estimates are available which suggest they were on the order of 2–8 tritium units across the continental USA (Thatcher, 1962). Tritium concentrations in precipitation rose rapidly following the atmospheric bomb tests and were found to have a strong dependence on location and season (Libby, 1962; Gat et al., 1962; Eriksson, 1965). Tritium concentrations inland tended to be much higher than those at coastal or mid-ocean locations due to the dilution of atmospheric tritium concentrations by the low concentrations found in ocean waters. There is also a major seasonal difference caused by the interaction of the stratosphere and troposphere. During the northern hemisphere Spring of each year, the warming of the land masses causes an instability in the tropopause between 30° and 60°N. This break-up results in the mixing of stratospheric air into the troposphere. The stratosphere is the main repository for atmospheric tritium, and since water vapour in the stratosphere cannot exchange directly with water vapour in the ocean, the tritium concentrations in that reservoir remain higher than those in the troposphere. As a result, there is an increase in tritium concentrations in the troposphere of the northern hemisphere each year, frequently referred to as the “Spring Leak”. This atmospheric pattern, combined with the fact that most of the major nuclear tests occurred in the northern hemisphere, has resulted in a strong latitudinal gradient in tritium concentrations within the atmosphere. Tritium concentrations are higher in the northern hemisphere with the maximum tritium concentrations occurring at about 50° to 60°N. Tritium concentrations tend to be much lower in the southern hemisphere. By now (following the weapon test moratorium) the tritium levels are again approaching the pre-bomb levels, except for areas with local contamination.

Realizing the importance of knowing the tritium input properly to interpret tritium data from groundwater, ocean water and surface waters, the IAEA set up a sampling network for isotopes in precipitation (the GNIP network) in 1960 (Gourcy et al., this volume).. For a variety of reasons, many of the data sets are not complete from 1960 to the present. However, the IAEA has developed correlations to estimate data for years or months when measurements were not made (IAEA, 1981; 1992).These data sets, both reconstructed and measured, provide the basis for the interpretation of tritium data in hydrologic systems throughout the world. Figure 1 shows some of these records as taken from the GNIP data set.

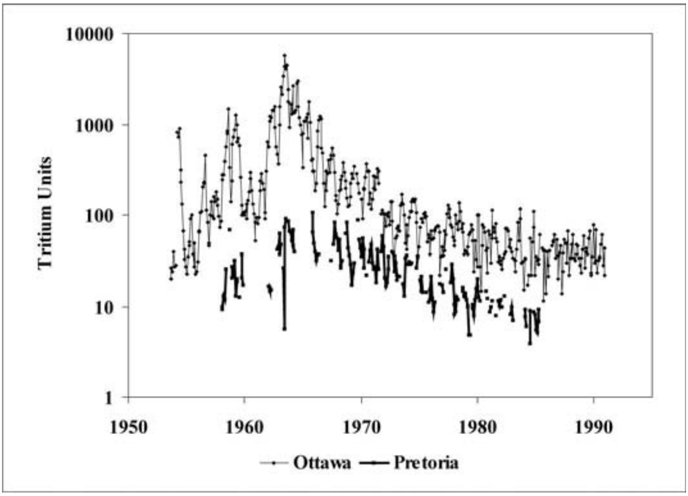

FIG. 1. Tritium concentrations in precipitation at Ottawa, Canada, and Pretoria, South Africa.

Another atmospheric reservoir for tritium is found in hydrogen and methane gases (Martell, 1963; Mason and Ostlund, 1979). Although the total quantities of tritium in these gases are small relative to that in water, the specific concentrations of tritium in the gases are much higher than in the water molecules since the main sources of these tritiated gases are nuclear power and fuel-rod reprocessing plants. Approximately 98% of the tritium in gas form is assumed to be in hydrogen and 2% in methane (Burger, 1979).

3. Unsaturated zone studies

Tritium has frequently been employed as a tracer for the movement of precipitation through the unsaturated zone into the groundwater system. Initially, it was assumed that tritium moved via a simple piston-flow through the vadose zone with some accompanying dispersion. Recharge estimates could be obtained by measuring the distance the 1963 peak had migrated through the unsaturated zone and the amount of water above the peak. These types of studies were most prevalent in the decade after major weapons testing and worked well in locations with relatively moist conditions and shallow unsaturated zones (Andersen and Sevel, 1974). Efforts were also made to calculate tritium inventories in the unsaturated zone and estimate recharge by relating the inventory to the total amount of tritium deposited at the site. However, because of the large seasonal signal, it is difficult to apply this technique when extensive hydrologic information on soil moisture contents is not available (Foster and Smith-Carrington, 1980). In locations with high recharge or shallow water tables, the tritium transient has already migrated through the unsaturated zone, making it difficult to obtain recharge rates. Thus, present-day studies are generally restricted to arid regions with deep unsaturated zones, where tritium is still an extremely useful tool (Cook et al., 1994).

Modelling tritium concentrations in groundwater requires understanding how tritium is delivered to the aquifer. In aquifers where transport through the unsaturated zone is the dominant mechanism for recharge, time scales and dispersion processes associated with the movement of water must be understood. There have been studies which modelled processes in both the saturated and unsaturated zones to determining recharge and groundwater flow in an aquifer system (Engesgaard et al., 1996; Dillon and Aggarwal, 1999). Understanding pollutant transport in such systems also requires an integrated approach involving processes in both the unsaturated and saturated zones (Zoellmann et al., 2001).

In arid areas, care must be taken in interpreting tritium distributions in the unsaturated zone. Work by Phillips et al. (1988) showed that both vapour and liquid transport are factors in the migration of tritium through the unsaturated zone. In studies in an arid unsaturated zone in New Mexico, tritium was found to have penetrated further into the unsaturated zone than chlorine-36. The maximum production of chlorine-36 was during the sea level weapons tests of the mid-1950s, while the maximum tritium production occurred during the major atmospheric testing during the early 1960s. Thus, if both nuclides had been transported only by the liquid flux, it would be expected that the chlorine-36 maximum would occur deeper than the tritium peak. The occurrence of tritium at lower depths is an indication that tritium can move as a vapour past areas where no liquid connection exists. The point where vapour flux exceeds liquid flux is dependent on the soil porosity and water content, but in many arid zones it appears that vapour flux is the dominant process.

The movement of tritium as a gas has important consequences for issues such as disposal of nuclear waste as well as estimation of recharge (Smiles et al., 1995). Arid zones have frequently been targeted as the best choices for disposal of nuclear waste, since the lack of water moving through the soils would be assumed to make it easier to contain radioactivity. While this is likely true for substances that can only migrate as ions, for radionuclides that can migrate as a gas this strategy is less effective. Studies at the low-level nuclear waste site in Beatty, Nevada have indicated that both tritium and carbon-14 have migrated out of the containment area (Striegl et al., 1998).

The extremely low recharge rates in some arid areas make the use of tritium (and chlorine-36) unreliable. Cook and Walker (1996) have shown that below a recharge rate of about 10 mm/a, recharge rates calculated using these bomb tracers will tend to be too large. For these low recharge rates, the chloride-accumulation method appears to be the more reliable tool for obtaining recharge rates. Tritium data has also shown that recharge in many areas can be focused along features such as playas and stream beds (Wood and Sanford, 1995; Scanlon and Goldsmith, 1997). Recharge rates can be calculated for these features and added to the regional water balance.

Irrigation practices also affect tritium distributions and water movement in the unsaturated zone. Irrigation water can have a very different isotopic signal from the signal in local precipitation and this difference can actually be used to study the movement of irrigated water and precipitation through the unsaturated zone. Gvirtzman and Margaritz (1986) investigated water infiltration under a field that was irrigated during the dry part of the year and received precipitation otherwise. The precipitation had environmental concentrations of tritium while the irrigation water (which was obtained from groundwater) contained little tritium. A distinctive pattern was observed under the field with alternating zones of high and low tritium indicating the movement of both types of water in a piston-flow fashion. Tritium data from unsaturated zones collected by McMahon et al. (2003) in irrigated and non-irrigated fields in farming regions of the central USA demonstrated the importance of irrigation in both recharge and transport of contaminants to groundwater. In non-irrigated fields, very little recharge occurs, and no water or contaminants had reached the water table during the tritium transient. In irrigated fields, tritium and contaminants were found to be present at the water table as well as in the unsaturated zone. Transport of water (and tritium) through the vadose zone was found not to occur in a simple piston-flow fashion, but to involve lateral transport and/or macropore flow to move past some layers. It was also found that the method of irrigation has a pronounced affect on both recharge and transport of contaminants.

There is evidence that hydrogen gas can oxidize very quickly in the soil zone, much faster than in the atmosphere (Murphy, 1993). Around nuclear power plants where releases of tritiated hydrogen gas occur, this process can result in an excess of tritium in plant water and tissue (Murphy and Pendergast, 1979). Because of the very high tritium concentrations in hydrogen gas, Ehhalt (1973) suggested that oxidation of molecular hydrogen could account for a percentage of the tritiated water that migrates into the unsaturated zone and to the water table at all locations. However, most oxidation will occur near the soil surface, so much of the tritiated water produced from hydrogen may be lost to evapotranspiration prior to movement below the soil zone.

4. Surface- and groundwaters

The most important use of tritium as a hydrologic tool is in the study of residence times for surface and groundwaters. While tritium alone cannot give an accurate estimate of age, its concentration can place limits on the possible time scales for hydrologic processes being studied in the system. The best approach to use in these studies depends on the type of system being studied and the amount and type of supporting data available. Typically, tritium should only be used with other physical and chemical data to maximize the value of the data. It is also important to have tritium data over as wide a time scale as possible to assist in interpretation. As tritium is a transient tracer, the maximum benefit is derived from tritium measurements if they are available over a wide time range, preferably on a scale of a decade or longer. Typically, long time series are not available for most studies, and simplifying assumptions must be made. Some of the approaches to the use of tritium data for surface- and groundwater systems are discussed below.

4.1. SURFACE WATER

Larger rivers represent a more complex system, where the inflows come from a variety of sources, including smaller streams, groundwater, direct runoff and lakes and ponds. The tritium concentration in the river water will be determined by the relative combination of all these sources, and it is difficult to relate changes in tritium concentration to a simple physical process. However, tritium can be used to estimate effective flushing times of large river basins. This estimate is important in that it gives a time scale for the transport rate of a conservative contaminant out of a watershed. The removal rate of the contaminant will also depend on other properties such as reactivity and adsorption, but the time scale derived from tritium will be the baseline against which these other reactions can be compared. The tritium time scale can also be used to assist in the interpretation of other isotopic river data that is being used for studying issues such as climate variations and effects of changes in land use (Gibson et al., 2002). The tritium data can be used to determine what type of delayed response occurs in the waters of a river basin so the signal of the other isotopes can be unravelled and correctly interpreted.

Estimating time scales from tritium data is most effective if data have been collected over periods of a decade or more, preferably with some data from the period when the tritium transient was at its peak in the 1960s or 1970s. Data collected over a shorter time, especially if samples were taken well after the maximum of the transient, can result in some ambiguities in their interpretation. However, some of the uncertainties may be limited by other isotopic or hydrologic information. Very few data are available from the pre-bomb period, but a few samples of river water collected prior to nuclear testing were analysed later. Figure 2 shows the range of these data for river water samples from the 1940s. Tritium concentrations in rivers prior to weapons testing reflect a steady-state situation with the tritium in precipitation. Most concentrations in Fig. 2 are less than four tritium units, slightly lower than what rainfall would be expected to be during the pre-bomb period.

One of the earliest uses of tritium to estimate residence times was by Brown (1961) in outflow of the Ottawa Basin. Using several years' worth of data in precipitation and river water collected during the 1950s, he was able to estimate turnover times for the basin. Michel (1992) used tritium data collected over a 25-30-year span to estimate residence times of a series of river basins in the USA. The model used divided the input into the river into a long-term fraction that was derived from the aquifers that drained into the river and a prompt fraction composed of runoff of water that had resided in the basin for less than one year. From the parameters of this model, he was able to reconstruct the tritium concentrations in river water during the tritium transient. As river water is frequently used in urban and agricultural settings before aquifer recharge, its concentration represents the real input of tritium into the hydrologic system. Thus, knowledge of tritium concentrations in river water can be more relevant than concentrations in precipitation for many systems.

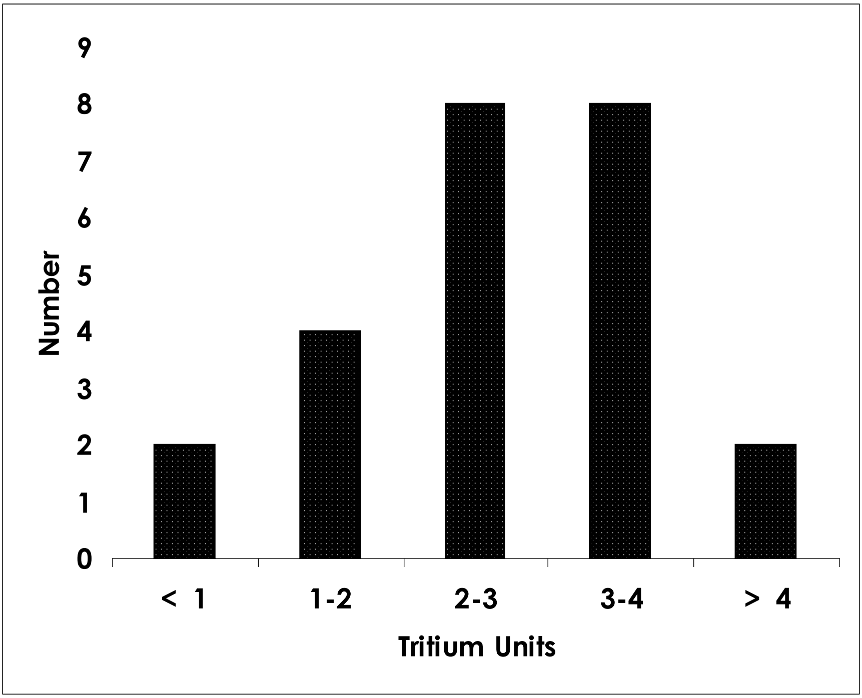

FIG. 2. Tritium concentrations in pre-bomb river waters. Data from Grosse et al., (1951) and G. Ostlund, personal communication (2003)

Rank et al. (1998) used tritium and stable isotopes of water to study the hydrology of the Danube River. A residence time of about three years for water in the basin above the sampling location was obtained from the tritium data. This information was then used with the stable isotope data to study changes in climate for the basin.

Tritium data has also proved very useful in lake and inland sea studies, both in helping to define water balances and determine rates of internal circulation. As with river basins, tritium concentrations increased in lakes quickly following the major bomb-tritium pulses and have decreased since then at a rate dependent on turnover times and internal mixing processes. The tritium distributions in the lake reflect the internal dynamics of mixing within the lake. If the lake overturns to the bottom, there should be no vertical gradient in the tritium concentration. Studies on Lake Tahoe by Imboden et al. (1977) showed that although it did not mix to the bottom every year, it had done so within a year or two before it was sampled in 1973, so no vertical gradient was present. A long series of tritium profiles in the Dead Sea indicated that it was highly stratified and had not turned since the advent of nuclear weapons testing. Beginning in the mid-1970s, the stability of the thermocline seemed to decrease, associated with a lowering of the surface level. In early 1979 the Dead Sea mixed to the bottom, resulting in a complete mixing of tritium within the sea (Steinhorn, 1985). For many lakes, the vertical gradient in tritium concentrations persists, either because the physical requirements for complete mixing never occur, or there is an influx of groundwater into the deep layer with a concentration different than surface lake water. This gradient can exist for large lakes (Scripps Institution of Oceanography, 1974) as well as small lakes (Miller and Aiken, 1996). Occasionally in large lakes and inland seas, complex concentration gradients exist which are determined by mixing and exchange processes within the system, and differences in tritium concentrations from incoming sources such as rivers and precipitation. These gradients can be used to obtain internal mixing time scales and dynamics for lakes. Torgersen et al. (1977) pointed out the value of combining tritium with helium-3 to obtain information on vertical diffusivity and effective ages of subsurface waters in studies on three of the Great Lakes in North America. This work has been expanded and several studies now exist on the use of tritium with helium-3 and other tracers to study the dynamics of large lake systems (Hohmann et al., 1998; Peeters et al., 2000; Hofer et al., 2002). Such information has also made it possible to calculate rates of chemical reactions within the deep waters of the lake (Torgersen et al., 1981; Vollmer et al., 2002).

Tritium data has also been used to study water balances in lakes. Isotopic lake balances involve inflow and outflow, both as surface and groundwater, and evaporation, precipitation and molecular exchange. It is best to have a long time series, as where there is only one measurement available multiple solutions may be possible (Michel and Suess, 1978). Herczeg and Imboden (1988) used tritium time series data to study the physical parameters on four closed-basin lakes in the western USA. They were able to use the tritium time series to place limits on properties such as relative humidity and gas exchange. Even with one measurement in a well-mixed lake, it may be possible to obtain useful information as estimates can be made on some parameters and not all solutions are physically feasible. Michel and Kraemer

(1995), using tritium and physical measurements on surface flow and meteorological data, determined that groundwater inflow must be an important component of two of the eleven Finger Lakes in New York.

4.2. GROUNDWATER

Groundwaters and the surface expressions of groundwaters such as small springs and seeps, have the widest range of tritium concentrations of any water type. They are also the systems to which tritium has been applied most extensively. At the simplest level, the presence of tritium in groundwater implies that at least a fraction of the water in the aquifer has been recharged since the beginning of the bomb era. Tritium should always be measured when collecting carbon-14 samples to insure that no leakage of recent water has occurred which would bias the age calculated. Approximate age ranges can be given for groundwater samples if one assumes that the highest concentrations represent the tritium peak (Fontes et al., 1980). To obtain more information from the tritium data, it is desirable to have a time series of tritium data over decadal time scales. When available, tritium time series can help to put constraints on models. Frequently, time series are not available, but measurements along a flow path can help overcome this deficiency. Over the years, a series of models and approaches have been developed to work with these types of data sets. The simplest method used was the piston-flow method, which assumes that the tritium peak migrates through the aquifer and retains its shape. By sampling an aquifer system along a flow path, rates of flow and recharge could be calculated by assuming that the location of the maximum tritium concentration was in water from 1963, and that the front where tritium disappeared entirely was the location of water from 1953. This method has proved very effective for systems where very little data is available, and it is assumed that tritium migrates in a simple manner (Siegel and Jenkins, 1987). It is still of use today in systems where recharge occurs in a limited area, flow is unidirectional (either laterally or vertically), and the flow path is sufficiently long that a tritium peak is still evident.

Another simple model that has been utilized is the well-mixed reservoir model, frequently referred to as the “black box” model, which was initially introduced into oceanographic studies (Revelle and Suess, 1957). This model assumes that the system being studied is well mixed and that the tritium concentration is the same everywhere within the system. Then, by measuring the tritium concentration in the system and knowing the input function, information about the time that water resides in the system can be obtained. This approach has worked well for lakes and river basins as described above, but did not give a realistic representation of groundwater systems.

Nir (1964) produced a more realistic interpretation of tritium movement through aquifers by using hydrodynamic dispersion coefficients. He found that the use of dispersion with a piston-flow model could result in a better representation of the tritium distribution in systems where laminar flow was the dominant mechanism of movement. Przewlocki and Yurtsever (1974) produced a model that used a series of well-mixed reservoirs connected in series to represent water movement. This method had flexibility and could be used for different sizes of reservoirs and allowed for additional input through the unsaturated zone as the water moved along the flow path. It was able to reproduce time series of tritium measurements found in several springs. Its main disadvantage was that the choice of reservoir size and its nature required an understanding of the system and a large number of fitting parameters had to be estimated. Małoszewski and Zuber (1982) developed new approaches that combined elements of the piston-flow model with the exponential (well-mixed reservoir model) and linear-flow model to simulate tracer distributions in aquifer systems. Zuber (1986) discussed the limitations of these models and their applicability with specific cases and tracers. Amin and Campana (1996) developed a general model, which involved perfect and partial mixing with piston flow, and discussed differences in tracer response to specific cases of the general model. All the approaches require knowledge of the source concentrations as well as measurements of the outflow concentrations. The models can then place limits on the physical parameters of the system.

Ideally, tritium data should be used in conjunction with a wide range of other data, including other tracers, chemical data and physical data. Thus, tritium will be one part of a database that can be used to calibrate models. An example of the use of tritium with other tracers and flow models is found in the work of Reilly et al. (1994) on an aquifer system in Maryland. Using tritium with chlorofluorocarbons and models such as MODFLOW and Method of Characteristics (MOC), they were able to refine their estimate of the location and quantity of recharge to the aquifer and determine flow lines within the system. Of particular interest was their calculation of dispersion, which is always a source of difficulty in tracer studies. They determined that in their aquifer system dispersion was much lower than numbers frequently calculated and that what appears to be dispersion may actually be an artifact of the finite size of the screen in wells. The tritium peak is so narrow in most systems that the screen size on most wells includes water from periods several years above and below the peak, resulting in concentrations that are well below the tritium maximum. This lower concentration is frequently thought of as the result of dispersion in the aquifer system when in reality, it may simply be the result of the inability to sample at a fine enough scale. The use of tritium/helium-3 measurements has also increased as the pulse from weapons testing has decreased. This method has the advantage of overcoming uncertainties of the input concentration as well as giving more accurate dates for young waters (Solomon et al., 1992; Carmi and Gat, 1994; Plummer, 2004).

5. Artificial tracer experiments and contaminant studies

Tritium, like most radioactive tracers, has not received much use as an added tracer to hydrologic systems. This fact most likely stems from the reluctance of the public to allow the introduction of radioactive substances into the environment. However, in the few instances that it has been allowed, tritium has furnished an effective tracer to study the movement of water through hydrologic systems. One of the earliest injection studies was carried out by Kaufman and Todd (1962) in the San Joaquin Valley in California. They introduced tritium into their site to study the seepage and loss of water from unlined canals. Houle et al. (2004) used tritium and sulphur-35 to trace the movement of sulphur relative to water in a forested watershed in Canada. Quay et al. (1980) used tritium to study the movement of tritium injected into a lake thermocline.

Contaminant sites furnish the equivalent of tracer injections in some cases. Frequently the main concern in studies of these sites is the movement of radioactive contamination. However, it is also possible to use the contaminant signature for hydrologic studies. Several studies have used the tritium signature found in the Savannah River below the Savannah River DOE Site. The tritium signature has been used to estimate the flushing rate of the estuary at the mouth of the river and the influence of river water on the coastal shelf (Hayes, 1979; Bush, 1988). Hoehn and Santschi (1987) used an accidental release of tritium in a river in northern Switzerland to study the rate of infiltration of river water into the local aquifer. They were able to calculate linear flow velocities of river water flowing into the aquifer which compared well to other tracer tests.

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6. ASSESSING SOURCES AND TRANSFORMATIONS OF SULPHATE AND NITRATE IN THE HYDROSPHERE USING ISOTOPE TECHNIQUES

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1. Introduction

Dissolved sulphate and nitrate are common constituents of surface water and groundwater. Identifying their sources and biogeochemical histories is often of significant interest for water resource managers. Sulphate contributes to the hardness of water, whereas nitrate may lead to acidification and eutrophication of water bodies. The World Health Organization (WHO) recommends a maximum of 10 mg NO_3^--N as an upper limit for drinking water. Hence, knowing the sources of nitrate and sulphate may be essential for providing suitable and safe water for human use and consumption. Stable isotope techniques have emerged as a valuable tool in this endeavour, since the isotopic compositions of dissolved sulphate ($\delta^{34}S$ and $\delta^{18}O$) and nitrate ($\delta^{15}N$ and $\delta^{18}O$) in surface water and groundwater often provide information about the sources of these solutes. Additionally, spatial or temporal patterns of increasing or decreasing sulphate and nitrate concentrations in concert with changing isotope ratios may reveal biogeochemical processes governing the occurrence of sulphate and nitrate in aquatic systems. This chapter summarizes the analytical developments which have enabled isotope hydrologists to use the isotopic composition of sulphate and nitrate in water resources research and management. A few selected historical and contemporary case studies are briefly reviewed to demonstrate the usefulness of isotope techniques in assessing sources and transformations of dissolved sulphate and nitrate in the hydrosphere.

2. The isotopic composition of sulphate in the hydrosphere

Sulphur isotope ratio determinations on the sulphate ion (SO_4^{2-}) have been performed since more than five decades (e.g. Thode et al., 1949). Sulphur has four stable isotopes, ^{32}S, ^{33}S, ^{34}S, and ^{36}S, occurring naturally with respective abundances of circa 95.02, 0.75, 4.21, and 0.02 % (MacNamara and Thode, 1950). Because of

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their more favourable abundances, ^{32}S and ^{34}S are usually chosen for sulphur isotope measurements, which are expressed using the delta scale defined as:

$$\delta^{34}S\,[‰] = \left[\frac{{}^{34}S/{}^{32}S_{sample}}{{}^{34}S/{}^{32}S_{reference}} - 1 \right] \cdot 1000 \qquad (1)$$

The traditional reference is the troilite (FeS) phase from the Cañon Diablo meteorite (CDT). The increasing scarcity of this standard combined with its slight inhomogeneity (Beaudouin et al., 1994) has prompted the International Atomic Energy Agency (IAEA) to recommend a V-CDT scale, on which a standard IAEA-S-1 has a defined δ34S value of -0.30 ‰ (Coplen and Krouse,1998). Further reference materials such as IAEA-S-2 (+22.67 ‰) and IAEA-S-3 (-32.55 ‰) with widely differing δ34S values (Coplen et al., 2002) are available from the IAEA for calibration and normalization purposes.

Using stable isotope techniques to assess sources and transformations of sulphate in the hydrosphere has been particularly successful when not only the sulphur isotope ratio, but also the oxygen isotope ratio of SO_4^{2-} has been determined. Of oxygen's three stable isotopes ^{16}O, ^{17}O, and ^{18}O, with abundances of circa 99.76206, 0.03790, and 0.20004 % respectively (Baertschi, 1976; Li et al., 1988), ^{16}O and ^{18}O are usually measured and reported using the $\delta^{18}O$ scale defined as:

$$\delta^{18}O[‰] = \left[\frac{{}^{18}O/{}^{16}O_{sample}}{{}^{18}O/{}^{16}O_{reference}} - 1 \right] \cdot 1000 \qquad (2)$$

The reference for oxygen isotope ratio determinations on SO_4^{2-} is V-SMOW (Vienna Standard Mean Ocean Water). Unfortunately, there is a lack of well-calibrated reference materials for oxygen isotope measurements of sulphate. The barium sulphate NBS 127 has reportedly a $\delta^{18}O$ value of +9.34 ‰ (IAEA, 1995). New $BaSO_4$ reference materials with widely differing oxygen isotope ratios are currently under development.

2.1. ANALYTICAL DEVELOPMENTS

To determine both sulphur and oxygen isotope ratios, dissolved SO_4^{2-} must be converted to pure $BaSO_4$. This is best achieved by filtering the water sample with 0.45 μm membranes and acidification to pH values between 3 and 4 to remove HCO_3^-. Subsequent addition of $BaCl_2$ solution results in the formation of a white $BaSO_4$ precipitate, which is recovered by filtration and dried at moderate temperatures. For samples with very low sulphate concentrations (<10 mg/L), pre-concentration of the dissolved sulphate using ion exchange resins may be desirable (e.g. Mizutani and Rafter, 1969a). For water samples containing sulphur species other than sulphate (e.g. HS^- or H_2S), it is essential to prevent their conversion to SO_4^{2-} during sampling. A detailed summary of suitable sampling procedures for different types of water samples has been published by Carmody et al. (1998).

Historically, the most common procedure for measuring sulphur isotope abundances involved the off-line preparation of SO_2 and subsequent analysis in a dual inlet isotope ratio mass spectrometer (DI-IRMS). Numerous techniques have been proposed for converting $BaSO_4$ to SO_2 (e.g. Bailey and Smith, 1972; Coleman and Moore, 1978; Fritz et al., 1974; Halas and Wolacewicz, 1981; Haur et al., 1973; Holt and Engelkemeir, 1970; Ricke, 1964; Robinson and Kusakabe, 1975; Ueda and Krouse, 1986; Yanagisawa and Sakai, 1983). One complication with SO_2 is that $^{34}S^{16}O_2^+$ is not resolved in a typical mass spectrometer from $^{32}S^{16}O^{18}O^+$. Producing SO_2 with a constant oxygen isotope composition (e.g. Yanagisawa and Sakai, 1983) is therefore desirable for simplifying the correction for the oxygen isotope contribution (Coleman, 2004). Sulphur hexafluoride (SF_6) has also been used for sulphur isotope abundance measurements using DI-IRMS (e.g. Hulston and Thode, 1965; Puchelt et al., 1971; Rees, 1978; Thode and Rees, 1971). There are no isobaric interferences for this gas, but fluorinating compounds are chemically very active and hence extreme caution is necessary during preparation of SF_6. In recent years, on-line conversion of $BaSO_4$ to SO_2 in an elemental analyser followed by continuous-flow isotope ratio mass spectrometry (CF-IRMS) has gained increasing popularity (Giesemann et al., 1994; Pichlmayer and Blochberger, 1988). The major advantage of this technique is that it can realize rapid sulphur isotope analyses (<15 min per sample) on small samples (<250 µg $BaSO_4$). A comprehensive summary of techniques for sulphur isotope abundance measurements was recently published by Mayer & Krouse (2004).

The oxygen isotope composition of sulphate has been historically determined on CO_2 generated by reacting a mixture of pure graphite with $BaSO_4$ in platinum or molybdenum boats at circa 1000°C (Longinelli and Craig, 1967; Rafter, 1967). Some CO is produced in this reaction, which is usually converted to CO_2 at platinum electrodes in a high voltage discharge cell (Rees and Holt, 1991). Recently, an alternative technique to this rather cumbersome and slow procedure has emerged. High temperature (~1450°C) pyrolysis in a glassy carbon reactor is capable of quantitative conversion of $BaSO_4$-oxygen into CO (e.g. Kornexl et al., 1999). The oxygen isotope ratio of the CO can be subsequently determined by CF-IRMS. This technique has greatly reduced both sample size requirements and analysis time. It is, therefore, likely that oxygen isotope ratio determinations on SO_4^{2-} will soon be more widely used in hydrological studies than has been the case in the past. However, assuring the accuracy of such measurements remains problematic due to the scarcity of well calibrated reference materials.

2.2. IDENTIFICATION OF SOURCES OF SULPHATE

Numerous case studies investigating the isotopic composition of sulphate in precipitation (e.g. Grey and Jensen, 1972; Jensen and Nakai, 1961; Östlund, 1957), river water (e.g. Chukhrov et al., 1975; Hitchon and Krouse, 1972; Longinelli and Corteccci, 1970), lake water (e.g. Deevey et al., 1963; Matrosov et al., 1975), and groundwater (e.g. Fontes and Zuppi, 1976; Müller et al., 1966; Rightmire et al., 1974; Zuppi et al., 1974) have been conducted throughout the last five decades with the objective to determine the sources of sulphate. Generally, dissolved sulphate in the hydrosphere can be of atmospheric, pedospheric, or lithospheric origin.

Typical ranges of $\delta^{34}S$ and $\delta^{18}O$ values for these sulphate sources are shown in

Fig. 1. Additionally, anthropogenic sulphate sources with varying isotopic compositions are ubiquitous in most watersheds worldwide.

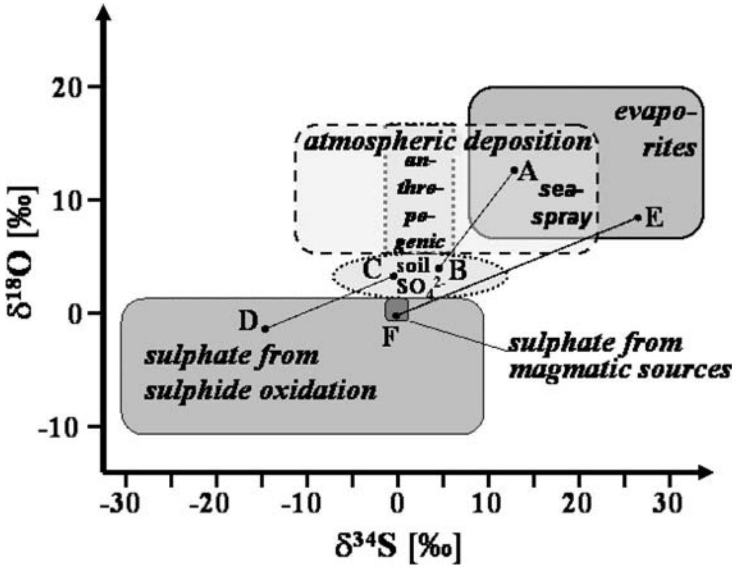


FIG. 1. Typical ranges for δ^{34}S and δ^{18}O values of sulphate from a) evaporites, b) atmospheric deposition, c) soil solutions, d) sulphide oxidation, and e) magmatic sources. Also shown are trends expected from mixing of sulphate from evaporites and soil solutions (A-B), sulphate from soil solutions and sulphide oxidation (C-D), and sulphate from evaporites and magmatic sources (E-F).

In industrialized countries, the majority of the sulphur in atmospheric sulphate deposition is of anthropogenic origin (e.g. Benkovitz et al., 1996). δ^{34}S values between -1 and +6 ‰ were found to be characteristic for atmospheric sulphate deposition in these regions (Alewell et al., 2000; Cortecci and Longinelli, 1970; Herut et al., 1995; Mizutani and Rafter, 1969b; Moerth and Torssander, 1995; Wadleigh et al., 1994; Wakshal and Nielsen, 1982). Elsewhere, natural sulphur compounds may contribute significantly to atmospheric sulphate deposition. Sulphur from volcanic emissions often has δ^{34}S values near +5 ‰ (Lein, 1991) and hence may be isotopically indistinguishable from atmospheric sulphur of anthropogenic origin. Emissions of reduced biogenic sulphur gases from wetlands may result in negative δ^{34}S values of atmospheric sulphate deposition (Nakai and Jensen, 1967; Nriagu and Coker, 1978). In coastal regions, seaspray is often the dominant source of atmospheric sulphate and δ^{34}S values as high as +21 ‰ have been observed (Chivas et al., 1991; Nielsen, 1974; Wadleigh et al., 1994; Wadleigh et al., 1996).

The oxygen isotope composition of atmospheric sulphate is dependent on the oxidation conditions in the atmosphere and the $\delta^{18}O$ value of the moisture involved in the oxidation of precursors compounds such as SO_2. Comprehensive reviews on the relevant oxidation mechanisms and the associated isotope effects have been provided by Holt & Kumar (1991) and Van Stempvoort and Krouse (1994). In temperate regions, $\delta^{18}O$ values between +5 and +17 ‰ are typical for sulphate in atmospheric deposition (e.g. Cortecci and Longinelli, 1970; Rafter and Mizutani, 1967), with the lower values observed in winter and the high values associated with summer precipitation.

Lithospheric sulphur occurs predominantly in sedimentary rocks, either as sulphate minerals (gypsum, anhydrite, etc.) in evaporite deposits or as reduced inorganic sulphur in minerals such as pyrite, which are common in shales and many other rock types. The isotopic composition of evaporite sulphate deposited throughout Earth's history has been summarized by Claypool et al. (1980) and more recently by Strauss (1997). As shown in Fig. 1, typical $\delta^{34}S$ values range between 35 ‰ (late Precambrian and Cambrian) and 8 ‰ (Permian). The respective $\delta^{18}O$ values for evaporite sulphate vary between +7 and +20 ‰ dependent upon geological age (Claypool et al., 1980). Current ocean water sulphate has a $\delta^{34}S$ value of 21 ‰ (e.g. Rees et al., 1978) and a $\delta^{18}O$ value near 9.5 ‰ (Lloyd, 1967). Reduced inorganic sedimentary sulphur compounds often (but not always) have negative $\delta^{34}S$ values (e.g. Migdisov et al., 1983; Strauss, 1999). The $\delta^{34}S$ value of sulphate generated via oxidation of reduced inorganic sulphur is often similar to that of the precursor minerals, since there tends to be only minor sulphur isotope fractionation during oxidation (Price and Shieh, 1979). The oxygen isotope ratios of sulphate generated by sulphide oxidation are often lower than those of sulphate from evaporitic or atmospheric sources. During the oxidation of sulphide minerals to SO_4^{2-}, four oxygen atoms are incorporated into the newly formed sulphate, which are either derived from H_2O or atmospheric O_2. The proportion of water and atmospheric oxygen incorporated into the sulphate molecule is dependent on whether the reaction occurs abiologically or biologically under reducing or oxidizing conditions (e.g. Taylor and Wheeler, 1994; Taylor et al., 1984). Regardless of the exact stoichiometry, sulphate derived from oxidation of sulphide minerals often has a distinct isotopic composition with comparatively low $\delta^{34}S$ and $\delta^{18}O$ values (Fig. 1). Other lithospheric sources of sulphate are magmatic and volcanic sulphur compounds (e.g. SO_2, H_2S), which are after oxidation usually characterized by $\delta^{34}S_{sulphate}$ and $\delta^{18}O_{sulphate}$ values near 0 ‰ (Fig. 1).

Additionally, anthropogenic sources may contribute sulphate with characteristic, but widely differing isotope compositions depending on location, to groundwater and surface water. For example, municipalities using surface water for their drinking water supply often use aluminium sulphate as an additive for settling particulate matter during water processing. Soaps and detergents contain considerable amounts of sulphate ($\delta^{34}S$ values often near +1 ‰, Varner and Mayer, unpublished data) which is released into rivers via waste water effluents. Drywalls in leaky landfills or by-products of the sour gas industry are alternative examples for anthropogenic sulphate point sources. Ammonium sulphate is a widely used fertilizer in agriculture and on golf courses. The fertilizer-derived sulphate may infiltrate into groundwater or surface water bodies since it is usually applied in rates far exceeding the sulphur requirements of the biosphere.

2.3. IDENTIFICATION OF PROCESSES

Atmospheric deposition contains sulphate typically in low concentrations (often < 10 mg/L) which is transported into groundwater and surface water during recharge and runoff. It is interesting to note that sulphate in the water unsaturated soil zone has often $\delta^{34}S$ values similar to those of atmospherically-derived sulphate, but its oxygen isotope ratios are significantly depleted in ^{18}O (Fig. 1). This indicates that sulphate does not behave conservatively in the water-unsaturated zone during groundwater recharge (Caron et al., 1986; Mayer et al., 1995). Particularly in forest soils, SO_4^{2-} may be converted to carbon-bonded S compounds (immobilization). During the subsequent re-oxidation of these organic S compounds (mineralization), new oxygen atoms are incorporated into the generated sulphate molecule as described above for sulphide oxidation. This explains why soil sulphate, and consequently sulphate in freshly recharged groundwater, may have lower $\delta^{18}O$ values than sulphate in atmospheric deposition.

Evaporation during groundwater recharge or from surface waters increases the concentration of dissolved sulphate without causing changes in its $\delta^{34}S_{sulphate}$ and $\delta^{18}O_{sulphate}$ values. Van Stempvoort et al. (1990) provided evidence from laboratory and field studies that adsorption and desorption of sulphate proceed with minor isotope selectivity for both sulphur and oxygen, despite claims to the contrary in earlier publications (Corteccci, 1978; Nriagu, 1974). Crystallization of sulphate minerals slightly favours the heavier isotopes in the precipitates. For example, the $\delta^{34}S$ and $\delta^{18}O$ values of gypsum minerals have been determined to be 1.7 and 3.6 ‰ higher than those for dissolved sulphate, from which they formed (Holser and Kaplan, 1966; Szaran et al., 1998). Consequently, solution sulphate becomes slightly depleted in ^{34}S and ^{18}O along a line of about slope 2 on a $\delta^{34}S$ versus $\delta^{18}O$ diagram (FIG. 2). Dissolution of sulphate minerals is accompanied by negligible isotope selectivity since it proceeds in a layer-by-layer fashion. Therefore, groundwater sulphate derived from evaporite dissolution is characterized by an isotopic composition similar to that of the gypsum and anhydrite minerals in the bedrock.

It has long been known that the light isotopes ^{32}S and ^{16}O are preferentially metabolized during bacterial (dissimilatory) sulphate reduction (e.g. Harrison and Thode, 1958; Mizutani and Rafter, 1969a). Consequently, the remaining sulphate becomes progressively enriched in ^{34}S and ^{18}O as sulphate concentrations decrease. Isotope fractionation factors for sulphur during bacterial (dissimilatory) sulphate reduction can be quite variable, dependent upon environmental conditions (Canfield, 2001), but often range between 1.010 and 1.020 in hydrological settings (e.g. Strebel et al., 1990). Early work by Mizutani and Rafter (1973) suggested that the $\delta^{34}S$ and $\delta^{18}O$ values in the remaining sulphate increase at a ratio of 4:1 (Fig. 2). It has, however, been shown that this is not generally the case, possibly because of back-reactions with intermediate species that facilitate oxygen isotope exchange with H_2O (Fritz et al., 1989; Mizutani and Rafter, 1969a). Spence et al. (2001) demonstrated for a phenol-contaminated aquifer that bacterial (dissimilatory) sulphate reduction may proceed with significant sulphur isotope selectivity but no concurrent change in the oxygen isotope ratios of the remaining sulphate (Fig. 2). In contrast to bacterial dissimilatory sulphate reduction, sulphur isotope selectivity during bacterial assimilatory sulphate reduction is small (Trust and Fry, 1992).

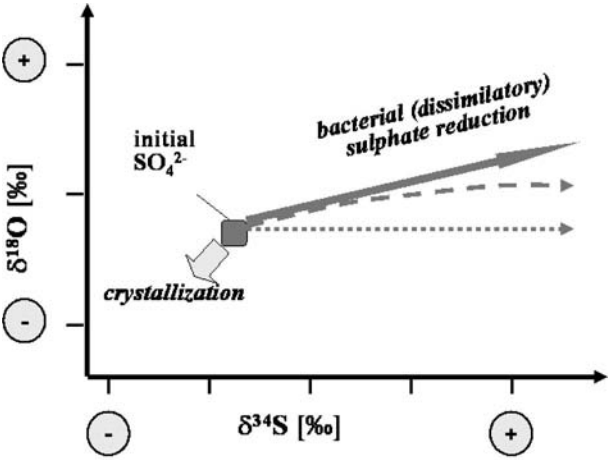


FIG. 2. Typical trends of $\delta^{34}S$ and $\delta^{18}O$ values of the remaining dissolved sulphate resulting from bacterial (dissimilatory) sulphate reduction and crystallization of sulphate minerals.

Isotope exchange reactions between sulphur compounds in the hydrosphere (e.g. SO_4^{2-} and HS^-) proceed very slowly at low temperatures and neutral pH values (e.g. Robinson, 1973; Sakai, 1968). The same is the case for oxygen isotope exchange between SO_4^{2-} and H_2O (e.g. Chiba and Sakai, 1985). Therefore, sulphur and oxygen isotope exchange reactions are usually not significant in relatively young (<100 years) low temperature (<50°C) groundwater with neutral pH values. However, isotope exchange reactions have been postulated for geothermal waters and groundwater with long residence times and have been repeatedly employed for geothermometry (Dazy et al., 1987; Giggenbach et al., 1983; Panichi and Gonfiantini, 1981; Rightmire et al., 1974; Zuppi et al., 1974).

2.4. TRENDS AMONG CONCENTRATIONS AND ISOTOPIC COMPOSITIONS OF SULPHATE

In some situations, a plot of $\delta^{34}S_{sulphate}$ and $\delta^{18}O_{sulphate}$ values may conclusively reveal the mixing of sulphate from two sources (Fig. 1). However, simultaneous monitoring of spatial or temporal trends in concentrations and isotopic compositions of sulphate in groundwater and surface water has proved to be a more effective approach for revealing addition of sulphate from various sources and for identifying sulphate transformation processes than interpreting the isotopic composition of sulphate alone. Generally expected trends are depicted in Fig. 3, assuming that initial sulphate in freshly recharged groundwater or surface water has $\delta^{34}S$ and $\delta^{18}O$ values of circa +4 ‰ respectively and a concentration of circa 10 mg/L. Note, however, that deviations from these trends may occur depending on the isotopic compositions of the various sulphur sources and that of the initial dissolved sulphate in a given study area.

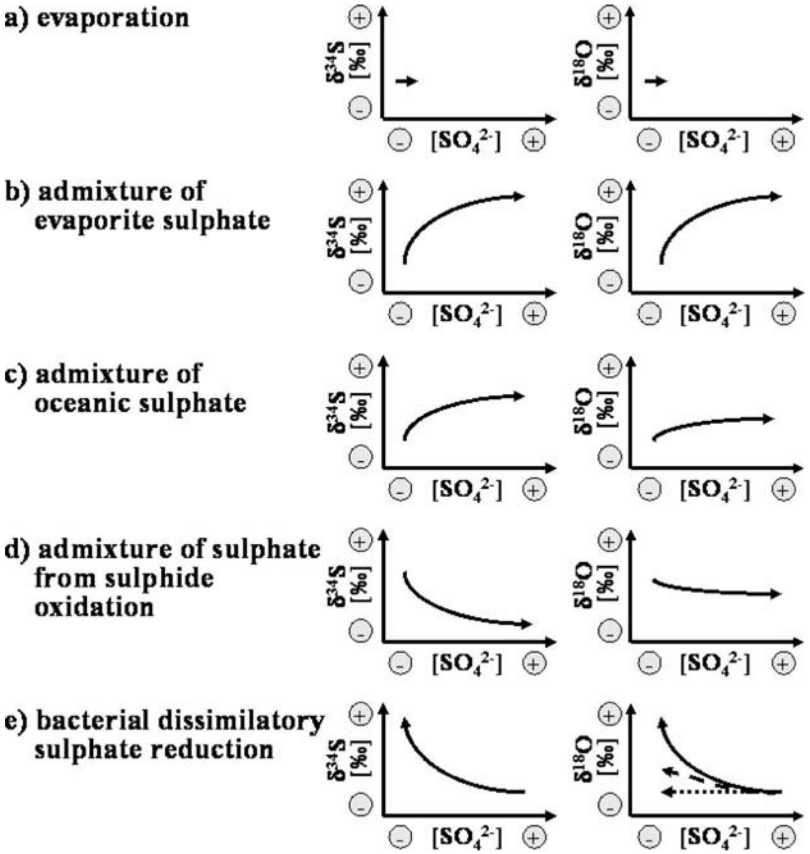


FIG. 3. Trends of concentration and isotopic composition of sulphate during a) evaporation, b) admixture of evaporite sulphate, c) admixture of oceanic sulphate, d) admixture of sulphate from oxidation of sulphide minerals, and e) bacterial (dissimilatory) sulphate reduction.

Figure 3a is characteristic for a situation in which atmospheric deposition is the dominant source of hydrospheric sulphate. Therefore, the isotopic composition of sulphate is identical to that of atmospheric or pedospheric sulphate in the region. Sulphate concentrations are slightly elevated compared to those in atmospheric deposition due to evapotranspiration during recharge. Edmunds et al. (1996) proposed that the isotopic composition of sulphate in the East Midlands Triassic aquifer (UK) reflects primarily that of atmospheric deposition recharging the aquifer. Robertson et al. (1989) described a similar situation for the Sturgeon Falls aquifer in Ontario (Canada). These authors suggested that it is feasible to reconstruct the level of atmospheric sulphate deposition for the period 1950-1985 based on groundwater dating, sulphate concentrations in the aquifer, and the insight derived from isotope measurements that sulphate was almost entirely derived from atmospheric sources in their study area.

Admixture of sulphate from lithogenic sources is usually accompanied by a marked increase in sulphate concentrations and the isotopic composition of sulphate in groundwater or surface water will rapidly approach that of the lithogenic sulphur source. Admixture of sulphate from evaporite dissolution typically results in increasing sulphate concentrations accompanied by increasing $\delta^{34}S_{sulphate}$ and $\delta^{18}O_{sulphate}$ values (Figure 3b). Fritz et al. (1988) demonstrated for an aquifer influenced by evaporites from the Silurian Salina formation in Ontario (Canada) that $\delta^{34}S$ values of groundwater sulphate can exceed +30 ‰. Nielsen demonstrated that sulphate in numerous aquifers in Germany is derived from dissolution of evaporites of Phanerozoic age. Infiltration of ocean water sulphate (e.g. Barker et al., 1998) results also in increasing concentrations of sulphate with its $\delta^{34}S$ and $\delta^{18}O$ values trending towards +21.0 and +9.5 ‰, respectively (Fig. 3c). In contrast, increasing sulphate concentrations accompanied by decreasing $\delta^{34}S_{sulphate}$ values usually point to oxidation of sulphide minerals as the dominant source of sulphate (Fennell and Bentley, 1998; Hendry et al., 1989), as depicted in Figure 3d. Admixture of sulphate from magmatic or volcanic sources results in increasing sulphate concentrations with $\delta^{34}S_{sulphate}$ and $\delta^{18}O_{sulphate}$ values trending towards 0 ‰ (Governa et al., 1989).

Bacterial (dissimilatory) sulphate reduction is a process that produces trends of decreasing sulphate concentrations with increasing $\delta^{34}S_{sulphate}$ and usually also increasing $\delta^{18}O_{sulphate}$ values (Figure 3e). One of numerous excellent examples was published by Strebel et al. (1990) for the Fuhrberger Feld aquifer in the vicinity of Hannover (Germany), where bacterial (dissimilatory) sulphate reduction was identified by a combination of chemical and isotopic techniques.

3. The isotopic composition of ammonium and nitrate in the hydrosphere

First nitrogen isotope ratio measurements on water samples were reported in the 1950s by Hoering (1955; 1957) but it was not until the early 1970s that determinations of $\delta^{15}N$ values of dissolved ammonium and nitrate in surface water and groundwater samples gained more widespread use in hydrological studies (e.g. Edwards, 1973; Kohl et al., 1971; Kreitler, 1979; Kreitler and Jones, 1975). Nitrogen has two stable isotopes, ^{14}N and ^{15}N, with approximate natural abundances of 99.6337 and 0.3663 %, respectively (Junk and Svec, 1958; Rosman and Taylor, 1998). Nitrogen isotope measurements are expressed using the delta scale:

$$\delta^{15}N[‰] = \left[\frac{^{15}N/^{14}N_{sample}}{^{15}N/^{14}N_{reference}} - 1 \right] \cdot 1000 \tag{3}$$

The accepted primary reference for nitrogen isotope abundance measurements is atmospheric N_2 (Mariotti, 1983). Reference materials such as IAEA-N-1 (+0.43 ‰) and IAEA-N-2 (+20.32 ‰) with widely differing $\delta^{15}N$ values (Coplen et al., 2002; IAEA, 1995) are available from the International Atomic Energy Agency (IAEA) for calibration and normalization purposes. Since the late 1980s, a variety of different analytical methods have been developed also to determine the oxygen isotope ratio of NO_3^- (e.g. Amberger, 1987; Bräuer and Strauch, 2000; Casciotti et al., 2002; Revesz et al., 1997; Silva et al., 2000). The combined interpretation of nitrogen and oxygen isotope ratios has greatly facilitated the ability to trace the sources of dissolved nitrate and conclusively to identify processes that nitrate may have undergone in many hydrological settings. Oxygen isotope ratios are reported in delta units in per mil (‰) relative to Vienna Standard Mean Ocean Water (V-SMOW) as shown in Eq. (2). A sufficient number of reference materials with widely differing $\delta^{18}O_{nitrate}$ values have recently become available (Böhlke et al., 2003). Their use will greatly improve the world-wide comparability of the reported oxygen isotope ratios of nitrate in the near future.

3.1. ANALYTICAL DEVELOPMENTS

In order to avoid inter-conversions of potentially labile nitrogen compounds such as ammonium (NH_4^+), nitrate (NO_3^-), dissolved (DON) or particulate organic nitrogen (PON), it is recommended to filter water samples in the field with 0.45 µm membranes and to transport the filtered samples in cool and dark containers. Samples should be processed as soon as possible upon return to the laboratory or stored frozen until further analysis.

Determining the nitrogen isotope ratios of NH_4^+ and NO_3^- is commonly achieved in three steps: (1) extraction of NH_4^+ or NO_3^- from a water sample, (2) conversion of the extracted NH_4^+-N or NO_3^--N into di-nitrogen gas (N_2), and (3) determination of the nitrogen isotope ratio of the produced N_2 using an isotope ratio mass spectrometer (IRMS). Nowadays, the latter two steps are usually performed by thermal decomposition of a synthesized solid nitrogen compound in an elemental analyser (EA) and subsequent sweeping of the produced N_2 with a He carrier gas into an isotope ratio mass spectrometer (IRMS) in continuous flow (CF) mode (Barrie and Prosser, 1996). Prior to the invention of CF-IRMS techniques, N_2 gas was produced off-line by hypobromite oxidation (Bremner, 1965) or by combustion in quartz ampules (Kendall and Grim, 1990) and measured via dual inlet isotope ratio mass spectrometry.

A number of different techniques have been suggested throughout the last half century for the extraction of NH_4^+ and NO_3^- from aqueous samples. Historically, nitrogen isotope ratios of ammonium (NH_4^+) and nitrate (NO_3^-) have been determined using variations of the Kjeldahl technique, which was initially developed for soil science applications (Bremner and Keeney, 1965). In a large Kjeldahl distillation apparatus that accommodates samples of up to 1000 mL, NH_4^+ in a water sample is converted to NH_3 gas by raising the pH of the solution to ~9.5 via addition of NaOH or MgO (e.g. Cline and Kaplan, 1975). The liberated NH_3 gas is distilled, trapped in an acidic solution, and converted to $(NH_4)_2SO_4$. Subsequent to the complete removal of NH_4^+ from the original water sample, NO_3^- can be reduced to NH_4^+ via addition of Devarda's alloy (Bremner and Keeney, 1965) and treated as described above to yield a second $(NH_4)_2SO_4$ precipitate that is representative for NO_3^--N. An alternative to the distillation method is the diffusion of the released NH_3 gas onto glass fiber filters acidified with sulphuric acid mounted in the headspace of closed containers (Brooks et al., 1989) or floating enclosed in gas-permeable but hydrophobic PTFE membranes on the water sample (Holmes et al., 1998; Sigman et al., 1997; Sorenson and Jensen, 1991; Stark and Hart, 1996). Zeolites (Velinsky et al., 1989) and cation exchange resin beads (Lehmann et al., 2001) have also been used to recover NH_4^+ from aqueous solutions. Nitrogen contained on precipitates, filters, resin beads or zeolites is subsequently converted to N_2 typically by combustion in an elemental analyser and the $^{15}N/^{14}N$ ratio is determined by isotope ratio mass spectrometry. All Kjeldahl distillation or diffusion techniques have the disadvantage that the nitrate-oxygen is removed during the reduction of nitrate to ammonium, making oxygen isotope measurements impossible.

Analytical techniques capable of determining the oxygen isotope ratio of dissolved nitrate initially relied on the synthesis of nitrate-containing solids and their conversion to CO_2 or CO. These gases were subsequently analysed for their $^{18}O/^{16}O$ ratios either by off-line combustion in sealed quartz tubes followed by dual inlet IRMS, or by on-line pyrolysis-CF-IRMS techniques (Revesz and Böhlke, 2002). Amberger and Schmidt (1987) generated KNO_3 using $Hg(CN)_2$ as a combustion reagent, but their procedure never gained wide-spread popularity. Revesz et al. (1997) proposed a technique in which KNO_3 was reacted with catalyzed graphite to generate CO_2, K_2CO_3 and N_2. Since there is oxygen isotope fractionation between CO_2 and K_2CO_3, corrections are necessary to obtain the true $\delta^{18}O$ value for nitrate. Silva et al. (2000) described an analytical procedure, in which nitrate is retained on ion exchange resins, subsequently eluted, and quantitatively converted to pure $AgNO_3$. Despite of relatively high costs (ion exchange resins, silver oxide, etc.), this technique has gained wide-spread popularity for the analysis of the isotopic composition of nitrate from freshwaters. However, analysis of water samples with high contents of dissolved organic carbon (DOC) or high contents of total dissolved solids remained challenging. These problems were recently overcome by the so-called denitrifier technique. In this procedure, dissolved nitrate is quantitatively reduced to N_2O by denitrifying bacteria that lack N_2O-reductase activity. The generated N_2O gas is subsequently used for nitrogen (Sigman et al., 2001) and oxygen (Casciotti et al., 2002) isotope analyses.

3.2. IDENTIFICATION OF SOURCES OF NITRATE

Numerous attempts have been made to use nitrogen isotope ratios to determine the sources of nitrate in surface water and groundwater. These were particularly successful in situations were nitrate from one source with a unique $\delta^{15}N$ value (e.g. from sewage or manure) was dominant (e.g. Mariotti, 1984), but assessing the respective contributions from two or more sources remained challenging. Kohl et al. (1971) were among the first to utilize nitrogen isotope ratio variations for determining the sources of nitrate in surface waters. In an agriculturally used watershed in Illinois, USA, they observed a trend of decreasing $\delta^{15}N$ values (from 10 to 4 ‰) with increasing nitrate concentrations. Based on a simple two end-member mixing model ($\delta^{15}N_{\text{soil N}} = +13$ ‰; $\delta^{15}N_{\text{fertilizer}} = +3$ ‰) they concluded that at times of peak nitrate concentration more than 50 % of the nitrate-N in the surface water originated from synthetic fertilizers. This approach was widely criticized (e.g. Edwards, 1973; Hauck et al., 1972) partially because there are often variable isotope effects during nitrogen transformations in the biosphere and pedosphere that need to be considered in source apportionments based on nitrogen isotope ratios. Feigin et al. (1974) demonstrated that isotope effects during nitrification of anhydrous ammonia fertilizer can exceed 10 ‰, depending on pool size and nitrification rates.

Even larger nitrogen isotope fractionation effects have been described for volatilization of NH_3 (e.g. Heaton, 1986; Hübner, 1986) and denitrification (e.g. Wellman et al., 1968), making a quantitative assessment of contributions from various nitrate sources based on nitrogen isotope ratios alone in many situations problematic.

The dual isotope approach based on the determination of $\delta^{15}N$ and $\delta^{18}O$ values of nitrate has improved the ability of isotope hydrologists to identify sources of nitrate in aquatic systems. Nitrate derived from manure or sewage is usually characterized by $\delta^{15}N$ values between +7 and more than +20 ‰ (Aravena et al., 1993; Aravena and Robertson, 1998; Gormly and Spalding, 1979; Kreitler, 1979; Kreitler and Browning, 1983; Wassenaar, 1995). It is therefore distinct from nitrate in atmospheric deposition (-10 to +8 ‰), nitrate in synthetic fertilizers (near 0 ‰), and nitrate generated via nitrification processes in soils (Kendall, 1998 and references therein). Usually, the latter three sources can not be differentiated by nitrogen isotope analyses alone because of their overlapping ranges of $\delta^{15}N$ values (Fig. 4). However, recent research has shown that nitrate in atmospheric deposition has quite positive $\delta^{18}O$ values ranging from circa +30 to +80 ‰ (Durka et al., 1994; Kendall, 1998; Voerkelius, 1990). Nitrate-containing synthetic fertilizers have $\delta^{18}O_{nitrate}$ values near +22 ± 3 ‰ (Amberger, 1987; Voerkelius, 1990; Wassenaar, 1995). Nitrate derived from nitrification processes in soils has typically $\delta^{18}O$ values of less than +15 ‰ (Durka et al., 1994; Hollocher, 1984; Mayer et al., 2001) and nitrate in manure and sewage has similarly low $\delta^{18}O$ values (Aravena et al., 1993; Wassenaar, 1995). Hence, the combined determination of $\delta^{15}N$ and $\delta^{18}O$ values of dissolved nitrate provides a tool for distinguishing between four major nitrate sources: (1) atmospheric nitrate deposition, (2) nitrate-containing synthetic fertilizers, (3) nitrate derived from nitrification e.g. in soils, and (4) nitrate in manure and sewage (see Fig. 4).

3.3. IDENTIFICATION OF TRANSFORMATION PROCESSES

Isotope tracing of nitrogen-containing compounds in the water-unsaturated and water-saturated zone is not straightforward, since numerous transformation processes in the nitrogen cycle are associated with significant but variable isotope effects. During volatilization, the conversion of NH_4^+ to NH_3, ^{14}N is preferentially converted to NH_3 leaving the remaining NH_4^+ enriched in ^{15}N (Letolle, 1980; Heaton, 1968; Hübner, 1986). Nitrification, the conversion of NH_4^+ to NO_3^-, can also proceed with significant nitrogen isotope fractionation accumulating ^{14}N preferentially in the produced NO_3^-, provided that the substrate is not limited (Mariotti et al., 1981). During the nitrification process, three new oxygen atoms are introduced into the newly formed nitrate molecule. Typically, two of these oxygens are derived from ambient water and one from O_2 (Hollocher, 1984), resulting in $\delta^{18}O_{nitrate}$ values between 0 and +15 ‰ depending on environmental conditions (e.g. Amberger and Schmidt, 1987; Durka et al., 1994; Mayer et al., 2001).

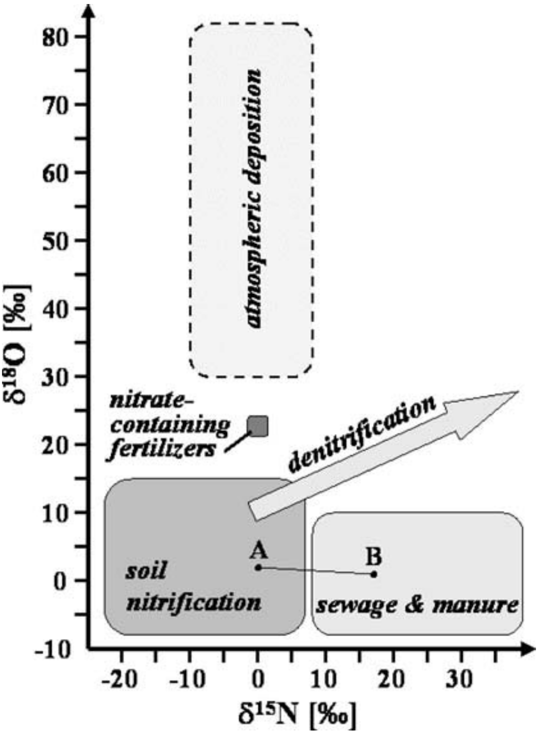


FIG. 4. Typical ranges for $\delta^{15}N$ and $\delta^{18}O$ values of nitrate from a) atmospheric deposition, b) synthetic nitrate-containing fertilizers, c) nitrification processes in soils, and d) sewage and manure. The arrow indicates the trend of $\delta^{15}N$ and $\delta^{18}O$ values of the remaining nitrate during denitrification assuming initial nitrate with $\delta^{15}N \sim 0$ ‰ and $\delta^{18}O \sim 10$ ‰. Also shown is a trend line expected for mixing of nitrate from nitrification in soils (A) and nitrate from manure or sewage (B).

Another process causing significant alterations of the isotopic composition of nitrate in aquatic systems is microbial denitrification, during which the lighter isotopes ^{14}N and ^{16}O are preferentially metabolized by microorganisms causing an enrichment of the heavy isotopes ^{15}N and ^{18}O in the remaining nitrate as concentrations decrease (Mariotti et al., 1981; Mariotti et al., 1982). The increase in $\delta^{15}N_{nitrate}$ values due to microbial denitrification appears to be about twice that of $\delta^{18}O_{nitrate}$ (e.g. Böttcher et al., 1990). Hence, the remaining nitrate eventually assumes elevated $\delta^{15}N$ and $\delta^{18}O$ values, which are unique for nitrate that has undergone denitrification under closed system conditions (Fig. 4).

Interestingly, nitrate in surface water or groundwater rarely has the same isotopic composition as nitrate in atmospheric deposition or in synthetic fertilizers. The typically low δ^{18}O values (<15 ‰) of aqueous nitrate provide stong evidence that nitrate from atmospheric deposition ($\delta^{18}O_{nitrate}$ > +30 ‰) and nitrate from synthetic fertilizers ($\delta^{18}O_{nitrate}$ ~ 23 ‰) does not behave conservatively in the water-unsaturated zone, but rather undergoes an intense immobilization–mineralization cycle in the soils (e.g. Mengis et al., 2001). The three original oxygen atoms of the nitrate molecule are removed during the immobilization process and hence nitrate from atmospheric deposition or from synthetic fertilizers looses its original oxygen isotope signature. Three new oxygens are acquired during the subsequent mineralization process and the δ^{18}O value of the newly formed nitrate (typically <15 ‰) is indicative of nitrate from soil nitrification. Mengis et al. (2001) demonstrated in lysimeter experiments that tracing of fertilizer nitrate with the dual isotope approach (δ^{15}N and δ^{18}O) is only possible under conditions of very low microbial activity (e.g. winter), but fails under the biologically active conditions during the growing season because of the rapid immobilization – mineralization turnover of nitrogen in soils.

3.4. TRENDS AMONG CONCENTRATIONS AND ISOTOPIC COMPOSITIONS OF NITRATE

In some situations, a plot of $\delta^{15}N_{nitrate}$ and $\delta^{18}O_{nitrate}$ values may conclusively reveal the mixing of nitrate from two sources (Fig. 4). However, simultaneous monitoring of spatial or temporal trends in concentration and isotopic composition of nitrate has proven to be a more effective approach for revealing nitrogen sources and transformation processes in aquatic systems. Decreasing nitrate concentrations with increasing $\delta^{15}N_{nitrate}$ (Mariotti et al., 1982; Mariotti et al., 1988) and $\delta^{18}O_{nitrate}$ values (Böttcher et al., 1990) are indicative for denitrification (Fig. 5a). Using a combination of hydrological, chemical, and isotopic techniques, denitrification has been identified in groundwater systems (Aravena and Robertson, 1998; Böttcher et al., 1990), riparian zones (Cey et al., 1999; Mengis et al., 1999), and surface waters (Kellman and Hillaire-Marcel, 1998).

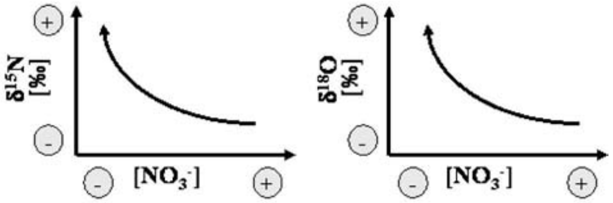
Trends of increasing nitrate concentrations accompanied by increasing $\delta^{15}N_{nitrate}$ values are often typical for admixture of nitrate from an anthropogenic source (Fig. 5b). Nitrate derived from sewage (Aravena et al., 1993) or manure (Karr et al., 2001; Rock and Mayer, 2004) have been identified in surface waters and groundwater using a combination of chemical and isotopic techniques.

4. Combined assessment of isotopic compositions of sulphate and nitrate

Denitrification is considered the most important process attenuating nitrate in groundwater. Heterotrophic denitrifiers oxidize organic compounds, which serve as both energy and carbon sources. In contrast, autotrophic denitrifiers have the ability to oxidize reduced inorganic sulphur such as pyrite. This process results in characteristic trends of concentrations and isotopic compositions of sulphate and nitrate in aquatic systems (Aravena and Robertson, 1998). Whereas the δ^{15}N and δ^{18}O values of the remaining nitrate progressively increase as nitrate concentrations decrease during the denitrification process, sulphate concentrations increase and the $\delta^{34}S_{sulphate}$ values approach those of the inorganic sulphur source in the subsurface.

Hence, isotope measurements are a unique tool to reveal the connection between denitrification and sulphide oxidation during autotrophic denitrification.

a) denitrification



b) admixture of nitrate from manure or sewage

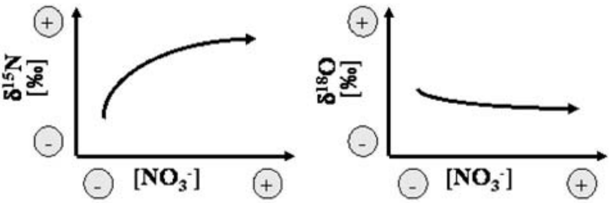


FIG. 5. Trends of concentration and isotopic composition of nitrate during a) denitrification and b) admixture of nitrate from manure or sewage.

5. Current and anticipated future developments

The determination of δ^{34}S values of sulphate or δ^{15}N values of nitrate alone does not always result in unequivocal information about the sources and processes these solutes have undergone in aquatic systems. However, if interpreted in concert with solid hydrological information and with an abundance of chemical data, it is often possible conclusively to determine the sources and the biogeochemical history of sulphate and nitrate in groundwater and surface water. This is particularly true if both the δ^{34}S and δ^{18}O values of sulphate and the δ^{15}N and δ^{18}O values of nitrate are determined. The availability of new continuous flow techniques for the rapid determination of oxygen isotope ratios of sulphate and nitrate will undoubtedly result in an increased use of this dual isotope approach.

Recently, analytical techniques have been developed to determine the ^{17}O/^{16}O ratios of sulphate (Bao et al., 2001a; Bao et al., 2001b) and nitrate (Michalski et al., 2002) and it has been shown that atmospheric sulphate and nitrate is affected by mass independent isotope fractionation. Therefore, Δ^{17}O values of sulphate and nitrate will likely become a useful additional parameter for tracing atmospheric sulphate and nitrate in the environment. The cosmogenic radioactive isotope ^{35}S can also be used as an additional tracer for atmospheric sulphate in young waters (Sueker et al., 1999), but so far few studies have attempted to combine radiocative and stable isotopes to trace sulphur cycling in aquatic systems (Shanley et al., in review).

6. Conclusion

Development of water resource management plans to preserve or improve water quality requires knowledge of the sources of dissolved constituents and an understanding of the processes these solutes may have undergone. Determining the isotopic composition of sulphate ($\delta^{34}S$ and $\delta^{18}O$) and nitrate ($\delta^{15}N$ and $\delta^{18}O$) has a tremendous potential in providing this information, if the isotope ratios are interpreted in conjunction with hydrological and chemical data.

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7. RARE GASES

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Noble gases have decisive advantages for applications as tracers in earth sciences because of their chemical inertness. Therefore considerable progress has been achieved in the last decades in noble gas measurements. In Fig. 1 the different measuring techniques are depicted schematically and in Fig. 2 a selection of methods applied for groundwater age determination are summarized. It has to be emphasized, however, that the determination of the age and mixing structure of a groundwater system is only one aspect of their applications. Short term subsurface and atmospheric processes can be studied, for example, by Rn isotopes determined by α-spectroscopy (Lehmann et al., 1999, 2000). Long-term geochronical and cosmochemical processes are investigated , for example, by He and Ar isotopes. Climate signals are obtained from noble gas recharge temperatures (NGRT). For a comprehensive description see the articles in the book "Noble Gases in Geochemistry and Cosmochemistry" (Porcelli et al., 2002).

Most frequently the determination of noble gases in earth and solar system sciences is based on mass spectrometry (MS) (Fig. 1). In recent years the precision of measurements as well as the automation and capacity of sample preparation and measurement has increased in several laboratories (e.g. Kipfer et al., 2002). This progress enabled considerable improvements in the principal conclusions obtained earlier from research done on meteorites, lunar and terrestrial rock samples, on groundwater, ocean water and in lakes. Subsurface processes and evolution in the lithosphere are studied by applying He and Ar isotopes. The $^3H/^3He$ method, for instance, has improved our knowledge of ocean and groundwater circulation and these isotopes allow the study of release rates from the sea floor and soil–atmosphere fluxes (Schlosser et al., 2002).

The method of calculating NGRT from the dissolved atmospheric noble gases Ne, Ar, Kr, and Xe was developed a long time ago by Emanuel Mazor and John Andrews (Mazor, 1972). Today NGRTs are determined routinely by MS and allow important conclusions to be drawn about climate history on earth. Correction models to separate atmospheric from subsurface radiogenic components and especially to

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correct for supersaturation by the so-called "excess air" component improved the reliability of calculated recharge temperatures (Kipfer et al., 2002).

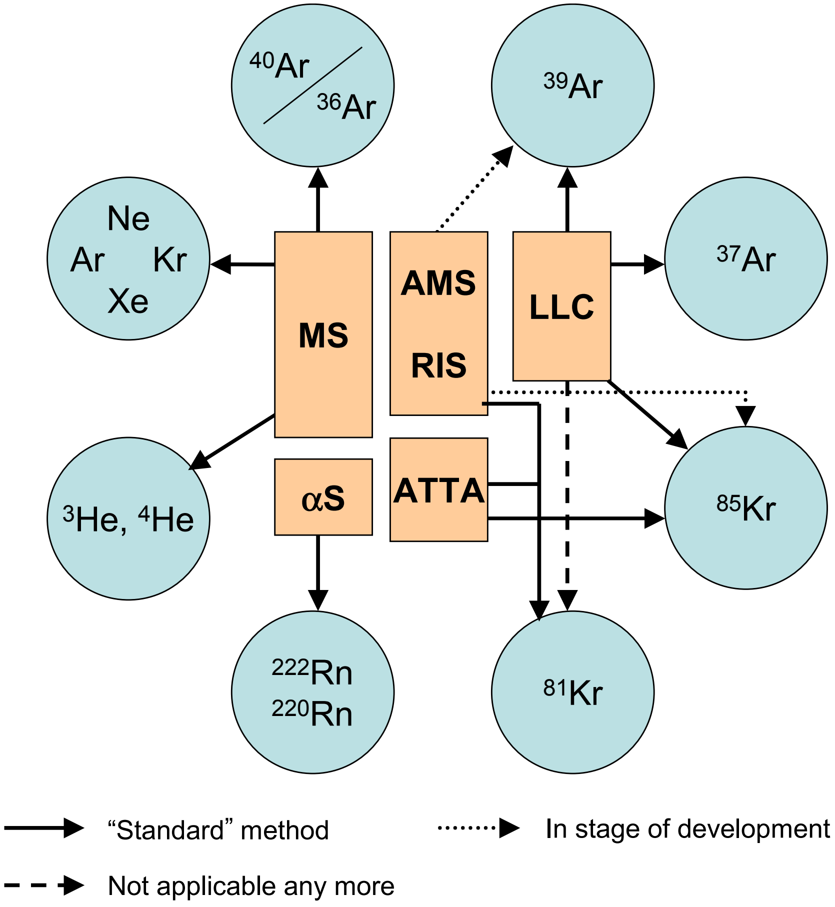

FIG .1. Analytical techniques used for noble gas measurements.
***MS**: **M**ass **S**pectrometry, **AMS**: **A**ccelerator-**MS**, **RIS**: **R**esonance **I**onisation-**S**., **LLC**: **L**ow **L**evel **C**ounting, **ATTA**: **A**tomic **T**rap **T**race **A**nalyses. (Aeschbach-Hertig et al., 1999).*

The isotopes ^{37}Ar and ^{39}Ar are used for studying atmospheric circulation and mixing (Loosli et al., 1986), subsurface processes (Pearson, Jr et al., 1991, Purtschert et al., 2001) and for dating of groundwater and ocean water up to about 1000 years (Loosli et al., 1999, Schlosser et al., 1994). Krypton-81 is the ideal tracer for dating very old groundwater (Lehmann et al., 2003), whereas ^{85}Kr, which has to be considered a man-made isotope, yields information in the time range of the most recent decades for water systems (Ekwurzel et al., 1994; Loosli et al., 1999; Corcho et al., 2002).

For decades low level counting (LLC) was the only method for detecting radioisotopes of argon and krypton at an atmospheric level. Even for the first determination of the ^{81}Kr activity in the atmosphere proportional counting was used on a sample of about 5 L of pre-bomb krypton (Fig. 1). For routine measurements in isotope hydrology, about 15 to 20 ^{39}Ar results (with a statistical error of about 5 %) and about one hundred ^{85}Kr results are produced each year by the low level counting method at the Physics Institute of the University of Bern. The sample size for ^{39}Ar analyses has been reduced by about a factor of ten, from about 5 L of argon (Loosli, 1983) to about 0.3 l (Loosli et al., 1999). One to two ^{85}Kr samples can be extracted per day from typically a few hundred litres of water.

A considerable reduction of the sample size is possible by applying RIS (Resonance Ionization Spectroscopy) and AMS (Accelerator Mass Spectroscopy) techniques (Fig. 1). The determination especially of the ^{39}Ar activity in water samples of 10 L size increases the field of applications considerably, especially in oceanography. Recently, first experiments were carried out to measure ^{39}Ar activities by AMS (Collon et al., 2003). The authors "believe that the reported results are a first indication that measurement of ^{39}Ar concentrations with precisions below 5% can be achieved". An electron cyclotron resonance source produced ^{39}Ar^{8+} ions, which were then accelerated by the ATLAS machine. For comparison a ^{78}Kr^{16+} pilot beam was used. The main problem was to avoid in the spectrum the overlap of the ^{39}Ar signal by the contaminating ^{39}K background. For control, a dated argon sample from old groundwater (Watson Creek, (Lehmann et al., 2003)) was measured; the results agree: the low level counting result was <8%, the AMS result was 5.4 ± 2.6% (Collon et al., 2003). However, up to now all measurements "only" demonstrated the feasibility of the measurement; these determinations are not yet used on a routine basis for applications with low statistical errors.

The first successful application of the RIS method was developed for ^{81}Kr determinations in Oak Ridge (Thonnard et al., 1987), using a tuneable laser beam for isotope selection, yielding for the first time a ^{81}Kr activity below the atmospheric concentration and a ^{81}Kr age for the Milk River groundwater (Lehmann et al., 1991). The uncertainty however was relatively large, mainly due to the errors in estimating the different enrichment factors during sample preparation. For ^{81}Kr measurements recently the Atomic Trap Trace Analysis ATTA (Chen et al., 1999) has been used, where by tuning laser frequency metastable atoms of a single isotope are trapped and forced to photon burst emissions. Currently the ^{81}Kr/^{85}Kr ratio is measured because both isotopes have 10^{-11} to 10^{-12} abundances relative to stable krypton in the atmosphere. First preliminary results indicate very old ages for the deep groundwater from the Nubian aquifer (Egypt) (personal communication, Lu and Purtschert, 2003).

The AMS technique was first successfully applied to measure ^{81}Kr activities on samples extracted from water of the Great Arthesian Basin in Australia. Calculated ages from four samples range between 200 to 400 ka (Lehmann et al., 2003). For the first time possibilities and limitations of the ^{36}Cl dating method have been quantified using the new ^{81}Kr groundwater ages combined with ^{4}He measurements. Cyclotron accelerated ^{81}Kr^{17+} ions were stripped totally of Kr^{36+} and separated from interfering Br^{35+} ions by mass spectroscopy (MS). (Collon et al., 1997). About 16 tonnes of water had to be degassed and 0.5 cc krypton gas was purified in several steps (Collon et al., 2000).

For groundwater dating, relative measurements of the ^{81}Kr/Kr ratios are sufficient. However, for the comparison of calculated and measured ratios, the absolute value of the atmospheric ^{81}Kr concentration is required. (Lal, 2004, this volume). ^{81}Kr/Kr ratios determined by gas proportional counting, by RIS and AMS techniques show to date some differences, which probably are due to systematic errors.

The application of ^{85}Kr in isotope hydrology is generally based on the gas proportional counting method (Fig. 1). Yearly about 100 samples are analysed, especially investigating groundwater being recharged in the last few decades (Loosli et al., 1999). Although the AMS and RIS techniques of ^{85}Kr were developed in parallel to the ^{81}Kr technique, it remains questionable whether the sophisticated and expensive RIS or AMS technique will be used in the near future on a routine basis for service ^{85}Kr measurements. The present atmospheric level of about 1.4 Bq/m^3 of air is high enough to use the radioactive decay for detection. Even if the size of water sample to be degassed can be reduced for RIS and AMS technique, some steps in sample purification remain similar for all techniques, e.g. the separation of CH_4 from krypton.

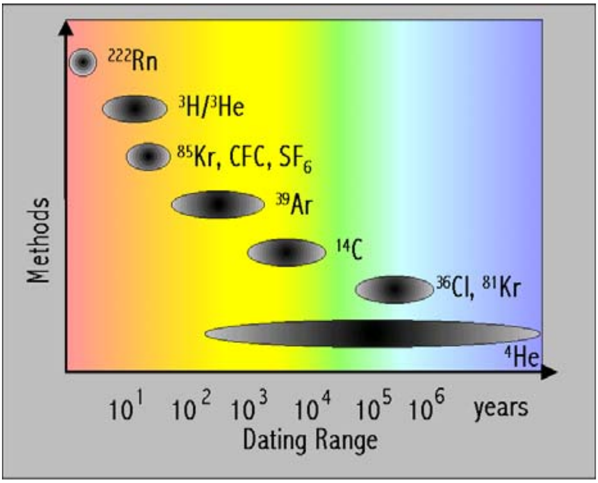

FIG. 2. Selection of environmental tracer methods used for groundwater dating and their dating ranges.

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8. U AND Th SERIES NUCLIDES IN NATURAL WATERS

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1. Introduction

The three naturally occurring radioactive decay series (those of ^{238}U, of ^{235}U and of ^{232}Th) together include 45 nuclides (A=206 to 238) of 12 elements (Z=81 to 92). It took the discoverers of radioactivity about 17 years (1896 till about 1913; Romer, 1970) to unravel the complex properties and interrelationships of these mysterious new substances: that the radioactive decay process converts one nuclide to another (transmutation); that helium ions are spontaneously expelled from the nuclei of some and electrons from the nuclei of others (alpha and beta particle emission); that some are the same element as others but have different radioactive properties (isotopes); that each has a characteristic disintegration rate (half-lives), etc. But even before all these phenomena were understood, some early workers already started studying the distribution in nature of the few substances they were already familiar with. Joly (1908), for example, speculated whether the concentration of radium (he was as yet unaware that there was more than one isotope of this element) was uniform throughout the ocean. (It was not until the GEOSECS project of the 1970s that the degree to which these concentrations were variable was clarified (Turekian and Cochran, 1978)).

Except for uranium and thorium prospecting (minerals bearing these elements were the economic sources of the ingredients used to colour glass and to make lantern mantles, respectively), much of what was learned about the geochemical distribution of these new substances before the 1930s was primarily a by-product of the research into the nature of radioactivity. During World War II the Allied governments initiated a large amount of nuclear weapons-related research. Then, in the post-war period, much of the research was ecology-related, concerning nuclear waste disposal and environmental damage evaluation. At the same time that the

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latter was being conducted, however, a significant geochemical effort was made to understand the distribution patterns of natural radioactive nuclides in order to determine those geophysical and geochemical parameters that involved the element of time. Several examples of the latter will be discussed in the last section of this article.

Of the 45 nuclides in the three natural decay series, only ^{222}Rn, ^{226}Ra and ^{238}U were investigated widely in natural waters in the earlier period because almost all of the other 42 had too low a "hydrologic range", which was defined by Osmond and Cowart (1992) as the product of solubility and half-life. The latter nuclides were studied much less often till about the mid-1960s. This was because their concentrations are low, because they do not persist very long in natural waters, given the rapidity with which they either decay by radioactivity or are removed by chemical precipitation or adsorption. (The reason ^{235}U and ^{234}U were not studied in the earlier period despite their high "hydrologic range" was that it was assumed that their concentrations were always in a constant ratio to that of ^{238}U.) Accordingly, the techniques for measuring the above three nuclides were developed earlier and the number of early investigations involving them is much higher than are those of the other 42, and any account of the evolution of techniques would naturally emphasize the techniques for measuring these three.

The above, though true for all natural waters, is especially true for groundwater and rivers, where the ubiquity of solid particles provides a ready source of adsorbing substrate. In lakes and oceans, on the other hand, the adsorption process (and hence the scavenging by particles) is much slower because of the sparsity of adsorbing surfaces. It was, in fact, for the purpose of investigating the variations in scavenging rates in lakes and oceans that a significant number of studies were performed of ^{234}Th, ^{232}Th, ^{230}Th, ^{228}Th, and ^{210}Pb concentrations. In addition to studies of these five, those of the nuclides ^{234}U and ^{228}Ra also made their appearance when their special interest became apparent. Accordingly, the techniques for measuring these latter seven nuclides will also be described.

2. Radon and radium

Radon-222, being the only one of the nuclides of interest which is a gas, is the easiest to measure because no chemical processing is required for the liquid in which the ^{222}Rn is to be determined. In the time-honoured "emanation method" (Strutt, 1906; Curtiss and Davis, 1943), the liquid sample was placed in a vessel which could be attached to a vacuum line where the sample was boiled while flushing with N_2 into a pre-evacuated chamber. In a second stage, interfering impurities (mainly water and CO_2) were removed from the gas, which was transferred to a radiation detector. The latter took the form of an electroscope in the very early years (Strutt, 1906), of an ionization chamber in the 1930s (Evans, 1935), and of a scintillation counter in the 1950s (Lucas, 1957). Broecker (1965) developed a shipboard version of the emanation method apparatus so that measurements could be made of the in situ ^{222}Rn concentrations in open ocean water before its 3.8 day half-life reduced the decay rate to unmeasurable low levels.

Determinations of ^{226}Ra were made indirectly by this same technique. Since ^{226}Ra is the immediate precursor of ^{222}Rn, after all of the latter was flushed out of the sample as above, the collection vessel was sealed for about three weeks during which time a new generation of ^{222}Rn grew back to secular equilibrium with the ^{226}Ra in the sample. By measuring this newly ingrown ^{222}Rn after the three weeks, one in effect actually determined the ^{226}Ra. (At secular equilibrium, the decay rate of the daughter nuclide (in this case, ^{222}Rn) equals its formation rate which equals the decay rate of its mother nuclide (in this case, ^{226}Ra)). The very earliest measurements of radioactivity in natural waters (Joly, 1908) were performed on sea water in this way.

This method of determining ^{222}Rn and ^{226}Ra was absolute. Since ^{222}Rn could be stripped from a water sample with a known and reproducible efficiency close to 100%, no yield tracer was needed. What is more, the ^{226}Ra thus determined could, itself, be used as an "internal spike" for the isotope dilution determination of other radium isotopes that were usually pre-concentrated by a $BaSO_4$ coprecipitation. The chemical yield of this coprecipitation and of subsequent purification steps could be established by means of a second ^{226}Ra determination.

With its 5.8 year half-life, ^{228}Ra was far more interesting than the other naturally occurring radium isotopes, ^{223}Ra and ^{224}Ra, whose half-lives are no longer than weeks. But ^{228}Ra, being a weak beta-emitter, would be almost impossible to measure directly in the presence of ^{226}Ra and all its daughters. Therefore, the earlier techniques for determining it were indirect, being based on the measurement of one of ^{228}Ra's daughters: either strong-beta emitting ^{228}Ac or alpha-emitting ^{228}Th, whose concentrations could be related mathematically to that of ^{228}Ra (Moore, 1969). The daughter nuclide was first removed from the sample and the latter was then stored for sufficient time to permit the growth towards secular equilibrium of a new generation of that daughter nuclide.

Two changes were made in the radium technique in the early 1970s, which both required less effort and which led to greater sensitivity and precision, thus permitting the determination of ^{224}Ra as well as of ^{228}Ra (Moore, 1976). The first of these changes involved the determination of the ^{224}Ra/^{226}Ra and ^{228}Ra/^{226}Ra ratios by gamma spectrometry (which together with a separate determination of the absolute ^{226}Ra concentration by a variation of the emanation method, yielded the absolute concentrations of ^{224}Ra and ^{228}Ra). The second change involved the method of concentrating the radium isotopes. Where larger samples were needed, the earlier $BaSO_4$ precipitation was replaced by a procedure wherein the water sample was passed through a cell containing MnO_2-impregnated acrylic fibres. The radium isotopes in very large volumes (up to 2000 L) were adsorbed on the fibres, and in a second stage, the radium was desorbed with hydroxylamine-hydrochloride, coprecipitated with $BaSO_4$, and transferred to a gamma-counting cell.

In 1991, a mass spectrometric technique was developed for the measurement of radium in solid samples (Volpe et al., 1991) which could be applied also to aqueous samples. This technique enabled the determination of as little as 4 femtog of ^{226}Ra. (This is the quantity in, for example, 100 mL of seawater as opposed to the 10 or more litres processed by previous workers). The dissolved sample was spiked with ^{228}Ra, evaporated to dryness, redissolved and passed through ion exchange columns.

The purified radium isotopes were then measured in a thermal ionization mass spectrometer (TIMS). This great sensitivity of the TIMS technique applies only to ^{226}Ra. Because the atomic abundance of ^{228}Ra is very much lower, a sample would have to be at least 100 times as large in order for the latter to be measurable by TIMS.

3. Uranium and thorium

Because sea water uranium concentrations are so low (they are even lower in most other natural waters), early estimates were often based, not on actual uranium measurements but rather, on the assumption that ^{226}Ra (which was much easier to measure) was in secular equilibrium with ^{238}U. Direct uranium measurements in sea water (which showed that the concentration of ^{238}U was actually about an order of magnitude higher than that of ^{226}Ra) were first made only after the perfection of the fluorimetric technique (Hernegger and Karlik, 1935) in which a sample's uranium concentration is derived from the intensity of the fluorescence excited by ultraviolet light in a NaF bead which included the uranium from that sample. Nevertheless, the measurements of uranium in sea water were not entirely satisfactory till Rona et al. (1956), applying a mass spectrometric technique with ^{235}U as yield tracer, achieved consistent results which are close to those accepted today.

When it became clear that the ^{234}U/^{238}U activity ratios in natural waters were generally greater than unity (Thurber, 1962), investigators went over to the alpha spectrometer technique (Koide and Goldberg, 1964). By adding a ^{232}U tracer to the sample and comparing the number of pulses in each alpha energy interval of the purified uranium, they determined both the ^{238}U concentration and the ^{234}U/^{238}U ratio.

The development of techniques for measuring thorium in natural waters came later than for uranium because the concentrations of the former are much lower than those of the latter. Koczy et al. (1957) performed a study of the thorium isotopes in Baltic Sea water using the double nuclear emulsion technique (Picciotto, 1949) in which one determines the thorium isotopes by counting all the alpha particle trajectories of each isotope in a photographic emulsion. The various isotope trajectories are distinguishable because their track lengths are proportional to their disintegration energy. As for uranium, the precision of the thorium isotope measurements was improved in the 1960s when investigators went over to the alpha spectrometric technique for the alpha emitters, ^{232}Th, ^{230}Th and ^{228}Th (Moore and Sackett, 1964). At about the same time a technique was also developed to determine beta-emitting ^{234}Th by flow proportional counting (Bhat et al., 1969).

The alpha spectrometry technique started giving way to the TIMS technique for ^{238}U, ^{234}U and ^{232}Th in the mid-1980s, when a new filament loading procedure was perfected (Chen et al., 1986) which gave rise to a very substantial improvement in both the sensitivity and the precision. TIMS and alpha spectrometry (where TIMS is unavailable) are still the commonly used techniques for aqueous samples, though the newer ICP-MS technique when applied to solid samples (Shen et al., 2002) requires less analysis time and smaller sample sizes. Furthermore, though TIMS is not sensitive enough to be satisfactorily applicable to ^{230}Th in sea water, ICP-MS probably would be. Neither of these two techniques is, as yet, sensitive enough to enable the measurement of ^{228}Th in sea water.

Huh et al. (1989) showed that most of the oceanic ^{232}Th concentrations reported previous to 1980 were questionable because they were typically about an order of magnitude higher than those reported after 1980. This was observed to be the case not only when the post-1980 measurement was by the newer techniques (i. e. mass spectrometry or neutron activation (Huh and Bacon, 1985)), but even when it was by alpha spectrometry, the technique used for most pre-1980 measurements. For this reason, the discrepancy appears not to be due to a faulty measuring technique but primarily to contamination during sampling. The accuracy of the pre-1980 ^{230}Th and ^{228}Th concentrations, on the other hand, was affected much less than was that of the ^{232}Th concentrations because the former are, in fact, generally about 20 times as high (in activity units) as are the ^{232}Th concentrations.

4. Lead-210

Lead-210 emits a low-energy beta particle and because much of even this energy is absorbed within the sample, it was decided early that it was preferable to determine ^{210}Pb by actually counting its strong-beta emitting daughter, ^{210}Bi. Since the latter has a 5-day half-life, one could add stable lead to the water sample as a yield tracer, purify the lead of bismuth, prepare a counting source and wait 2–3 weeks for ingrowing ^{210}Bi to approach secular equilibrium with ^{210}Pb; by counting the former, one actually determined ^{210}Pb. Rama et al. (1961) applied this technique to sea water and Crozaz et al. (1964) to Antarctic snow.

The above technique was slowly replaced by one analogous to it, but which used ^{210}Po, the daughter of ^{210}Bi (and hence the granddaughter of ^{210}Pb), rather than ^{210}Bi itself (Flynn, 1968). Since ^{210}Po is an alpha emitter, it could be measured by the more precise isotope dilution alpha spectrometry. Balistieri et al. (1995) added ^{209}Po tracer at the start before removing the ^{210}Po in the sample and then added ^{208}Po tracer after the ingrowth period. This permitted them to correct for any ^{210}Po that was not removed before the ingrowth period

5. Sample size and precision

The evolution of the measurement techniques described above is shown in summary form in Table 1. The intention here was to select a single type of sample (open ocean water) and to show the degree to which two indicators of technique success (sample size required and precision obtained) improved with time when applied to that sample type. Open ocean water was selected as the water type in order to provide the most reasonable comparison possible since (i) it is the only material in which all ten nuclides of interest were measured; and (ii) the concentrations of these nuclides vary from point to point in the open ocean, much less than in other water bodies. The studies cited in the table are not necessarily the ones in which the specific techniques were first described, but rather the first ones in which a significant number of measurement results were presented.

Table 1. Changes in measurement techniques for the ten most investigated natural radioactive nuclides.

Period	**Nuclide**	Rn-222	Ra-226	Ra-228	U-238
	Half-Life	3.83 days	1602 a	5.75 a	4.47x109 a
1908-51	Reference,year	[1] 1935	[2] 1908		[3] 1951
	Technique	Ioniz. Chamber	Electroscope		Fluorimetry
	Location	Calif. Coast	Irish Coast		N. Pacific
	Sample Size(L)	2	3		0.2
	Uncertainty(%)	n.r.	22		10
1955-57	Reference,year		[4] 1955		[5] 1956
	Technique		Ioniz. hamber		Mass Spec.
	Location*		World		World
	Sample Size(L)		n.r.		2
	Uncertainty(%)		n.r.		3
1961-70	Reference,year	[7] 1967	[7] 1967	[8] 1969	[9] 1969
	Technique	Scintill. Counter	Scintill. Counter	PROP(228Ac)	A.Spec.
	Location*	N. Pacific	World	World	Indian
	Sample Size(L)	30	30	700	30
	Uncertainty(%)	6	3	14	8
1970-82	Reference,year	[13] 1970	[14] 1976	[15] 1973	[16] 1977
	Technique	Scintill. Counter	Scintill. Counter	A.Spec(228Th)	A.Spec.
	Location*	N. Pacific	NE. Pacific	World	World
	Sample Size(L)	20	20	700	12
	Uncertainty(%)	5	3	9	3
1984-87	Reference,year	[20] 1984	[21] 1987	[22] 1985	[23] 1986
	Technique	Scintill. Counter	Scintill. ounter	Gamma Spec.	TIMS
	Location*	NW. Pacific	W. Indian	N. Atlantic	World
	Sample Size(L)	23	20	270	0.01
	Uncertainty(%)	3	3	6	0.1

**=Location was designated as "World" if samples were from more than one ocean.*

n.r.= not reported; PROP = proportional counter: A. Spec. = alpha spectrometer

Table 1 (cont.). Changes in measurement techniques for the ten most investigated natural radioactive nuclides.

U-234	Th-232	Th-230	Th-228	Th-234	Pb-210
248,000 a	13.9x109 a	75,200 a	1.91 a	24.1 days	22 a
	[6] 1957	[6] 1957	[6] 1957		
	Nucl. Emuls.	Nucl. Emuls.	Nucl. Emuls.		
	North Sea	North Sea	North Sea		
	40	40	40		
	37	70	8		
[10] 1966	[11] 1970	[11] 1970	[8] 1969	[9] 1969	[12] 1961
A.Spec.	A.Spec.	A.Spec.	A.Spec.	PROP	PROP(Bi-210)
NW.Pacific	NW. Pacific	NW. Pacific	Atlantic	Indian	Calif.Coast
n.r.	n.r.	n.r.	700	30	20
3	22	20	12	7	10
[16] 1977	[17] 1982	[17] 1982	[17] 1982	[18] 1975	[19] 1973
A.Spec.	A.Spec.	A.Spec.	A. Spec.	PROP	PROP(Bi-210)
World	N. Pacific	N. Pacific	N. Pacific	N. Pacific	World
12	200	200	200	50	30
3	36	12	18	10	5
[23] 1986	[23] 1986	[24] 1987	[24] 1987	[25] 1987	[26] 1986
TIMS	TIMS	A.Spec.	A.Spec.	PROP	A.Spec(Po-210)
World	Atlantic	N. Pacific	N. Pacific	E. Pacific	E. Pacific
0.01	0,25	500	500	30	3
0.5	2	19	12	4	5

[1] Evans, 1935
[2] Joly, 1908
[3] Nakanashi, 1951
[4] Kroll, 1955
[5] Rona et al., 1956
[6] Koczy et al., 1957
[7] Broecker et al., 1967
[8] Moore, 1969
[9] Bhat et al., 1969
[10] Miyaki et al., 1966
[11] Miyaki et al., 1970
[12] Rama et al., 1961
[13] Broecker & Kaufman, 1970
[14] Chung, 1976
[15] Kaufman et al., 1973
[16] Ku et al., 1977
[17] Bacon & Anderson, 1982
[18] Matsumoto, 1975
[19] Craig et al., 1973
[20] Gamo & Horibe, 1984
[21] Chung, 1987
[22] Moore et al., 1985
[22] Moore et al., 1985
[23] Chen et al., 1986
[24] Nozaki et al., 1987
[25] Coale and Bruland, 1987
[26] Nozaki et al., 1986

Unfortunately, there are a few cases where the only relevant investigations were performed not in open ocean waters but in coastal waters where the nuclide concentrations may be quite different from those of the open ocean. Also, not all measurements were made of water collected from the same oceanic depth and concentrations often vary significantly with depth. Still, the general trend of improvement of precision with time is apparent, and especially so for those which occurred in the measurement of ^{238}U, ^{234}U, and ^{232}Th when the TIMS technique was applied. It should be noted that many of the articles cited in the table report a significant spread in the uncertainties of the different samples measured. Therefore, in order to make the precisions reported in the table comparable to one another, an average was computed for the median two-thirds of the uncertainties listed.

6. The determination of geophysical parameters

Because the concentration of a radioactive nuclide in any water body decreases spontaneously with time, the spatial distribution of that concentration has often been used to determine the parameters of the process that causes that nuclide's concentration to vary from point to point. This is illustrated below by four very different attempts to determine such parameters in natural waters. Obviously, the uncertainty in any such calculated parameter is dependent on the precision with which the nuclide concentrations have been measured.

A relatively straightforward example of such a parameter is the gas evasion rate of ^{222}Rn from the ocean surface (Peng et al., 1974). This nuclide, which is generated by the decay of its mother, ^{226}Ra, is in secular equilibrium with the latter below a depth of about 80 m, but is more and more depleted relative to ^{226}Ra as the surface is approached. From the shape of the curve of degree of equilibrium vs depth, it was found that the effective upward transfer velocity of ^{222}Rn is of the order of 4 m/day and increases with the square of the wind velocity.

Henderson and Maier-Reimer (2002) addressed the concentration patterns of ^{210}Pb actually observed in open ocean water as a function of location and depth. To account for the differences between these concentrations and the ones predicted from in situ production from ^{226}Ra and atmospheric and riverine inputs, they proposed a model of scavenging and advection. One outcome of this model is that the mean residence time of ^{210}Pb in the open ocean is about 48 years.

Li et al. (1977) made the surprising discovery that the ^{226}Ra concentration in the Hudson River estuary was greater than in those of either the upstream river water or the oceanward sea water. Based on a long series of studies in several other estuaries (largely by Moore and co-workers; references in Hancock and Murray, 1996), the accepted explanation for this is that the estuarine environment causes radium isotopes (^{226}Ra, ^{228}Ra, ^{223}Ra and ^{224}Ra) to desorb from particles upon whose surfaces their thorium isotope precursors (^{230}Th, ^{232}Th, ^{227}Th and ^{228}Th, respectively) had been adsorbed. The consequent high concentrations of radium isotopes enabled the estimation of a number of parameters: the flux of ^{226}Ra from the Hudson River into the open ocean (Li et al., 1977); the current speed in the Caribbean Sea (Moore and Todd, 1993); the exchange rate between marsh water and estuarine sediment porewater (Bollinger and Moore, 1993); the depth of estuarine sediment from which radium is flushed (Webster et al., 1994); etc.

Groundwaters generally have higher ^{234}U concentrations than would be in equilibrium with the concentrations of the mother, ^{238}U. This is so because the alpha decay causing the creation of ^{234}U is accompanied by a nuclear recoil which weakens the bonds which hold it in its lattice position and the ^{234}U atom is therefore more easily leached out of the aquifer minerals by the groundwater flow. Since the excess of ^{234}U over its equilibrium amount should decrease with the 248,000 year half-life of ^{234}U as the groundwater gets older, several investigations have been performed to ascertain that such a decrease exists and whether the ages calculated from it are reasonable. These investigations have met with only limited success because the uranium concentration increases steadily in the upstream part of the aquifer, and even in the downstream part it seems to undergo a cycling of precipitation and redissolution (Osmond and Cowart, 1992). In a very thorough study of the Milk River aquifer of Alberta, Ivanovich et al. (1991) applied two different models to the uranium data and compared the results to independent estimates of the groundwater flow rates. Whereas the more elaborate phenomenological model (which included removal and mixing estimates) yielded reasonable flow rates of about 0.3 m/a, the lower flow rate of the simpler model was interpreted as the velocity of uranium migration rather than that of groundwater flow. (In another chapter in the present volume, Geyh (2003) discusses the latter study as well as one of three Israeli aquifers (Rogojin, 1998) where a correlation was found between the ^{14}C ages of young groundwaters and their excess ^{234}U concentrations).

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9. OPTICAL ISOTOPE RATIO MEASUREMENTS IN HYDROLOGY

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1. Introduction

In this Paper we present an overview of spectroscopic methods for measuring the stable isotope ratios of water, as alternatives to isotope ratio mass spectrometry (IRMS). We do not deal with methods in which lasers are merely used to prepare the sample by means of ablation. Also, for a more detailed and wider discussion of stable isotope ratio infrared spectrometry of small molecules of environmental and biological importance, the reader is referred to a recent review (Kerstel, 2004).

IRMS is the conventional method for measuring isotope ratios and has benefited from over 40 years of research and development. Nowadays IRMS instrumentation is commercially available that reaches impressively high levels of precision, as well as throughput. Unfortunately, IRMS is incompatible with a condensable gas or a sticky molecule such as water. Therefore, in general, chemical preparation of the sample is required to transfer the water isotope ratio of interest to a molecule that is more easily analysed. For the ^{18}O isotope the method most used is the so-called Epstein-Mayeda technique: oxygen-exchange between water and carbon dioxide through the bicarbonate reaction (Epstein and Mayada, 1953). Equilibration requires several hours and an accurate temperature stabilization is needed in order to quantify the isotope fractionation associated with the reaction. The same technique also transfers the ^{17}O signature to CO_2; but the $^{17}O^{12}C^{16}O$ molecule appears in the same mass channel as the much more abundant $^{16}O^{13}C^{16}O$ molecule, making an accurate determination difficult, if not impossible. For the $^{2}H/^{1}H$ ratio, one can reduce water to hydrogen gas at an elevated temperature, using a suitable reducing agent, such as uranium (Bigelstein et al., 1952), zinc (Socki et al., 1999), or chromium (Gehre et al., 1996). (The latter two have been used in continuous flow arrangements.) Care

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has to be taken that the reaction is run to completion, in order to avoid severe systematic errors. In addition, a significant correction has to be made for the formation of H^{3+} in the ion source. Competing methods are the use of platinum catalytic equilibration of a water sample and hydrogen gas (Horita and Gat, 1988; Coplen et al., 1991). But this method too has its disadvantages: the equilibrium state is accompanied by a very large isotope fractionation (about -740‰ at room temperature), which is also extremely temperature dependent (~6‰/ºC). The gas sample arriving at the IRMS contains approximately one-quarter the original amount of deuterium, considerably decreasing the (already low) mass-3 signal, with obvious consequences for errors due to background correction, amplifier offset, and, above all, the H^{3+}-correction. Furthermore, the amount of water required is rather large (typically 4-5 mL), prohibiting the use of this method in quite a number of possible applications. The same is true for electrolysis (Meijer and Li, 1998). In fact, the only realistic alternative appears to be on-line pyrolysis of water in combination with a continuous-flow IRMS (Begley and Scrimgeour, 1997; Phillips et al., 2000). The latter method is able to deal with very small sample sizes (of the order of 1 μL), provides a high throughput, and is able to achieve good precision.

It may be clear that for the larger part these chemical conversion steps are time-consuming, sometimes hazardous (in the case of uranium reduction) and often compromise the overall accuracy and throughput (Brand et al., 1996; Meijer, 2001). Moreover, the two distinct sample preparations for δ^2H and $\delta^{18}O$ determinations potentially lead to uncorrelated (systematic) errors that do not (partially) cancel in the difference of the two measurements. As we will see later, this is of importance in biomedical doubly labelled water studies, and in the determination of the so-called deuterium excess parameter used in ice-core research. Apart from these drawbacks specific to water, IRMS instrumentation is expensive, voluminous and heavy, confined to a laboratory setting, and usually requires a skilled operator. All or most of these issues may be addressed by optical measurement techniques, although for the ^{18}O isotope one may have to accept a reduced level of precision in most, but not all, cases.

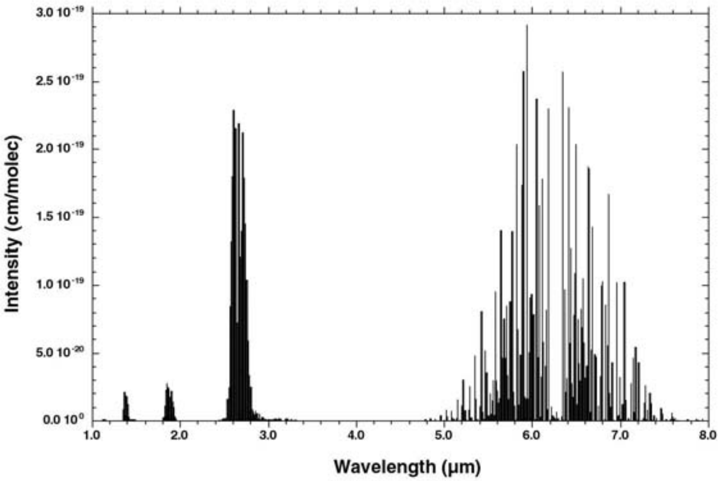
2. Infrared spectrometry

The near and mid-infrared absorption spectrum of gas phase water shows a large number of highly characteristic rotational-vibrational transitions (so called because they can be associated with rotational and vibrational stretching and bending motions of the molecule) that are very sensitive to isotopic substitution (in fact, such is the case for most small molecules). Figure 1 shows the spectrum of water over a wide range in the infrared. At sufficiently low vapour pressure and high instrumental resolution the individual ro-vibrational transitions are easily resolved, and can be uniquely assigned to a water molecule of particular isotopic composition (isotopologue). Even at higher pressure, or in the liquid phase, the unresolved vibrational bands of the deuterium isotopologue may be sufficiently displaced to be useful for a quantitative determination of the deuterium to hydrogen isotope ratio. Since the intensity of the experimentally recorded spectral features (whether individually resolved ro-vibrational transitions, or an unresolved vibrational band) may be directly related to the abundance of the absorbing species, recording the spectrum containing abundant and rare isotopologue features, in both an unknown sample and an isotopically well-known reference material, enables one to relate the isotopic composition of the sample to that of the reference material.

3. Direct absorption spectroscopy

In direct absorption spectroscopy, the attenuation of infrared light of frequency ν and intensity I_0, when traversing an optical path of length l through a gas cell filled with the material of interest, is given by Beer's law of linear absorption (see, for example, Demtröder, 1982.

$$\frac{I_t}{I_0} = e^{-\alpha(\nu)} = e^{-S\cdot f(\nu-\nu_0)\cdot n\cdot l} \quad or:\ \alpha(\nu) = -\ln\left(\frac{I_t}{I_0}\right) \tag{1}$$



Here, I_t is the transmitted intensity and α the dimensionless absorbance. The latter is proportional to the line strength S, which depends on the transition dipole matrix element connecting the lower and upper states of the transition, as well as on the number of molecules in the lower state.

FIG. 1. Simulated (near) infrared spectrum of water based on the HITRAN 1996 database. The individual ro-vibrational transitions are assumed to be infinitesimally small.

The absorbance is also proportional to the normalized line shape function $f(\nu-\nu_0)$, where ν is the frequency of the light and ν_0 the frequency for which f is maximum. Finally, the absorbance is proportional to the number density n of the absorbing molecules, and the optical path length l.

Typically, the signal-to-noise ratio (SNR) of a direct absorption measurement reaches a maximum for an absorbance α not too far from unity. If α approaches zero, the ratio of two almost equal quantities (I_0 and I_t) will have a large uncertainty, whereas for very large α the measurement of a very small transmitted intensity I_t will carry a large relative error. In practice, it is most often the path length l that is adjusted such that α is between roughly 0.3 and 3 for the majority of the samples to be analysed. Of course, for weak molecular absorptions, or in the case of very small sample sizes, this may simply mean maximizing the optical path length.

4. The Groningen colour centre laser setup

In Figs 2 and 3 we illustrate the principal of an isotope ratio measurement by means of infrared spectroscopy, using our own colour centre based experiments as an example (Kerstel et al., 1999).

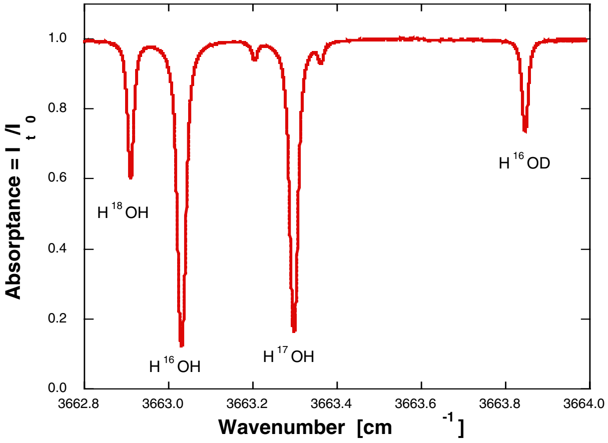


FIG. 2. Experimental registration of the absorption spectrum of a natural water sample. The four major isotopologues have absorptions of the same order of magnitude in a small spectral range around 3663 cm^{-1} (2.73 μm). The small absorptions on the shoulders of the $H^{17}OH$ line are due to $H^{16}OD$.

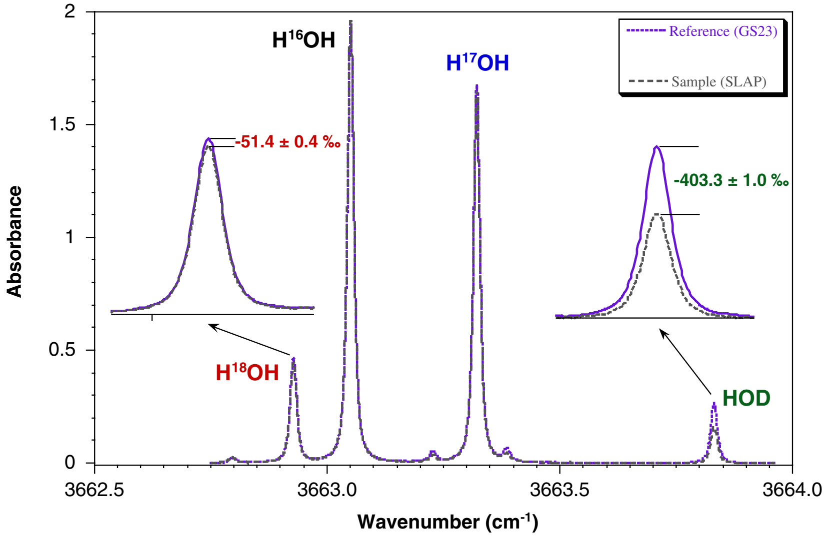


FIG. 3. Principle of the isotope ratio determination. In this figure, the absorbance spectra of sample and reference have been scaled to give equal H^{16}OH absorbances. The isotope ratio may then be "read" directly from the ratio of the corresponding line intensities. In this case, the reference material was a local (Groningen) standard ($^2\delta$=–41.0‰, $^{17}\delta$=-3.36‰, and $^{18}\delta$=-6.29‰) and Standard Light Antarctic Precipitation was used as "unknown" sample ($^2\delta$=–428.0‰, $^{17}\delta$≈-29.7‰, and $^{18}\delta$=-55.5‰).

Figure 2 shows an experimental registration of absorption by a vapour-phase, natural water sample as a function of the light frequency ν in a small spectral region near 2.73 μm (3664 cm^{-1}). The absorption features correspond to ro-vibrational transitions in the most abundant isotopologue, H^{16}OH, and the rare isotopologues H^{17}OH, H^{18}OH, and H^{16}OD. The absorption spectrum can be converted to an absorbance spectrum, as shown in Fig. 3, using the Beer law of Eq. (1).

Figure 3, in fact, shows two spectra recorded in the same region, one belonging to the “unknown” sample, the other to a reference material (back-traceable to an international standard material such as Vienna Standard Mean Ocean Water, VSMOW). The relative deviation $^x\delta_r(s)$ of the isotopic ratio of the sample (xRs), with respect to that of the reference (^xR_r) is given by:

$$ {}^{x}\delta_{r}(s) \equiv \frac{{}^{x}R_{s}}{{}^{x}R_{r}} - 1 = \frac{\left({}^{x}n/{}^{a}n\right)_{s}}{\left({}^{x}n/{}^{a}n\right)_{r}} - 1 \tag{2} $$

The subscript *s* refers to the sample, *r* to the reference material. The superscripts *a* and *x* refer to the most abundant ($H^{16}OH$) and the rare isotopologue species ($H^{17}OH$, $H^{18}OH$, or $H^{16}OD$), respectively. With a proper choice of experimental conditions, the δ-value follows directly from the intensities in the spectra:

$$ {}^{x}\delta_{r}(s) = \frac{\left({}^{x}\alpha/{}^{a}\alpha\right)_{s}}{\left({}^{x}\alpha/{}^{a}\alpha\right)_{r}} - 1 \tag{3} $$

Here, $\alpha = \alpha(\nu_0)$ represents the experimentally determined (maximum) absorbance at centre-line frequency, provided that the exact same line shape applies for all transitions. Alternatively, one may use the integrated line intensity. In Eq. (3) the assumption has been made that the optical path length *l* is the same for each isotopic species, or for the sample and reference spectra, or for both.

Since the line strength *S* depends on the number of molecules in the lower level of the transition, it is in general temperature-dependent: a change in temperature will redistribute the population over the rotational levels of the ground vibrational state (see, for example, Kerstel, 2004). Sample and reference spectra should therefore be measured at exactly the same temperature, and/or the isotopologue lines should be chosen such that their temperature coefficients are nearly equal. In general, this implies that the transitions should originate from ground state rotational levels with very nearly the same energy.

Table 1 lists the relevant parameters for the transitions used in our study. It may be seen that the most unfavourable situation occurs for the deuterium measurement: for a measurement taken at room temperature, the $^{2}\delta$-value would change by –7.8‰ for each degree of temperature difference between sample and reference cells. However, since to good approximation the measurement does not depend on the absolute temperature, but rather the difference between the sample and reference gas cells, passive stabilization with a good thermal contact between both gas cells is sufficient to make the temperature induced error negligible (i.e. < 0.1‰).

It should be noted that the isotope ratios thus determined are molecular isotope ratios. However, it can be shown that for all practical purposes these are equal to the more commonly used atomic isotope ratios (Kerstel, 2004).

The experimental layout is shown in Fig. 4. The laser is tuned in frequency under computer control. A fraction (~2%) of the output of the laser is directed to each gas cell (four in total, to allow for the simultaneous measurement of one reference material and three samples – this in order to increase the throughput of the apparatus), of which again a fraction (10%) is used to measure the power entering each gas cell, while the remainder makes multiple passes through the cell between specially designed reflective optics for a total path length of 20 m. Before a measurement, the gas cells are flushed with dry nitrogen, evacuated, and then filled with 10 μL of liquid water.

Table 1. The ro-vibrational transitions used in this study [a)]

Frequency [cm^{-1}]	Intensity [b)] [$cm\cdot molecule^{-1}$]	Temp. coeff. [c)] at 300 K [K^{-1}]	Isotope
3662.920	$1.8\cdot 10^{-23}$	$1.3\cdot 10^{-3}$	$^1H^{18}O^1H$
3663.045	$7.5\cdot 10^{-23}$	$4.4\cdot 10^{-3}$	$^1H^{16}O^1H$
3663.321	$6.4\cdot 10^{-23}$	$-1.5\cdot 10^{-3}$	$^1H^{17}O^1H$
3663.842	$1.2\cdot 10^{-23}$	$-3.4\cdot 10^{-3}$	$^1H^{16}O^2H$

a) All values are taken from the HITRAN 1996 spectroscopic database (http://www.hitran.com).

b) The intensities are for a natural water sample with abundances: 0.998, 0.00199, 0.00038, and 0.0003 for $^1H16O^1H$, $^1H^{18}O^1H$, $^1H^{17}O^1H$, *and* $^1H^{16}O^2H$, *respectively.*

c) The temperature coefficients give the relative change with temperature in absorption intensity of the selected transitions. They are calculated using the HITRAN 1996 database.

The power and signal beams are amplitude modulated at incommensurate frequencies around 1 kHz and detected by the same detector. A phase-sensitive detector (lock-in amplifier) recovers both signal and power measurements. The use of one optical detector and one lock-in amplifier (Perkin-Elmer 7265) per gas cell ensures that these devices contribute the same coherent noise and drifts to both the signal and power measurement, such that these cancel out in the ratio of signal to power. In this manner we are able to measure the $^2\delta$, $^{17}\delta$, and $^{18}\delta$ values of naturally occurring water samples with an accuracy of better than 1‰, 0.5‰, and 0.5‰, respectively, and a throughput of about 4 to 5 samples per hour (including gas cell evacuation and sample injection). The accuracy for $^2\delta$ is comparable to that which can be obtained by IRMS. As mentioned above, $^{17}\delta$ is difficult to determine by means of IRMS, making the laser determination quite unique. The $^{18}\delta$ accuracy is about one order of magnitude lower than possible with IRMS, but at higher enriched ^{18}O concentrations, the accuracy of IRMS and our laser instrument become comparable (see Table 2).

Table 2. Comparison of calibrated accuracy routinely obtained with the Groningen colour centre laser (FCL) setup and IRMS instrumentation.

Isotope ratio	δ-range [‰]	1σ-accuracy [‰] FCL	 IRMS
$^{2}H/^{1}H$	-500 – 15,000	0.6 – 55	1 – 100
$^{17}O/^{16}O$	-100 – 300	0.4 – 2	
$^{18}O/^{16}O$	-250 – 1,200	0.5 – 3.5	0.05 – 3

We have successfully used the colour centre laser based isotope spectrometer in applications in biomedicine (energy expenditure measurements by means of the so-called doubly labelled water method) (Trigt et al., 2001; Trigt et al., 2002a) and in ice-core studies to reconstruct the Earth's past climate and (Trigt et al., 2002b). The biomedical studies determine the CO_2 production as a direct measure of energy expenditure (Speakman, 1997). This is done by injecting a small amount of water, highly enriched in both ^{2}H and ^{18}O and following the decay of their concentrations. The ^{18}O concentration diminishes as ^{18}O leaves the body in the form of CO_2 (through the bicarbonate O-exchange reaction, which is accelerated by the anhydrase enzyme) or H_2O, whereas ^{2}H can leave the body only in the form of H_2O. Therefore the area between the ^{18}O and ^{2}H decay curves gives the CO_2 production over a certain period in time. The energy expenditure calculation thus involves the differences of $^{2}\delta$- and $^{18}\delta$-determinations. The overall error benefits in particular from the fact that both isotope ratio measurements take place simultaneously on the same sample, without requiring different chemical pretreatments for each measurement. Moreover, since these studies use highly enriched samples, the accuracy of laser and IRMS instrumentation is comparable and the laser technique can compete effectively with IRMS, also in this respect.

The ice-core studies measured the $^{2}\delta$-value (versus depth) as a proxy for the local (palaeo-) temperature, but also the so-called deuterium excess value, which can be shown to depend on other important climate variables (such as the temperature and relative humidity in the source region of the precipitation). The deuterium excess is defined as $^{2}\Delta = {}^{2}\delta - 8 \cdot {}^{18}\delta$. A precise determination of $^{2}\Delta$ thus requires a precise determination of $^{2}\delta$, and in particular $^{18}\delta$. Here, the laser setup cannot (yet) compete with IRMS. Still, the laser measurements proved rather useful as a check on the absolute accuracy (a possible shift of the δ scale), as they are much less sensitive to sample contamination, in this case by residual drilling fluid.

The colour centre laser is an excellent laboratory research instrument, mainly because of its very wide spectral coverage. Almost all infrared active small molecules have one or more strong absorption bands within its tuning range from 2.4 µm to 3.4 µm. Unfortunately, it is also a rather complicated, expensive, and large laser system, making it much less well suited for portable applications, and it is unlikely that the spectrometer will be copied by other isotope laboratories. For these reasons we have started using high quality diode lasers of designs originally developed for telecommunications (Kerstel et al,. 2002). These are not (yet) available in the same favourable spectral region of the colour centre laser, but operate near 1.4 µm in the region of water overtone and combination band vibrations. As can be seen in Fig. 1, the transitions in this region are at least one order of magnitude weaker than in the 2.7 µm region. Still, the low-noise properties of the diode laser in combination with the sensitive detection technique of wavelength modulation, has enabled us to obtain very favorable preliminary results with precision (i.e., not calibrated to an international standard) levels of 0.2‰ for $^{18}\delta$ and 0.5‰ for $^{2}\delta$ and $^{17}\delta$ (Gianfrani et al., 2003).

5. Other direct absorption techniques

In the above-mentioned spectrometers, wavelength selection is obtained by the use of a very narrow bandwidth laser. On the time scale of a typical isotope ratio measurement (from seconds to several minutes) our lasers exhibit line widths of several MHz, or typically at least two orders of magnitude smaller than the molecular absorption width (~0.01 cm-1). Such a high resolution is difficult to obtain by dispersive elements like prisms or gratings, but may not always be required.

6. Grating spectrometer

In fact, in one of the earliest infrared isotope ratio studies, Gaunt used a broad band light source in combination with a grating spectrometer near 4 µm to measure $^{2}H/^{1}H$ ratios between 0.015% and 0.08% with a relative error of 2% in liquid water samples from integrated vibrational band intensities (Gaunt, 1956). Much later, Fusch used the same experimental technique, but improved the measurement precision to <30‰, while at the same time reducing the sample requirement by a factor of 10, down to about 0.1 mL (Fusch, 1985).

7. Fourier transform spectrometry

An alternative detection technique is Fourier transform infrared (FTIR) spectrometry, in which a broadband light source illuminates the sample held in a gas cell inside the stationary arm of a Michelson interferometer. As the length of the second arm is changed in a periodic manner, an interferogram is recorded that is the Fourier transform of the sample gas absorption spectrum. The resolution of the instrument is proportional to the path length difference travelled by the mirror in the second arm. In practice this limits the resolution of an FTIR instrument to about 0.01 cm^{-1}. At this level of resolution the instrumentation quickly becomes rather expensive and bulky. Although most small molecules of environmental interest have an average rotational line spacing of the order of 1 cm^{-1}, allowing for a relatively compact FTIR apparatus, this is not true for water. Using a high-resolution FTIR spectrometer, Griffith and co-workers have been able to measure carbon and oxygen isotope ratios in natural air CO_2 and oxygen and nitrogen isotope ratios in pure N_2O with excellent precision (0.1‰ for $\delta^{13}C$, 1-2‰ for $\delta^{15}N$, and ~4‰ for $\delta(N_2{}^{18}O)$ and $\delta(N_2{}^{17}O)$) (Esler et al., 2000a,b; Turatti et al., 2000). However, we are aware of only one, low-resolution (8 cm^{-1}), FTIR study on water: Fusch et al. determined δ^2H over a very wide range of enrichments (–500‰ to 16,000‰) in 60 µL liquid water samples with an accuracy ranging from 3‰ to about 45‰ (Fusch et al., 1993).

8. Non-dispersive infrared spectrometry

Finally, we would like to mention the technique of non-dispersive infrared (NDIR) spectrometry, which has been applied with quite some success to the measurement of $\delta^{13}C$ in exhaled breath analyses. In its most common form NDIR uses an amplitude modulated broad band light source (lamp) and gas-specific detector units. Gas- and isotopologue specificity of the detectors is achieved by filling a small chamber with the pure isotopologue gas. Heating of the gas is detected with a microphone (photoacoustic detection), or alternatively, the transmission through the chamber is measured with an infrared detector. NDIR is by definition a spectrally low-resolution technique yielding a signal that is the integrated absorption over a relatively large fraction of the absorption spectrum of the molecule of interest (in practice limited by a narrow band-pass filter). As described here, it requires that at least part of the isotopologue absorption is well separated from that of the most abundant molecule. The selectivity can be high for ^{13}C-analysis in CO_2, as the asymmetric stretching band used in this scheme is shifted considerably (66 cm^{-1}) upon ^{13}C substitution. An entirely different implementation of NDIR is possible that actually depends on the overlap of the isotopologue bands. In this heterodyne scheme, the signal is derived from the absorption of amplitude modulated infrared radiation by a pressure-modulated gas (Dimeff, 1972; Irving et al., 1986). The latter technique in particular may be applicable to water isotope ratio measurements, but we have not encountered such an implementation in the literature.

9. Indirect techniques

In indirect detection techniques, the absorption of infrared radiation is not detected directly, but rather by its influence on other properties of the gas, such as heat dissipation (photoacoustic spectroscopy) or the electrical response of a gas discharge (opto-galvanic effect). The detection signal therefore depends in general on other parameters in addition to those seen in Eq. (1), most notably the laser power. As the signal now depends directly on the number of absorbing molecules, indirect absorption techniques are characterized by a zero background and thus potentially very sensitive. This is not necessarily an advantage for isotope ratio measurements, where SNR and signal linearity are often more important.

10. Photoacoustic detection

The technique of laser photoacoustic detection was used by Matsumi et al. to determine the $^{18}O/^{16}O$ isotope ratio in small (5 µL) gas phase water samples (Matsume et al., 1998). They used a pulsed dye laser in the visible region of the spectrum (720 nm) to excite a weak third overtone OH stretching vibration. The sound wave generated in the gas cell containing the sample was detected with a sensitive microphone. The measurement precision was disappointing (~16‰), mainly because of the weakness of the third overtone transition, but perhaps also because of the poor noise characteristics of the pulsed laser source.

11. Opto-galvanic detection

The opto-galvanic effect has been used for isotope ratio measurements ($\delta^{13}C$ and $\delta^{18}O$) in exhaled breath CO_2 analyses, using a powerful CO_2 laser to boost the weak opto-galvanic signals in a CO_2 RF discharge (Murnick et al., 1998). As far as we know, the technique has not been used with water.

12. Discussion

Optical isotope ratio measurements of the $^{2}H/^{1}H$ ratio in water have proved competitive with IRMS in terms of accuracy. In this respect, fractionation effects during sample handling constitute the dominant source of analytical errors. It appears unlikely that an optical method will be able to reach the very high accuracy possible with IRMS for $\delta^{18}O$ determinations on natural samples. However, for highly enriched samples laser spectrometry may already be a viable alternative to IRMS. The possibility of using laser spectrometry to measure $\delta^{17}O$ easily may be used for independent verification of $\delta^{18}O$ measurements on the same sample (Trigt et al., 2000b), or in exotic applications. For example, we have determined the ^{17}O concentration in the heavy water used in a solar neutrino experiment (Kerstel, 2001) and, in collaboration with the group of D. Romanini in Grenoble, we have recently built a very low water-concentration isotope spectrometer to measure the isotopic composition (and in particular $\delta^{17}O$) of stratospheric water. The latter instrument is based on the extremely sensitive detection technique of cavity ring-down spectroscopy, which is essentially a clever way to increase the effective optical path length in direct absorption spectroscopy by determining the life-time of a photon inside a high finesse (high reflectivity) optical cavity (see, for example the review in Berden et al., 2000).

Of course, accuracy is not the only factor to be considered when comparing laser spectrometry to IRMS. There are certainly applications for which other aspects are more important. One could think of industrial plant or volcanic emission monitoring, requiring, for example, robustness, portability, remote operation in a hostile environment, compactness, and real-time measurements. Other advantages of optical methods that may be considered are the high selectivity, thus avoiding the need of chemical sample pretreatment, the non-destructive nature of the measurement, making it possible to recover the sample if needed, and low cost. Last but not least, methods based on direct absorption are conceptually simple, which helps reduce the required scale correction and normalization with respect to IRMS.

Finally, we would like to quote one of the recommendations made by the IAEA Advisory Group meeting on new approaches for stable isotope ratio measurements (IAEA, 2001):

> During the past few years a variety of new techniques have appeared. Here we discuss in particular clinical applications of isotope measurements and laser spectrometry techniques. The requirements for clinical use are similar to those required for field deployment – easy of use, self diagnostic, robust, and moderate cost.

[…]

> For such new techniques to be accepted by the isotope community they should be adequately compared with existing state-of-the art equipment and checked against isotope reference materials that are back-traceable to (IAEA) primary standards. Publications should distinguish between precision, accuracy, as well as instrument stability. In addition they should clearly state the procedure followed for calibration (defining the scale zero) and normalization (scale multiplication factor). In practice this means, e.g. for the case of water, that VSMOW, SLAP, GISP and a number of local standards should be measured.

Unfortunately, the terms precision (a measure of the reproducibility of the result) and accuracy (a measure of the deviation from the true value) are sometimes used too loosely in the literature. Moreover, since measurements should be made with respect to a local reference material, instead of the international standard material (which is simply too expensive and rare to be used on a daily basis), the total variance can be decomposed into at least two components: the variance of the local reference material with respect to the international standard, and that of the sample with respect to the local reference (Jasper, 2001). Both should be reported. Conformity with the procedures outlined above is essential if optical isotope ratio instrumentation is to move from the physics laboratory to the isotope ratio work floor.

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HYDROLOGIC PROCESS AND SYSTEMS

10. SOME CLASSICAL CONCEPTS OF ISOTOPE HYDROLOGY:

"Rayleigh fractionation, Meteoric Water Lines, the Dansgaard effects (altitude, latitude, distance from coast and amount effects) and the d-excess parameter"

Their inception, the role they played in the evolution of the discipline and how they have stood the test of time

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Following the discovery of variations of isotopic abundance of the isotopes of light elements in natural materials (in excess of those resulting from radioactive decay and transmutations), mass-dependent processes were invoked to explain the occurrence of such variations. In the newly emerging field of isotope geology (as reviewed by Rankama, 1954) the unequal distribution of isotopes between co-existing molecules or phases was explained by the quantum mechanical effects on the partition function of the molecules concerned, the so-called equilibrium or thermodynamic isotope effects; it was then suggested that the process of fractionation between isotopes in the hydrologic cycle was also controlled by such effects. A major role was attributed to the phase transitions of water, namely between ice/liquid/vapour, respectively. The mathematical description of the change in the isotopic composition which accompanies such a process follows that attributed to Lord Rayleigh more than 100 years ago in order to describe the enrichment of alcohol in an alcohol/water mixture by distillation (Rayleigh, 1902). The Rayleigh fractionation formula, as applied to isotope fractionation, is given in differential form by the equation:

$$\mathrm{dlogR/dlogN} \equiv \mathrm{d}\lambda/\mathrm{dlogN} = (\alpha^{*}-1) \qquad (1)$$

where R is the ratio of the numbers N_i and N of the isotopic molecules concerned and α^* is the equilibrium fractionation factor. Strictly speaking, this formulation is

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intended to apply to a case of a well-mixed system from which material is removed under the condition of equilibrium with the residual material. An example was the attempt to describe the changing isotope composition of rain in a precipitating air mass by integration of this equation. It was realized, however, that the fractionation factor during the evolution of the rainout process could not be constant, since more and more water precipitates only when the air-mass cools down. In this particular case, then, the fractionation factor increases because of the negative temperature dependence of the quantum mechanical processes; integration over the entire rainout process has thus to be performed with a continuously changing isotope fractionation factor. Such a model was then widely invoked to explain the different isotope composition of precipitation over the globe as observed by the GNIP programme (Dansgaard, 1964). To what extent this also provides an explanation of the Global Meteoric Water Line (GMWL) (Craig, 1961) will be discussed below.

Integrating the classical Rayleigh equation for the case of removal of liquid from an air-mass at local isotopic equilibrium for both the hydrogen and oxygen isotopes, based on fixed isotopic fractionation factors, yields a straight-line dependence in λ-space for the enrichment of the oxygen and hydrogen isotopes, with the slope of this line given by:

$$d\lambda^{2}H / d\lambda^{18}O = (\alpha^{*}-1)^{2}H / (\alpha^{*}-1)^{18}O \qquad (2)$$

where $\lambda \equiv \log R$ and λ-space is the representation of λ^{2} H vs. λ^{18}O. Translation of this relationship into δ-space (i.e. the representation of λ^{2} H vs. λ^{18}O) based on the definition of δ as:

$$\delta \equiv \{(R - R_{standard}) / R_{standard}\} \qquad (3)$$

is given by the following equation wherein the δ values, which are small numbers, are expressed in ‰ form:

$$d\lambda = d\log(1+\delta/10^{3}) = (d\delta/10^{3})/(1+\delta/10^{3}) \qquad (4)$$

This results in a deviation from a straight-line dependence when $\delta(^{2}H)$ ‰ is plotted vs $\delta(^{18}O)$ ‰, due to the term of $(1+\delta/10^{3})$ which can differ considerably from unity, especially for the case of the hydrogen isotopes (since their fractionation factors are larger by almost one order of magnitude than of the other elements). It is further to be noted that the deviation of the δ‰ scale from that of the logarithmic λ scale depends on the choice of the standard for the former. As was first shown by Taylor (1972), the temperature correction for the fractionation factor under a regime of changing temperature during the rainout process fortuitously compensates almost exactly for the effect of the $(1+\delta/10^{3})$ term, provided the δ scale is based on the SMOW standard (Craig, 1961a).

At about the time that these formulations were first being discussed, Harmon Craig (1961b) proposed the relationship of:

$$\delta(^{2}H) = 8\bullet \delta(^{18}O)+10 \tag{5}$$

as the locus line of the isotopic composition of meteoric waters in the water cycle, i.e. those waters directly derived from precipitation, when the ‰ notation is used. This relationship, later named the Global Meteoric Water Line (GMWL in δ-space), was based on a very limited database and it is evident, on a closer look, that the linear relationship of the GMWL is dictated to a large extent by the one sample of Antarctic precipitation with $\delta(^{18}O) \approx -50‰$. Already the first data set used by Craig excluded data from "African lakes", i.e. systems where additional water loss by evaporation had occurred.

Three aspects of the relationship are noteworthy:

- the offset from the composition of the source of water in the hydrologic cycle, namely the oceans;
- the slope of that line approximates that dictated by the ratio of the equilibrium fractionation factors (α^*-1) for the liquid to vapour phase transition at ambient temperatures, respectively for the hydrogen and oxygen isotopes.
- The supposedly linear relationship over a wide range of isotopic compositions.

These facts suggested that the formation of the atmospheric vapour by evaporation of oceanic waters was a non-equilibrium process, as was described later by the Craig-Gordon model (Craig and Gordon, 1965), whereas the reverse process of rainout from the atmosphere was supposed to occur under close-to-equilibrium conditions. This notion implied that the additive parameter in the Meteoric Water Line (namely 10‰) was inherited from the initial isotope composition of the maritime airmass as determined by the air-sea interaction regime and that this then remains invariant as rainout occurs. Later particular regional patterns were observed which appeared to result in a series of Meteoric Water Lines essentially in parallel with Craig's GMWL, described by the equation:

$$\delta(^{2}H) = 8\bullet \delta(^{18}O)+d \tag{6}$$

This was interpreted in the sense that different oceanic or other source areas are characterized by different air-sea or air-land interaction modes. The parameter d, which was named the *d-excess parameter* by Dansgaard (1964), is then taken to refer to the source condition of the vapour; obviously it can then also be applied even to a singular datum point, on the assumption that all rainout processes which took place in the air mass prior to the particular sample would have described a line of slope=8 in δ-space.

The notion that the whole range of meteoric waters, from precipitation in the oceanic source regions and up to the snow accumulation in the Antarctica, is formed by a continuous "Rayleigh rainout process" also established itself, although this was not originally implied. Indeed Craig (private communication) had suggested that the primary fractionation process, which fixes the slope of the GMWL, might occur in the towering tropical clouds, followed by the poleward drifting of the upper air masses with their isotopically very depleted vapour.

Early on it was realized that not all *mass-dependent* processes which result in isotopic fractionation are equilibrium effects; different reaction rates in chemical or biological reactions have to be considered, as well as processes such as diffusion or effusion which are characterized by the different transport properties of the isotopic molecules concerned. A special important case in the hydrologic cycle is that of evaporation from a liquid into either the free turbulent atmosphere (as was treated by the above-mentioned Craig-Gordon model) or through a stagnant air layer, as is the case when soilwater evaporation takes place through a soil column (Barnes and Allison, 1988), in which cases a combination of equilibrium and transport processes is involved. In principle, Rayleigh equations can still be applied provided they are based on the appropriate fractionation factors. The term *Rayleigh-type processes* has been used to describe such cases where the mathematics of the Rayleigh process applies, without however implying an equilibrium process based on the thermodynamic "unit separation factor".

While the system to which the classical Rayleigh equation applies is one where material is continuously removed under conditions of isotope fractionation as determined by the appropriate fractionation factor (so that the residual isotope composition is found by integrating the differential equation given above) there are other systems in which the same fractionation factor applies, but where the integration has to be performed under different boundary conditions. One such system, the so-called "two-phase equilibrium model", is one where the material removed from one phase accumulates in a second one in such a manner that isotopic equilibrium between the phases is maintained throughout; an example being the in-cloud process when vapour condenses into floating water droplets (Epstein, 1965; Gat and Dansgaard, 1972). Another situation is that of an open model where the outgoing fractionated flux is replaced by an inflow, for example in a through-flow or a terminal lake. In the latter case, the isotopic compositions of the inflowing and outgoing fluxes become equal under steady-state conditions, whereas the isotope composition in the reservoir then differs by one unit fractionation factor from that of both these fluxes. Figure 1 shows the evolution of isotopic change under these three situations. Evidently then, the changes of the isotopic composition in any system should not be interpreted without also considering the boundary conditions that have to be applied.

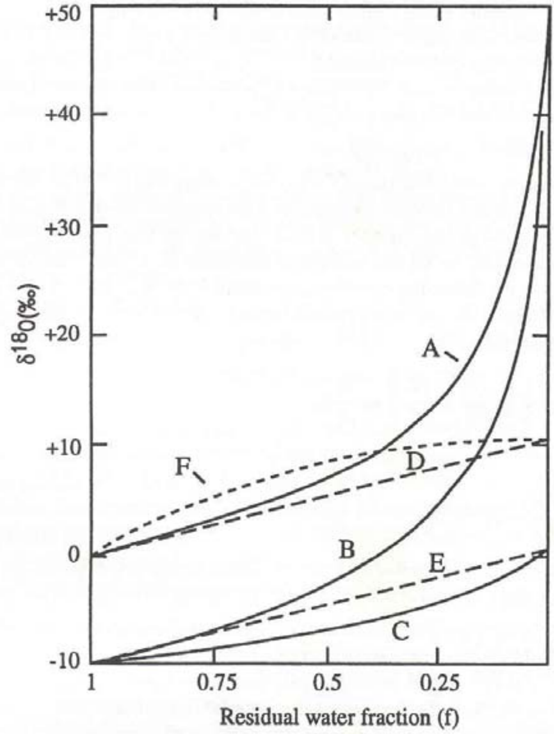

FIG. 1. Change of the isotope composition under Rayleigh, closed and steady-state conditions, respectively, for an initial composition in the liquid of δ = 0 and assuming a unit fractionation factor of α = 1.01. Lines A, B and C apply to the case of the Rayleigh conditions and stand for the composition of the residual water, the instantaneously removed vapour and the integrated composition in the vapour, respectively. Lines D and E show the isotopic composition of the liquid and vapour in a co-existing two-phase system. Line F shows the composition of a liquid approaching steady-state (with the x-axis taken as a time axis in units not in proportion).

A very considerable amount of isotope data of precipitation have been collected within and in supplement to the GNIP program. These constitute either monthly averaged or event-based data at the chosen precipitation collection sites, worldwide. Very often then a "Local Meteoric Water Line" (LMWL) is defined for a given location, being the best linear fit of all the precipitation data in δ-space, namely:

$$\delta(^{2}H) = a \bullet \delta(^{18}O) + b \tag{7}$$

Obviously, unless "a" has the value of a=8, one should not equate b with the *d-excess* concept, as has often been done erroneously.

The LMWL can serve some useful purpose in a descriptive capacity, in order to define the range of input parameters to those hydrologic systems that are fed directly by the precipitation (the "meteoric waters"). Beyond that its validity is quite limited, for the following reasons:

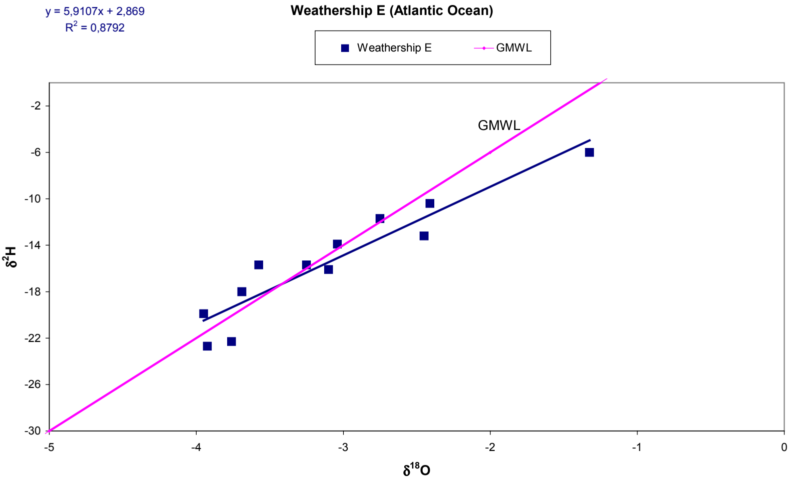

FIG. 2. Monthly average isotope composition of precipitation at selected representative stations, based on the GNIP data set (IAEA, 1992). Two lines shown are the GMWL and the best-fit linear local MWL. Data for Weathership E in the North-Atlantic Ocean.

- In a marine or coastal setting, where the precipitation is often a first-condensate of the accumulated moisture, the data are distributed on a δ-plot within a circle or ellipsoid rather than along a line , as shown for example in Fig. 2 by the GNIP monthly data (IAEA,1992) from Weathership E in the northern Atlantic Ocean. Under some circumstances, especially in relatively arid settings, the evaporation from falling droplets (to be discussed below) dictates the course of the line, which then resembles the "*Evaporation Lines"* of surface waters, as exemplified for the case of Flagstaff, Arizona in Fig. 3.
- On the other extreme, snow samples are generally characterized by higher d-excess values than precipitation from the same air mass,due to transport fractionation in super-cooled clouds (Jouzel and Merlivat, 1984) and this affects the depleted winter data (see data from Ottawa in Canada in Fig. 4), thus also imposing a slope of less than 8 on the local MWL, which could be erroneously interpreted as resulting from evaporation.
- Often the LMWL simply joins two or more separate clusters of data, for example, representing summer and winter data, as is exemplified in Fig 5 by the GNIP data from Tokyo (IAEA, 1992) or rain events associated with air masses of different origin, as is the case in climate transition zones, for

example at the stations in southern Israel reported by Gat and Rindsberger (1985). Drawing a composite best-fit line for all the data is then obviously just an artifact.

Going back to the fundamentals, one must realize that the classical concept of the Rayleigh Rainout Process applies to an air mass, with whatever isotopic properties acquired before, whereby precipitation is removed under equilibrium conditions. It is thus basically a Lagrangian property of the air mass and describes a spatially distributed data set which follows the evolution of a particular precipitating air mass, and cannot be observed at any fixed point unless subsequent precipitation events all result from air masses of similar origin. Thus this process can in principle describe the altitude effect of air masses ascending a mountain range as well as the distance-from-coast and latitude effects; One should realize, however, that in these cases the depletion of the heavy isotopes is a function of the total integrated amount of precipitation along the trajectory, and not the rain amounts accumulated at the observation point. To a first approximation, the d-excess during this process remains invariant, even though at higher elevations (and the lower temperatures associated with these locations) there is a tendency for an increase in this value (Gonfiantini et al., 2001).

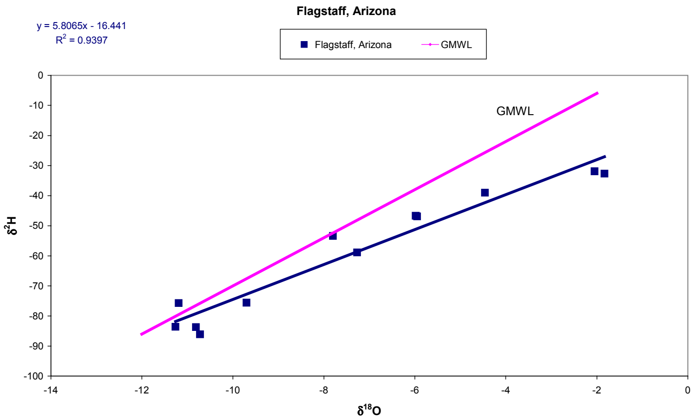

FIG.3. Monthly average isotope composition of precipitation at selected representative stations, based on the GNIP data set (IAEA, 1992). Two lines shown are the GMWL and the best-fit linear local MWL. Data for Flagstaff, Arizona, USA,

Unlike the three Dansgaard effects mentioned above, namely the altitude, latitude and continental (i.e. distance-from-coast) effects, which are in a sense straightforward measures of the wringing out of moisture from the air mass as the air cools, the amount effect, namely the relation between the rain amount at any location and the depletion in the heavy isotopes, has a more complex structure, although this is not always realized. The problem is, of course, that it is not the local rain amount but the spatially integrated one which is expected to show a proportionality to the depletion of the isotopes, as was indeed demonstrated recently (Gat et al., 2001). The factors that often make it appear as if there is also a direct local amount effect are not directly related to the Rayleigh rainout process: one of these other factors, for example, is the enrichment of the heavy isotopes during the evaporation from the falling droplets below the cloud base, because this effect is of greater consequence in the case of small rain amounts.

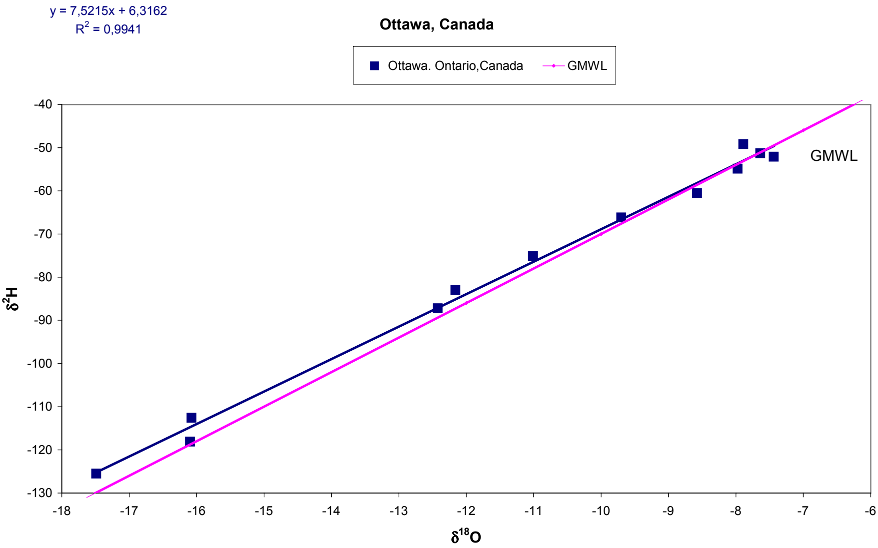

FIG.4. Monthly average isotope composition of precipitation at selected representative stations, based on the GNIP data set (IAEA, 1992). Two lines shown are the GMWL and the best-fit linear local MWL. Data for Ottawa, Canada.

The formation of precipitation elements in the clouds is not necessarily in equilibrium with the average air at its ambient mean temperature, but occurs under the much colder conditions of the higher elevation.. The physical reality that yet enables a satisfactory formulation of the rainout process in terms of the Rayleigh equation is the isotopic exchange between the falling droplets and the ascending air in the cloud (Friedman et al.,1962), which results in precipitation which essentially “forgets” the isotopic values imprinted by the in-cloud process, establishing isotopic equilibrium with the ambient air, strictly speaking close to the cloudbase. An exception to this scenario is encountered when snow or hail reaches the ground, in which case the isotopic exchange cannot take place, or by precipitation from strongly convective systems which are accompanied by strong local downdrafts. In these two cases the precipitation is more depleted than the true equilibrium precipitation and under such a situation then the extent of isotope depletion as a function of rainout is moderated (Gat, 2000). However, the d-excess value will still be more or less conserved in the air mass, except for a slight reduction in those cases where the isotopic composition of the snow shows the kinetic fractionation effect described above. This fact is one of the reasons that the *d-excess parameter*, in addition to the depletion or enrichment of the isotopic species, has such a high diagnostic value.

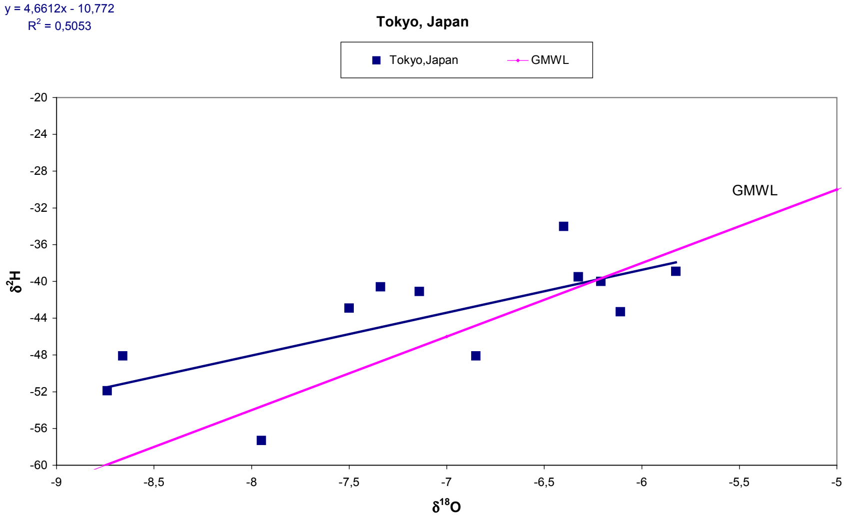

FIG.5. Monthly average isotope composition of precipitation at selected representative stations, based on the GNIP data set (IAEA, 1992). Two lines shown are the GMWL and the best-fit linear local MWL. Data for Tokyo, Japan.

The evaporation from falling rain droplets beneath the cloudbase not only results, in the first instance, in the enrichment of the heavy isotopes in the remnant rain droplets and a decrease of the *d-excess parameter,* similar to the effect seen in evaporated surface waters (see, for example, Stewart, 1975) but the more far-reaching (and often apparently puzzling) effect is that of precipitation with a large d-excess value, which results from the downwind admixture of the evaporated moisture into the air masses concerned. This effect was first observed by Dansgaard (1964) for precipitation in Ethiopia. Later an increase inland of the d-excess value inprecipitation was observed in the Amazon basin (Salati et al.,1979) and interpreted as due mainly to the evaporate from surface waters and water intercepted on the canopy of the vegetation (Gat and Matsui,1991). One should notice, however, that the recycling of the meteoric water by evapotranspiration will affect the d-excess of the water vapour in the atmosphere only when this process is one of evaporation, as shown in the case of the Great Lakes of north America by Gat, Bowser and Kendall (1994) whereas transpiration or the complete evaporation of a surface water pool (or for that matter, of a falling droplet) will apparently decrease the depletion of the heavy isotopes in later stages of the Rayleigh rainout process (Rozanski et al., 1982) without however affecting the d-excess value. In order to estimate the total water balance of an air mass the isotope content, the d-excess value of the precipitation (or preferably of the associated vapour) as well as the total integrated rain amount along the trajectory should be recorded. This record, in comparison to the expected value according to the Rayleigh model, can then be very informative both regarding the water balance in the atmosphere and of the meteoric water systems on ground and the nature of the evaporative flux. Indeed more and more basin-wide studies are being pursued with these objectives in mind.

The classical representation of the isotopic data of the meteoric waters has been either on a δ-plot or of a representation of $\delta(^{18}O)$ and the d-excess in the precipitation and the associated ground- or runoff waters as a function of time or space. Alternate representations can be as revealing in relation to the processes at play. The first of these, namely the presentation of d-excess parameter as a function of $\delta(^{18}O)$ (as suggested by Bowser) shows up the origin of the atmospheric moisture. Alternative representations, either the plotting of $\{8x\delta(^{18}O)+10\}$ and $\delta(^{2}H)$ as a function of time or space (i.e. the comparison of values expected on the GMWL with the actual data) or the TAMI plot (the comparison of $\{8x\delta(^{18}O)\}$ with $\delta(^{2}H)$) have been used. The first obviously highlights the variations relative to the GMWL, whereas the second plot is useful when the data are not constrained along that line. Both these representation have been used mainly in order to detect evaporative water losses in the systems investigated, by comparing the isotope data of the precipitation with those of river runoff or groundwater.

A major handicap in the full utilization of isotope data has been the deficient data set of atmospheric vapour; this has to be inferred, in most situations, from the data of precipitation events, assuming isotopic equilibrium between the precipitation and the ambient moisture. This of course leaves wide open gaps, especially under more arid conditions. A worldwide isotopic water vapour monitoring network, (Global Network of Isotopes in Atmospheric Moisture, GNIAM) is long overdue, in support of the GNIP and the Isotopes in River Runoff Programmes.

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11. ISOTOPES IN LAKE STUDIES: A HISTORICAL PERSPECTIVE

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1. Introduction

Lakes, together with other surface water bodies such as wetlands and artificial surface reservoirs, cover millions of km^2 of continental area and constitute an important component of the regional and global water cycles. They are complex dynamic systems, connected to the water cycle through both surface and underground inflows and outflows, as well as via precipitation/evaporation fluxes. The interaction with the local environment includes also chemical constituents and mineral phases that are transported from the catchment area to the lake via surface and underground inflows. Lakes vary greatly in size, from small water bodies with a volume of just a few thousand m^3, up to the Caspian Sea covering the area of 374,000 km^2 and encompassing 780,000 km^3 of water. In many areas of the world lakes are exploited as a source of potable water. Nowadays lakes are seen also as important contributors to the carbon, nitrogen and phosphorus cycles on continents through various processes such as production of autochthonous organic matter, sedimentation of detrital organic matter, and precipitation of carbonates and evaporites. Lacustrine sediments belong to the most important continental archives of climatic and environmental changes.

Scientific foundations for using environmental isotopes as tracers in lake (sea) studies were laid down shortly after the discovery of the respective isotopes in

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nature. For example, natural tritium in lake water was measured by W. Libby and A. Kaufmann in samples taken in 1952 and 1953 from Lake Michigan, USA (Libby, 1954). The average value found for two samples taken in 1952 and 1953, was about 1.5 TU, and the tritium content in Chicago rainwater at this time was ca. 5.5 TU. The lower tritium value of the lake water in comparison to that of precipitation indicates a residence time of water in Lake Michigan on the order of some tens of years.

The small natural variations in the abundance of ^{2}H and ^{18}O could only be measured on a routine basis after Nier built a light and versatile mass spectrometer, the grandfather of the present-day highly precise isotope ratio mass spectrometers (Nier, 1940). Later, the pioneering studies of Urey (1947), and Bigeleisen and Mayer (1947) on the thermodynamics of isotopic fractionation processes enabled interpretation of these natural variations in terms of processes in the hydrologic cycle. In 1953, Epstein and Mayeda (^{18}O) and Friedman (^{2}H) demonstrated that the isotopic variations were sufficiently great to provide an excellent tracer for hydrologic research, including lake studies. Craig and Gordon, finally, developed the model which provided the basis for the interpretation of these natural variations in terms of oceanographic and lake processes (Craig and Gordon, 1965).

Since then, numerous lake studies using these isotopes as tracers have been carried out. In addition, a variety of other environmental isotopes, including stable isotopes of carbon and nitrogen, radioactive isotopes and other environmental tracers such as noble gases and chlorofluorocarbons (CFCs), have also been applied. The problems addressed by environmental isotopes include water balance of lakes and surface reservoirs, lake dynamics (e.g. vertical and horizontal mixing processes), interaction between lakes and adjacent groundwater, lake sedimentation processes, and palaeo-hydrologic and palaeo-climatological problems.

This contribution focuses on lake studies using isotopes of the elements of the water molecule hydrogen and oxygen. It describes major results achieved to date and outlines future research needs. The use of artificial radioisotopes in lake studies will not be discussed, because nowadays the injection of radioactive tracers, including tritium, to water bodies is prohibited in most countries.

2. Water balance of lakes

Lake water is often enriched in ^{18}O and ^{2}H with respect to local precipitation and tributaries, because water molecules containing heavy isotopes are removed from lakes by evaporation at a lower rate than the light ones. Craig and Gordon (1965) described this isotopic fractionation as a two-step process. In the first step, the fractionation occurs at equilibrium between liquid water and saturated water vapour confined to a very small layer above the liquid surface. This fractionation is a consequence of the different saturation vapour pressures of isotopic vapour molecules and, hence, a function of the temperature and salinity. The isotopically lighter molecules have a higher vapour pressure, so that the heavy isotopes are depleted in the vapour phase with respect to the liquid phase. At a typical ambient temperature of 15°C, this depletion is about 10‰ in ^{18}O and 90‰ in ^{2}H. The second isotope fractionation step is represented by the diffusion of water vapour from this layer to an upper layer that is completely mixed by turbulence and in which therefore no further isotope fractionation takes place. This diffusion/turbulence-controlled fractionation is a function of the different diffusion rates of isotopic vapour molecules in air, the strength of the turbulence and the humidity deficit over the evaporating surface.

The Craig-Gordon model provides an expression for the isotopic composition of the net evaporating moisture δ_E by the following expression:

$$\delta_E = \frac{\delta_S / \alpha_e - h \cdot \delta_A - \varepsilon}{1 - h + \Delta\varepsilon} \tag{1}$$

in which h = humidity normalized to the lake surface temperature, α_e = equilibrium fractionation factor, $\varepsilon = \varepsilon_e + \Delta\varepsilon$ = total enrichment factor, $\varepsilon_e = (\alpha_e - 1)$ = equilibrium enrichment factor, $\Delta\varepsilon = (1 - h)\cdot c^*_K$ and c^*_K = empirical constant describing the kinetic fractionation during the evaporation process. δ_S is the isotopic composition of the lake water at the surface, and δ_A is the isotopic composition of the water vapour in the 'free air', whose properties are independent of the evaporation process.

Assuming a reliable value of δ_E has been derived, the use of ^{18}O and/or ^2H in lake studies provides a balance equation additionally to other balance equations such as that of the water mass and the salinity. This enables an independent determination of relevant parameters, especially of the inflow/evaporation ratio. A typical example is demonstrated by the following expression that follows from water and isotope balance equations (see, for example, Froehlich, 2000):

$$I_{tot}/E = \frac{h \cdot (\delta_A - \delta_{IT}) + \varepsilon_e + (1 - h) \cdot c^*_K}{\Delta \cdot (1 - h)} - \frac{h}{1 - h} \tag{2}$$

where I_{tot} and E are the inflow and evaporation (rates), respectively, and Δ is difference between the steady-state isotopic composition of the lake water and the isotopic composition of the total inflow δ_{IT} to the lake. The latter two quantities can directly be measured in samples taken from the lake and its inflow. The humidity and ambient temperature (for the calculation of ε_e) are easily measurable. The determination of the parameter c^*_K is discussed in Gat (1996).

The status reached in certain periods during the past 40 years in research and application of these isotopes in lake studies, has been reviewed in a number of publications, including Dinçer (1968), Gat (1968), Pearson and Coplen (1978), IAEA (1979), Zuber (1983), Gonfiantini (1986), Gat (1995 and 1996), Froehlich (2000), and Rozanski et al. (2001). The IAEA played a significant role in fostering the use of isotopes in such studies. Two prominent examples of the Agency's contributions to this field are represented by the Proceedings of an Advisory Group Meeting, held in 1977 at the IAEA Headquarters in Vienna, Austria (IAEA, 1979) and of the final co-ordination meeting of a Co-ordinated Research Project, held in March 1997 in Rehovot, Israel (IAEA, 2001).

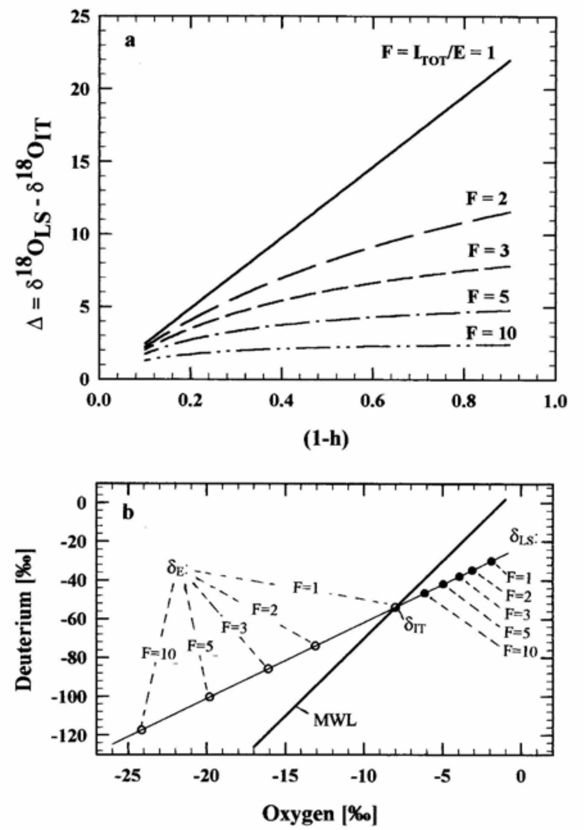

FIG.1(a). The calculated steady-state ^{18}O isotopic enrichment of a lake water ($\Delta\delta^{18}O = \delta^{18}O_{LS}-\delta^{18}O_{IT}$) as a function of humidity deficit ($1–h_N$) and the ratio of total inflow to evaporation rate($F=I_{tot}/E$) characterizing the water balance of the studied system. The isotope enrichment was calculated from the isotope and mass balance equations with several simplifying assumptions: (i) the system is in hydrologic and isotopic steady state; (ii) the mean annual temperature of the surface water in the lake is identical to the mean annual surface air temperature in the area; (iii) the weighted mean annual isotopic composition of local rainfall is the same as the isotopic composition of the shallow groundwater in the area, and (iv) the mean isotopic composition of the atmospheric water vapour above the lake is in isotopic equilibrium with the local precipitation.Fig 1(b) Evolution of the isotopic composition of lake water and the net evaporation flux with changing water balance of the system (varying ratio of the total inflow to evaporation). The calculations were performed with the simplifying assumptions listed above, isotopic composition of the total inflow ($^{18}\delta_{IT}$ = -8‰ and $^{2}\delta_{IT}$ = -54‰) located on the Global Meteoric Water Line and with relative humidity $h_N = 0.75$.

Figure 1(a) illustrates how the isotopic enrichment of lake water depends on the water balance of the system and on local climate. The isotope enrichment, $\Delta\delta^{18}O$, defined as the difference between the ^{18}O content of the lake water and the total inflow, is plotted as a function of humidity deficit for different ratios of the total inflow to the evaporation rate (I_{tot}/E). This figure may serve as a quick reference for identifying the type of water balance of the studied system (evaporation-controlled or through-flow system). It is apparent that the isotope enrichment can be quite remarkable, reaching more than 10‰ for ^{18}O in some cases.

Figure 1(b) shows how the isotopic composition of a lake evolves in the δ^2H-$\delta^{18}O$ space with the changing water balance. It is apparent that the steady-state isotopic composition of lake water (δ_{LS}) and that of the evaporating vapour (δ_E) are found on a straight line that is called the *evaporation line*. The slope of the evaporation line may vary according to environmental conditions (Gat, this volume).

The most critical parameter in the isotopic balance equations is the isotopic composition of the net evaporation flux δ_E, which cannot be measured directly. Its determination requires knowing, among other things, the isotopic composition of the water vapour δ_A in the "free air" (Eq.1). This parameter should be determined by measuring vapour samples to be taken from vertical moisture profiles above the lake surface (to arrive at the "free-atmosphere" value included in Eq.(1)). In many cases, however, δ_A is estimated from the isotopic composition of precipitation in the nearest possible station, assuming isotopic equilibrium between the vapour above the lake surface and the precipitation. However, this assumption is not always justified. Craig and Horibe (1967) found close to equilibrium in a continental setting (Bern, Switzerland) and less near a coastal site (LaJolla, USA). The relationship between the isotopic composition of rain and vapour in Brazil has been studied by Matsui et al. (1983). Long-term time series of isotopic composition in rain and atmospheric vapour at Heidelberg, Germany, were discussed by Jacob and Sonntag (1991).

For small lakes, the contribution of evaporated water to the bulk of air moisture is assumed to be small or negligible, so that the regional air moisture circulation mainly controls the isotopic composition of the atmospheric vapour above the small lake. However, moving from the shore across the water surface of large lakes, the vapour released by the lake itself becomes rapidly predominant and the external vapour less and less important (Fontes and Gonfiantini, 1970; Gat et al., 1994).

The existing isotopic data on atmospheric vapour above lakes confirm the validity of the Craig-Gordon model. However, the data available are still scarce, owing to the difficulties and cost of vapour sampling, and therefore our knowledge of the isotopic interrelations between lakes and atmospheric vapour is still inadequate. Repeated sampling of atmospheric vapour in different seasons and different aerodynamic conditions is required to improve our current knowledge on the isotopic balance of lakes. Research efforts along these lines should be encouraged. For large lakes, this will also help to assess recycling of the lake vapour by precipitation. The IAEA is currently supporting an isotopic investigation of Lake Titicaca, including the determination of the isotopic composition of atmospheric vapour, both directly by sampling it and indirectly through evaporation pan experiments. In fact, evaporation pan experiments can drastically reduce the uncertainties connected with the critical parameters of the isotopic balance equations (especially δ_A). Evaporation pans, placed on the lake shore or on a floating platform, can be operated either as constant-volume systems simulating the behaviour of a terminal lake (Gat, 1970; Allison and Leaney, 1982; Gibson et al., 1999) or as drying out systems initially filled with the lake water (Froehlich, 2000).

3. Lake–groundwater inteactions

Groundwater usually conserves its stable isotope composition unless mixed with water of a different isotopic signature. Therefore, recharge from isotopically distinct and well characterized water sources, such as surface water bodies (see, for example, Krabbenhoft et al., 1990) can often easily be identified. However, to characterize potential sources of recharge accurately, sampling must represent any temporal variability that exists in the isotopic composition. Lake water can isotopically be distinct from adjacent groundwater due to isotopic enrichment caused by evaporation of lake water and/or due to the isotopic composition of the inflow, which can represent a completely different precipitation source than the local groundwater. Provided that the isotopic composition of lake and groundwater remain sufficiently distinct from each other, the proportion of lake water in adjacent groundwater or vice versa can be determined by a simple mixing equation. A recent application of this approach, by which the relative contributions of different water sources to groundwater near the Lake Erie, Canada, were determined, has been published by Huddart et al. (1999). Infiltration of surface water (lakes, dams, rivers) into adjacent groundwater can also be studied in arid and semi-arid regions, where the difference in the isotopic composition between surface water and adjacent palaeo-groundwater can be remarkably large, up to more than 10‰ in $\delta^{18}O$ (Aly et al., 1993). This isotopic approach can also be used to determine the inflow of groundwater to a lake (Yehdegho et al., 1997).

In the case of young artificial lakes, for example dredging lakes, the bottom silting by sediments is usually negligible. Thus, exchange with groundwater can be quite active and constitutes the major mechanism for water renewing in the lake. Seasonal variations of lake isotopic composition allow estimation of the rate of water exchange with groundwater. If the lake is very young and a quasi-steady isotopic composition has not yet been attained, the seasonal isotopic variations can be superimposed by a long-term trend of increasing heavy isotope content (Zimmermann and Ehhalt, 1970). Combining isotope and hydrologic modelling techniques, effects of lake water infiltration into adjacent aquifers and hydraulic aquifer parameters have been studied. It has been shown that isotope data reduce parameter uncertainty in numerical groundwater modelling and predicting groundwater quality changes due to lake water infiltration (Stichler et al., 1999).

In the case of natural lakes whose isotopic composition is enriched in heavy isotopes by evaporation the investigation is performed on surrounding groundwater bodies, searching for isotopic anomalies that indicate infiltration of lake water. Lake losses to groundwater might be diffuse, so that they can be significant for the lake balance but insignificant as source of groundwater recharge with respect to other recharge sources (rivers, precipitation). Only few cases have been reported in which significant lake losses were concentrated in limited areas (Seiler et al., 1992).

4. Lake water mixing

Many lakes, even large and deep lakes with long residence time of the water, are well mixed, i.e., the chemical and isotopic composition of the lake water is uniform, indicated by negligible spatial gradients. Studies of mixing processes in lakes are important, for instance for assessing paths and fate of contaminants. Isotopes complement other physical and chemical methods for studying mixing rates in lakes.

Winds and seasonal overturns promote the mixing in lakes. For instance, the major water body of Lake Titicaca, the Lago Mayor, containing 97% of the lake water, is well mixed (Gonfiantini et al., 2002). When, however, two lake sectors have limited connections, they often have also different chemical and isotopic composition. This happens especially when the water movement across the connection has a preferential direction, which hinders the water exchanges between the two sectors and produces different water budgets (ratio of evaporation losses to water inflow). For this reason the Lago Menor, which is connected to the Lago Mayor of Lake Titicaca through a narrow strait, is found to be enriched in the heavy isotopes and dissolved compounds. The same happens to the Lake Kara-Bogaz, a terminal lake that is the only surface outlet of the Caspian Sea (Ferronsky et al., 2001).

There are lakes that are not well mixed, either vertically, due to the occurrence of permanent or seasonal stratification, or horizontally, when the seasonal pulses of the inflow to the lake follow preferential paths and the residence time is not long enough to smooth out the isotopic and chemical differences. Such conditions were studied, among others, in Lake Kanji, Nigeria using the different stable isotope content of the two seasonal floods (Dinçer et al., 1979). To determine mixing processes in Lakes Geneva and Constance, the variations of bomb-tritium during the period 1960-1970 could be used as natural tracers (Meybeck et al., 1970). The permanent stratification of tritium (and stable isotopes) found in Lakes Tanganyika and Malawi was used to model the lake mixing dynamics (Gonfiantini et al., 1979).

Deep-water renewal by exchange with surface waters (‘ventilation’) controls the internal redistribution of water properties, and in this way “the time-dependent response of the lake to its own chemical and biological processes, as well as to natural and anthropogenic external disturbances” (Weiss et al., 1991). Using time-dependent isotopic and chemical tracers, such deep-water renewal processes can be studied. The time-dependent isotopic tracers (i.e. tracers with a characteristic time-dependent input concentration into the hydrologic system) include bomb-tritium and tritiugenic ^{3}He (Torgersen et al., 1978). Chlorofluorocarbons (CFCs) represent time-dependent chemical tracers. Deep-water exchange with both tracer types have been studied in Lake Baikal (Peeters et al., 1997) and the Caspian Sea (Peeters et al., 2000). Unfortunately, ^{3}H-^{3}He and CFCs data on lakes are still rather scarce. It is expected that the applications of these methods will become more common in the near future.

5. Sedimentation rate in lakes

The variations of sedimentation rate in lakes depend mainly on changes of the water balance and/or of the environmental conditions. For instance, deforestation induces an increase of sediment transport by rivers and, as a consequence, of sedimentation rate in lakes. Therefore, the estimate of sedimentation rate is useful for assessing recent and palaeo-environmental changes and predicting the life of artificial reservoirs.

The isotopic methods for estimating the sedimentation rate in lakes are based on radioactive isotopes, which are incorporated in sediments and decay (Schell and Barnes, 1986). Carbon-14 (half-life 5730 years) and lead-210 (half-life 22.6 years) are continuously supplied, the first through exchange with the atmospheric CO_2, aquatic plant respiration and groundwater input, and the second by decay of atmospheric radon and deposition of its daughter products. Therefore, the sedimentation rate can be deduced from the decrease of ^{14}C and ^{210}Pb concentrations with depth in lake sediment cores.

The concentration of caesium-137 (half-life 30.2 years) in atmospheric waters reached a peak value in 1963, i.e. one year after the maximum injection into the atmosphere by atmospheric nuclear tests. Therefore, from the depth of the 1963 peak in the sediment column the sediment layer deposited since 1963 can be estimated (Schell and Barnes, 1986).

6. Lakes as palaeoclimate archives[1]

Lacustrine deposits are among the most valuable continental materials for palaeo-climatic reconstructions (Stuiver, 1970). They can provide high resolution, relatively continuous records of Late Pleistocene/Holocene climatic changes. Lake sediments often contain authigenic carbonates and fossil shells (ostracodes) whose oxygen isotopic composition is mainly controlled by that of the lake water and by temperature. The $\delta^{18}O$ and δ^2H values of open lakes, located at medium latitudes and characterized by relatively fast water turnover, primarily respond to changes of the isotopic composition of precipitation over the lake basin, which in turn is temperature-dependent. Consequently, the periods of cold and mild climate are reflected by minima and maxima in $\delta^{18}O$ of the deposited calcite (e.g. Siegenthaler et al., 1984; Goslar et al., 1995; von Grafenstein et al., 1999). For closed lakes, the isotopic composition of water is largely determined by evaporation and exchange with atmospheric moisture; dry periods, usually characterized by an increased ratio of evaporation to inflow, are marked by high $\delta^{18}O$. In the tropics, $\delta^{18}O$ of authigenic calcite deposited in lakes generally reflects the extent of evaporative enrichment of the lake water, which in turn is connected with the residence time of the water in a given lake system. Therefore, $\delta^{18}O$ then predominantly reflects the changes in the precipitation regime. In monsoon-controlled regions the isotopic composition of precipitation primarily responds to the amount of rainfall and, consequently, to the intensity of monsoon circulation. Records of $\delta^{18}O$ and δ^2H of ancient precipitation

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[1] See also Gasse, this volume.

preserved in various continental archives located in such regions may thus provide important information about the extent and intensity of the major monsoon systems in the past (e.g. Morinaga et al., 1993; Lister et al., 1991).

Of particular importance for high resolution climatic reconstructions on continents are lacustrine archives that contain annually laminated sediments. Seasonally varying sedimentation patterns in some lakes may lead to the formation of varves, thus providing a chronological time scale of climatic proxies preserved in sediments, such as pollen and stable isotopes in authigenic carbonates and organic matter. In most cases such scales are floating, i.e. they are not fixed on the calendar time scale although they can provide an annual resolution for various periods of time. Only in rare cases is the absolute calibration of floating chronologies possible, for instance through ^{14}C dating of terrestrial macrofossils preserved in such sediments (e.g. Hajdas et al., 1993; Goslar et al., 1995; Kitagawa and Van der Plicht, 1998).

7. Other isotopes used in lake studies

Data on $^{11}B/^{10}B$ ratio in lakes are scarce. Very positive ^{11}B values ($\delta^{11}B$ up to +60 ‰) have been reported in brines from Australian lakes, which were attributed to preferential uptake of ^{10}B in absorption processes from an initial isotopic composition similar to that of sea water. A preliminary $\delta^{11}B$ in Lake Titicaca (Lago Mayor) is around -8‰, and the origin of ^{11}B depletion will be explained by establishing the boron isotope budget of the lake. Because of the large range of variations in nature, the boron isotope geochemistry of lakes appears to be a promising field of investigation.

8. Major lakes in which isotope techniques have been used

Major lakes that have been investigated with environmental isotopes include in Africa Lakes Chad, Victoria, Tanganyika, Malawi, and Kanji (Nigeria); in northern America Lakes Tahoe (California and Nevada, USA), Erie, Huron and Ontario (USA and Canada); in Central America Lakes Nicaragua (Nicaragua) and Atitlán (Guatemala); in southern America Lakes Titicaca (Peru and Bolivia), Valencia (Venezuela) and Laguna Mar Chiquita (Argentina); in Asia the Dead Sea (Israel and Jordan), the Caspian Sea (Azerbaijan, Russian Federation, Kazakhstan, Turkmenistan, Iran), Lakes Kinneret (Israel), Egridir and Behysehir (Turkey) and Baikal (Russian Federation); in Europe Lakes Geneva (Switzerland and France), Constance (Switzerland, Germany and Austria), and Neusiedl (Austria and Hungary). References to most of these studies can be found by means of the list below.

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12. A REVIEW OF ISOTOPE APPLICATIONS IN CATCHMENT HYDROLOGY

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1. Introduction

Isotope methods were introduced into catchment hydrology research in the 1960s as complementary tools to conventional hydrologic methods for addressing questions of where water goes when it rains, what pathways it takes to the stream and how long water resides in the catchment (McDonnell, 2003). Despite slow incorporation into routine research applications, the last decade has seen a rapid increase in isotope-based catchment studies. These have been mainly carried out in small well-instrumented experimental catchments, on the order of 0.01 to 100 km^2 and located typically in headwater areas (Buttle, 1998). In contrast, little has been done in terms of application and transfer of these concepts and methodologies to large (>100s to 1000s of km^2), less instrumented basins. Much potential also waits to be realized in terms of how isotope information may be used to calibrate and test distributed rainfall-runoff models and to aid in the quantification of sustainable water resources management. In this chapter, we review the major applications of isotopes to catchment studies, and address a variety of prospective new directions in research and practice. Our discussion is based primarily on catchments in temperate to wet zones.

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2. Review of research

2.1. HISTORICAL OVERVIEW OF ISOTOPES EMPLOYED IN CATCHMENT HYDROLOGY

Natural ^{14}C was discovered in the late 1940s and natural ^{3}H (tritium) was discovered in the early 1950s (Grosse et al., 1951). Shortly thereafter, atmospheric nuclear weapon tests substantially increased the ^{3}H content in the rapidly circulated parts of the hydrologic cycle, with the peak around 1963. Tritium was therefore used for the first systematic estimations of water age in catchments (Eriksson, 1963). While bomb spike ^{3}H is now rarely used for water age-dating, oxygen-18 and/or deuterium (^{2}H) became and remained common tools for dating waters up to about five years of age, which typically occur in shallow aquifers connected to streams (Epstein and Mayeda, 1953). Noble gases such as ^{3}He (Torgersen et al., 1979), ^{85}Kr (Rozanski and Florkowski, 1979) and ^{222}Rn (Rogers, 1958), solutes such as ^{35}S (Lal and Peters, 1966), and the anthropogenic compounds, CFC (Thompson et al., 1974) and SF_6 (Maiss and Levin, 1994), date water ages from days up to decades.

In addition to water age dating, hydrograph separation approaches employed tritium (Crouzet et al., 1970) and stable isotopes of ^{18}O and ^{2}H (Dinçer et al., 1970) in two-component mixing models (Pinder and Jones, 1969). These early studies opened the way for an expansion of studies of runoff generation and runoff components (event vs pre-event water) on experimental hillslopes and in catchments. The paper by Sklash and Farvolden (1979) is a benchmark study that documented the dominant role of the subsurface pre-event water in runoff generation. Solute isotopes such as ^{87}Sr (Stueber et al., 1987), ^{13}C, ^{34}S and ^{15}N (Kohl et al., 1971) have provided important information on biological and geological sources of solutes recharging groundwater and delivery to surface water. Several other cosmogenic (^{7}Be, ^{10}Be, ^{24}Na, ^{41}Ca) and lithogenic (^{6}Li, ^{37}Cl, ^{11}B, ^{143}Nd, ^{206}Pb, ^{207}Pb, ^{208}Pb, ^{210}Pb) isotopes have been introduced into catchment hydrology research within the last two decades and many potential applications are yet to be realized.

Thus, the expansion of isotope techniques in catchment hydrology in recent decades generated two major sets of applications: (1) assessment of the temporal variations of the major stocks and flows of water in catchments between events, such as estimation of water residence times and quantification of recharge travel times, and (2) assessment of catchment hydrologic processes, such as quantification of the sources of runoff and delineation of infiltration and exfiltration zones along streams.

2.2. TEMPORAL VARIATIONS OF HYDROLOGIC PROCESSES IN CATCHMENTS

The hydrologic cycle in catchments varies in time (Ohmura and Wild, 2002) and the runoff generation is a complex of highly nonlinear processes (Phillips, 2003). Water infiltrates at different rates, mixes in the subsurface and thus has different travel times to the stream. The mean residence time (MRT) or "age" of water in a catchment is the average time elapsed since a water drop entered the catchment and the time it is observed in the catchment outlet, well or soil depth (adapted after

Yurtsever, 1995). It describes functionally the catchment response to water withdrawals, contamination, or land use changes, and provides a basis for assessing sensitivity to imposed catchment management practices (Alley et al., 1999). To date, stable water isotopes ^{18}O and ^{2}H have been the dominant age-assessment tool, generally because of the conservative nature of those isotopes and the ease in field and laboratory processing of water samples. Table 1 summarizes recent estimates of the MRT of water exiting a catchment; a few applications have been also carried out also on water exiting a spring (Małoszewski et al., 2002) or the base of a hillslope (Asano et al., 2002). These approaches are typically based on residence time distribution models presented by the pioneers in this field (e.g. Kreft and Zuber, 1978; Małoszewski and Zuber, 1982; Zuber, 1986a). These techniques have been recently formalized into a variety of software packages, such as FLOWPC (Małoszewski and Zuber, 1996), MULTIS (Richter et al., 1993), TRACER (Bayari, 2002), BOXmodel (Zoellmann et al., 2001), and TRANSEP (Weiler et al., 2003). Most of these models combine deconvolution of isotope input (i.e. the isotopic composition of precipitation or throughfall) with a system response function (also called weighting function) to calculate the time of the isotope output (i.e. the isotopic composition of streamwater) from the catchment. Adjusting the response function to optimize the fit between measured and computed streamwater isotope content provides a mean water residence time. Finally, the optimized model parameters provide the distribution of residence times for a designated point on the water flowpath. Other applications of this approach range from simple sine-wave and isotope damping analysis (Burns and McDonnell, 1998; DeWalle et al., 1997; Soulsby et al., 2000; Stewart and McDonnell, 1991 to mathematically more complex approaches such as multi-parameter response function models (Amin and Campana, 1996; Haitjema, 1995; Zuber 1986b). Less common approaches, which require special data or precisely defined boundary conditions, include power spectra techniques (Kirchner et al., 2000; Manga, 1999), direct simulation (Etcheverry and Perrochet, 2000; Goode, 1996), and stochastic-mechanistic models (Simic and Destouni, 1999). Some workers have also tried to define surrogate indicators of water residence times based on the hydraulic and topographic features of the subsurface (Wolock et al., 1998; Vitvar et al., 2002).

In addition to the use of stable isotopes and tritium, other environmental isotopes and anthropogenic tracers have been used as dating tools, including ^{35}S and ^{7}Be (Cooper et al., 1991), $^{3}He/^{3}H$ (Solomon et al., 1993), CFCs and SF_6 (Plummer and Busenberg, 2000), and ^{85}Kr (Smethie et al., 1992). The range of potential “datable” ages obtained can vary from a few days (using ^{35}S and ^{7}Be), up to decades (using ^{3}H, $^{3}He/^{3}H$, CFCs and ^{85}Kr). Multitracer studies in shallow aquifers (Ekwurzel et al., 1994; Plummer et al., 2001, Plummer in this volume) estimated the age of groundwaters at different depths. Notwithstanding, the use of noble and atmospheric gases is still limited to groundwater applications, since the interaction of these isotopes with the atmospheric air compromises their use in streamwaters. Schlosser et al. (1988) introduced a method of calculating streambed infiltration velocities using the $^{3}H/^{3}He$ ratio. These techniques have been suitable in areas of both high and low recharge rates; however, diffusion dominates the ^{3}He transport in the unsaturated zone and provides little information on vertical transport of water

(Solomon and Cook, 1999). The infiltration velocities obtained by $^{3}H/^{3}He$ dating are also useful as a calibration tool in numerical 3-D groundwater flow models (Mattle et al., 2001).

The relationship between basin area and baseflow residence time remains equivocal. Though no studies have reported a relation between residence time and catchment size, McDonnell et al. (1999) and McGlynn et al. (2003) found that the internal flowpath composition may be a first-order control on stream baseflow age. Recent ^{18}O and ^{2}H studies comparing small catchments in Japan and New Zealand by Uchida et al. (2004) show how bedrock permeability may control the direction of water aging. In the impermeable bedrock case (Fig 1a), Stewart and McDonnell (1991) observed a lateral downslope increase in soil water mean residence time. Asano et al (2002) tested this hypothesis on a comparable slope configuration, but with permeable bedrock, and found that water aged vertically through the soil profile, with no evidence of a downslope age increase. In this case, the communication of water vertically between the soil and underlying bedrock did not “force” a downslope component to soil water age (Fig. 1b).

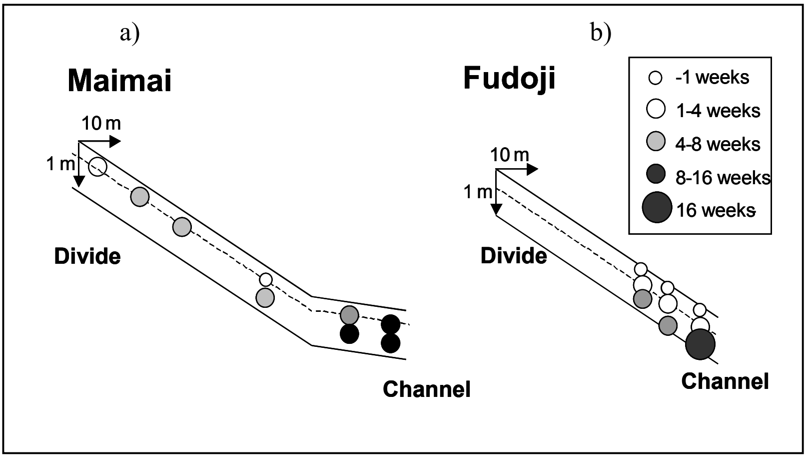

FIG. 1. Comparison of mean water residence times in two small catchments (a)Maimai (New Zealand) and (b) Fudoji (Japan). Differences in runoff generation processes cause increase in mean water residence times along the depth (Fudoji) and distance from the catchment divide (Maimai). Adapted after Uchida et al. (2004).

In most streams, there are two storm hydrograph discharge components: (1) surface and near-surface quickflow in response to rain or snowmelt, and (2) baseflow, which is water that enters from persistent, slowly varying sources and maintains streamflow between water-input events (Dingman, 2002: p. 342). The relative contributions of these sources differ in each watershed, and depend on the physical setting of the drainage basin (topography, soil type, depth to bedrock, vegetation, fractures, etc.), climatic parameters (precipitation amount, seasonal variations in precipitation, temperature, potential evapotranspiration, etc.), and human activities, such as dams, reservoirs, irrigation usages, clearing of agriculture, channel restructuring, etc. (Kendall and Coplen, 2001). The baseflow runoff component originates predominantly from unconfined shallow groundwater reservoirs, which are less than 50 years old and range in depths between 10 and 100 m (Seiler and Lindner, 1995), and exfiltrate through river banks and the bottom of river beds (Wittenberg and Sivapalan, 1999). Since the late 1960s, ^{2}H and ^{18}O have been used routinely to delineate the baseflow component of a stormflow event. where event water is represented by the distinct isotopic composition of rainfall/throughfall, and pre-event water is represented by the distinct isotopic composition of pre-storm stream water or adjacent groundwater. This approach has been applied to a large number of studies of stormflow events in small catchments (recent thorough reviews in Genereux and Hooper, 1998; Turner and Barnes, 1998). In general, these studies have revealed a much greater baseflow proportion in the stream discharge hydrograph (theoretical discussion in Kirchner, 2003), which differs markedly from the early conceptual models of streamflow generation and graphical hydrograph-separation analysis (Hewlett and Hibbert, 1967). In almost all cases the mobilized pre-event water accounts for over half, and usually about three-quarters of the runoff and/or peakflow associated with rainstorms (Genereux and Hooper, 1998). These results contradict the traditional engineering assumption of Hortonian overland flow generation (Horton, 1933) as the dominant component of streamflow. A large number of publications describe the subsurface hydraulic mechanisms of rainfall-induced release of the pre-event water; however, comprehensive reviews can be found e.g. in Bonell (1998), for snowmelt-dominated catchments in Rodhe (1998) and for tropical rainforest catchments in Elsenbeer (2001). Hydrograph-separation techniques have evolved and become more sophisticated — adopting methods to quantify errors and uncertainties (Genereux, 1998, Joerin et al., 2002) and incorporating additional solute tracers that separate three or more runoff components (DeWalle et al., 1988). These methods have allowed simultaneous identification of both the origin (pre-event and event water) and the geographical sources (soil, aquifer, riparian zones, hillslopes, etc.) of runoff components.

2.3. SPATIAL DISTRIBUTION OF HYDROLOGIC PROCESSES IN CATCHMENTS

Regardless of the age of streamwater, runoff in streams is generated from a variety of spatial sources and along various flow pathways. This complexity increases with catchment size, so that large rivers often represent highly heterogeneous mixtures of water types. Craig (1961) was among the first to compile water isotope content information in selected rainfall, stream discharge, and groundwaters to demonstrate the effects of evaporative enrichment and water-rock interactions. His work was based largely on the deviations of the stream water isotopic composition from the global meteoric water line. This information and methodology have been further integrated into longitudinal surveys of larger streams, which has allowed the identification of recharge waters isotopically enriched due to evaporative effects in lakes, streams, drainage channels and shallow river banks (Simpson and Herczeg, 1991; McKenna et al., 1992), and waters isotopically depleted from irrigation use and return in arid areas (Friedman et al., 1992). On a small scale Burns and McDonnell (1998) used this approach to identify how streamwater in a small catchment in the Adirondack Mountains, New York, contained water that was seasonally isotopically enriched due to summer evaporation from the adjacent small beaver ponds (Fig. 2). Lee and Hollyday (1991) determined the location of groundwater recharge to streams using ^{222}Rn.

Table 1. Principal works in peer-reviewed journals on streamflow residence time estimations since 1990. A review of previous works is presented in Herrmann (1997).

Reference	**Catchment**	**Area**	**MRT**	**Isotope**
Burns et al., 1998	Winnisook, USA	200 ha	330 d 247-319 d	^{18}O ^{35}S
Burns and McDonnell, 1998	two catchments in the Adirondack Mountains, USA	41.3 and 61.2 ha	100 d	^{18}O
DeWalle et al., 1997	three catchments in the Appalachians, USA	34, 39 and 1134 ha	1.4-5 a	^{18}O
Frederickson and Criss, 1999	Meramec River, Missouri, USA	10.300 km^2	100 d	^{18}O
Holko, 1995	Jalovecky potok, Slovakia	23 km^2	31 mo	^{18}O, ^{2}H
Małoszewski et al., 1992	Wimbachtal, Germany	33.4 km^2	4.1 a 4.2 a	^{18}O ^{3}H
McGlynn et al., 2003	four nested subcatchments of Maimai, New Zealand	280, 80, 17 and 2.6 ha	1.1-2.1 a	^{3}H
McGuire et al., 2002	Mahantango, Leading Ridge, Pennsylvania, USA	14ha, 100ha	9.5 mo 4.8 mo	^{18}O

Table 1. (cont.)

Reference	**Catchment**	**Area**	**MRT**	**Isotope**
Rodhe et al., 1996	Gårdsjön, Sweden	63 ha	7.5 mo	^{18}O
Rose, 1993	three catchments in Piedmont Province, Georgia, USA	347, 109 and 6.5 km^2	15-35 a	^{3}H
Soulsby et al., 2000	Allt a' Mharcaidh, Scotland	30 km^2	5 a	^{18}O
Stewart and McDonnell, 1991	Maimai, New Zealand		100 d	^{2}H
Sueker et al., 1999	3 catchments in High Rockies, Colorado, USA	780-1320 ha	200-400 d	^{35}S
Taylor et al., 1992	Wairau, New Zealand	170 km^2	10 a	^{3}H
Vitvar and Baldeder, 1997	Rietholzbach, Switzerland	3.14 km^2	12.5 mo	^{18}O
Vitvar et al., 2002	Winnisook, USA	200 ha	11.5 mo	^{18}O

In larger drainage basins, the process of infiltration from rivers into river banks can be successfully addressed using isotopic approaches. Schlosser et al. (1988) have quantified this connection using ^{3}H and ^{3}He. Ellins et al. (1990) showed how ^{222}Rn could be used for studying leakage of river water into shallow aquifers and delineation of exfiltration and infiltration zones along river reaches. In zones where river baseflow exfiltrates into the adjacent aquifers, recharge velocities and residence times of the recharged water can be obtained by use of ^{3}He/^{3}H techniques (Solomon et al., 1993). Conversely, the source and residence times of groundwater seepage to streams have been evaluated by using chlorofluorocarbons (Modica et al., 1998). These approaches have been further developed in stream recharge studies in urban areas, such as Calcutta (Sinha et al., 2002) and Dhaka (Darling et al., 2002). Several of these studies have documented increased recharge of shallow aquifers in developed areas (Foster et al., 1998), due to leakage from

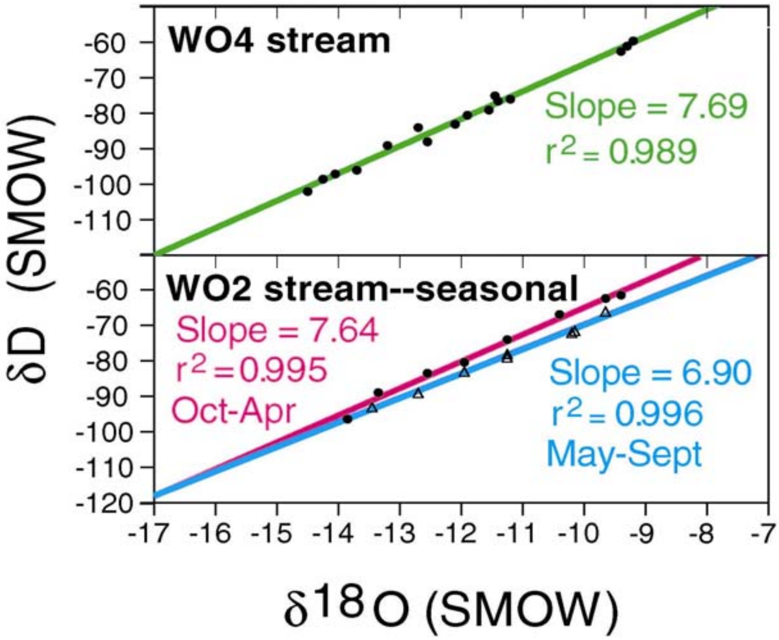

FIG. 2. Relation between ^{18}O and D (or ^{2}H) content in streamwater of two small catchments in the Adirondack Mountains, New York, USA. The stream in catchment WO4 contains no lakewater, whereas the stream in catchment WO2 contains water from beaver pond lakes, isotopically enriched during summer. Adapted from Burns and McDonnell, 1998.

water supply pipes and storm sewers (review in Lerner, 2002), and septic leach-fields (Sherlock et al., 2002). These findings apparently contradict the common view of urban catchments as being sources of enhanced rapid runoff on impervious areas (review in Hirsch et al., 1990) and indicate a substantial need for further investigations of processes in developed catchments.

Simultaneous analysis of isotopes and solutes in hillslope and small catchment studies have identified the geographic sources of the subsurface runoff component that had been stored in the catchment prior to the rain event. Buttle (1998) described two principal mechanisms to explain the presence of this "old" water in streamflow: (1) subsurface stormflow, and (2) groundwater ridging. Subsurface stormflow of the "old" pre-event water is explained as macropore flow through large conduits in the soil and "translatory flow", a flux of water stored in soil micropores with soil water contents close to saturation. Groundwater ridging is caused by flux of groundwater to the stream, enhanced by the saturation of the capillary fringe, or tension-saturated zone, during infiltration. These mechanisms, and the presence of "old" pre-event water in streams, have been noted in a number of field and laboratory studies at the plot and hillslope scales (Ward and Robinson, 2000) and identified on the catchment scale through multi-tracer hydrograph-separation techniques (DeWalle et al., 1998).

However, runoff in undisturbed catchments is generated typically through a combination of mechanisms, varying temporally and spatially in each catchment. A large number of isotope-based studies on runoff generation exist; recent comprehensive reviews can be found in publications on well-known leading experimental watersheds, such as Brugga in Germany (Uhlenbrook et al., 2002), Haute-Mentue in Switzerland (Jordan et al., 1994) Panola (Freer et al., 2002), Hubbard Brook (Hogan and Blum, 2003) and Sleepers (Shanley et al., 2002) in the USA, Maimai (McGlynn et al., 2002) in New Zealand, Hydrohill (Kendall et al., 2001) in China and Fudoji (Uchida et al., 2004) in Japan.

The combination of water stable isotopes and selected solutes, such as silica and calcium, has been particularly effective in determining flow sources and flowpaths. Isotope of solutes (for a thorough review, see Lal, Horita, this volume), such as ^{15}N and ^{18}O of nitrate, have been developed and successfully applied on the catchment scale as tracers of nitrate sources in catchments. Böhlke and Denver (1995) showed that in a small catchment draining into Chesapeake Bay the outflowing water continued to be contaminated with nitrates for 2–3 decades after cessation of the N-input. A large number of studies also provided information on the contributions of nitrate from precipitation and from microbial nitrification (Burns and Kendall, 2002), from microbial denitrification in shallow aquifers (Böttcher et al., 1990), from septic tank leakages and animal waste (Aravena et al., 1993), and from natural soil (Kreitler and Browning, 1983). Mayer et al. (1995) used ^{34}S for tracing runoff sources from atmospheric deposition and mineral weathering. A review of studies on nitrogen isotopes is presented in Kendall (1998) and a review of studies on sulphur isotopes can be found in Mitchell et al. (1998).

Isotopes of solutes such as ^{87}Sr and ^{210}Pb have become useful tools for identification of the evolution and origin of river waters via tracing the geochemical reactions along water pathways in the catchment (Bullen et al., 1994; Bullen et al., 1996, Bullen and Kendall, 1998). ^{11}B (Vengosh et al., 1994) and ^{37}Cl (Van Warmerdam et al., 1995) have been used for identification of anthropogenic sources of water pollution, whereas several cosmogenic isotopes, such as ^{7}Be and ^{10}Be (Brown et al., 1995) have addressed the identification of runoff sources from horizons under strong chemical weathering.

Multi-tracer separation methods of runoff sources have been formalized into the concept of End-Member-Mixing-Analysis EMMA (Christophersen et al., 1990), based on the multivariate statistics and quantification of runoff sources as statistical end-members. EMMA has become a popular technique for interpretation of isotopic (and solute) data, and has great potential in extended future applications (Table 2).

Table 2. Principal works in peer-reviewed journals on the End Member Mixing Analysis (EMMA) in catchments.

Reference	**Catchment**	**Area**
Brown et al., 1999	Shelter Creek, USA	161 ha
Burns et al., 2001	Panola, USA	41 ha
Christophersen and Hooper, 1992	Panola, USA, and Birkenes, Norway	41 ha both
Elsenbeer et al., 1995	South Creek, Australia	25.7 ha
Genereux et al., 1993	Walker Branch, USA	97.5 ha
Katsuyama et al., 2001	Matsuzawa, Japan	6 ha
McHale et al., 2002	Archer Creek, USA	135 ha
Mulholland, 1993	Walker Branch, USA	97.5 ha
Soulsby et al., 2003	Newmills burn, United Kingdom	14.5 km^2

One of the lingering challenges in the application of the runoff tracer-based data is in parameterization and calibration of distributed rainfall-runoff catchment models. Although the isotopic investigations on runoff generation substantially changed the conceptualization of the catchment rainfall-runoff process, they have not been widely incorporated into models, model structures and model parameter testing. Thus, while the hydrologic community continues to develop and operate sophisticated rainfall-runoff models (such as those summarized in Beven and Freer, 2001, Döll et al., 2003, Gurtz et al., 2003, and Leavesley et al., 2002), simulated runoff components are rarely calibrated by results of isotopic hydrograph separations. Some recent work has seen calibration of the rainfall-runoff models using the isotopically obtained proportion of runoff components as one of main model parameters. Seibert and McDonnell (2002) showed that although these "soft data" slightly decrease the absolute quality of the fit of the simulated versus measured discharge, they provide a higher quality of the understanding of the runoff components within the model routing procedure. These approaches are considered as a promising way to enhance the relation between isotope-based and conventional hydrologic methods in catchment hydrology (see also Uhlenbrook and Leibundgut, 2002).

3. Future directions

The application of isotopes to track sources and movement of water in catchments over the past 40 years has resulted in a substantial improvement in the understanding of runoff processes. This is especially true in small, dominantly forested humid experimental catchments with a high level of instrumentation and long data records (Burns, 2002). However, moving beyond these traditional catchment types and scale remains a challenge (Gibson et al., 2002). Recent trends indicate a continuously growing interest in isotopic applications to solve practical problems in hydrology and water resources management in large scale catchments.

In particular, application of isotope methods from small catchments to large river basins is a promising area of research. Owing to the ever-decreasing bomb tritium signal in natural systems, development of new methods for tracing older waters (with mean residence time >50 a) is essential. In particular, the use of dissolved gases ^{3}He and ^{222}Rn, solute isotopes ^{15}N, ^{35}S, ^{87}Sr, ^{208}Pb, ^{41}Ca, ^{11}B and anthropogenic gases CFCs and SF_6 needs to be further investigated and addressed in catchment studies. A movement towards multi-isotope studies is highly desirable; yet, many researchers and sub-communities are still too fixated on one particular isotope. A significant potential also remains in novel applications of isotopes coupled with solutes and artificial tracers in complex approaches such as EMMA or the geochemical model NETPATH (Burns et al., 2003). In addition, calibration and verification of rainfall-runoff catchment models is an area where isotopic applications could aid significantly process and parameter interpretation.

Large basins are very heterogeneous and are typically driven by a large variety of runoff processes. Therefore, methods developed in small natural catchments might be limited in large basins (Blöschl, 2002). Techniques and indicators are required, that describe the principal processes in large catchments without the need of spatially intensive experimental datasets. Large-scale catchment studies may be able to utilize well known isotopic effects (the altitude effect, the continental effect, etc.) to assess gross first order controls on flow generation (Kendall and Coplen, 2001; Schotterer et al., 1993). More attention to the catchment groundwater system and its coupled relation to the large river is required. At larger river basin scales, it is likely that a mean water residence time in the channel is a weak indicator of process. A synoptic survey longitudinally up/down the main channel might better characterize the variety of runoff processes contributing from different catchment positions to streamflow. A more intensive merging of isotopic survey data in rivers with conventional hydrologic data is needed, such as statistical characteristics of stream low-flow and runoff recession, which would help broaden insight into streamwater–groundwater interactions in catchments on different scales. New techniques of storing and presenting isotopic data in catchments should be created, especially those which link monitoring and mapping of isotopic input from the atmosphere (e.g. GNIP) with mapping and monitoring of isotopic content in streamwaters and groundwaters.

Finally, integration of isotope-based solutions of hydrologic problems in catchments into the solutions of water resources sustainability is an essential challenge for the further development of isotopic methods in catchment hydrology. Sustainability indicators of water resources are focused typically on local water scarcity (Atkinson et al., 1997). New approaches should be developed to generate, quantify and integrate indicators of runoff processes in catchments, and evaluate them in terms of potential sustainability.

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13. CONTRIBUTION OF ISOTOPIC AND NUCLEAR TRACERS TO STUDY OF GROUNDWATERS

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1. Introduction

The application of environmental isotopes in hydrology dates back to 1935, when oxygen isotope ratios were first measured on Lake Michigan water by Dole (1935). However, the first substantive scientific papers on the application of stable isotopes of oxygen and hydrogen to natural waters had to wait until after the second world war (Epstein and Mayeda, 1953; Friedman, 1953). Then, the first systematic application of these isotopes in natural waters was spurred by the classic paper by Craig (1961) which showed systematic differences in the isotopic composition of different waters. This gave the basis for their use in tracing water movement and origins in groundwaters as well as surface waters. The first paper specifically referring to groundwaters was by Münnich (1957) dealing with the possibility of radiocarbon dating. This step was greatly assisted by the injection of tritium (and other radioisotopes) into the global water cycle from thermonuclear weapons testing in the 1950s and early 1960s. In subsequent decades the wider scientific community, notably hydrogeologists and geochemists, took up the development of isotope techniques in groundwater studies. At the present day, and after 40 years of research, stable and radio-isotope techniques have become embedded in hydrogeological curricula and applications, where they are essential in defining conceptual models, establishing groundwater circulation processes, evolution of water quality, tracing the origins of both water and solutes, groundwater residence time studies and palaeohydrology.

Several excellent reviews of the application of environmental isotopes in hydrogeological studies have been published (Fritz and Fontes 1980; Clark and Fritz, 1997; Cook and Herczeg, 1999; Geyh, 2000). These texts more than adequately summarize the systematics as well as the applications of isotope techniques applied to groundwaters, as well as demonstrating the very wide range of isotope tools now available. Many of the developments and first applications in

P.K. Aggarwal, J.R. Gat and K.F.O. Froehlich (eds), Isotopes in the Water Cycle: Past, Present and Future of a Developing Science, 171-192.

isotope hydrology are contained in the proceedings of symposia of IAEA, which form an essential archive for following developments in the science over 4 decades. In this paper some of the key papers of the past 40 years' work are used to illustrate how isotope applications have changed ways of thinking about, and understanding groundwater systems.

2. Recharge processes and estimation

Tritium was widely used in the late 1960s and 1970s to advance our scientific knowledge of recharge processes, especially using unsaturated zone profiles in temperate regions (Zimmerman et al., 1967; Andersen and Sevel, 1974) – Fig. 1. The study from Denmark (drilling in 1966) shows the high soil mosture tritium and the modelled results which confirm piston (displacement) flow with some dispersion. These studies in deep sandy unsaturated zone profiles showed that piston displacement of moisture generally occurred, although in dual-porosity media such as chalk, some by-pass flow was possible (Smith et al., 1970). These studies also showed that it was possible to use the position of the tritium peak to measure recharge rates, although using tritium for mass balance studies proved problematic. Studies using $\delta^{18}O$ and $\delta^{2}H$ in shallow profiles of a chalk lysimeter were also applied to indicate that homogenization of any seasonal rainfall signature took place within the upper few metres of the unsaturated zone (Darling and Bath, 1988).

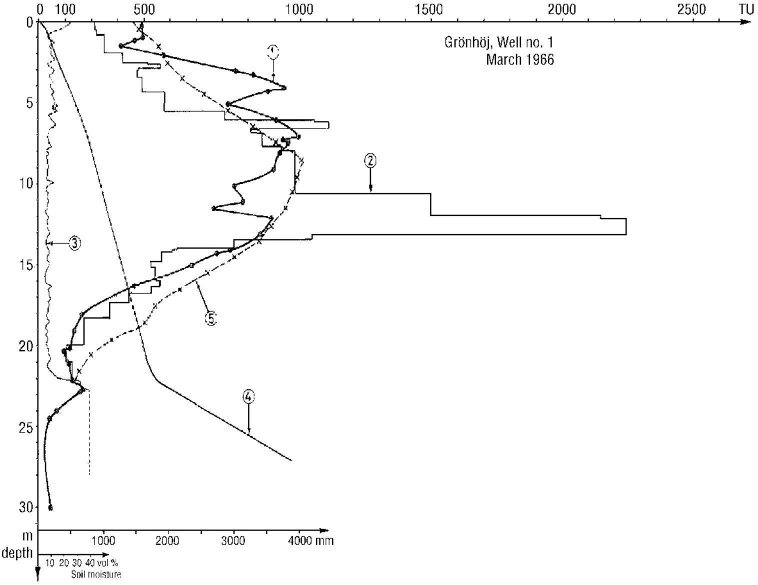

FIG. 1. Tritium profile (1: black dots) from Grønhøj, Denmark (Andersen and Sevel, 1974). Various model calculations are shown: 2) displacement flow model; 5) displacement flow with dispersion (best fit). Also shown are the soil moisture content (3) and total soil-moisture accumulated with depth (4).

Tritium was also tested as a tracer under semi-arid/arid conditions, for example in Saudi Arabia (Dinçer et al., 1974) and it was under much drier climates that isotope methods combined with other tracers were subsequently proved to be an essential tool for investigating not only recharge processes but also recharge rates and recharge history. Under arid conditions with low rainfall and high rates of evapotranspiration, classical physical water balance techniques break down. This problem, at least in the case of sandy terrain, was overcome using chloride mass balance in conjunction with the tritium peak method and also with studies of stable isotope movement. Chloride, unlike tritium, is conserved in the soil profile and providing the rainfall Cl inputs are known then a Cl mass balance may be conducted. This approach was developed in the late 1970s in Australia and Cyprus (Allison and Hughes, 1978; Edmunds and Walton, 1980). These studies were then extended to many other areas, including North Africa (Edmunds and Gaye, 1996), and North America (Phillips et al.,1994). However studies by Eriksson and Khunakasem (1969) pioneered the use of the chloride mass balance in studies of aquifers at a regional scale, work which has not been followed since as actively as it deserves for study of the spatial variability of recharge.

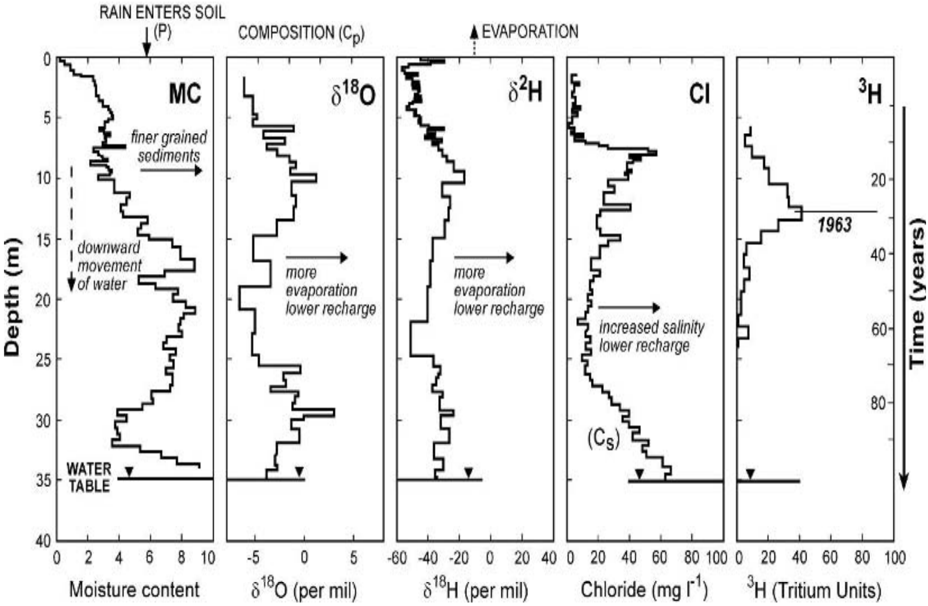

FIG. 2. Chemical and isotopic signatures in unsaturated zone moisture from Louga, Senegal as indicators of recharge amount, recharge process and recharge history (here recording the severe drought of the late 1970s. The severe drought of the late 1970s is recorded as the chloride peak between 6-10m depth and mirrored by enrichment in the stable isotope signal.

In Senegal, for example, the tritium peak in the early 1990s was still preserved at a depth of between 12–20 m (Aranyossy and Gaye, 1992) with no by-pass flow. In this region the combined use of tritium and chloride provided confirmation of recharge rates over decadal scales in sands with low moisture content (2–4 wt%), an impossible task using physical methods (Gaye and Edmunds, 1996); the additional use of stable isotopes demonstrates the extent of evaporation of moisture, in line with the increase in Cl concentration (Fig. 2). These studies demonstrate that low, but continuous rates of recharge occur in many porous sediments in semi-arid regions. In some areas dominated by indurated surface layers, deep vegetation or very low rates of recharge, the tritium peak is less well defined (Phillips, 1994), indicating some moisture recycling to greater depths (up to 10 m), although overall penetration of modern water can still be estimated. Some problems in estimating recharge using tritium (and other tracers) have been created through sampling above the zero-flux plane, where recycling by vegetation or temperature gradients may occur (Allison et al., 1994).

The usefulness of tritium as a tracer has now greatly diminished due to weakness of the signal following cessation of atmospheric thermonuclear testing and radioactive decay (half-life 12.3 years). It may still find application though when measured with its daughter product (as $^3H/^3He$ ratios) in studies of shallow groundwater. It may still be possible to find the peak in unsaturated zones, but this is likely to be at depths of 10–30 m, based on those areas where it has been successfully applied. Other radioisotope tracers, especially ^{36}Cl (half-life 301,000 years), which were also produced during weapons testing, still offer ways of non-routinely investigating unsaturated zone processes and recharge estimation. However, in studies where both ^3H and ^{36}Cl have been applied, there is sometimes a discrepancy between recharge indications from the two tracers, due to the non-conservative behaviour of tritium (Cook et al., 1994; Phillips, 1999). Nevertheless, the position and shape of the tritium peak in unsaturated zone moisture profiles provides convincing evidence of the extent to which 'piston displacement' occurs during recharge, as well as providing reliable estimates of the recharge rate.

The use of ^{36}Cl in unsaturated zone studies is illustrated in Fig. 3, adapted from Cook and Herczeg (1999) showing profiles from Australia and USA. The profile from Australia (Murbko) is from sandy soil in an area cleared of native eucalyptus vegetation since the early 20th century and used for dry land farming. The profile illustrates the leaching of Cl due to the increase in soil water flux following clearance. However, as suggested earlier, there is poor agreement between the water fluxes obtained using ^3H, ^{36}Cl and stable chloride. This is because the two former estimate soil water flux from the soil surface, whereas the stable Cl is estimating flux below the plant root zone. Thus the results to date indicate that little or none of the ^{36}Cl has traversed the root zone and that this isotope can only give an upper limit for recharge rate.

In indurated or heterogeneous sediments in (semi-) arid systems, shallow by-pass (macropore or preferential) flow is also an important process. Below a certain depth the pathways of soil macropore movement commonly converge and a more or less homogeneous percolation is re-established. In some areas, such as the southern USA, by-pass flow via macropores is found to be significant (Wood and Sandford, 1995; Wood 1999). In areas of Botswana it is found that preferential flow may account for at least 50% of fluxes through the unsaturated zone (Beekman et al., 1999; De Vries et al., 2000). All of the above studies show that it is important to be able to sample to sufficient depths to account for by-pass flow and then to check through water table samples (using suitable tracers such as tritium, CFCs) that there is continuity of flow through the saturated zone.

Although the atmospheric concentrations of TU are now at a new baseline (around 7–10 TU in the northern hemisphere and below 2 TU in the southern hemisphere) low level measurements are still possible (0±0.2 TU), allowing its qualitative use in groundwater studies. Thus, a value of 0 TU will signify the absence of modern recharge, an important indicator especially when used alongside other tools, such as CFCs. The application of tritium, especially in studies of shallow

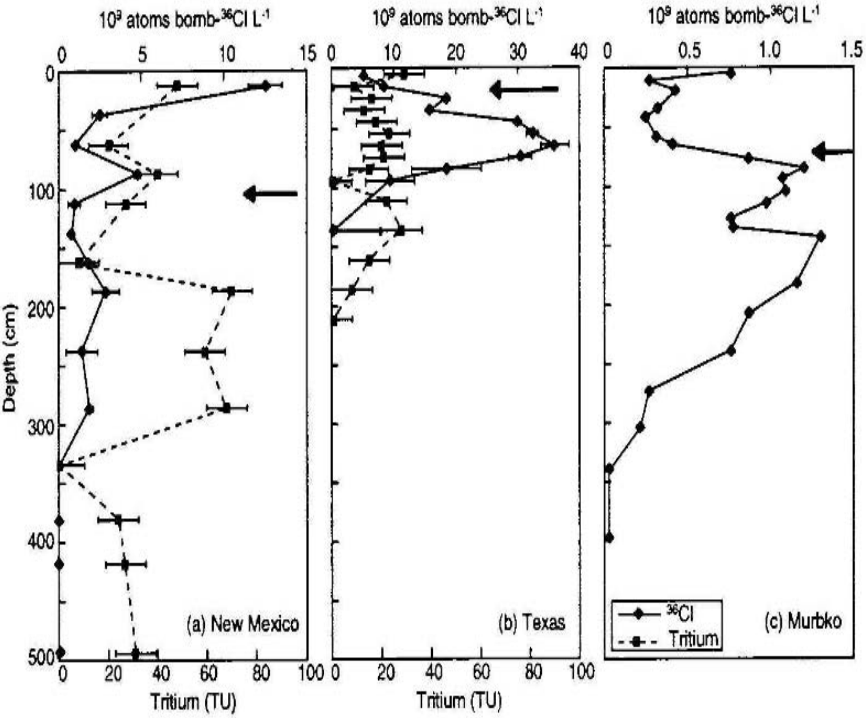

FIG. 3. Profiles of 36Cl concentration and tritium in soil water at sites in the western United States and Australia. The arrows indicate the predicted depth of penetration of the bomb 36Cl pulse calculated by the chloride mass balance method. Sources of data are Phillips et al. 1988 (New Mexico); Scanlon 1992 (Texas) and Cook et al. 1994 (Murbko, Australia).

groundwater, is greatly enhanced by simultaneous measurement of its stable decay product ^{3}He. This is applicable where there is no hydrodynamic dispersion (i.e. piston flow applies) and has the advantage that initial atmospheric tritium input concentrations need not be known (Solomon and Cook, 1999). Thus the presence of ^{3}He at 3TU equivalent would signify the possibility for modern recharge, although care is needed to define aquifer ^{3}He/^{4}He background. This technique is particularly useful for verification of groundwater flow models in shallow environments and has been used for example to measure flow velocities in the Danube flood plain (Stute et al., 1997) and in mapping groundwater flow around contaminant plumes (Solomon et al., 1995).

3. Groundwater age determination

Perhaps the most important contribution by the isotope community to hydrogeology has been the concerted effort to determine the absolute age of groundwater, most particularly using radiocarbon. The principles of radiocarbon dating of groundwaters were first set out by Vogel and Ehhalt (1963), although one of the first field applications was to confirm the Late Pleistocene age of the very fresh waters beneath the Egyptian Sahara (Degens. 1961). Although in theory the radiocarbon dating range can extend to 60 000 years, in practice the limit is found to be much less than this due to the fact that radiocarbon is a reactive (non-conservative) tracer and that there are uncertainties in deriving initial input values from soils as well as potential for contamination (see also Geyh, this volume). Various studies have shown that the resolution of radiocarbon dating of groundwaters is rather low, perhaps not better than ±1000 years, despite the ability to resolve ^{14}C activities well below this range.

The initial radiocarbon values used in dating are a primary source of uncertainty due to the amount of dilution (reservoir effect) in the soils; this value is shown to be variable for different rock/soil types (Geyh, this volume), although a commonly used value is 85% of the “modern” pre-bomb radiocarbon. A further problem relates to the non-linearity of atmospheric ^{14}C production, which affects all radiocarbon dating over the timescale of interest due to solar radiation.

During the 1970s it was realised that a geochemical approach to radiocarbon interpretation was required (Pearson and Hanshaw, 1970). This was based on the wider understanding of carbonate equilibria through the pioneering work of Garrels (Garrels and Christ, 1965) and co-workers. Thus, knowledge of the total dissolved inorganic carbon (TDIC) behaviour was needed, since congruent and incongruent reactions diluted the radiocarbon, initially on a 1:1 ratio but, with time, reducing the radiocarbon in groundwater still further as water–rock interactions proceeded. The understanding of the geochemical reactions was assisted greatly by the parallel measurement of ^{13}C in groundwaters, soils and host rocks. In fine-grained aquifers such as the Chalk of Europe (Smith et al., 1976; Elliott et al., 1999) highly enriched groundwaters were identified showing that it was possible for the radiocarbon to be progressively incorporated in the solid phase, with groundwater ages appearing to be far too old, and the water isotopic compositions approached that of the host rock. This work then led to development of a series of groundwater geochemical models to handle the ranges in input functions as well as the extent of possible water–rock reactions (for example, Pearson and Hanshaw, 1970; Reardon and Fritz, 1978; Fontes and Garnier, 1979). These models have been used with varying degrees of success since that time. It has been shown for example that reliable model interpretation may be achieved for non-carbonate aquifers but that the incongruent reactions in carbonate aquifers, resulting in ^{13}C-enriched groundwaters, cannot be reliably dated (Darling et al., 1997).

Other complications in ^{14}C interpretation may arise with the in situ production of carbon dioxide from breakdown of organic matter or from the incorporation of metamorphic CO_2 from tectonically-active areas (Andrews et al., 1993; Clark and Fritz, 1997). However the use of soil-derived dissolved total organic carbon (TOC) offered promise of an alternative technique for dating alongside use of TDIC (Aravena and Wassenaar, 1993), although this method has its own problems, including the dilution of active carbon with dead carbon in the soils.

Partly because of the problems inherent in ^{14}C dating, much effort and isotopic ingenuity has been expended in finding other tools for dating of palaeowaters. The main contenders for this purpose have been the “inert” noble gas radioisotopes – ^{37}Ar, ^{39}Ar, ^{81}Kr, (Lehmann et al., 1993; Loosli et al., 1999). These have often been used in parallel with ^{14}C and, despite the relative effort and expense of collection, have, with relatively few samples, provided a major contribution to understanding groundwater age distributions, insight into the limitations of other tools and also better understanding of groundwater flow systems. Recently the use of ^{81}Kr has enabled groundwaters in the Great Artesian Basin to be dated to between 200,000–400,000 years, the oldest confirmed ages for groundwater residence to date (Lehmann et al., 2003). The other major contribution of the noble gas isotopes such as ^{85}Kr has been in confirming (with other tracers such as CFCs and ^{3}H) the extent of mixing of old and modern groundwaters and improving our understanding of age stratification in aquifers (Ekwurzel et al., 1994). Some of these examples are considered below in the context of multi-tracer studies of the key reference aquifers. These studies have also allowed reinterpretation of ^{4}He and ^{36}Cl as dating tools for very old waters.

4. Palaeohydrology

The significance of stable isotopes (δ^{18}O, δ^{2}H) as climatic fingerprints was implicit in the earliest studies of the science (e.g. Craig, 1961). Their application to palaeohydrologic and palaeoclimatic studies was focused on groundwaters where ancient waters were likely to be preserved. Palaeowater studies were mainly initiated in northern Africa during the 1960s and early 1970s (Conrad and Fontes, 1970; Gonfiantini et al., 1974), where the distinctive isotopically depleted groundwater signatures were first recognised in “dated” groundwaters. These and subsequent studies emphasized the differences found in unconfined as compared to confined aquifers. In the deeper artesian basins sequential piston flow evolution of isotopes was confirmed with generally much slower water movement, but far greater storage than in the unconfined systems.

Subsequent early studies resolved the climatic significance of the isotope signatures both at the local as well as the continental scales. The progressive isotopic depletion in palaeo-groundwaters across Africa was interpreted as evidence of a continental effect as Atlantic air masses travelled away from their source, and also that the trajectory of the rainfall was more to the south of that of the present day during the cooler Late Pleistocene climates (Sonntag et al., 1978). The results from a range of studies of aquifers in Africa and the Arabian peninsula, carried out over the period 1972-1987, are summarized in Fig. 4, which shows the distinctive compositions of palaeowaters across the continent (Clark and Fritz, 1997).

Other detailed studies, in Africa especially, showed heterogeneity and stratification in the unconfined aquifers. In Libya, for example, a Holocene-age freshwater channel could be identified superimposed on the Late Pleistocene groundwaters, being isotopically distinct and which corresponded to the line of a former large river derived from the central Sahara (Edmunds and Wright, 1979). Similar stratified waters were also identified in Kenya (Pearson and Swarzenski, 1974).

During the 1980s, much of the development in isotope hydrology relating to palaeoclimate was focused on application of different techniques in a number of inter-comparative case studies across the globe, some of which are described below. In the past decade, groundwaters have become palaeoclimatic archives in their own right alongside ice cores, sediments and other proxy records (Loosli et al., 1998; Edmunds et al., 2003). The main tool for this work has been the noble gas palaeothermometer (Stute and Schlosser, 1993). The use of isotopes and hydrochemistry combined with noble gas ratios in dated groundwaters allows a number of palaeoclimatic and environmental parameters to be reconstructed. The present author discusses this field of application is discussed in more detail in a subsequent Paper in this volume.

5. Saline groundwaters

Salinity represents the primary limitation to groundwater use. Natural salinity boundaries exist in aquifers due to geological factors controlling the maximum depth of circulation, as well the interface between marine and fresh water. Salinity is strongly controlled by climatic factors so that continuous low rates of recharge in arid areas (as over much of the Australian continent for example), lead to widespread salinity of groundwaters (Allison et al., 1990). Human factors exacerbate salinity directly by pollution or indirectly by agricultural activities and excessive pumping leading to invasion of saline groundwater into freshwater aquifers. A check list of potential isotopic tools used alongside chemical tracers is given in Table 1, slightly modified from Edmunds and Droubi (1997).

Over the past 40 years isotope methods have proved to be of unique value in understanding the origins of salinity as well as the process of salinization in groundwaters (see also Horita, this volume). Overviews are provided in Fontes (1980), Payne (1983); Edmunds and Droubi (1997).

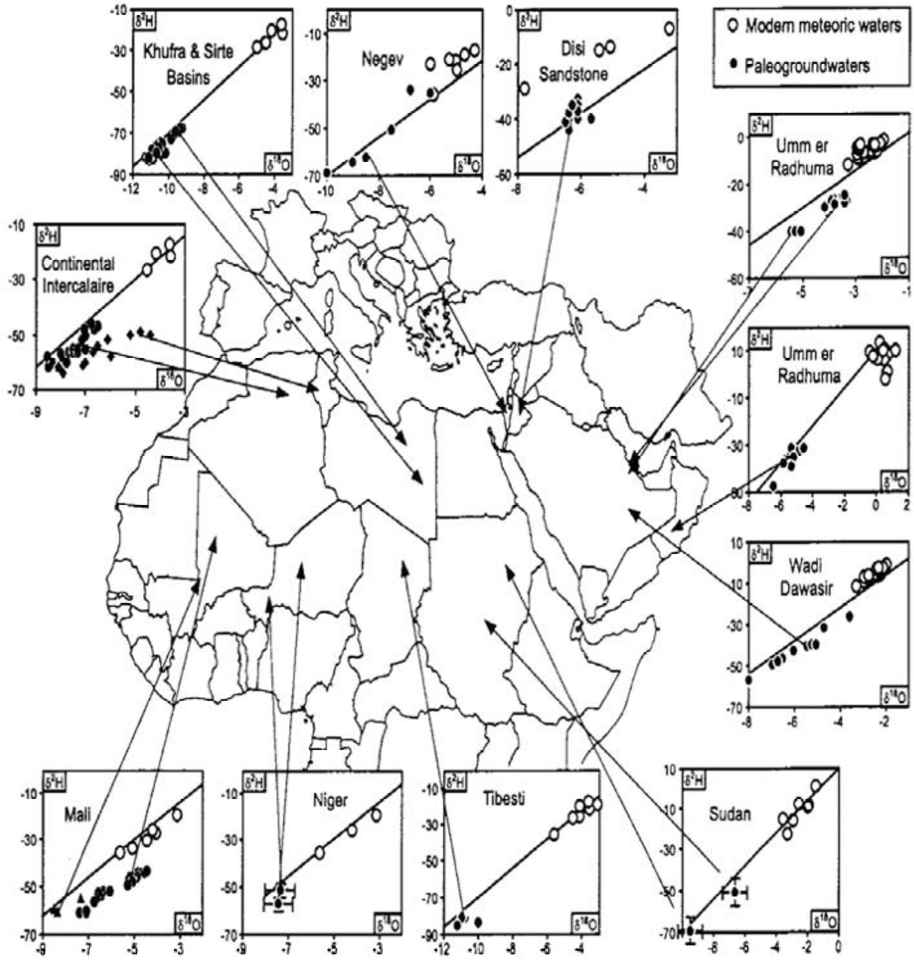

FIG. 4. Stable isotope signature of palaeogroundwaters from North Africa and the Middle East and North Africa (based on Clark and Fritz 1997 which provides more information on data sources).

The extent of rainfall evaporation can be characterized and in some cases quantified (Allison et al., 1984) using the combined ratios of oxygen and hydrogen isotopes. This classic method is also reinforced with the parallel measurement of chloride; in fact the combined use of chloride and the stable isotopes of water ($\delta^{18}O$, δ^2H) has provided a powerful technique in numerous studies of the evolution of groundwater salinity as well as recharge/discharge relationships, especially in semi-arid regions (Fontes, 1980; Dinçer et al., 1984; Gonfiantini et al., 1974b)

A major challenge in the investigation of groundwater salinity was to distinguish saline water of different origins, not least sea water of different generations and for this both chemical and isotopic techniques are needed. The ratio Br/Cl is an important tool for narrowing down different sources of salinity, discriminating specifically between evaporite and marine Cl sources (Edmunds, 1996; Davis et al., 1998). With prolonged water–rock contact the seawater chemical composition (e.g. decrease in Mg/Ca ratio) may change but the salinity source may still be ambiguous. In such cases the stable isotope composition provides an independent variable to confirm the marine origin of the salinity. Modern sea water should also have an increased activity of ^{14}C due to the inclusion of precipitation from thermonuclear fallout. In a coastal area of Madras State, India, for example, Sukhija et al. (1996) have been able to distinguish palaeomarine (up to 20 ka BP) and modern sea water intrusion on the basis of a combined approach using hydrogeochemical markers, radiocarbon and organic bio-markers, specifically the distribution of different suites of fatty acids.

Salinity is derived in many aquifers from time-dependent reactions between water and rock. The build up of salinity may be in part derived from solution of formational evaporites, but progressive geochemical reactions may also allow the build-up of ionic concentrations. Chemical interpretations alone may be ambiguous and the use of various isotope ratios (^{15}N, ^{87}Sr, ^{11}B, for example) has been useful to help constrain the origins and evolution of salinity (Heaton, 1984; Bassett, 1990; Yechieli et al., (1992); Marie and Vengosh, 2001). Some of the most successful solutions of salinity interpretations come from the use of multiple tracers where both chemical and isotopic tools have been used. The genesis of formation brines and also the study of salinity in crystalline rocks such as the Canadian Shield (Frape and Fritz, 1987) and Carnmenellis Granite (Edmunds et al., 1984) and the German Continental Deep Borehole (Stober and Bucher, 1999) provide good examples of this type of integrated study of salinity. The isotopes of Cl have also be used: ^{36}Cl to determine the extent of infiltration of salinity of modern origin (Phillips, 1994; Cook et al., 1994) and $\delta^{37}Cl$ to determine the origins of chlorine in saline formation waters (Weaver, 1999). The precision of measurement around ± 0.1‰ makes the use of chlorine stable isotopes a potential new tool for studies of environmental salinity.

Table 1. Isotopic and related chemical tools used for evaluating salinity sources; additional tracers such as 4He may be useful for evaluating residence times.

Geochemical/ isotopic tool	**Role in evaluating salinity**
Cl	Master variable: inert tracer in nearly all geochemical processes, use in recharge estimation and to provide record of recharge history
Br/Cl	Use to determine geochemical source of Cl
^{36}Cl	Half life $3.01x10^5$ a. Thermonuclear production - use as tracer of Cl cycling in shallow groundwater and recharge estimation. Potential value for dating over long timespans and also for study of long term recharge processes. However, in situ production must be known
^{37}Cl/^{35}Cl	Fractionation in some parts of the hydrologic cycle, mainly in saline/hypersaline environments may allow fingerprinting
Inorganic tracers Mg/Ca Sr, I, etc	Diagnostic ratio for (modern)sea water Diagenetic reactions release incompatible trace elements and may provide diagnostic indicators of palaeomarine and other palaeowaters
Nutrients (NO_3, K, PO_4), $\delta^{15}N$	Nitrate accumulations may accompany Cl in aerobic arid environments. Nutrient elements characteriztic of irrigation returns. Characterization using $\delta^{15}N$

Table 1. (cont.) Isotopic and related chemical tools used for evaluating salinity sources; additional tracers such as ^4He may be useful for evaluating residence times.

Geochemical/ isotopic tool	**Role in evaluating salinity**
$\delta^{34}S$	Indicator of evolution of seawater sulphate undergoing diagenesis. Characterization of evaporite and other SO_4 sources of saline waters
$\delta^{11}B$	Additional indicator of salinity source
^3H	Recognition of modern sources of salinity (half life 12.3 years)
$\delta^{13}C$, (^{14}C)	Additional indicator for modern sea water and with ^{14}C for dating of saline waters. Understanding of carbon geochemistry is essential to interpretation.
Organics	Indicator species (e.g. fatty acids) to characterize marine waters of different age. Pesticides, etc., diagnostic of irrigation sources of salinity

6. Classic aquifer studies

Probably the most important studies on groundwater in recent decades are those detailed investigations made using multidisciplinary and repeated studies. Research may have been conducted simply for better understanding of hydrogeology and water–rock interaction of flow systems, as for the East Midlands aquifer (UK), the Milk River aquifer (USA, Canada); other studies may have had a specific target such as suitability of aquifers for storage of radioactive wastes, e.g. Stripa Granite (Sweden), the Molasse Basin (Switzerland/Germany), or the Canadian Shield to study the origins of salinity (Fritz and Frape, 1987). These serve as good reference aquifers for study of the uses and limitations isotope applications, and three of them are described here.

6.1. THE MOLASSE BASIN

The Molasse Basin (Pearson et al., 1991) is a complex sequence of sediments, part of the Alpine foreland, ranging in age from Permo-Carboniferous to Quaternary, which is highly faulted and folded. It represents the most detailed integrated study of a sedimentary basin system of aquifers so far carried out and also looks at the groundwaters in the crystalline basement. Its focus is squarely on the testing of isotopic tools, yet it also interprets these in full conjunction with supporting chemical (including dissolved gas), mineralogical and hydrogeological data. The study is published in full with all supporting data and discussion of sampling errors, contamination problems, as well as storage and analytical errors, making this a unique reference study. The shallow groundwaters are sampled from 140 readily available groundwater sources but the programme concentrated on accessible deep groundwaters including seven specially drilled deep drill holes.

Isotopes that were studied to investigate flow rates included ^{3}H, ^{3}He, ^{4}He, ^{14}C, ^{36}Cl, ^{36}Ar, ^{39}Ar, ^{40}Ar, ^{85}Kr, ^{234}U and ^{238}U. Investigation of recharge conditions were studied using the dissolved noble gases (Ne, Ar, Kr, Xe) as well as δ^{18}O and δ^{2}H. A wide range of isotopes was also included to investigate the geochemical evolution of groundwaters, including δ^{13}C, δ^{34}S, ^{87}Sr/^{86}Sr, ^{36}Cl/Cl, ^{37}Ar/Ar, ^{40}Ar/^{36}Ar, as well as the concentrations and ratios of a range of uranium and thorium isotopes and their daughter products. In many cases the results from more than one participating laboratory were compared.

The range of groundwater ages in the basin sequence ranges from modern to “very old”. Resolution of the younger groundwaters, for example using ^{39}Ar, is quite good, although limitations on radiocarbon age interpretation is imposed by the carbonate reactions. The upper age limits are qualitative, mainly due to in situ production of some of the longer-lived isotopes such as ^{36}Cl, as might be expected from contamination from drilling fluids and mixing, although the measurement of short-lived isotopes helps to constrain the contribution of younger waters.

This study demonstrates the active circulation of groundwater through the upper formations of the Molasse Basin and also the dominance of carbonate and sulphate mineral equilibria (both rock forming and secondary fracture fillings) in controlling the chemistry of groundwater. In the deeper formations isotope studies show that the waters are slow-moving and saline, with little evidence of cross-formational flow, and any original signature of age or origin is obliterated by extensive water–rock interaction. Overall this is an honest and very detailed “state-of-the-art” study, which is at the same time a classic showpiece for isotope applications, yet a warning on the limitations of obtaining simple answers from complex aquifer systems.

6.2. THE EAST MIDLANDS AQUIFER

The East Midlands Triassic Sandstone aquifer represents the most detailed study of a fresh water aquifer used exclusively for public supply. Although it was the target for the first IAEA-led international comparative study of groundwater dating techniques (Andrews et al., 1983), it has also been a regular test bed for isotopic and geochemical applications over the past 25 years. It also represents a relatively uncomplicated aquifer system for studies of groundwater flow and evolution. The sandstone is a relatively homogeneous, gently dipping sequence, overlain by Triassic mudstones and confined at the base by a Permian marl and limestone sequence. The sandstone was once cemented with evaporites (mainly anhydrite and dolomite), but these have largely been removed by groundwater circulation over geological timescales, resulting in the present porosity and also the remarkably fresh groundwater chemistry to a depth of 500m (Fig. 5). The absence of salinity to this depth indicates that upward leakage of saline water does not occur and that chemical and isotopic evolution takes place entirely within the sandstone.

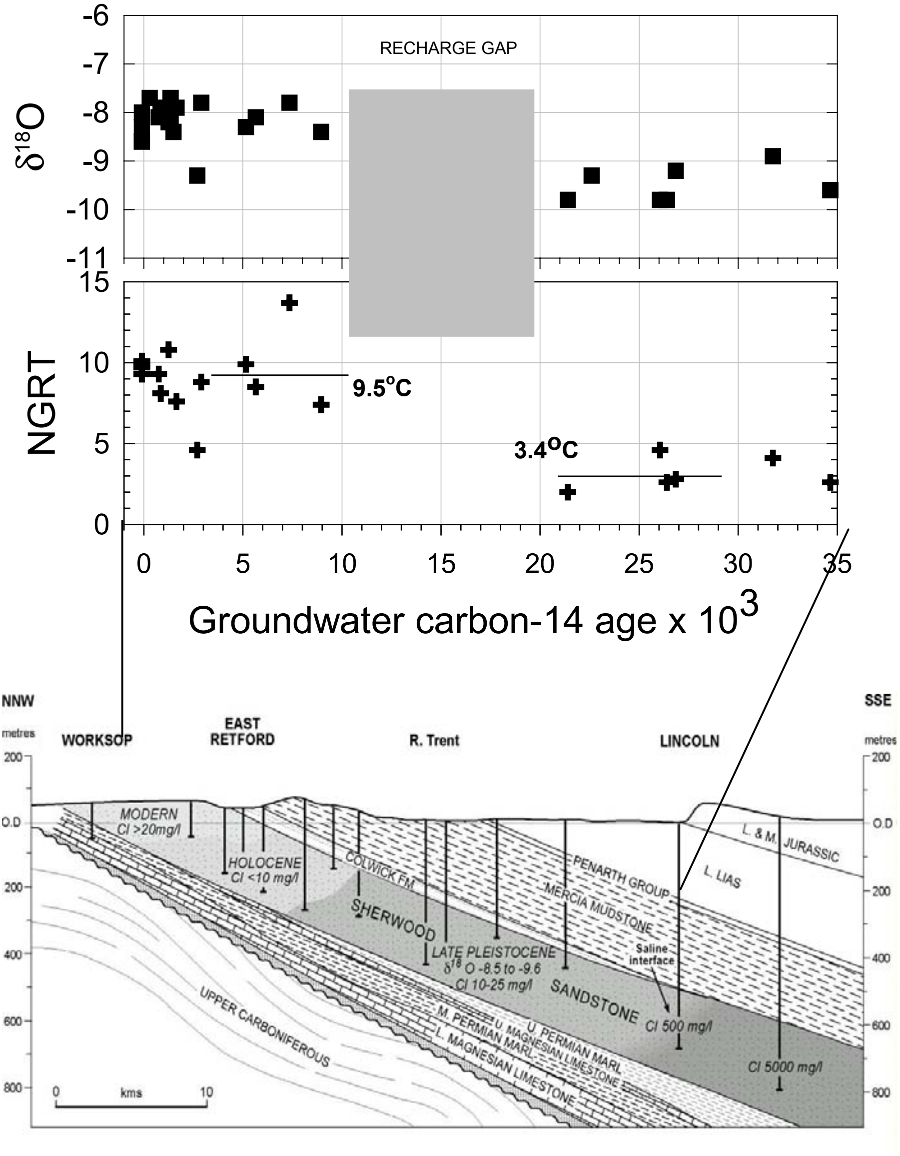

FIG. 5. East Midlands aquifer, UK. Summary of the age relationships along the flow line with the $\delta^{18}O$ and noble gas recharge temperatures for the line of section (note that corrected radiocarbon age is roughly proportional to distance along flow line). The recharge gap due to frozen terrain during the Pleistocene is indicated.

Radiocarbon and other age indicators (Bath et al., 1978 and Andrews et al., 1983; Darling et al. 1997) show that there is a progressive sequence of flow downgradient over a period in excess of 30 ka. In this aquifer the systematic hydrochemical changes also allow extrapolation of the age range to suggest residence times up to 100 ka (Edmunds and Smedley, 2000). Use of $\delta^{13}C$ allows absolute age correction and this aquifer very clearly shows a characteristic “recharge gap” between around 10-20 ka corresponding to frozen conditions during the Last Glacial Maximum (LGM). The stable isotopic evidence ($\delta^{18}O$, $\delta\ ^{2}H$) as well as the dissolved noble gases also indicate cooler conditions in the pre-glacial groundwaters. There is also a smooth trend in the Holocene groundwaters indicated by ^{39}Ar, which suggests piston-type flow; modern influx is also well demonstrated using a suite of short-lived isotopes. A unique feature of this low-Cl aquifer is the application of $^{36}Cl/Cl$ isotope ratio to estimate that rates of evapotranspiration were lower in the Late Pleistocene as compared with the modern era (Andrews et al., 1994); this study also illustrates the in situ production of ^{36}Cl, as well as its use, with tritium, to fingerprint modern (post bomb) waters.

The East Midlands aquifer also records a sequence of geochemical evolution in which isotope ratios assist the interpretation. Sulphur isotope ratios in conjunction with the chemistry allow the modern “foreign” pollutant sulphate to be distinguished from the main source of sulphate derived from anhydrite (Edmunds et al., 1995). However since the groundwaters are of very low salinity, the pre-industrial groundwaters are shown to contain the isotopic composition of the pristine rainfall. The steady increase in $\delta^{13}C$ also indicates the direction and progress of carbonate dissolution in the aquifer from secondary calcite, to incongruent dolomite dissolution driven in turn by anhydrite dissolution. Overall, this aquifer demonstrates clearly the linkages between progressive sequences of hydrochemical change and groundwater evolution, illustrated by isotopic studies over a 100 ka period.

6.3. THE MILK RIVER AQUIFER

The Milk River Cretaceous sandstone aquifer (Fig. 6) is recharged mainly from Montana, USA, but its flow is northwards into Canada. It is a relatively thin (30–60 m) sandstone unit but with a flow path of 80–100 km, with hydraulic estimates of flow times in excess of 500 ka (Hendry et al., 1991). Radiocarbon was known to be undetectable a short distance downflow of the recharge area and this aquifer was chosen for the second IAEA-led international comparative study on dating of very old groundwaters (Ivanovich et al., 1991).

The range of isotopic tools tested in the Milk River study was similar to those for the Molasse Basin but with the addition of the long lived cosmogenic ^{129}I alongside ^{36}Cl. As in the other two studies the comprehensive investigation of the aquifer hydrochemistry alongside the isotope studies proved essential, whilst having good independent hydraulic estimates of flow rates and residence times enhanced the value of the work.

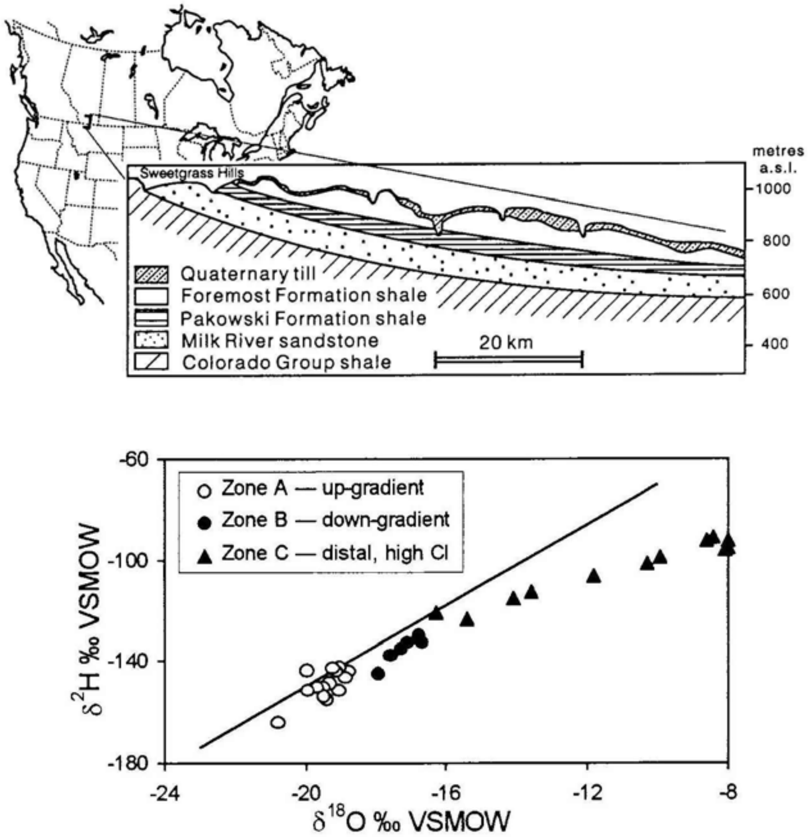

FIG. 6. Stable isotope variation in groundwaters from the Milk River aquifer (combined from Clark and Fritz, 1997). A steady enrichment in isotopes is observed along the flow direction in the aquifer.

It is fair to say that the Milk River study provided challenges to the interpretation of most of the individual isotopic tools and that simple application of any one method for age determination proved to be impossible. The reasons for this were several, including in situ production of the isotope due to neutrons produced from minerals containing uranium, water–rock interaction and the extreme difficulty of obtaining enough measurements in such a heterogeneous system. For the cosmogenic isotopes the very low cosmic abundances may be swamped by in situ production in this and other aquifers with other radionuclides in the sediments, producing a high background neutron flux. Nevertheless where the in situ production of ^{36}Cl could be determined and where the stable Cl origins are well understood, it was possible to make age estimates; in the case of the Milk River aquifer the flow velocities measured were 0.04 to 0.14 m/a and the ages of groundwater from 0.6 and 2 Ma across the aquifer (Nolte et al., 1991). The use of U-isotopes also proved to be valid for dating in this aquifer where the U-residence time is the same order as the ^{234}U half-life, and ages comparable to those derived from ^{36}Cl were obtained.

This study has proved of value from a hydrogeological viewpoint. It shows that there is a limit to the application of hydrodynamic models in groundwater systems that are heterogeneous and with long residence times. Here the isotopic tools allow testing of the model ages and show that parameters measured using present day hydraulic heads may be inapplicable. Estimates of flow and residence times calculated using isotopic tools might be more realistic in such an aquifer affected by glaciation and climatic changes. The Milk River study also shows the value of the previously established hydrochemistry in determining the flow patterns and the zones of higher transmissivity.

7. Future directions for research

This brief review has shown the evolution of ideas in four decades of the application of isotope hydrology in hydrogeological studies. The great strengths of the available techniques have been in absolute (as well as relative) age estimation both of young and very old groundwaters, the application to the characterization of groundwaters in arid and semi-arid regions, in palaeohydrologic studies and in the validation of flow models. Isotopic techniques have also significantly clarified understanding of hydrologic processes taking place in unsaturated zones, and the amount as well as the sources of recharge to aquifers. In effect the isotopic and chemical methods have often been useful in solving physical problems such as recharge estimation and flow velocities. The classic aquifer studies have also shown how single tracers used alone are much less effective than isotopic tracers, used in combination with each other, in hydrogeologically well-characterized systems. In almost all studies the combined uses of geochemical and isotopic tracers has proved to be highly effective. In fact many of the earlier studies lose their valu, since little or no chemical data was reported alongside the isotopic data. It is also important to note that isotope studies, even used on their own, have proved to be useful reconnaissance tools in areas where mainstream hydrogeological data are sparse.

Isotope studies are now embedded in the training of most hydrogeologists and can be considered alongside other tools available. Access to specialist laboratories remains a problem in many countries and every effort needs to be made to support isotope applications in developing countries. There are two types of application of isotopes in groundwater studies. Firstly, it is necessary to continue detailed, multi-tracer studies of well-chosen reference aquifers on a global scale, using tools that may be prohibitively expensive for general use. These help not only to fine-tune the various isotopic methods, but also provide teaching examples of type aquifer systems. Secondly, a widespread application of certain isotopic tools (e.g. δ^{18}O, δ^{2}H) must be encouraged as standard practice. This can easily be justified in terms of cost and in their value in relation to groundwater management.

A number of new opportunities are also emerging. The growing accessibility of AMS analysis for radiocarbon measurement allows smaller sample volumes to be considered. Apart from easier field procedures and transportation, there is the possibility of collecting much smaller sample volumes (well below one litre for most groundwaters). This offers a number of possibilities of determining age stratification in aquifers using well-chosen depth samples and in studies where TDIC can be extracted from pore waters. There is also a need for better recognition of the properties and extent of younger groundwaters, most vulnerable to contamination. In the absence of detectable (above background) thermonuclear tritium, there is the possibility of using several other tracers for the timescale 0–50 years, including tritiogenic helium (^{3}He), SF_6, CFCs and ^{85}Kr.

Finally, the groundwater community needs to look beyond its strictly quantitative and qualitative water resources remit, to view aquifers as archives of important palaeoenvironmental information Conversely these palaeowaters, often of good chemical quality and free of pathogens, form an important strategic reserve.

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14. DATING OF YOUNG GROUNDWATER

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1. Introduction

In developing management strategies for groundwater systems, dating can be a useful tool to determine recharge rates to aquifers, calibrate models of groundwater flow, extract information on the rates of geochemical and microbiological processes occurring in aquifers, classify hydrogeologic environments on the basis of contamination potential, retrieve historical records of contaminant loading to aquifers, and estimate remediation times for groundwater systems that are already contaminated.

Historically, groundwater age information has primarily been obtained from measurements of ^{3}H in water and ^{14}C in dissolved inorganic carbon. Recognizing the limitations of these methods and driven, in part, by the need for more detailed age information, additional environmental tracers have been sought that can provide information on the age of "young groundwater". Here, "young groundwater" refers to water recharged within approximately the past 50 years, a time scale defined largely by the dating range of a small group of environmental tracers that encompasses, at least in part, groundwater that has potentially been impacted by anthropogenic contamination.

Significant advances on aspects of dating young groundwater have been presented at past symposia on isotope hydrology convened by the IAEA. For example, at the 1978 IAEA Symposium, pioneering papers on tritium/helium-3 dating (Torgersen et al., 1979), argon-39 dating (Loosli and Oeschger, 1979), and krypton-85 dating (Loosli and Oeschger, 1979; Rozanski and Florkowski, 1979) were presented. Much literature exists on the subject of dating young groundwater and new tools continue to be developed. Numerous papers have reviewed aspects of groundwater dating on a range of time scales (Davis and Bentley, 1982; Fontes, 1983; Moser and Rauert, 1983; Evans, 1983; Florkowski and Rozanski, 1986; Fröhlich, 1990; Plummer et al., 1993; Lehmann et al., 1993; Małoszewski Małoszewski and Zuber, 1996; Cook and Solomon, 1997; Kipfer et al., 2002). Many aspects of the subject of dating young groundwater appear in Cook and Herczeg

P.K. Aggarwal, J.R. Gat and K.F.O. Froehlich (eds), Isotopes in the Water Cycle: Past, Present and Future of a Developing Science, 193-218.

(2000), and in “Guidebook on the Use of Chlorofluorocarbons in Hydrology” (IAEA, in preparation). Radiocarbon dating is discussed by Geyh (this volume).

The term “groundwater age” is used to refer to the time elapsed since recharge, and, although reference is often made to “dating of groundwater”, it is important to recognize that what is actually being “dated” is a dissolved solute, or dissolved gas, or isotope that has an atmospheric origin, and has been transported through the unsaturated zone, into and through the aquifer to the point of sampling. While it is often possible to measure reliably the concentrations of environmental tracers in groundwater samples, groundwater age is model-dependent, being based on an interpretation of the recharge mechanism, groundwater flow conditions and other physical and geochemical processes that may have affected the concentrations measured in the sample. As an initial reference point, an “apparent age”, which assumes shallow recharge and unmixed samples (piston flow) is often reported, although, in general, the environmental tracer data need to be evaluated in terms of all the hydrodynamic and geochemical processes that can affect the measured concentrations.

In the following, advances in development and application of selected environmental tracers that are currently used to interpret groundwater age information on the 0-50-year time scale are discussed. Environmental tracers that have proven most useful in providing groundwater age information can be grouped according to their systematics: (1) methods based on the measurement of the activity of a single radionuclide of atmospheric origin in groundwater, such as in applications of ^{3}H, ^{85}Kr, ^{39}Ar, ^{32}Si, and ^{35}S in groundwater dating, (2) the ^{3}H/^{3}He method, which is based on measurement of the concentrations of both parent and daughter isotopes in groundwater, and (3) methods based on measurement of the concentrations of atmospheric gases of anthropogenic origin in groundwater, such as in applications of chlorofluorocarbons (CFCs) and sulphur hexafluoride (SF_6).

2. Dating with the parent isotope

In the first group of environmental tracers used in dating young groundwater, it is only feasible to measure the concentration of the parent isotope. Age information is then derived from the measured concentration of the radionuclide in the aquifer, the decay equation, and a priori knowledge of historical variations of the concentration of the parent isotope in the atmospheric source. Examples of this dating technique apply to uses of ^{3}H, ^{85}Kr, ^{39}Ar, ^{32}Si, and ^{35}S.

2.1. TRITIUM[1]

Tritium is a radioactive isotope of hydrogen that has a half-life of 12.32 years (Lucas and Unterweger, 2000). Environmental tritium occurs in precipitation from two sources — tritium of cosmogenic origin and tritium derived from anthropogenic

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[1] See also Michel, this volume.

sources, principally from the atmospheric testing of nuclear weapons and nuclear reactors. Small amounts of tritium can also be produced in situ in the lithosphere by neutron irradiation of ^{6}Li. Andrews et al. (1989) calculated that tritium activities in the range of 0.07 to 0.7 TU were possible for water in fractures of porosities of 1 to 0.1%, respectively, from in situ production in the Stripa granite, Sweden.

Prior to atmospheric testing of nuclear weapons, middle and low latitude precipitation and surface water contained tritium in the range of 2 to 10 TU (von Buttlar and Libby, 1955; Thatcher, 1962; Roether, 1967). However, between 1951 and 1980, tritium from atmospheric tests of nuclear weapons overwhelmed the natural cosmogenic source. As a result, ^{3}H input from precipitation is represented by a series of pulses, with the largest pulse occurring during 1963-1964. The shape of ^{3}H input differs significantly from the relatively smooth input functions for ^{85}Kr, CFCs and SF_6. The spiked nature of the tritium input function results in considerable ambiguity in age interpretation; nevertheless, the presence of tritium in water samples is a reliable indicator of samples that contain at least a fraction of post-1950s water. It is also useful to locate the depth of the mid-1960s bomb pulse in aquifers, which can still be detected in ^{3}H, and more clearly in "initial tritium", i.e. tritium plus tritiogenic helium-3 ($^{3}H+^{3}He_{tri}$) (Solomon et al., 1993; Szabo et al., 1996; Shapiro et al., 1999). Tritium concentrations in precipitation are much lower in the southern hemisphere than in the northern hemisphere. Significant spatial variations also occur on smaller scales, so that uncertainty in input function can sometimes limit interpretation.

Because of various meteorological processes and atmospheric moisture sources (Rozanski et al., 1991), it is often necessary to construct a local record of "^{3}H-in-precipitation" for a particular region being studied. Several scaling procedures exist for re-construction of local ^{3}H records on the basis of records from parts of the USA (Michel, 1989, and reports from the International Atomic Energy Agency, IAEA). Since 1961, the IAEA, in cooperation with the World Meteorological Organization (WMO), has maintained a database of the isotopic composition of monthly precipitation world-wide based on GNIP, the global network of isotopes in precipitation (Gourcy et al., this volume).

Because of the multiple peaks in ^{3}H content of precipitation, multiple possible years of recharge may come into question. Nevertheless, ^{3}H data can be quite useful in recognizing post-bomb waters, waters that at least contain a fraction of post-bomb water. In conjunction with other atmospheric tracers, the ^{3}H concentration can be very useful in recognizing ground-water mixtures. Terrigenic sources of ^{3}H are usually negligible, and ^{3}H is not affected by microbial degradation processes. There is much literature on applications of ^{3}H in hydrology; much of which has appeared in past proceedings of the IAEA (see also Münnich et al., 1967, Eriksson, 1983; Rozanski, 1991; Schlosser, 1992; Michel, this volume).

2.2. KRYPTON-85

Krypton-85 is a radioactive noble gas with a half-life of 10.76 years. Although there is a cosmogenic source, ^{85}Kr released in the reprocessing of fuel rods from nuclear reactors has overwhelmed the natural background concentration by some six orders of magnitude (Rozanski and Florkowski, 1979; Florkowski and Rozanski, 1986; Weiss et al., 1992). Applications of ^{85}Kr in dating young groundwater continue to hold considerable promise in the hydrologic sciences. Dating is based on the specific activity of ^{85}Kr (i.e. the ratio of ^{85}Kr to stable Kr), which is insensitive to recharge temperature, altitude, and Kr solubility. The specific activity of ^{85}Kr in the atmosphere has steadily increased since the mid-1950s, avoiding the ambiguity in age interpretation that can result from input functions that are spiked, such as is the case with ^{3}H, and lessening some of the problems caused by hydrodynamic dispersion of tracer signals in aquifers. Krypton-85 is produced almost entirely in the northern hemisphere (Zimmermann, 1989). Due to slow mixing across the Intertropical Convergence Zone (Rozanski, 1979; Weiss et al., 1983), the specific activity of ^{85}Kr in the southern hemisphere is about 20% below northern hemisphere values (Weise et al., 1992). There are no significant anthropogenic sources of ^{85}Kr other than those mentioned above that result in an increase in the atmosphere and, being a noble gas, ^{85}Kr is not altered by microbial degradation or other geochemical processes. When ^{85}Kr is used to date groundwater that was recharged through thick unsaturated zones, the time lag for transport of the atmospheric gas through the unsaturated zone should be considered (Cook and Solomon, 1995).

Procedures for water degassing, Kr separation and counting of ^{85}Kr are given in Rozanski and Florkowski (1979) and Smethie and Mathieu (1986). Sample volumes range from 120 to 360 L; extraction efficiencies have ranged from 50-80%, and counting times are typically 1 week (Loosli et al., 2000). Krypton-85 dating would be widely used today if collection and analytical procedures were not so labour-intensive. Currently, laser-based methods of analysis of ^{85}Kr are being developed. They could reduce the sample volume to the range of 2-5 L (Thonnard et al., 1997; Fairbank et al., 1998).

Although difficult to collect and analyse, ^{85}Kr has few other limitations. Therefore, even a few determinations of ^{85}Kr can often help resolve questions and ambiguities that can remain in interpretation of other environmental tracer data, such as ^{3}H and CFC data, for which large numbers of samples can be collected fairly easily in hydrologic investigations, but which are subject to greater uncertainty in interpretation (Loosli et al., 2000). Because of its relatively high detection limit, ^{85}Kr may be less reliable than CFCs for waters recharged more than 30 years ago. It is also difficult to use ^{85}Kr to detect newly recharged water in mixtures, if the content of the young fraction is less than about 10% in a mixture with old water. In studies of very old groundwater, ^{85}Kr measurements are sometimes used to determine whether the sample has been contaminated with modern air during collection. However, the problem can be complicated by in situ production due to spontaneous fission of ^{238}U (Andrews et al. 1989; Loosli et al., 1989).

In some shallow aquifers where flow is not affected significantly by mixing, ^{85}Kr dating can directly yield the piston-flow age of groundwater, if sampled from wells with narrow screens (Smethie et al., 1992; Ekwurzel et al., 1994). In general though, as with all environmental tracer data, the mixing process needs to be investigated. The ^{85}Kr technique alone cannot be used to identify mixing between old and newly recharged waters. Combined with other tracers, ^{85}Kr can be used to calculate the mixing percentage and provide a check on results obtained from other tracers. For example, plots comparing concentrations of one tracer against another, such as ^{85}Kr vs ^{3}H can be used to recognize mixing of young and old water (Loosli et al., 2000). Ratios of ^{3}H to ^{85}Kr have proved useful in eliminating some mixing models and refining estimates of mean residence time (Salvamoser, 1984; Loosli, 1992; Loosli et al., 2000). Atmospheric concentrations of ^{85}Kr are expected to continue to increase in the foreseeable future. This will allow the technique to be used in the next decades. Further development of the technique and increase of ^{85}Kr in the atmosphere will probably make this technique more practical.

2.3. ARGON-39 AND SILICON-32

For many years, there has been an effort to investigate nuclear dating techniques that can fill the gap between dating with ^{3}H (and other environmental tracers on the 0-50-year time scale) and ^{14}C dating (approximately 1000-30,000-year time scale). The cosmogenic radioisotopes ^{39}Ar (half-life 269 years) and ^{32}Si (half-life 140 years) have favourable half-lives for groundwater dating on the 50-1000-year time scale, and the systematics of ^{39}Ar dating (Loosli and Oeschger, 1968, 1979, 1980; Loosli, 1983; Andrews et al., 1984; Florkowski and Rozanski, 1986; Loosli et al., 1989, 1991, 1992, 2000; Loosli and Lehmann, 1991; Forster et al., 1992) and ^{32}Si dating (Lal et al., 1970; Andrews et al., 1984; Fröhlich et al., 1987; Morgenstern et al., 1995, 1996; Morgenstern, 2000) have been carefully investigated.

Argon-39 is produced in the stratosphere by cosmic-ray secondary neutrons in the reaction $^{40}Ar(n,2n)^{39}Ar$. The atmospheric activity of ^{39}Ar has been nearly constant over the past 1000 years (Loosli, 1983), and groundwater from some carbonate aquifers has apparently been successfully dated using ^{39}Ar (Loosli, 1983; Loosli et al., 1989). However, in crystalline rocks with high U and Th content, there is a significant source of ^{39}Ar from subsurface production (Loosli, 1983; Loosli et al., 1989; Loosli and Lehmann, 1991; Andrews et al., 1991; Florkowski, 1992) making dating applications impossible in such environments. Measurement of ^{222}Rn provides an effective means of recognizing water samples that may be contaminated with ^{39}Ar from subsurface production (Forster et al., 1992). Sample collection is probably the most serious detriment to the ^{39}Ar dating method; modern water contains only about 8.5 atoms of ^{39}Ar per mL (Lehmann et al., 1993), requiring gas-stripping of approximately 10-12 m^3 of groundwater (Forster et al., 1992; Loosli et al., 2000). Currently, there are few laboratories capable of measuring the specific activity of ^{39}Ar (Forster et al., 1992; Loosli et al., 2000).

Silicon-32, produced by cosmic-ray spallation of argon by the $^{40}Ar(n,4p5n)^{32}Si$ process in the upper atmosphere, was first detected in the environment by Lal et al. (1960) and soon found successful applications in the dating of glacial ice (Dansgaard et al., 1966a, 1966b; Clausen et al., 1967; Clausen, 1973; Morgenstern et al., 1996). Early estimates of the half-life of ^{32}Si were too high, and initial investigations in groundwater targeted aquifers for study that were too old, as pointed out by Fröhlich et al. (1987). Some favourable dating applications seem possible for sand and limestone aquifers (Fröhlich et al., 1987; Morgenstern et al., 1995). Silicon-32 reaches the land surface as both dry deposition and silicic acid dissolved in precipitation. There are lower concentrations in snow than rain and there is seasonality of the input function, similar to that of tritium (Morgenstern et al., 1995). Collection and analytical procedures are given in Gellermann et al.

(1988). Subsurface production is negligible (Florkowski et al., 1988). Unfortunately, dissolved silica is reactive in the soil and groundwater environment, and can be strongly sorbed during infiltration through the soil; consequently, dating applications in the groundwater environment are quite limited (Morgenstern et al., 1995). Yet there are still important applications of ^{32}Si in dating snow and ice, and recently, ^{32}Si was demonstrated to provide useful chronologies for marine sediments (Morgenstern et al., 2001).

2.4. SULPHUR-35

Sulphur-35 is produced in the atmosphere by cosmic-ray spallation of Ar (Lal and Peters, 1967; Tanaka and Turekian, 1995; Sueker et al., 1999), and decays with a half-life of 87 days. Sulphur-35 has been used successfully to estimate mean ages of water discharging from springs and runoff in small mountainous watersheds (Michel, 2000, 2002) in Colorado (Michel and Turk, 1995; Sueker et al., 1999; Michel et al., 2000), Virginia (Böhlke et al., 1996), and New York (Burns et al., 1998). Plummer et al. (2001) found low activity of ^{35}S in young water from springs in the Blue Ridge Mountains of Virginia and concluded that transport of dissolved sulphate was probably retarded by uptake and exchange of sulphate in plants, and/or soil sorption. The young ages obtained from SF_6 and ^{3}H/^{3}He dating of the spring waters suggested that at least 50% of the ^{35}S was lost to the biomass. If unaffected by uptake processes, ^{35}S has a piston-flow dating range of approximately 0 to 1.5 years.

3. Dating with parent–daughter isotopes; tritium/helium-3 dating

In dating with parent-daughter isotope pairs, 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 ability to reconstruct the initial radionuclide concentration for a single sample has considerable advantage over dating methods that require prior knowledge of the initial concentration of the environmental tracer recharged. Tolstikhin and Kamensky (1969) were the first to suggest the possibility of dating with tritium (half-life 12.32 years) and the decay product, tritiogenic helium-3 ($^{3}He_{tri}$). Torgersen et al. (1977, 1979) applied ^{3}H/^{3}He dating to lakes and suggested the application to dating groundwater. ^{3}H/^{3}He dating has been extensively used in oceanographic studies since the mid-1970s (see for example Jenkins, 1977 and numerous subsequent papers). In the 1980s, several studies further developed the systematics of ^{3}H/^{3}He dating and demonstrated its applicability in studies of groundwater systems (Małoszewski and Zuber, 1983; Weise and Moser, 1987; Takaoka and Mizutani, 1987; Poreda et al., 1988; Schlosser et al., 1988, 1989).

The ^{3}H/^{3}He age is based on ^{3}He and ^{4}He isotope mass balances used to calculate the amount of $^{3}He_{tri}$ derived from radioactive decay of ^{3}H (Schlosser et al., 1988, 1989) in water samples that can contain He from several other sources, including solubility equilibrium with air, excess air dissolved during recharge, ^{4}He derived from in situ U- and Th-series decay, ^{3}He derived from decay of ^{3}H produced in situ in the ^{6}Li(n,α)^{3}H reaction, and helium of mantle origin that is elevated in ^{3}He.

Determination of the $^3H/^3He$ age requires measurement of ^3H, ^4He, Ne, and the $^3He/^4He$ ratio of dissolved He in the sample (Bayer et al., 1989).

There are several requirements that can permit solving the helium isotope mass balance for $^3He_{tri}$ and calculation of the $^3H/^3He$ age in groundwater samples: (1) The sample must contain detectable tritium (^3H greater than approximately 0.5 TU), (2) Ne data are needed to correct for excess air in calculating $^3He_{tri}$ in samples that contain terrigenic He (helium from mantle and crustal sources), and (3) If the amount of terrigenic He is greater than about 5% of the dissolved ^4He, the $^3He/^4He$ ratio of the terrigenic He, R_{terr}, must be known within approximately 1% or better.

The validity of the $^3H/^3He$ dating method was demonstrated in a series of studies (Poreda et al., 1988; Schlosser et al., 1988, 1989; Solomon and Sudicky, 1991; Solomon et al., 1992, 1993, 1995; Ekwurzel et al., 1994; Szabo et al., 1996; Schlosser et al., 1998) in which apparent age determined by $^3H/^3He$ dating was compared with age information determined from other tracers and/or models utilizing data collected from narrow-screened piezometers in shallow, sandy aquifers.

In mixtures of young and old (pre-1960s) water, the $^3H/^3He$ age, being based on an isotope ratio, applies to the young fraction (Plummer et al., 1998b; Aeschbach-Hertig et al., 1998). This property has considerable value over all other dating procedures, which require some a priori means of correction for dilution in mixtures of young and old water. Mixtures of young and old water can be recognized by comparing the reconstructed initial tritium ($^3H + {}^3He_{tri}$) as a function of the $^3H/^3He$ age to historical records of ^3H in precipitation, or by comparing ^3H measurements as a function of age to historical records of ^3H in precipitation that have decayed to the date of sampling (Dunkle et al., 1993; Ekwurzel et al., 1994; Shapiro et al., 1998; Plummer et al., 1998b; Aeschbach-Hertig et al., 1998). In a study of leakage of river water into old (pre-1960s) water of the Floridan aquifer system in Georgia, USA, the $^3H/^3He$ age of the river fraction was calculated in samples containing 10 to 100% river water (Plummer et al., 1998b), but in samples containing less than 10% river water the uncertainties were too great to permit resolution of $^3H/^3He$ age of the river-water fraction.

The $^3H/^3He$ dating method depends on ^3He gas confinement following recharge. Model calculations (Schlosser et al., 1989) indicated that loss of ^3He of less than 20% occurred when the vertical water velocity was greater than 0.1 $m.a^{-1}$, equivalent to a recharge rate of about 30 $mm.a^{-1}$ with a porosity of 30% (Solomon et al., 1993; Solomon and Cook, 2000). Reasonable confinement was demonstrated in water samples from a multi-level well in a sand aquifer in Germany where the quantity $^3H+{}^3He_{tri}$ in samples from 26-41 m below the bomb pulse was in the range of 3-6 TU and consistent with the estimated 5 TU for pre-bomb precipitation (Schlosser et al., 1989). In areas of low recharge rate, diffusion dominates ^3He transport and little age information can be obtained (Solomon and Cook, 2000). Similarly, when groundwater samples contact air, such as during infiltration (Weise et al., 1992), in re-aeration (Shapiro et al., 1999) or irrigation return flow (Plummer et al., 2000), there is loss of ^3He and the $^3H/^3He$ clock is essentially re-set. In $^3H/^3He$ dating, it is usually assumed that excess air is dissolved without fractionation, having the Ne/He ratio of air, as has been demonstrated for several sample sets of young waters

(Aeschbach-Hertig et al., 1998; Plummer et al., 2001). However, some paleowaters have been shown to be fractionated (Stute et al., 1995; Aeschbach-Hertig et al., 1999, 2000, 2002; Kipfer et al., 2002) and further study of the mechanism of formation of excess air during recharge is needed.

As is often the case in some fractured-rock systems, and/or mixtures pumped from crystalline rocks, the old fraction in groundwater mixtures may contain a large excess of terrigenic helium for which the $^3He/^4He$ ratio cannot be defined with sufficient precision to permit calculation of the $^3H/^3He$ age of the young fraction, even in samples that contain only a few per cent of old water (Plummer et al., 2000; Burton et al., 2002).

4. Dating with atmospheric gases of anthropogenic origin

In the third case, age information is derived from a priori knowledge of the atmospheric input function of an anthropogenic gas, its solubility in water, and the measured concentration in the water sample. The most notable examples are dating applications with CFCs (Plummer and Busenberg, 2000) and SF_6 (Busenberg and Plummer, 2000). Dating groundwater with atmospheric gases, particularly with respect to CFCs, is treated extensively in a forthcoming publication of the IAEA (Guidebook on the Use of Chlorofluorocarbons in Hydrology).

4.1. CHLOROFLUOROCARBONS

Chlorofluorocarbons (CFCs) are volatile, synthetic compounds of carbon, chlorine and fluorine that were produced commercially beginning in the early 1930s for uses in refrigeration. CFC-12 (dichlorodifluoromethane, CF_2Cl_2), produced commercially from 1930, and CFC-11 (trichlorofluoromethane, $CFCl_3$) produced from 1936, found wide applications in air conditioning and refrigeration, blowing agents in foams, insulation, and packing materials, propellants in aerosol cans, and as solvents. Many other CFC compounds have since been produced, most notably CFC-113 (trichlorotrifluoroethane, $C_2F_3Cl_3$), produced commercially from 1944. CFC-113 has been used primarily by the electronics industry in the manufacture of semiconductor chips, in vapour degreasing and cold immersion cleaning of microelectronic components, and as a solvent in surface cleaning procedures (Jackson et al., 1992). Release of CFCs to the atmosphere and subsequent incorporation into the Earth's hydrologic cycle has closely followed production (Gamlen et al., 1986; Midgley and Fisher, 1993).

Early studies in the hydrologic sciences demonstrated the potential of CFCs as tracers of recent recharge and indicators of groundwater age (Thompson et al., 1974; Schultz et al., 1976; Randall and Schultz, 1976; Thompson, 1976; Hayes and Thompson, 1977; Randall et al., 1977; Thompson and Hayes, 1979; Schultz, 1979). Early attempts to date a water sample with CFCs were based on (1) comparison of a measured CFC-11 concentration to an analysis of another water sample of assumed age, and (2) estimation of sample age using Henry's law and relating implied air concentrations to atmospheric values (Randall and Schultz, 1976). Randall and Schultz (1976) recognized the need for reconstruction of atmospheric mixing ratios of CFCs to improve dating capability, the possibility of detecting both CFC-11 and

CFC-12 in the same analysis (at that time, analytical procedures were capable of detecting only CFC-11), and potential for dating using ratios of CFCs. Thompson (1976), Hayes and Thompson (1977), and Thompson and Hayes (1979) refined field gas chromatography with electron-capture detector (GC-ECD) analytical procedures for CFC-11 and tested the feasibility of dating with CFC-11 in groundwater systems in parts of New Jersey, Arkansas, and Texas, USA.

Since the late 1970s, chlorofluorocarbons have been used extensively in oceanographic studies as tracers of oceanic circulation, ventilation, and mixing processes. As a part of the oceanographic research, the Henry's law solubilities of CFC-11, CFC-12 and CFC-113 were measured to high precision as a function of temperature and salinity (Warner and Weiss, 1985; Bu and Warner, 1995), and purge-and-trap GC-ECD analytical procedures (Bullister and Weiss, 1988) were refined, permitting measurement of CFC-11, CFC-12 and CFC-113 in the same sample. A global network of air monitoring stations established by the Climate Monitoring and Diagnostics Laboratory (CMDL) of the National Oceanic and Atmospheric Administration (NOAA), U.S. Department of Commerce and the ALE/GAGE/AGAGE network (Cunnold et al., 1997) has provided air composition data from the mid-1970s. CFC mixing ratios in air prior to 1976 have been reconstructed from production data (see Plummer and Busenberg, 2000, and references therein). Air-mixing ratios of CFCs can be elevated in urban areas and particularly in western Europe (Oster et al., 1996), requiring consideration of local enrichment factors (Ho et al., 1998).

Much of the work developed by the oceanographic scientific community and atmospheric sciences was adopted for groundwater studies in the early 1990s (Epler, 1990; Busenberg and Plummer, 1991, 1992). In the USA, because of Nuclear Regulatory Commission (NRC) licensing requirements for the radioactive ^{63}Ni source used in the ECD of the gas chromatograph, it is not practical to measure CFC concentrations on site for most groundwater investigations. Sampling procedures introduced by Busenberg and Plummer (1992) permitted collection and storage of water samples without contacting air, and transport of the samples in fused borosilicate ampoules to an NRC-licensed laboratory for analysis by purge-and-trap GC-ECD. Sample collection in glass bottles with metal-lined caps (L.-F. Han, IAEA, written communication, 2003; G. Casile, USGS, written communication, 2003) greatly simplifies sample collection procedures (see http://water.usgs.gov/lab/cfc).

For water recharged at approximately 10°C and 1 atmosphere total pressure, the detection of 1 pg.kg^{-1} permits recognition of groundwater recharged in the years 1945, 1950, and 1957 based on CFC-12, CFC-11 and CFC-113. The presence of CFC-12 indicates post-1945 recharge or older water samples that contain a fraction of post-1945 water. And similarly, detection of CFC-11 and CFC-113 indicates post-1950 and post-1957 water, or their mixtures, respectively.

During the past decade, a series of studies investigated potential applications of CFCs in the hydrologic sciences (see for example Busenberg and Plummer, 1991; 1992; Dunkle et al., 1993; Plummer et al., 1993; Ekwurzel et al., 1994; Reilly et al., 1994; Cook and Solomon, 1995; Böhlke and Denver, 1995; Katz et al., 1995; Cook et al., 1995; 1996; Szabo et al., 1996; Oster et al., 1996; Cook and Solomon, 1997;

Thorstenson et al., 1998; Johnston et al., 1998; Ho et al., 1998; Plummer et al., 1998a,b; Modica et al., 1998; Beyerle et al., 1999; Goode et al., 1999; Weaver and Talma, 1999; Plummer and Busenberg, 2000; Kipfer et al., 2000; Talma et al., 2000; Plummer et al., 2000; Plummer et al., 2001; Katz et al., 2001; Busenberg et al., 2001; Bauer et al., 2001; Burton et al., 2002). CFCs have provided useful tools for tracing and dating post-1945 water (Busenberg and Plummer, 1992; Plummer et al., 1998a; Plummer et al., 2000), estimating groundwater mixing properties (Plummer et al., 1998b; Plummer et al., 2000; Katz et al., 2001; Burton et al., 2002), calibrating groundwater flow models (Reilly et al., 1994; Szabo et al., 1996), and assessing susceptibility of drinking water sources to anthropogenic contamination (Nelms et al., 2003).

The primary advantage that CFCs have relative to noble gas and other radionuclide dating techniques is that, at least in comparison, the collection and analytical procedures are relatively less labour-intensive, permitting tracer data to be collected and analysed from a large number of sites within a given study area. The most serious detriment to dating with CFCs is the possibility of anthropogenic contamination of the aquifer with CFCs from sources other than the atmosphere, resulting in a young, or impossibly young, bias. Although CFCs are not degraded in aerobic environments, microbial degradation can occur in anoxic environments, particularly with respect to CFC-11.

As a result of the *Montreal Protocol on Substances That Deplete the Ozone Layer*, air mixing ratios of CFC-11 and CFC-113 peaked in about 1994 and 1996, respectively. The air mixing ratio of CFC-12 increased slowly through the 1990s, remained nearly constant from about 2000 through 2002, and is expected to begin declining in 2003. Because of nearly level atmospheric input functions of CFC mixing ratios in the 1990s and early 2000s, it is not possible to resolve “modern” CFC ages as precisely as can be done with waters recharged earlier when atmospheric mixing ratios were increasing rapidly. Yet there are still important future uses of CFCs in dating groundwater.

Although the apparent ages of “modern” waters have relatively large uncertainties, the CFC record of recharge over the past 60 years remains in aquifers and most of this record can be sampled and dated with lower uncertainty than for modern samples. The pre-1990s groundwater CFC record remains useful in establishing chronologies for parcels of water recharged to aquifers spanning some 50 years (from the 1940s to the 1990s).

As atmospheric mixing ratios of CFCs fall, it will once again be possible to use CFCs to date modern waters, though an additional caution is that dual ages will be possible. CFC-12 atmospheric mixing ratios are expected to decline more slowly than those of CFC-11 and CFC-113. Consequently, relatively large uncertainties will apply to “modern” ages based on CFC-12 data. As the various CFCs are expected to decline at differing rates, it is anticipated that CFC ratios will once again be useful in dating, particularly in resolving cases of dual apparent ages.

Because of the relatively smooth changes in CFC atmospheric mixing ratios, the possibility of determining multiple ages is not nearly so critical as results from attempts to deduce apparent ages for tritium data alone. It is also anticipated that the effects of hydrodynamic dispersion will be relatively small for CFCs due to the relatively smooth changes in atmospheric mixing ratios. Hydrodynamic dispersion will cause greatest uncertainty for waters with CFC ages corresponding to concentrations close to the peak values.

4.2. SULPHUR HEXAFLUORIDE

Sulphur hexafluoride is a predominantly anthropogenic gas that is used as an electrical insulator in high voltage switches and transformers. Industrial production of SF_6 began in 1953 with the introduction of gas-filled electrical switches and annual production has increased from nearly zero in 1953 to 85,700 tonnes of SF_6 in 1995 (Maiss and Brenninkmeijer, 1998). The troposphere mixing ratio of SF_6 has increased from a steady-state value of 0.054 ± 0.009 to about 5 pptv during the past 40 years (Busenberg and Plummer, 1997; 2000). The atmospheric history of SF_6 is now well established (Maiss and Levin, 1994; Maiss and Brenninkmeijer, 1998) and the mixing fraction of SF_6 is currently increasing at a rate of about 6% per year while those of the CFCs are nearly constant or decreasing (Geller et al., 1997). SF_6 has received significant recent interest because of its high greenhouse warming potential (Climate Change 1995), and SF_6 was one of the six gases covered by the Kyoto Global Warming Protocol Agreement of 1997.

Sulphur hexafluoride is primarily of anthropogenic origin but also occurs naturally (Harnisch and Eisenhauer, 1998; Harnisch et al. 2000; Busenberg and Plummer, 2000). The natural background concentration, 0.054 ± 0.009 pptv, constitutes about 1.0% of the 2001 total atmospheric partial pressure. Small but significant concentrations of SF_6 were measured in 16 minerals and rocks of igneous, metamorphic, hydrothermal, and sedimentary origin (Busenberg and Plummer, 2000). Concentrations of SF_6 were generally highest in silicic igneous rocks and lowest in mafic rocks. Significant concentrations of SF_6 may be present in some diagenetic fluids. Concentrations of SF_6 significantly higher than that of modern air–water equilibrium were measured in groundwater from fractured silicic igneous rocks, from some hot springs, and in some groundwater from volcanic areas (Busenberg and Plummer, 2000). Where the terrestrial flux of SF_6 from igneous rocks and mineral grains is high, groundwater cannot be dated by the SF_6 method.

As with CFCs, SF_6 is measured by purge-and-trap GC-ECD procedures (Busenberg and Plummer, 2000). Corrections for excess air are very important for SF_6, due to its low solubility in water (Busenberg and Plummer, 2000). The Henry's law solubility of SF_6 was determined at 1 atmosphere total pressure between 0 and $40^{\circ}C$ and salinities of 0 to 40‰ (Bullister et al., 2002). There is no evidence that SF_6 is degraded in anoxic waters (Busenberg and Plummer, 2000), and anthropogenic sources other than the atmosphere are uncommon. The dating range of water with SF_6 is from 1970 to modern.

Sulphur hexafluoride has been successfully used to date groundwaters in a number of multi-tracer studies (Busenberg and Plummer, 2000; Bauer et al., 2001; Zoellmann et al., 2001a; Katz et al., 2001; Plummer et al., 2001; Hofer et al., 2002; Vulava et al., 2002). The SF_6 dating method yields excellent results in clastic sediments even in urban areas that are often contaminated with CFCs and other volatile organic carbons (VOCs). However, results have been less reliable for groundwaters obtained from glacial tills, fractured igneous rocks (Busenberg et al., 1998, 2001) and from carbonate aquifers (Katz et al., 2001; Busenberg and Plummer, 2000) where the natural background SF_6 was often significant, and in some cases, exceeded the anthropogenic fraction. The SF_6 method is particularly useful in dating very young (post-1993) groundwater, if there are no terrigenic sources of SF_6, and as atmospheric CFC concentrations fall, the SF_6/CFC ratios will provide strong indicators of modern ages.

5. Event markers

The simple presence or absence of some substances in groundwater can place limits on age, as pre- or post-event. Event markers include dyes or other chemical or isotopic substances that are intentionally introduced into aquifers or karst systems – their detection at a discharge point marks waters or fractions of waters that are post-injection. Location of the bomb-pulse in tritium with depth in aquifers marks water from the mid-1960s, and detection of bomb-pulse ^{36}Cl marks waters or fractions of waters that are post-1958. There are many possible tracers that can be used as event markers, including some VOCs, additives to gasoline such as methyl tertiary-butyl ether (MTBE), surfactants, pharmaceuticals; some of which are discussed in Davis et al. (1980), IAEA (1982), IAEA (1991), and Plummer et al. (1993).

6. Quasi-age indicators

Although the prospects of developing practical nuclear dating methods for groundwater recharged on the 50-1000-year time scale have been limited by a number of technical and geochemical problems (see discussion of ^{39}Ar and ^{32}Si above), two other means of "filling the gap" between ^{3}H and ^{14}C dating have been demonstrated. It has long been recognized that ^{4}He accumulates with time in minerals (Hurley, 1954, attributes the idea to Ernest Rutherford shortly after the discovery of the radioactivity of U and Th; see Solomon, 2000) and in groundwater from radioactive decay of U and Th. If the abundance of U and Th is relatively constant in minerals along the flow path, the release rate of ^{4}He to groundwater will be approximately constant. The accumulation of ^{4}He as an age indicator is attractive because ^{4}He is a stable, non-reactive gas that accumulates with time (rather than being lost to radioactive decay), and is uncomplicated by assumptions regarding atmospheric source, since it is derived from rocks (Marine, 1979). In some cases it is possible to quantify the release rate of ^{4}He from aquifer sediment in the laboratory and apply the measured rate to dating on the 10-1000-year time scale (Solomon et al., 1996), or to calibrate the ^{4}He release rate using measurements of ^{4}He accumulation in samples that can be dated by other dating methods. Longer time scales have also been considered using ^{4}He accumulation (see for example, Andrews and Lee, 1979; Torgersen, 1980, Andrews et al., 1982, 1985; Torgersen and Ivey, 1985; Andrews, 1991; Andrews, 1992; Stute et al., 1992; Mazor and Bosch, 1992; Marty et al., 1993; Castro et al., 1998a, 1998b, 2000; and references therein).

Another means of inferring groundwater age uses calibration of geochemical weathering reactions in aquifers. Some geochemical weathering reactions do not reach equilibrium or partial-equilibrium states in aquifers, and the rates of these irreversible reactions can be calibrated in parts of the aquifer where other dating methods still apply. Aeschbach-Hertig (1998) showed that ^{3}H/^{3}He ages correlated with changes in dissolved solute concentration. Several studies have combined geochemical mass balance models with ^{3}H/^{3}He and CFC dating to determine chemical weathering rates in crystalline-rock watersheds (Rademacher et al., 2001; Burns et al., 2003). Burton et al. (2002) calibrated the rate of release of Na and HCO_3 to groundwater in siliciclastic rocks in the eastern USA using CFC dating on the 0-30-year time scale to estimate ages of more than 100 years for waters with elevated Na and HCO_3. For the same waters, helium accumulation indicated ages of 100-200 years. The geochemical method has also been used to extend dating beyond the radiocarbon time scale in the East Midlands aquifer in England (Edmunds and Smedley, 2000).

7. Age interpretation

Several approaches are recognized for interpreting age information from measured concentrations of environmental tracers in groundwater. The subject can only be introduced here, but the reader is referred to several excellent references (below) for further information. One method calculates the response of the system to input of a tracer over time, assuming various age distribution models for the system. This approach, using lumped-parameter models, is well documented in the literature (Eriksson, 1958; Vogel, 1967; Małoszewski and Zuber, 1982; Grabczak et al., 1982; Małoszewski et al., 1983; Yurtsever, 1983; Zuber, 1986; Burgman et al., 1987; Zuber, 1994; Małoszewski and Zuber, 1996; Cook and Böhlke, 2000), and several software packages are available (Małoszewski and Zuber, 1996; Zoellmann et al., 2001b; Bayari, 2002; Ozyurt and Bayari, 2003; IAEA, 2003). In this case, the derived age information indicates a mean residence time of water in the system, and depending on the selected model, other parameters can be derived. As multiple lumped-parameter models can be considered, it is usually not possible to determine on the basis of a single tracer measurement which, if any, model describes the system under investigation. In cases of limited environmental tracer data, model selection is usually based on available geological and other technical information (Małoszewski and Zuber, 1996), and a mean residence time is estimated on the basis of the selected model. When reporting estimates of groundwater age, it is necessary to qualify the age with the model on which it is based.

In some cases, it is possible to use tracer data to better resolve which lumped-parameter model, and associated model parameters, best describes the system: (1) using a series of measurements of the tracer from the site over a period of time, (2) using measurements of multiple tracers collected from the site at a single time (see, for example Loosli et al., 2000), or (3) using measurements of the same tracer from multiple sites in the system, but, as pointed out by Zoellmann et al. (2001b), such an approach requires determining mean residence time at each site separately.

Each environmental tracer that can be considered for dating young groundwater has, to some extent, a unique temporal pattern of input, and, therefore, plots of one tracer against another, with comparison with theoretical relations expected for appropriate lumped-parameter mixing models, can sometimes be useful in distinguishing hypothetical mixing processes. If all tracers were reliable (no contamination, no degradation, no terrigenic sources, etc.), it should be possible to derive information about the age frequency distribution and the magnitude of the mean ages for a group of samples from the same system. For example, a water sample that is not a mixture should plot at a point along the piston-flow curve on plots of one tracer vs the other, at points corresponding to the single age of the water. Samples that do not plot on the piston-flow curves are more likely mixtures. Katz et al. (2001) examined a suite of environmental tracers (^{3}H, ^{3}H/^{3}He, CFC-12, CFC-113, and SF_6) in discharge from large springs in Florida, USA, showing that most of the data were consistent with either piston flow, or simple binary mixtures of young and old (pre-tracer) water. Loosli et al. (2000) used a plot of ^{3}H vs ^{85}Kr to demonstrate cases of binary mixing of young and old (pre-tracer) water. In fractured siliciclastics, Burton et al. (2002) demonstrated simple binary mixtures using plots of CFC-113 vs CFC-12. Talma et al. (2000) used plots of ^{14}C, ^{3}H, CFC-11, CFC-12, and CFC-113 in water from fractured rock in South Africa to demonstrate cases of piston flow and binary mixing. From plots of CFCs, SF_6, and ^{3}H in discharge from springs along the crest of the Blue Ridge Mountains of Virginia (Plummer et al., 2001), most tracer data indicated young ages of only a few years, and were insensitive to choice of model. While mixtures of young and pre-tracer water are often recognized in water samples from fractured-rock environments, it is likely that many of the mixtures previously recognized were created in the process of extracting water from boreholes (Burton et al., 2002; Shapiro, 2002). Yet, by using multiple tracers, it is sometimes possible to interpret age information on the young fractions in mixtures.

In mixtures of young and old (pre-tracer) water, the ^{3}H/^{3}He apparent age applies directly to the young fraction in the mixture, but in cases of dating with the parent isotope alone, or dating with anthropogenic atmospheric gases, the measured concentration must be corrected for dilution before attempts to estimate apparent age of the young fraction (see for example, Plummer et al., 1998b). Ratios of CFCs or SF_6/CFC ratios have proven useful in dating young fractions in some groundwater mixtures.

Another important consideration in interpreting age information from environmental tracer data is the thickness of the unsaturated zone and the mechanism by which the tracer is transported into the aquifer. Large differences in apparent age can result when environmental tracers are recharged through thick unsaturated zones. For example, the ^{3}H/^{3}He age will tend to be near zero at the water table beneath deep unsaturated zones, due to diffusive loss of $^3He_{tri}$ into the unsaturated zone air, while apparent ages based on ^{85}Kr and CFCs will be biased old by the diffusive transport from the land surface to the water table (Grabczak et al., 1982; Cook and Solomon, 1995).

In some instances, it may be possible to develop a groundwater flow model for the system, using the tracer data as observations to calibrate the model (see, for example, Reilly et al., 1994; Sheets et al., 1998; Zoellmann et al., 2001a; Mattle et al., 2001). Groundwater age information (travel time) is then calculated from the flow model at specific points in the system (Szabo et al., 1996). Goode (1996) showed that a solute transport model with zero-order source term could be used to directly simulate groundwater age. The simulation takes into account the effects of hydrodynamic dispersion on age, and in conjunction with measured environmental tracer data (Engesgaard and Molson, 1998), the model and age simulation can be refined.

8. Concluding remarks

As originally pointed out by Fabryka-Martin et al. (1985), ideal hydrologic tracers “should be inert, soluble and highly mobile in any hydrologic environment”, have a “known and limited number of sources and sink terms”, “should be widely dispersed but exhibit predictable variability in nature”, and “unbiased sampling techniques and precise analytical measurements must be available”. None of the tracers discussed here fully meet all of these requirements, but instead, each has advantages and limitations in comparison to others. Consequently, a multi-tracer approach is recommended (Grabczak et al., 1982; Beyerle et al., 1999; Bauer et al., 2001; Plummer et al., 2001). And, as we consider the effects of groundwater flow on transport of tracers through aquifers, unless the samples can be interpreted as piston flow, it is once again usually necessary to consider multiple tracers with differing input functions in attempts to interpret mixing processes and age information.

Until recently, much of the research conducted with environmental tracers suitable for dating young groundwater focused on development and testing of methodology. We are at a turning point now where there is need for application of dating tools to solve practical problems in hydrology, some of regional-scale proportions. Some of these problems require collection, analysis and interpretation of large (hundreds to perhaps a thousand) numbers of samples. From a practical standpoint, today it is often not possible to obtain large numbers of samples for noble gas determinations, such as ^{85}Kr or ^{3}H/^{3}He, even though, if available, they would probably prove more useful than tracers such as CFCs and SF_6 that can be collected and analysed in relatively large numbers, but are subject to more complications in interpretation. Recent experiences have shown that simple ^{3}H measurements, in conjunction with CFC-12, CFC-113, or SF_6 can yield a great deal of information on mixing processes and age interpretation. While it is often not practical to obtain as many ^{3}H/^{3}He (or ^{85}Kr) measurements as can be obtained for CFCs or SF_6, there often remain ambiguities in age interpretation that can be resolved from selected measurements of ^{3}H/^{3}He (or ^{85}Kr). In the future, collection and analytical procedures for ^{85}Kr may be improved permitting more routine applications.

Some of the practical problems being addressed today that are making use of environmental tracers include assessment of lag times for groundwater transport of contaminants to rivers and estuaries, reconstruction of historical records of loading of contaminants to aquifers, regional-scale assessment of susceptibility of aquifers in fractured rock and karst environments to anthropogenic contamination, determination of recharge rate and calibration of regional-scale groundwater flow models, and determination of rates of geochemical and microbiological processes in the environment. Even when age information cannot be interpreted, 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, septic tanks, and other contaminant sources, and can be used to assess susceptibility of water-supply wells to contamination from near-surface sources. To meet these environmental challenges, there is need for development of more laboratories capable of providing measurement and interpretation of environmental tracer data in groundwater.

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HYDROCLIMATIC PROCESSES AND SYSTEMS

15. DATING OF OLD GROUNDWATER – HISTORY, POTENTIAL, LIMITS AND FUTURE

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1. Introduction

After the discovery of the ^{14}C method as a chronometer for old groundwater in 1957, scientists concentrated their efforts first on the development of hydrochemical and isotopic models as well as empirical approaches to estimate the initial ^{14}C value of the dissolved inorganic carbon (DIC). Qualitative interpretation of ^{14}C dates was then used in a variety of fieldss to aid understanding the hydrology of groundwater systems. In the 1980s the quantitative interpretation of ^{14}C dates became the advanced practice, applying complex geohydraulic and hydrochemical conceptual models. The difficulty of converting ^{14}C dates into absolute water ages stimulated efforts to search for other isotopes as suitable chronometers for groundwater. In this regard, uranium isotope ratios, krypton-81, chlorine-36, helium-4 and ^{14}C in dissolved organic carbon (DOC) found potentially useful applications. The present challenge to isotope hydrology is the development of a theoretical and practicable platform for simple and direct implementation of absolute groundwater dates in numerical modelling.

2. History of ^{14}C dating of old groundwater

In the history of ^{14}C dating of old groundwater several phases can be distinguished:

- The elaboration of the principles of ^{14}C dating of old groundwater
- Designing models to convert ^{14}C dates of DIC into absolute groundwater ages
- Application of groundwater dating
- Qualitative interpretation of groundwater dates
- Designing conceptual models for quantitative interpretation of groundwater dates.

P.K. Aggarwal, J.R. Gat and K.F.O. Froehlich (eds), Isotopes in the Water Cycle: Past, Present and Future of a Developing Science, 221-241.

2.1. THE PRINCIPLE OF ^{14}C AGE DETERMINATION OF GROUNDWATER

The ^{14}C dating method developed by Libby and coworkers (Anderson et al., 1947) was basically considered as exclusively usable for organic samples related to archaeological and geoscientific studies. The initial ^{14}C value (A_o) of atmospheric CO_2 or contemporary organic matter is, by definition, 100 per cent modern carbon (100 pMC). The conventional ^{14}C age t of a sample with a measureed ^{14}C activity A is calculated as:

$$t = \frac{\tau}{\ln 2} \ln \frac{A_o}{A} \tag{1}$$

where τ is the conventional half life of ^{14}C of 5568 a. In groundwater dating the use of the physical half life of 5730 a is recommended.

In 1951 H.W.Franke proposed that ^{14}C ages could also be determined from inorganic carbon present in the carbonate of speleothem. Münnich (1957, 1968) applied Franke’s concept for dating old groundwater. The principle behind Münnich's concept was that rain water entering the top soil dissolves CO_2 (produced by root respiration and decomposition of contemporary organic matter) with a ^{14}C content of 100 pMC. Carbon dioxide dissolution in water forms carbonic acid, which in turn, dissolves lime in aquifer sediments (with a ^{14}C of nearly 0 pMC) to produce HCO_3^-:

$$CO_2 + H_2O + CaCO_3 \rightarrow Ca^{++} + 2\ HCO_3^- \tag{2}$$

Carbon-14 dates calculated from the results of ^{14}C measurements of DIC are relative, aquifer-specific numerical ages. They yield, however, absolute age differences if secondary hydrochemical and physical changes of ^{14}C can be excluded or corrected for. Such cases are identifiable by e.g. less variable pH and rather constant concentrations of both Ca^{++} and HCO_3^- along the flow path of groundwater (Geyh, 1992). These conditions are often met in confined fresh water resources. They enable the estimation of the tracer velocity, the delineation of the flow path, the determination of regionally valid hydraulic parameters as the hydraulic conductivity of aquitards, the improvement of water budgeting or the calibration of numerical models by means of ^{14}C ages.

2.2. MODIFICATION OF THE INITIAL ^{14}C VALUE OF DIC DURING GROUNDWATER RECHARGE

The hydrochemical process described by Eq. (2) occurs in the unsaturated zone and terminates shortly after the seeping water approaches the saturated zone. Because the carbonate in the unsaturated zone and the aquifer as one of the carbon-bearing components in Eq. (2) is usually nearly free of ^{14}C, the dissolved inorganic carbon (DIC = CO_2 + HCO_3^-) phenomenologically should contain only 50% of the ^{14}C concentration of contemporary organic matter represented by the CO_2 as second component. This means that ^{14}C age calculated with Eq. (1) yields about 5700 years for groundwater with an actual age of zero. This maximum correction of ^{14}C ages of DIC due to this so-called “hard water effect” (Münnich, 1957) or now “reservoir effect” (Olsson, 1979) is in practice smaller. One reason is that bicarbonate only remains in dissolution if CO_2 is dissolved in excess according to the law of mass action. Depending on the pH, this process results in an A_o(DIC) of 55-65 pMC, corresponding to a reservoir correction of -4940 to -3560 a.

A number of “ ^{14}C correction models” have been proposed to estimate A_o of groundwaters, and excellent reviews of these models are given by Fontes (1992) and Clark and Fritz (1997). Models based upon the concentration and/or stable isotope ratios (given as $\delta^{13}C$ values) of groundwater assume closed-system conditions, where only the initially dissolved soil CO_2 is involved (Pearson, 1964; Tamers, 1967; Salem, 1880; Gehy and Wendt, 1995). However, open-system conditions often prevail in the unsaturated zone where the isotopic composition is continously modified by exchange with soil gas CO_2 (Wendt et al., 1967, Wigley, 1977). This process results in an increase of A_o(DIC) to 70–90m pMC, corresponding to a much smaller reservoir correction of -2950 to -870 a. Mook (1972, 1976) included all the basic physical and chemical processes of dissolved carbon evolution in his most far-reaching conceptual model. This model considers isotope fractionation between all carbon-bearing compounds and geochemically distinguishes between open and closed system conditions.

A hydrochemically more complex model was developed by Reardon and Fritz (1978). It adjusted iteratively the simulated evolutionary path of ^{14}C for various initial pH controlled pCO_2 relationships to the measured results. Congruent and incongruent dissolution of carbonate, gypsum dissolution, and ion-exchange reactions for isotope and ionic mass balances were taken into account. An even more realistic mixing-exchange model (Fontes and Garnier, 1979) used a correction for sulphate dissolution, isotope exchange and mixing, as well as isotopic exchange between DIC and solid carbonate in the aquifer rock.

The initial ^{14}C values determined with these correction models usually deviate from each other considerably (Geyh, 1992). As a result many hydrogeologists have become confused in recommending and applying ^{14}C groundwater dating. One reason for the large deviation is the wide range of $\delta^{13}C$ values of the various carbon species in nature, resulting in errors of ^{14}C dating of up to ±5000 years (Tamers, 1975). But such wide confidence intervals of groundwater ages are not acceptable for both applied hydrologists and numerical modellers. When the specific $\delta^{13}C$ values of all dissolved carbon in the recharge area of an aquifer are known, the actual deviation of corrected and uncorrected ^{14}C ages is usually smaller than ±600 years, as demonstrated on a set of ^{14}C groundwater dates by Phillips et al. (1989). The reason for this narrow range is that the regional input parameters of any specific aquifer system scatter less than their worldwide ranges (Geyh, 1992). Pearson (1992) recommends an uncertainty analysis to approximate the parameters to be used for correction models. The few applications of his approach are promising.

A serious problem in the use of the ^{14}C correction models is that several basic assumptions of the models may not be consistent with local conditions. For example, most models assume that the $\delta^{13}C$ and ^{14}C values of lime in the unsaturated zone are zero. However, these values may notably deviate from the zero value (Geyh, 1970) due to the formation of ^{14}C-bearing secondary lime in the unsaturated zone during summertime and its dissolution during the groundwater recharge period in wintertime. A similar effect arises from the presence of young shells with high ^{14}C in the cover sands above coastal aquifers. Consequently, the ^{14}C ages in groundwater may be underestimated. The $\delta^{13}C$ and ^{14}C of soil CO_2 may also deviate from those assumed in the models. While the existing correction models all assume that the CO_2 dissolved in groundwater is produced in the root zone (with a high ^{14}C content), recent studies indicate that CO_2 production may also occur deep in the unsaturated zone from old sedimentary organic matter (Murphy et al., 1992; Buckau et al., 1998; Aggarwal and Dillon, 1998). Because of these and other effects, the assumed $\delta^{13}C$ range of soil CO_2 between -25 and -23‰ and ^{14}C value of nearly 100pMC may often be incorrect and lead to an overestimation of ^{14}C ages.

To overcome these difficulties, empirical approaches were developed to determine the A_o (DIC). They have the advantage that all of the involved regional parameters, hydrochemical reactions and isotope fractionations are automatically considered and A_o (DIC) of relatively high precision may be obtained. A statistical approach from Vogel and Ehhalt (1963) recommended the general use of an initial ^{14}C value of 85 pMC for DIC, corresponding to a reservoir correction of –1300 a. However, a generalized empirical estimate suffers from the same problems as a hydrochemical model. Geyh (1972) recommended the use of individual A_o(DIC) values adapted to the geology and ecology of the recharge areas (Table 1). They reflect the range of A_o(DIC) modelled for open and closed system conditions.

Table 1.Initial ^{14}C values and corresponding reservoir corrections for different recharge areas

geological setting	initial ^{14}C value pMC	reservoir correction a
volcanic rocks, shallow dunes	90 – 100	–1000 to 0
limy sediments, e.g. loess	80 – 90	–1500 to –1000
uncovered or barren karstified rocks, high dunes	65 – 80	–3500 to –1000

The decrease of the ^{14}C value in DIC by radioactive decay along the flow path of groundwater between the recharge and discharge area (Fig. 1) allows an estimation of the reservoir correction (Vogel, 1970) provided any other modification of the ^{14}C value during aging does not occur. If the recharge area is not known, a plot of ^{3}H versus ^{14}C values of DIC in young groundwaters is another often successful approach (Verhagen et al., 1974). A_o is given where ^{3}H disappears (Fig. 2) The concept behind this is that bomb ^{14}C in DIC should be absent if bomb ^{3}H is missing.

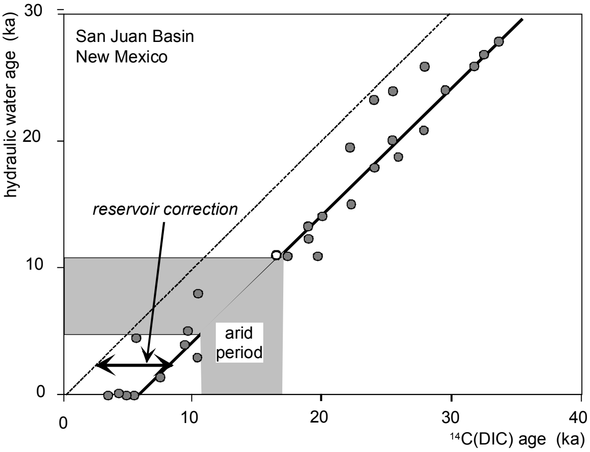

FIG. 1. Estimation of A_o(DIC) ye means of the increase of the water age along the flow path (Vogel and Ehhalt, 1963) demonstrated with ^{14}C dates by Phillips et al. (1989). The reservoir correction is about –5000 a. Groundwater recharge in New Mexico was interruped during the first part of the Holocene.

In order to avoid the problems encountered with the determination of A_o (DIC), attempts have been made to date dissolved organic carbon (DOC). This method might have a potential for dating old groundwater and reasonable ages have been obtained from ^{14}C in fulvic acides (Artinger et al., 1996: Wassenaar and Aravena, 1991). However, the A_o of DOC may considerably deviate from 100 pMC (Long et al., 1992), which would necessitate the use of models for esimating A_o (DOC) and may or may not prove to have advantages over the DIC-based age determimations.

3. Modification of ^{14}C of DIC in the aquifer groundwater

A_0(DIC) is the ^{14}C value immediately after the termination of groundwater recharge . The ^{14}C value of groundwater changes subsequently by radioactive decay during groundwater aging but also by secondary chemical reactions, and by physical as well as advective processes during the groundwater movement in the aquifer. The advanced models (Reardon and Fritz, 1978, Fontes and Garnier, 1979)

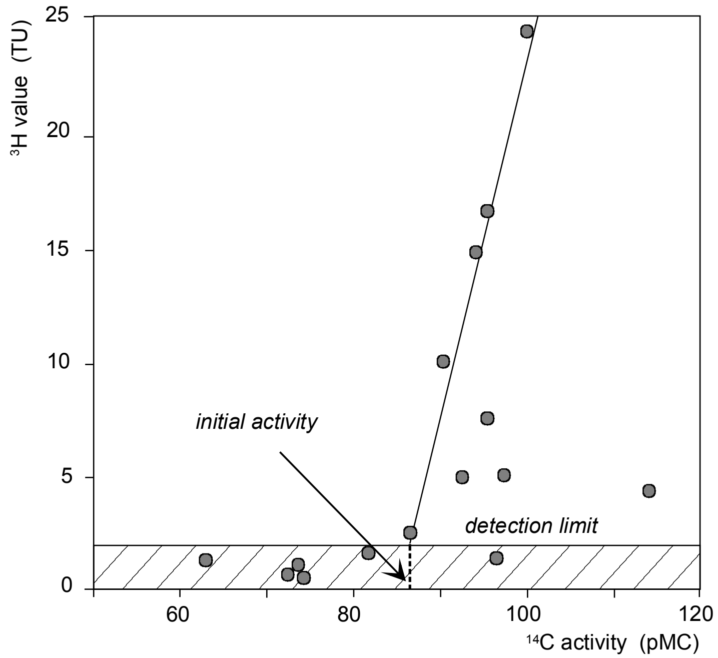

FIG. 2. A plot of ^{3}H versus ^{14}C values of DIC to determine A_o. Tritium below the detection limit (hatched area) verifies absence of bomb ^{14}C and ^{3}H. The initial ^{14}C value is about 87 pMC (Verhagen et al., 1974, Verhagen, 1984).

already consider several hydrochemical impacts, carbon isotope fractionation, and two component mixing to the ^{14}C value of DIC.

The secondary change of the isotopic and hydrochemical compositions along the flow path of groundwater are best simulated by reaction-path modelling (Plummer, 1977, Wigley et al., 1978, Pearson et al., 1983). This is based on an integrated mass-balance approach. The most advanced NETPATH model (Plummer et al., 1991) determines the ^{14}C value of DIC particularly for complex hydrochemical conditions such as redox reductions of sulphate and oxidation of organic matter, precipitation as well as dissolution of secondary calcite and admixture of fossil CO_2 from the earth crust and finally binary mixing. The usefulness of NETPATH is demonstrated by a palaeohydrologic study in Oman (Fig. 3, Clark et al., 1996). In general, the reliability of modelled ^{14}C water ages should be checked using archaeological and palaeoclimatic information (Figs 1 and 3).

Additional hydrochemical reactions have yet to be included in the correction models. One of them is silicate weathering, which is common in arid zones.The

HCO_3^- produced from silicate weathering is also free of ^{14}C, and neglecting the ^{14}C–free HCO_3^- resulting from silicate weathering may lead to ^{14}C ages being overestimated by up to one order of magnitude. Corrections can be made by

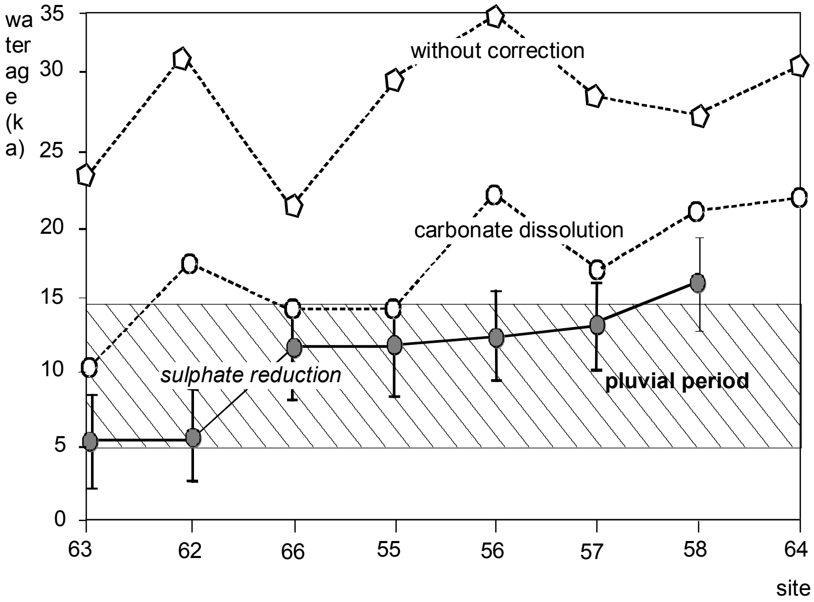

FIG. 3. Iterative hydrochemical correction of ^{14}C data of DIC from the Arabic Peninsula for various geochemical reactions using the NETPATH model. (Clark et al., 1996).

means, for instance, of the $^{86}Sr/^{87}Sr$ ratio (Harrington and Herczeg, 1999) or other stable isotope analyses (e.g. Phillips et al., 1989). A combination of hydrochemical and physical processes can also modify the specific activity of DIC in the aging groundwater. Isotopic exchange between DIC and the carbonate of aquifer rock as well as congruent dissolution and precipitation of carbonate may considerably increase the proportion of ^{14}C free carbon in DIC. As result the ^{14}C age of DIC is apparently too large (Wigley, 1976). Gonfiantini and Zuppi (2003) proposed an empirical correction for these processes by using effective half-lives of ^{14}C of 5000 to 3000 a for karst waters, instead of the physical half-life of 5730 a in Eq.(1).

In dual-porosity structured aquifers, isotopic exchange may occur between ^{14}C in DIC of the mobile groundwater in fractures with that of the less mobile porewater of a highly porous matrix (Elliot, 1999). Carbon-14 ages of DIC considerably increase due to tracer retardation, sorption and matrix diffusion , and deviate notably from the estimated transit time of the water in the fractures.

Małoszewski and Zuber (1984) proposed a simple solution for ^{14}C retardation which is related to both fracture and matrix porosities. In practice, how the matrix porosity can be reliably determined remains a problem.

In shallow aquifers containing very old groundwater, diffusion of $^{14}CO_2$ of the top soil into the groundwater may increase the ^{14}C value and decrease the ^{14}C water age. Palaeohydrologic information preserved in groundwater might become considerably truncated (Sonntag et al., 1979, Groening and Sonntag, 1993).

Advection and admixture processes also may control the ^{14}C value of DIC. One examples is sea-water intrusion. Geyh and Backhaus (1979) and Geyh et al. (1984) studied the advective mixing of groundwaters within multiple leaky aquifer systems. The seepage of young groundwater from the upper aquifer through an aquitard into the deep aquifer changes the water ages in such a way that the determined ages may even reflect an apparent inversion of the actual flow direction of the groundwater. This effect has to be taken into account for any groundwater date.

Lumped-parameter and conceptual models are usable for complex hydrodynamic systems such as fractured or multiple aquifers. Both approaches together may yield absolute dates or transit times in the aquifer required for palaeohydrologic studies and the assessment of non-renewable groundwater resources.

4. Application of the ^{14}C chronometer in applied hydrology

The first determined ^{14}C ages of DIC (Münnich and Vogel, 1959) surprised hydrogeologists, as groundwater in humid regions was found to be much older than previously expected. In the Sahara desert, groundwater ages were found to be more than tens of thousands of years (Knetsch et al., 1962).

Increasing experience in the interpretation of ^{14}C data of DIC has continuously opened new fields of application in hydrology, geohydraulics and palaeohydrology. Meanwhile the number of related publications is so large that only the topics can be mentioned.

4.1. STEADY-STATE CONDITIONS – RECHARGE EQUALS DISCHARGE

In humid regions or under pluvial palaeoclimatic conditions in present arid regions, the recharge rate of groundwater equals its discharge rate. This corresponds to hydrodynamic steady-state conditions, if not disturbed by man, and allows the determination of flow parameters of regional relevance. The difference between ^{14}C ages along the flow path – conventional or if necessary reservoir-corrected – allows calculation of the tracer velocity v_{tracer} in units of length over time. In piston-flow systems tracer is proportional to the Darcy velocity v_{Darcy} given in units of volume over t the cross-sectional area of flow and time. The factor of proportionality is the total porosity n_{total} (Geyh and Backhaus, 1979) rather than the effective porosity. Owing to the usually long residence time of groundwater in the aquifer isotopic exchange occurs between DIC of abstractable and non-abstractable groundwater.

$$v_{Darcy} = n_{\text{total}}\, x\, v_{\text{tracer}} \tag{3}$$

Equation (3) opens the possibility of determining the regionally valid total porosity by comparing the tracer and the modelled Darcy velocity. The tracer velocity is also proportional to the groundwater recharge rate which is required for the assessment of the groundwater budget and the calibration of numerical models (Verhagen et al., 1991). In addition, ^{14}C dates permit delineation of the flow path (Fig. 1) and therefore localization of the recharge area.

In open aquifers ^{14}C profiling of DIC delivers present or past recharge rates (Vogel, 1970, Geyh and Ploethner, 1995, Fig. 4). After the indispensable check that the ^{14}C value was solely controlled by radioactive decay, its depth gradient and the total porosity yields the recharge rate (Geyh and Ploethner, 1995).

The hydraulic conductivity of aquifers (and sometimes also aquitards) is generally determined by aquifer tests. The results are, however, only representative for the limited extension of the cone of depression. Regionally valid parameters require many such tests or ^{14}C dating. In leaky aquifer systems, ^{14}C values of DIC yield regionally valid hydraulic conductivities of the underlain or overlain aquitards (Geyh and Backhaus, 1979, Geyh et al., 1984).

4.2. PALAEOHYDROLOGY

^{14}C dating of groundwater is the usual way to reconstruct the palaeohydrologic history of a region within about the last 45,000 years. In regions with present temperate climate groundwater recharge was interrupted at least during the last glacial maximum. Precipitation was considerably reduced during this period and many recharge areas were blocked by permafrost (Geyh and Wendt, 1965, Andres and Geyh, 1970, Bath et al., 1979). Frequent changes between pluvial and arid periods were reconstructed for present arid and semi-arid areas in northern Africa (Sonntag et al., 1980), western Asia (Wagner and Geyh, 1999), the Arabic Peninsula (Clark et al., 1996, Fig. 3) and North America (Phillips et al., 1989, Fig. 1). Archaeological, historical, palynological and other palaeoclimatological time markers enable the calibration of the relative time scale of ^{14}C dates or checking of the validity of the applied reservoir-corrections (Figs 1 and 3). Important time markers are related to the beginning and end of periods of interrupted groundwater recharge.

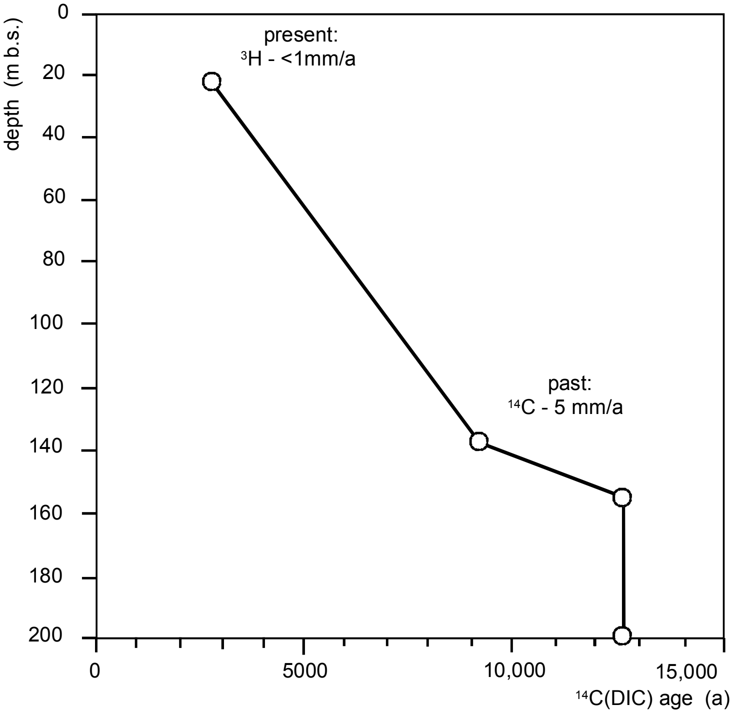

FIG. 4. Estimation of the recharge rate by ^{14}C profiling in the Thar desert. It yields 7 mm/a, which considerably deviates from the present recharge rate of < 1mm/a estimated by ^{3}H measurements of samples from dug wells (Geyh and Ploethner, 1995).

4.3. WATER BALANCE, NUMERICAL MODELLING, GEOHYDRAULIC PARAMETERS

Burdon (1977) suggested in the 1970s that the present piezometric surface of groundwater in arid and semi.arid areas is usually a relict of the decaying water table from a previous pluvial period. It may be only slighly modified by some present groundwater recharge. However, hydrogeologists and numerical modellers seldom consider that the gradient of the groundwater table may be a relict of former steady-state conditions between recharge and discharge.

Then, the present gradient reflects non-steady state conditions: groundwater discharge exceeds recharge. It has become evident for such cases that ^{14}C dating of groundwater is indispensable (e.g. Verhagen et al., 1991, Sanford and Buapeng, 1996) in order to distinguish continuous from discontinuous groundwater recharge. If discontinuous hydraulic conditions are not taken into account, numerical modelling considerably overestimates recharge rates by up to one order of magnitude (Geyh et al., 1995a, 1995b) and the estimation of the safe yield often fails. Conceptual modelling of isotope dates adapted to the palaeohydrologic situation yields more reliable results than numerical modelling, as shown for aquifers at the Nile River near Khartoum, Sudan (Verhagen et al., 1991, Geyh et al., 1995b) and in the Dawwa Basin south of Palmyra in Syria (Geyh et al., 1995a).

On the other hand, isotope hydrologists seldom realize that tracer velocities of groundwater calculated from ^{14}C dates of DIC only allow the estimation of geohydraulic parameters under steady-state conditions. Under non-steady state conditions (in arid and semi-arid areas as well overexploited aquifers) ^{14}C dates do not permit the calculation of reliable geohydraulic parameters. However, the spatial age distribution in such aquifers often permits estimation of upper and lower limits of the recharge rate, of the Darcy velocity or of hydraulic parameters.

Figure 5 elucidates the background for a present arid region. The upper diagram schematically shows three pluvial and arid periods of different intensity. According to this, only groundwater with ages of > 26,000 a, 23,000-18,000 a, and 8000-4000 a is present in the aquifer. Along the flow path of the groundwater four wells A, B, C and D were drilled and sampled for ^{14}C dating. The two apparent tracer velocities derived from the ^{14}C ages of DIC of the wells A-B and C-D correspond to those of the two oldest pluvial periods, respectively, when groundwater continuously recharged. The gradient of the water table of this fossil water resource decays as well as the actual flow velocity decreases. Therefore the ^{14}C dates do not allow an estimate of the past recharge rate or regionally valid geohydraulic parameters as the past piezometric surface and the size of the past recharge area cannot be reconstructed.

The tracer velocity derived from ^{14}C ages of the adjacent wells B-C or all wells A-D is meaningless, as the groundwater recharge was interrupted during the period bracket of the corresponding ^{14}C dates.

4.4. GROUNDWATER MINING

In urban, industrial and intensively used agricultural areas groundwater abstraction often exceeds the safe yield. Then, the groundwater table drops and natural and long-term balance of hydrodynamic conditions becomes disturbed. Young or old groundwater resources become mobilized and mixed. The spatial distribution of the water age in the aquifer may monitor this mining process.

Before the anthropogenic impact, ^{14}C ages of DIC reflect the undisturbed natural geohydraulic situation. Reliable estimates of the actual tracer velocity and regionally valid geohydraulic parameters as well as the delineation of the groundwater flow path are obtained. As soon as the groundwater is pumped excessively, the actual piezometric surface loses its relation to the water age distribution in the aquifer. If young groundwater from e.g. an overlying aquifer is mobilized apparently too young ^{14}C ages of the pumped groundwater are obtained. If old groundwater becomes involved groundwater ages apparently increase. By monitoring the ^{14}C age over many years a forecast of changes in groundwater

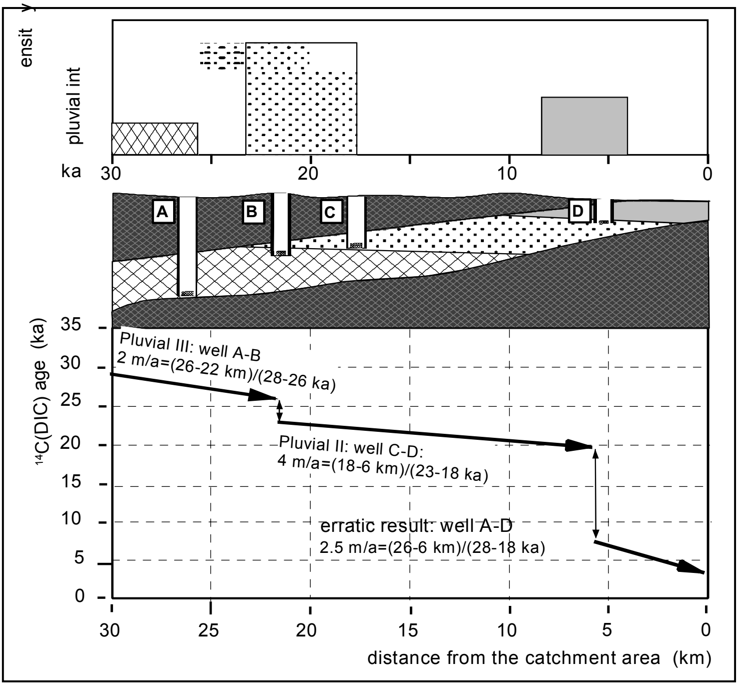

FIG. 5. Scheme of hydrodynamic non-steady state conditions: Groundwater recharge might have occurred before 26,000 a, between 23,000 and 18,000 a, as well as 8000 and 4000 a . The tracer velocities calculated from the ^{14}C *dates of the wells A–B and C–E are valid for the corresponding pluvial periods but* v_{tracer} *of the wells B-C and A-D are hydraulically meaningless as groundwater recharge was interrupted.*

quality can be made due to expected admixture of shallow groundwater polluted with pesticides or industrial and urban waste, by intrusion of ocean water or by advection of deep, often highly mineralized, groundwater or even brine. The resulting deterioration of the water quality due to the lowering of the piezometric surface can be recognized by long-term monitoring of the groundwater age (Geyh and Backhaus, 1979) earlier than by hydrochemical or other parameters (Geyh and Söfner, 1989).

Under suitable hydrologic conditions conceptual models applied to ^{14}C ages and hydrochemical analysis allow the quantification of such advective mixing processes (Verhagen et al., 1991, Fig. 6).

5. Other isotope dating methods

The difficulty of detecting secondary hydrochemical changes of ^{14}C in DIC and performing the corresponding corrections of ^{14}C ages has been one reason to search for other isotopes suitable for groundwater dating. Additional reasons for these efforts were the limited dating range of about 45 ka of the ^{14}C method and the exclusion of highly mineralized waters from ^{14}C age determination. However, one has to keep in mind that any chronometer similar to ^{14}C primarily determines the residence time of the tracer in the aquifer rather than the age of the hosting groundwater. Therefore, the effects of advective and dispersive flow dynamics to the isotope compositions have to be taken into account in any dating approach.

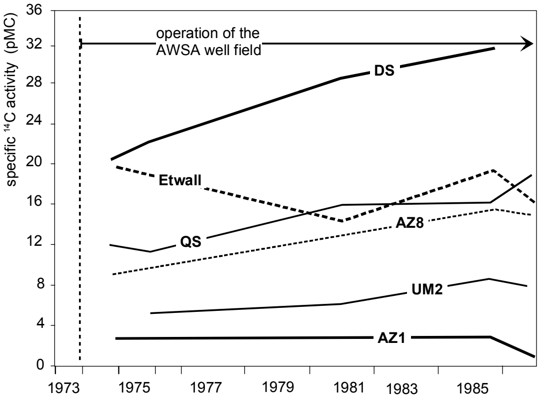

FIG. 6. Groundwater mining study in the Azraq spring area, Jordan: The increase of the ^{14}C value of DIC with time is interpreted as an increase of the proportion of fresh water, recharged within the basaltic outcrop, of the pumped fossil groundwater from the limestone aquifer (Verhagen et al., 1991).

Uranium isotopes appear to have a great potential for absolute groundwater dating between 100 ka and 1 Ma. The uranium concentration in groundwater is mainly controlled by the redox conditions and physicochemical interactions between the groundwater and the rocks in aquifers. The $^{234}U/^{238}U$ activity ratio in the groundwater changes principally as result of selective preferential leaching of ^{234}U, alpha recoil transfer from the aquifer rock and radioactive decay of ^{234}U with a half life of 245,000 years. In the oxygenated zone of the aquifer near the recharge area the uranium concentration rises, while it decreases in the reducing zone. There are several theoretical and empirical studies on uranium isotopes as a chronometer dealing with the isotope processes especially within the reduction zone (Pearson et al., 1983, Fröhlich, 1989). However, uranium concentrations in groundwater are subject to retardation by the complex interaction of reversible sorption as well as irreversible dissolution and precipitation. These processes are dificult to quantify, and therefore only relative ages can be derived from uranium isotope data, not absolute ages. However, reasonable agreement between ^{36}Cl and $^{234}U/^{238}U$ ages was found (Ivanovich et al., 1991).

Rogojin et al. (1998) made a successful attempt to use the change of the ^{234}U excess along the flow path in the aerated zone of a sandstone and of a limestone aquifer for age determination. They find a reasonable promising relationship between the ^{14}C age of DIC and the ^{234}U excess.

Large basins are usually filled with groundwater of ages exceeding the dating range of the ^{14}C method. Moreover, these groundwaters are often highly mineralized. Chlorine-36 as a cosmogenic isotope with a half life of 301 ka appeared to have a potential to determine the residence time of up to 3 Ma for Cl in an aquifer (Bentley et al., 1986a). The first successful attempt confirmed the initially doubted results of geohydraulic modelling in the Great Artesian Basin (GAB) in Australia (Calf and Habermehl, 1984). Chlorine-36 ages of up to 2 million years were determined (Bentley et al., 1986b). Other studies demonstrated the complexity of the interpretation of ^{36}Cl ages particularly for the mineralized groundwater in the Milky Aquifer of Canada (Phillips et al., 1986). Limits of ^{36}Cl dating of groundwater are obvious due to dissolution of salt, admixture of mineralized water and brine, ion filtration and underground production of ^{36}Cl (Andrews and Fontes, 1992). In order to counter the resulting effects, Mazor (1992) recommends performing complementary ^{14}C and Br determinations and including geohydraulic aspects as well as regional input parameters instead of global ones in ^{36}Cl studies.

Another promising cosmogenic isotope as a chronometer for brine and hydrocarbons has been ^{129}I with a half life of 16 Ma. ^{129}I is also emitted by volcanism. The theoretical dating range is 3-80 million years. Underground production may restrict its application in hydrology (Fabryka-Martin et al., 1987). But ^{129}I dates may successfully complement ^{36}Cl dating attempts.

Problems encountered with the dating of highly mineralized groundwater and brines of ages of up to 1 Ma may be solved by applying the cosmogenic ^{81}Kr with a half life of 210 ka. Interferences by hydrochemical interactions and underground production are absent. However, only up to 1100 ^{81}Kr atoms are present per litre of water. They are detected with accelerator mass spectrometers (AMS) after extremely laborious and complex gas extraction and preparation from a sample of about 15 m^3 of water. By introduction of even more advanced measurement techniques (Du et al., 2003) the application of the ^{81}Kr chronometer may became more widespread (Collon et al., 2000, Sturchio et al., 2003). Old brines with ages of up to 20 million years may also be datable with the in situ produced ^{21}Ne excess over that of the atmospheric neon (Weise et al., 1992).

Alpha decay of radionuclides of both the uranium and thorium series produces helium-4, which accumulates in groundwater. The production rate is controlled by the U and Th concentration in the aquifer rocks as well as the advective and diffusive helium flux from mainly the crust and the mantle of the earth. As a consequence the helium excess over that of the atmosphere in the groundwater of confined aquifers may increase over several million of years with rising age if helium loss by diffusion is negligible (Torgersen and Ivey, 1985, Kipfer et al., 2002). The relative time scale or the corresponding accumulation rates are best calibrated by other isotope dates e.g. ^{81}Kr ages (Beyerle et al., 1999, Weise et al., 1992).

6. Challenge to future activities

Many fields in applied hydrology and geosciences have benefited from the application of the methods in dating old groundwater. However, a direct and simple implementation of any numerical groundwater ages into numerical modelling is not yet satisfactory. Basic research is required.

Figure 7 elucidates the problem. For numerical modelling the aquifer to be studied is discretized into a large set of finite elements of very small volume. Geohydraulic parameters are assigned to each of them, based on available hydrogeologic information. The hydraulic pressure field is obtained by iterative adaptation of the finite element parameters until the modelled groundwater table fits the monitored piezometric surface. Solute-transport modelling of natural or artificial tracers calculates the particle way along hydraulic streamlines (particle tracking usually neglects dispersion, retardation and any physical and chemical reactions) or flow-paths between the recharge area and the well, applying statistical Monte-Carlo approaches (random walk, backwards pathline tracking which includes dispersion). For coupled finite-element hydraulic and solute-transport modelling the parameters of all physical and chemical processes during the transport of the tracers must be quantified. The result is the spatial distribution of the corresponding parameters in a structured model. Solute transport modelling is, however, still limited due to the excessive modelling time needed and the lack of verified quantitative parameters.

On the contrary, absolute isotope dating of groundwater is performed on a very small number of samples. Each date represents the weighted and integrated information on mixing, aging as well as physical and chemical modification of the groundwater between the recharge area and the well. The corresponding large involved aquifer volume consists of a very large but difficult to identify number of elements of the computer model. Hence, the measured ^{14}C value of each sample equals the weighted mean of the ^{14}C values of all elements around the well. In the case of flow-path modelling only a finite number of particle tracks along the groundwater flow can be modelled.

The weighted mean of the corresponding results may or may not agree with the measured ^{14}C value. The agreement depends on the reliability of the adapted hydraulic and transport parameters for each element. Erroneous geohydraulic, transport and reactive parameters of the numerical grid elements due to non-identified inhomogeneities in the aquifer result in disagreement.

In a case study (particle tracking) transit times of water particles in a partly confined aquifer are modelled between a few points along the total extension of the well filters and the recharge area (Frenzel et al., 1997). They differ by many thousands of years and do not steadily increase with the well depth. Even their weighted mean sometimes deviated from the corresponding ^{14}C water age.

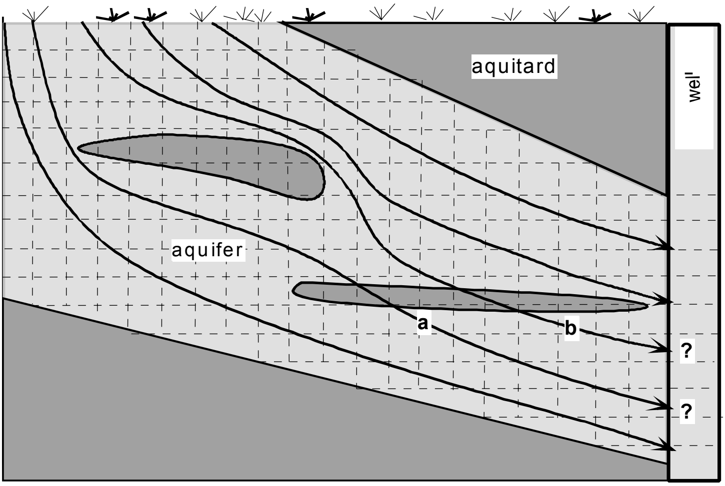

FIG. 7. Schematic sketch to elucidate the problem of implementation of isotope dates into numerical finite-element (squares surrounded by hatched lines) modelling: The ^{14}C *value of the well sample reflects the physical, chemical and advective processes of the groundwater within a large volume of the aquifer (light grey) with less conductive parts (dark grey). The modelled flow paths (arrows) represent only very restricted parts of this volume and may even yield erroneous results if geohydraulic inhomogeneities (a and b) cannot be correctly assigned to the corresponding grid elements.*

There is not yet a practical and often not even a theoretical platform to bridge the gap between numerical dating and numerical modelling. The number of dated samples will always remain small compared to the very large number of elements used in computer modelling. It is a physical, chemical and often a principal mathematical question whether the measured age of an unknown compartment agrees with the mean of modelled ages of a limited, but large number of elements and vice versa. The solution may be to join mathematically and statistically a non-identifiable compartment of the aquifer with geological and geohydraulic parameters.

7. Conclusion

The podium of the still lively, stimulating and often controversial discussion on pros and cons of the various methodical approaches for the interpretation of isotope dates as water ages has been the biannual IAEA conferences on isotope hydrology in Vienna over the last 40 years. They have become the platform for the very intensive scientific and interdisciplinary exchange and the premise of the progress and success of the isotope dating techniques in applied hydrology. The proceedings have become handbooks for the introduction in this field of geoscience as well as an indispensable source of comprehensive isotope hydrologic information for specialists as documented in the large number of IAEA papers cited in the reference list.

There are still hydrogeologists and even environmental physicists who have reservations against isotope dating of groundwater, although there is an uncountable number of successful applications. It is claimed that hydrochemical and other processes during the aging of the groundwater may not allow any reliable age determination. Considering the precision of geohydraulic or hydrologic assessments, seldom better than ±30%, isotope dates can successfully compete and be applied to calibrate numerical models as well as to augment palaeohydrologic knowledge of limited study regions or even in the world.

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16. GEOTHERMAL SYSTEMS

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1. Introduction

Geothermal energy, which is an abundant resource in the Earth's crust, has emerged as an important and clean alternative source of energy for electrical power generation and direct use (Muffler, 1981). Hot waters from thermal springs and shallow wells have been used extensively since prehistoric times for bathing, washing and cooking. For the last 50 years many countries have also used low enthalpy geothermal water (20º–150ºC) for agriculture, aquaculture, space heating, fruit drying, paper manufacturing and other applications (Fridleifsson, 1998). Electrical power generation using geothermal steam started at Larderello, Italy in 1912 (Ellis and Mahon, 1977), and currently a total of over 8000 MW of electricity are generated from geothermal systems in 22 countries, with the USA, Philippines, Italy, Mexico, Indonesia, Japan and New Zealand being the main producers (Duffield et al., 1994; Wright, 1998).

The δ^2H, δ^{18}O and tritium values of water, especially when integrated with the concentrations and isotopes of solutes and gases are powerful geochemical tools for determining the origin, nature, distribution and interactions of fluids in geothermal systems. The stable isotopes of water are especially useful because the relations governing their distribution in present-day surface and shallow groundwaters of an area (the local meteoric water) as well as their modifications in aquifers and geothermal systems are reasonably well known. The isotopes of meteoric water may be modified by evaporation and mixing in shallow aquifers and by mixing, boiling, and isotopic exchange with minerals in geothermal systems. For review articles and many references, see Truesdell and Hulston, 1980; Fournier, 1989; D'Amore, 1992; Kharaka and Thordsen, 1992, and Giggenbach, 1983.

In this summary review, we will discuss the major historical developments in the application of water isotopes and other geochemical tools to the study of geothermal systems. We will cover briefly the major advances in the last 25 years, including determination of isotopic and chemical compositions of solutes and noble gases, application of vapour-phase tracers, and improved geochemical modelling of

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chemical reactions in reservoir processes. These advances, as well as exploration in deep portions of known geothermal systems have led to a better understanding of vapour-dominated systems, associated ore deposits, the influence of magmatic heat sources, the origins of highly corrosive fluids, scaling and corrosion. These advances have helped to optimize injection strategies for improved production and helped to decrease waste disposal costs. Finally, we will discuss an integrated approach, using water isotopes and other geochemical and hydrologic parameters to investigate the recharge to the hydrothermal system at Yellowstone National Park, USA, the largest geothermal system in the world.

2. Water stable isotopes

Early studies of high-temperature hot-spring waters in Iceland, New Zealand, Japan, and Yellowstone National Park (USA) and of fumarolic steam at Larderello (Ita ly), The Geysers (USA), and Lassen (USA) could not determine the origin of the water and steam. Many workers thought that the water, like the heat, was magmatic, or was juvenile; others suggested that at least part of the water was meteoric based on seasonal changes in temperatures and flow rates (e.g. Allen and Day, 1927; White, 1957). This question could not be settled until Alfred Nier designed the first mass spectrometer in 1936, which was used first by Epstein and Mayeda (1953) to determine the $^{18}O/^{16}O$ ratios and by Friedman (1953) to determine $^{2}H/^{1}H$ ratios in natural waters. The meteoric origin of most geothermal water was largely settled when the pioneering studies of Craig and his colleagues showed that geothermal fluids are similar in deuterium content to local precipitation (Fig. 1) regardless of where the geothermal system was located (Craig, et al., 1956; Craig, 1963).

Craig (1963) showed that high-temperature geothermal systems have waters with the same $\delta^{2}H$ value as local precipitation but have variable amounts of enrichment in ^{18}O. This “oxygen-shift” is attributed to exchange of oxygen in the water molecule with oxygen in silicate and carbonate minerals in the confining rocks (~50% of the rock mass is oxygen atoms). Oxygen mass balance equations, together with isotope fractionation factors between water and minerals (Table 1), can be used to calculate the “oxygen-shift” in both water and rocks (e.g. Kharaka and Thordsen, 1992). Results show that high “oxygen-shifts” occur in water in high-temperature systems with fresh rock and relatively little water throughput. Small or negligible oxygen-shifts are observed in old systems where the isotopic composition of the rock have been shifted to equilibrium with the water and in low-temperature systems where the rate of exchange between the water and rock are too slow to cause a change in the isotopic composition of water as it passes through the system. Deuterium values of water do not usually change significantly by water–rock isotope exchange because most rock has very little hydrogen (<1% by mass). However, geothermal water in sedimentary or other rocks high in clay minerals can also undergo significant deuterium shifts (Kharaka and Thordsen, 1992; Kharaka et al., 2002).

Table 1. Oxygen isotope fractionation factors between water and minerals as a function of temperature (T) in °K (from Kharaka and Thordsen, 1992).

Equation	Reference
$1000\ell n\alpha(\text{quartz-}H_2O) = 3.38 \times 10^6T^{-2} - 2.90$	Friedman and O'Neil (1977)
$1000\ell n\alpha(\text{amorph. silica-}H_2O) = 3.52 \times 10^6T^{-2} - 4.35$	Kita et al. (1985)
$1000\ell n\alpha(\text{albite-}H_2O) = 2.39 \times 10^6\ T^{-2} - 2.51$	Matsuhisa et al. (1979)
$1000\ell n\alpha(\text{K feldspar-}H_2O) = 2.91 \times 10^6T^{-2} - 3.41$	O'Neil and Taylor (1967)
$1000\ell n\alpha(\text{calcite-}H_2O) = 2.78 \times 10^6T^{-2} - 2.89$	Friedman and O'Neil (1977)
$1000\ell n\alpha(\text{dolomite-}H_2O) = 3.34 \times 10^6T^{-2} - 3.34$	Land (1983)
$1000\ell n\alpha\ (\text{protodolomite-}H_2O) = 2.78 \times 10^6T^{-2} + 0.11$	Land (1983)
$1000\ell n\alpha(\text{ankerite-}H_2O) = 2.78 \times 10^6T^{-2} + 0.32$	Dutton and Land (1985)
$1000\ell n\alpha(\text{siderite-}H_2O) = 3.13 \times 10^6T^{-2} - 3.50$	Carothers et al. (1988)
$1000\ell n\alpha(\text{anhydrite-}H_2O) = 3.21 \times 10^6T^{-2} - 4.72$	Chiba et al. (1981)
$1000\ell n\alpha(\text{kaolinite-}H_2O) = 10.6 \times 10^3T + 0.42 \times 10^6T^{-2} - 15.34$	Savin and Lee (1988)
$1000\ell n\alpha(\text{smectite-}H_2O) = 2.58 \times 10^6T^{-2} - 4.19$	Savin and Lee (1988)
$1000\ell n\alpha(\text{illite-}H_2O) = 2.39 \times 10^6T^{-2} - 4.19$	Savin and Lee (1988)
$1000\ell n\alpha(\text{illite/smectite-}H_2O) = (2.58 - 0.19 \times I) \times 10^6T^{-2} - 4.19$	Savin and Lee (1988)
I = fraction of illite (0.0 – 1.0)	
$1000\ell n\alpha(\text{chlorite-}H_2O) = -8.38 \times 10^3T^{-1} + 4.81 \times 10^6T^{-2}$	Cole (1985)
$1000\ell n\alpha(\text{pyrophyllite-}H_2O) = 1.08 \times 10^3T^{-1} + 2.76 \times 10^6T^{-2} - 5.37$	Savin and Lee (1988)

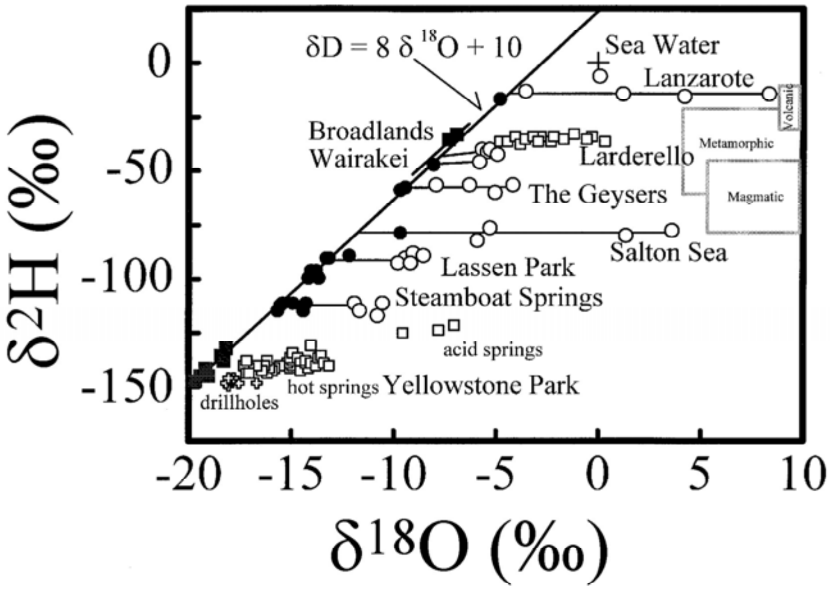

FIG. 1. Oxygen-18 and deuterium compositions of hot springs, fumaroles, and thermal wells (open symbols) and local meteoric waters (filled symbols). Modified from Truesdell and Hulston (1980).

Although oxygen exchange is the most important process that changes water isotopes as thermal fluids pass through the rock matrix at high temperature, other processes can modify the isotopic composition of thermal water as it rises from depth to discharge at the land surface. In high-temperature geothermal systems of large discharge, boiling and steam loss accompanied in some cases by mixing with cold groundwater can appreciably alter water isotope compositions. Boiling can occur at depth and the steam and boiled water remain in contact until discharged at the land surface (single-step steam separation) or boiling can occur constantly with the steam separating from the fluid as it rises to the land surface (continuous steam separation). Single-step steam separation is usually the dominant process and it has a larger effect on the isotopic composition of the water than continuous boiling. The effect of single-step boiling can be calculated from the isotope balance equation below:

$$\delta_o = \delta_s y_s + \delta_w(1-y_s) \tag{1}$$

where δ_o is the isotopic composition of the single liquid phase before separation, δ_s is the isotopic composition of the vapour phase after separation, δ_w is the isotopic composition of the liquid phase after separation, and y_s is the steam fraction. The value of y_s can be calculated (Eq. (2)) below, from the enthalpy of the single liquid phase prior to boiling (H_o), the enthalpy of the stream at the separation temperature (H_s), and the enthalpy of the liquid at the separation temperature (H_w).

$$y_s = (H_o - H_w)/(H_s - H_w) \tag{2}$$

Isotope exchange between liquid and vapour is fast enough at boiling temperatures so that isotopic equilibrium can be assumed and therefore the distribution of isotopes can be assumed to be governed by an equilibrium constant (α). The measured isotopic values for deuterium and oxygen-18 in water and steam are therefore related by the equilibrium equation

$$1000 \ln\alpha \approx 1000(\alpha-1) \approx \delta_w - \delta_s \tag{3}$$

by mass balance, and substitution of 1000 $\ln\alpha$ for $\delta_w - \delta_s$, we get

$$\delta_w \approx \delta_o + y_s (1000 \ln\alpha) \tag{4}$$

Table 2. Temperature dependence of Deuterium and Oxygen-18 fractionation factors between water and steam, $10^3\ln\alpha$. Values for integral I (single stage steam separation), and I_n (continuous steam separation). For details see Truesdell et al. (1977).

	Deuterium			Oxygen-18	
T °C	$10^3\ln\alpha$	I	I_n	$10^3\ln\alpha$	I
0	106.0	0.000	0.000	11.20	0.000
20	81.5	3.021	0.034	9.54	0.349
40	61.3	5.377	0.068	8.17	0.651
60	46.4	7.197	0.103	7.03	0.916
80	36.1	8.640	0.139	6.07	1.150
100	27.8	9.792	0.176	5.24	1.357
120	21.5	10.710	0.214	4.53	1.542
140	16.3	11.443	0.253	3.91	1.707
160	11.7	12.008	0.294	3.37	1.855
180	7.4	12.414	0.337	2.90	1.989
200	3.5	12.654	0.382	2.48	2.110
220	0.1	12.739	0.430	2.10	2.219
240	-2.2	12.680	0.482	1.77	2.319
260	-3.6	12.509	0.538	1.46	2.410
280	-4.0	12.261	0.602	1.19	2.494
300	-3.4	11.986	0.675	0.94	2.571
320	-2.2	11.735	0.764	0.70	2.644
340	-1.3	11.536	0.881	0.45	2.710
360	-0.5	11.374	1.073	0.19	2.769
374	0.0	11.279	2.018	0.00	2.805

Values for 1000 $\ln\alpha$ at various temperatures are listed in Table 2, compiled from data given by Truesdell et al. (1977) and Henley et al. (1984). Truesdell et al. (1977) derived Eq. (5) below, that relates initial isotope values to final isotope values by continuous steam loss

$$\delta_{wf} - \delta_{wo} \approx I_{to} - I_{tf} \tag{5}$$

where δ_{wf} is the isotopic composition of the water (deuterium or oxygen-18) after boiling, δ_{wo} is the initial isotopic composition of the water (deuterium or oxygen-18), I_{to} is a calculated value based on the initial water temperature and I_{tf} is a calculated value based on the final water temperature after boiling (Table 2).

Mixing of thermal and fresh waters can also modify the isotopic composition and concentrations of dissolved constituents of thermal waters as they move from an aquifer at depth to the land surface. However, mixing has sometimes been assumed without good evidence that it has actually occurred. The best evidence for mixing is a linear relation between δ^2H and dissolved chloride. Data of Mariner and Wiley (1976) for thermal springs and wells in Long Valley, California illustrate (Fig. 2) mixing in a relatively simple high-temperature geothermal system. In this system, recharge water of $\delta^2H = -115‰$ and $\delta^{18}O = -16.0‰$ is heated to 240°C, dissolving chloride, and undergoing oxygen shift to produce thermal water similar to that obtained from the geothermal well ($\delta^2H = -115‰$, $\delta^{18}O = -14.2‰$, 280 mg Cl/L). As the deep thermal water rises to the surface it mixes with a dilute groundwater to produce a range in spring compositions (Fig. 2). Boiling has modified the composition of two of the thermal springs and, to a small extent, the geothermal well causing these data to plot above the mixing line for the thermal springs. In large high-temperature systems various combinations of boiling, non-equilibrium evaporation, and mixing can produce a tremendous range in deuterium and chloride compositions, as was shown by Truesdell et al. (1977) for Norris Geyser Basin in Yellowstone National Park. In the Norris Basin, boiling (single stage or continuous) of a single high-temperature geothermal fluid, non-equilibrium evaporation, and mixing the products of boiling with dilute groundwater has produced thermal spring waters that range in chloride from near zero (acid-sulphate springs) to almost 800 mg Cl/L, and deuterium values that range from about $\delta^2H = -120‰$ (non-equilibrium evaporation) to $\delta^2H = -146‰$ (continuous steam separation).

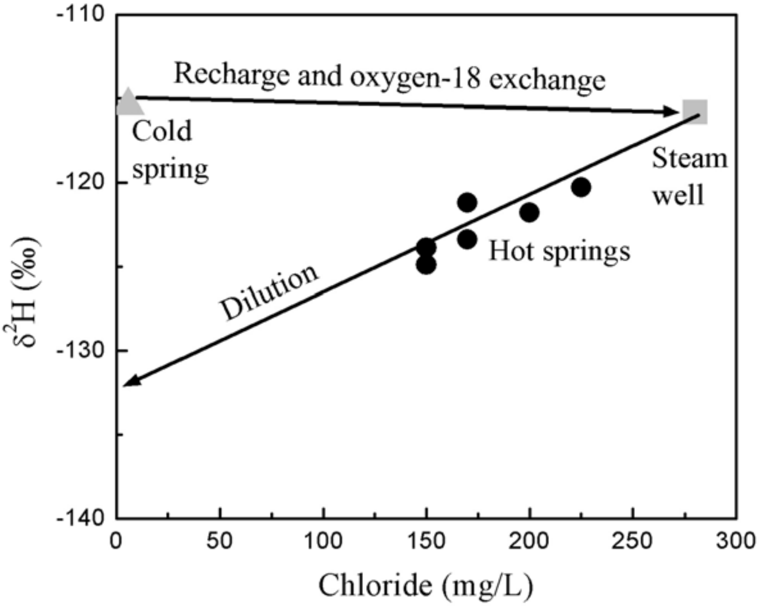

FIG. 2. Plot of δ^2H-Chloride for thermal springs, a cold spring, and a thermal well, Long Valley California, USA. Data from Mariner and Wiley (1976).

3. Noble-gas systematics

The isotopic compositions of noble gases (especially helium) have proved to be critical in detecting a magmatic component in geothermal fluids. Noble gases are excellent natural tracers because they are chemically inert (conserved during water–rock reaction or phase changes), moderately soluble in water (solubilities of the noble gases are known up to the critical point for water), and have distinctly different isotopic compositions depending on their origin (mantle, crust, atmosphere). ^{3}He/^{4}He values for mantle, crust, and atmosphere are ~(1.2 - 4.8) x 10^{-5}, ~3 x 10^{-8}, and ~1.4 x 10^{-6}, respectively. By convention the isotopic composition of a particular noble gas in the atmosphere is the standard against which noble gas isotope values for that gas are compared. Thus a ^{3}He/^{4}He value of 7 Ra indicates that the sample has a ^{3}He/^{4}He value that is 7 times the air value. Rock thought to originate in the mantle has ^{3}He/^{4}He values that range from ~9 Ra (Mid-Ocean Ridge Basalt – MORB) to ~32 Ra (Ocean Island Basalt – OIB). Crustal rocks have ^{3}He/^{4}He values as low as ~0.02 Ra. Although conserved during water–rock reaction and phase changes, large variations in ^{3}He/^{4}He values can occur across a basin as a result of boiling. Kennedy et al. (1985) showed that changes in ^{3}He/^{4}He values across Lower Geyser Basin in Yellowstone National Park (~2.7 to 7.7 times the air value) were due to deep boiling and steam separation. The extent to which deep fluids are diluted decreases from south to north across Lower Geyser Basin, thus more boiling occurs on the north side of the basin. Values of ^{3}He/^{4}He are higher to the south, where less boiling occurs. Boiling allows helium to escape from the liquid and concentrate in the vapour phase. The isotopic composition of the relatively little remaining helium in the residual liquid is then altered by addition of radiogenic helium from the local rock. This study illustrated the need for collecting multiple samples of even conservative constituents in geothermal systems that discharge over large areas.

4. Heavy solute isotopes

Isotopes of heavy atoms that do not fractionate during chemical reactions or phase changes (Pb, Sr, Nd, etc.) can provide insights into flow paths, flow directions, and chemical reactions. Lead isotopes can be particularly useful in determining the rock through which thermal fluids have circulated when there is a contrast in the lead isotope compositions of several possible aquifer-rocks. Low-temperature thermal systems along the south side of the Snake River Plain in southern Idaho illustrate how it is possible to determine the composition of the principal aquifer-rock from the lead isotope composition of the thermal water (Mariner et al., 1997). A very large volume of thermal water (25° to 70°C) is withdrawn from shallow wells in the Snake River Plain for space heating, agriculture, and aquaculture. All wells in the Plain are completed in Tertiary rock (Idavada volcanics) and waters produced from these wells are high in fluoride, silica, and pH (~8). A very few wells between the plain and the mountains of northern Nevada are completed in Palaeozoic limestones. Waters recovered from wells completed in the limestone are high in calcium, low in silica and fluoride, and have pH values between 6 and 7. Is the thermal fluid recovered from wells on the Snake River Plain circulating solely in the Idavada volcanics, or is at least some of the fluid being transported from the recharge area to the south (Humboldt Mountains of northern Nevada) in a Palaeozoic limestone? Lead isotope results for the thermal wells sampled in the Twin Falls area are shown on Fig. 3. Of the 29 thermal springs and wells sampled in the study, 26 form a strong linear trend ending in a field on the ^{208}Pb/^{204}Pb vs ^{206}Pb/^{204}Pb plot in which Palaeozoic limestones are located. Cuttings from a thermal well south of the plain that had been completed in the Palaeozoic limestone, and several rock samples from Palaeozoic limestone units in northern Nevada, were treated with weak acid to dissolve the rock sample partially and then the residue was dissolved in strong acid. Lead isotope values from the two samples (weak acid treatment and strong acid treatment) can then be used to establish a line along which waters which have dissolved more or less of the rock will plot. Most thermal waters recovered from wells in the Snake River Plain, plot along a line pointing to the composition of the limestone recovered from a thermal well south of the Plain. The few samples that do not plot along the trend line to the limestone

(Fig.3) have lead isotope values that plot between the limestone trend and the composition of the Tertiary volcanics. Clearly all of the thermal waters in the Twin Falls area circulate principally through one regional Palaeozoic limestone and it is the large storage capacity of this limestone that has permitted the tremendous increase in fluid extractions that have occurred in this area in the last 25 years. The gross chemical characteristics (high silica, fluoride, and pH) of the waters recovered from wells on the Snake River Plain is due to rapid water–rock reaction in the Tertiary rhyolite tuffs of the Idavada volcanics after the fluids left the limestone. The lead composition of the water changes much more slowly than the gross chemical characteristics. A few waters have picked up some lead that has the isotopic characteristics of the Idavada volcanics but most thermal waters still have lead compositions characteristic of the Palaeozoic unit.

5. Age of geothermal water

A number of radioactive isotopes produced primarily by cosmic rays interactions in the upper atmosphere, especially ^{3}H (Brown, 1961), ^{14}C (Clark and Fritz, 1997), ^{36}Cl (Andrews et al., 1994; Phillips, 2000) and ^{129}I (Moran et al., 1995; Fabryka-Martin, 2000), as well as dissolved ^{4}He (Torgersen and Clarke, 1985; Solomon, 2000) have been used, in conjunction with stable isotopes and calculated flow rates, for the determination of ages of natural waters, including geothermal fluids (Bethke et al., 1999, 2000). The half-life for ^{3}H (12.32 a) is relatively short for dating most geothermal systems, but Pearson and Truesdell (1978) used model calculations based on tritium values in thermal water from many geyser basins in Yellowstone National Park, USA to calculate an age of 200–1000 a. The half-life for ^{14}C, at 5.73 ka, makes it useful for dating geothermal and other natural waters of meteoric origin (up to ~40 ka), but ^{36}Cl ($t_{1/2}$ = 0.301 Ma) is applicable to dating water of up to ~2 Ma. The ratio of ^{129}I ($t_{1/2}$ = 15.7 Ma) to total I may be used to estimate ages of up to about 80 Ma, and even older ages are theoretically possible using ^{4}He generated from the decay of U and Th in rocks (Froehlich et al., 1991). All ages estimated from radioactive isotopes, however carry large uncertainties, because the isotopes may have several sources (e.g. Fabryka-Martin, 2000) and often are subject to fractionations from isotopic exchange and partitioning. In addition, the origin and age of H_2O in the formation water generally is different from that of the radiogenic and other isotopes used for age determinations (Froehlich et al., 1991; Kharaka and Thordsen, 1992; Clark and Fritz, 1997).

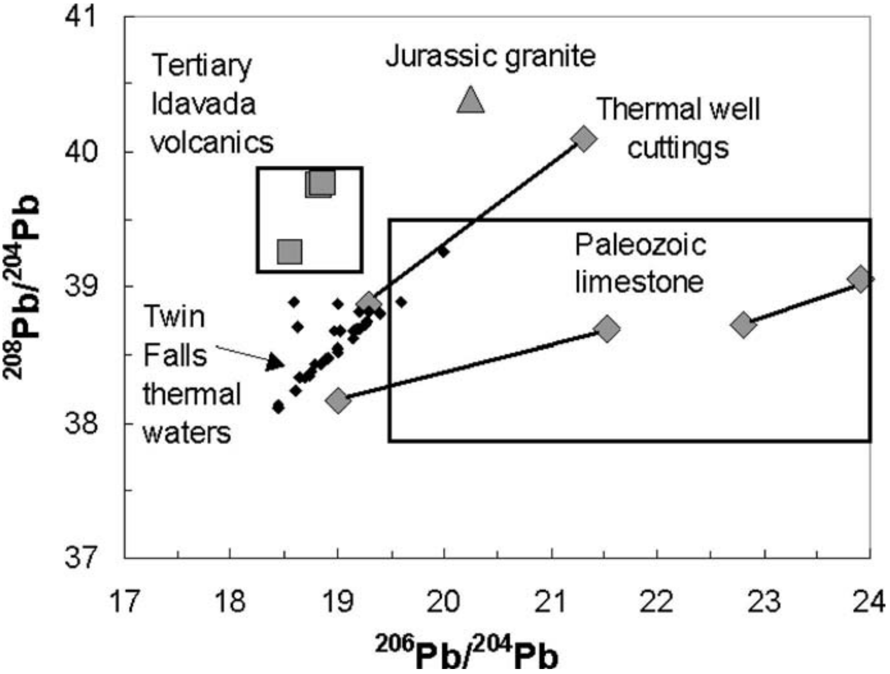

FIG. 3. Lead isotope data for thermal waters in the Twin Falls area, southern Idaho, USA. Possible aquifer-rock includes Palaeozoic limestone, Jurassic granite, and Tertiary Idavada volcanics. Two data points are shown for each Palaeozoic limestone because samples were treated initially with weak acid; residue from this treatment was then dissolved in strong acid.

6. Isotope and chemical geothermometry

6.1. WATER AND SOLUTE ISOTOPES

Several geothermometers utilizing some combination of hydrogen, oxygen, sulphur, or carbon isotopes have been proposed but are rarely used. An isotope geothermometer that deserves to be more widely used in water-dominated systems is based on the temperature dependent fractionation of ^{18}O between dissolved sulphate and water (Eq. (6); Mizutani and Rafter, 1969). Isotopic equilibration between sulphate and water is fast enough (~1 year at 250°C) to attain equilibrium in a reasonable length of time in geothermal reservoirs but still slow enough at lower temperatures so that the isotopic compositions of sulphate and water does not change prior to analysis (Truesdell and Hulston, 1980).

$$1000 \ln\alpha_{SO4\text{-}H2O} = 2.88 \times (10^6/T_{°K}^2) - 4.1 \qquad (6)$$

Conversion of H_2S to SO_4 after sample collection is a serious problem and must be prevented. Treatment with formaldehyde to kill the sulphur-oxidizing bacteria or removal of the sulphide as ZnS or CdS prevents this conversion. Any process that changes $\delta^{18}O_{SO4}$ or $\delta^{18}O_{H20}$ after the water leaves the geothermal reservoir will lead to erroneous sulphate-water isotope geothermometer results. A useful check in many geothermal systems is to use a solution-mineral equilibrium program to determine the temperature at which the water would be saturated with respect to anhydrite. If the temperature at which the water is theoretically saturated with respect to anhydrite is within a few degrees of the equilibrium temperature for fractionation of ^{18}O between the sulphate and water than it is very likely that the estimated temperature from the sulphate–water isotope geothermometer is a good indication of the temperature in the geothermal system. If the temperature of anhydrite saturation is appreciably lower than the temperature estimated from the sulphate–water isotope geothermometer then conversion of sulphide to sulphate or dissolution of a sulphate mineral between the geothermal reservoir and the spring (or well) is to be suspected. If the temperature of anhydrite saturation is higher than the temperature estimated from the sulphate–water isotope geothermometer then dilution or lack of anhydrite in the geothermal reservoir is to be suspected.

6.2. GAS ISOTOPES AND COMPOSITION

Gas composition data pioneered by Werner Giggenbach (Giggenbach, 1980), Franco D'Amore (D'Amore and Panichi, 1980, D'Amore, 1992), and Stefan Arnorsson (Arnorsson and Gunnlaugsson, 1985) and gas isotope data (Richet et. al., 1977; Panichi et. al., 1979) are powerful tools in geothermometry, especially in volcanic areas and vapour-dominated geothermal systems. Many gas geothermometers have been proposed utilizing gas concentrations or some ratio of them, including CO_2, CO, CH_4, H_2, H_2S, N_2, NH_3, or Ar (Table 3).

Arnorsson and Gunnlaugsson (1985) reported good agreement between measured temperatures in geothermal wells and the average of the temperatures estimated from the CO_2, H_2S, H_2, and CO_2/H_2 geothermometers in nearby fumaroles. Geothermal well temperatures ranged from 280° to 290°C in the Nesjavellir geothermal field, Iceland whereas average geothermometer temperatures for gas collected from nearby fumaroles ranged from 268° to 286°C.

The water–hydrogen and carbon dioxide–water isotope geothermometers, (Richet et al., 1977), have proven useful in fluids recovered from geothermal wells (Panichi et. al, 1979; Nuti, 1992).

Table 3.Equations for calculating temperature (t in °C) in geothermal systems from gas concentrations (mmoles gas per kg of steam at 1 atm) (modified from Arnorsson, 1992).

Geotherm	Equation	Temp. range °C
$CO_2\text{-}CH_4\text{-}H_2\text{-}H_2S$[1]	$t = 24775/(2Log(CH_4/CO_2)-6Log(H_2/CO_2)-3Log(H_2S/CO_2))$	(50°-300°C)
$H_2\text{-}CO_2$ [2]	$t = 190.3 + 55.97(LogH_2 + 0.5LogCO_2) - 0.14(LogH_2 + 0.5LogCO_2)^2$	(>200°C)
$H_2S\text{-}CO_2$ [2]	$t = 194.3 + 56.44(LogH_2S + 1/6LogCO_2) + 1.53(LogH_2S + 1/6LogCO_2)^2$	(>200°C)
CO_2 [3]	$t = -44.1 + 269.25(LogCO_2) - 76.88(LogCO_2)^2 + 9.52(LogCO_2)^3$	(100°-330°C)
H_2S [3]	$t = 246.7 + 44.81LogH_2S$	(>200°C)
	Use for water >300°C and 200°-300°C, with Cl >500 ppm	
H_2S [3]	$t = 173.2 + 65.04LogH_2S$	(>100°C)
	Use for water <200°C and 200°-300°C, with Cl <500 ppm	
H_2 [3]	$t = 277.2 + 20.99LogH_2$	(>200°C
	Use for water >300°C and 200°-300°C, with Cl >500 ppm	
H_2 [3]	$t = 212.2 + 36.59Log H_2$	(>100°C)
	Use for water <200°C and 200°-300°C, with Cl <500 ppm	
CO_2/H_2 [3]	$t = 341.7 - 27.58(LogH_2 + \frac{1}{2}LogCO_2)$	(>200°C)
	Use for water >300°C and 200°-300°C, with Cl >500 ppm	
CO_2/H_2 [3]	$t = 311.7 - 66.72(LogH_2 + \frac{1}{2}LogCO_2)$	(>100°C)
	Use for water <200°C and 200°-300°C, with Cl <500 ppm	
H_2S [3]	$t = 304.1 - 39.48(LogH_2S + 1/6Log CO_2)$	(>200°C)
	Use for water <200°C and 200°-300°C, with Cl >500 ppm	
$CO_2\text{-}CH_4\text{-}H_2$ [3]	$t = 244.6 - 17.44(LogCH_4 - Log CO_2 - 4LogH_2) - 0.136(LogCH_4 - Log CO_2 - 4LogH_2)^2 - 0.00524(LogCH_4 - Log CO_2 - 4LogH_2)^3$	(>100°C)
CO_2/N_2 [4]	$t = 135.9 + 63.14(Log(CO_2/N_2)) + 6.241(Log(CO_2/N_2))^2 - 1.813(Log(CO_2/N_2))^3$	(>100°C)
	Assumes N_2 in air was in equilibrium with recharge water at 25°C	
CO_2/N_2 [4]	$t = 135.9 + 63.14(Log(CO_2/N_2)) + 6.241(Log(CO_2/N_2))^2 - 1.813(Log(CO_2/N_2))^3$	(>100°C)
	Assumes N_2 in air was in equilibrium with recharge water at 25°C	

Source: [1] D'Amore and Panichi (1980); [2] Nehring and D'Amore (1984);
[3] Arnorsson and Gunnlaugsson (1985); [4] Arnorsson (1987)

6.3. CHEMICAL COMPOSITION

The ratios of Li/Na, K/Na, and Rb/Na in formation waters, including geothermal waters, generally increase with increasing temperatures. The proportions of alkali metals alone or combined with those of alkaline-earth metals (Mg and Ca in particular), and the concentrations of SiO_2 are so strongly dependent on subsurface temperatures that they have been combined into several chemical geothermometers (Table 4) that can be used to estimate these temperatures. The most useful "chemical markers" to indicate increasing subsurface temperatures in geothermal systems are the concentrations of silica, boron and ammonia, and the ratios of Li/Mg, Li/Na and K/Na. Excellent reviews of chemical geothermometry are reported in Fournier et al. (1974), Kharaka and Mariner (1989) and Pang and Reed (1998).

Table 4. Equations for the chemical geothermometers and their applicability for use in geothermal and other waters (after Kharaka and Mariner, 1989).

Geothermometer	Equation[a]	Recommendations
Quartz	$t = \frac{1309}{0.41 - \log(k \cdot pf)} - 273$ $k = \frac{\alpha H_4SiO_4}{\alpha H_2O^2}$; $pf = (1 - 7.862x10^{-5} e^{(3.61x10^{-3} \cdot t)} p)$	70°C – 250°C
Chalcedony	$t = \frac{1032}{-0.09 - \log(k \cdot pf)} - 273$	30°C – 70°C
Mg-Li	$t = \frac{2200}{\log(\sqrt{Mg/Li}) + 5.47} - 273$	0°C – 350°C
Na-K	$t = \frac{1180}{\log(Na/K) + 1.31} - 273$ *Do not use in oil-field waters*	
Na-K-Ca	$t = \frac{1647}{\log(Na/K) + \beta\left[\log(\sqrt{Ca/Na}) + 2.06\right] + 2.47} - 273$ *Do not use in oil-field waters* $\beta = 4/3$ for $t < 100$;$= 1/3$ *for* $t > 100$ *Mg-corrected* *Same as Na-K-Ca (above) with Mg-corrections*	
Na-K-Ca	$t = t_{Na\text{-}K\text{-}Ca} - \Delta t_{Mg}$ For $0.5 < R < 5$ $\Delta t_{Mg} = 1.03 + 59.971 \log R + 145.05(\log R)^2$ $- 36711 (\log R)^2/T - 1.67x10^7 \log (R/T^2)$; For $5 < R < 50$ $\Delta t_{Mg} = 10.66 - 47415 R + 325.87(\log R)^2$ $-1.032x10^5 (\log R)^2/T - 1.968x10^7 (\log R)^2 /T^2)$ $+ 1.605x10^7 (\log R)^3 /T^2$; *No correction should be attempted if R > 50.* $R = \frac{Mg}{Mg + 0.61\, Ca + 0.31\, K} \cdot 100$	0°C – 350°C
Na/Li	$t = \frac{1590}{\log(Na/Li) + 0.779} - 273$	0°C – 350°C

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[a] Concentrations in mg/L; t is temperature in °C; T in °K; p is pressure in bars; α is activity of the subscripted species. (For details and references see Kharaka and Mariner, 1989).

7. High temperature artificial tracers

Several new inorganic and organic tracers have been developed, and the temperature decay rates of others investigated over the last two decades to study the flow of water and steam in geothermal systems (Glover and Kim, 1993; Adams, 1995). The tracers, including halides, radioisotopes, fluorescent dyes, aromatic acids and halogenated alkanes, have been used primarily to detect and quantify the timing and fraction of water movement from an injection to a production well. Even the non-conservative tracers in the above list have been used in field tests to obtain information on reinjection of cooled thermal water and reservoir properties (Glover and Kim, 1993; Adams et al., 1999; Rose et al., 1999). Extensive tracer tests in 1989-90, using organic and inorganic compounds injected into water in sinkholes, travertine terraces and the Gardner River, established the flow paths, the mixing of thermal and cold surface and groundwaters and the hydraulic connections between the thermal features in the Mammoth area (Kharaka et al., 1991; Sorey et al., 1991; Spall et al., 1992).

8. Geothermal fluids in Yellowstone National Park

An integrated approach utilizing a broad spectrum of isotopes, chemical and other parameters is the most powerful way to study the geothermal resources and origin, history, and interactions of fluids in a geothermal system and this approach is essential to the understanding of the large and complex geothermal systems (e.g. Fournier, 1989). Lowenstern et al. (1999) use the integrated approaches to investigate the geothermal resources of a new prospective area, the Alid geothermal system, Eritrea. Truesdell et al. (1993) and Lowenstern and Janik (2003) used this approach to investigate the origin of fluids and heat in the well developed Geyser geothermal field in California. An example from a study of the possible relation of thermal waters outside Yellowstone National Park to thermal waters within the Park (Kharaka et. al., 1991) illustrates the utility of the multiple isotope approach, in addition to other chemical and hydrologic parameters. In this study, about 30 sites were sampled for major and minor dissolved constituents, water isotopes, free gas, dissolved gas, $^{3}He/^{4}He$, $\delta(^{36}Ar/^{40}Ar)$, $\delta^{13}C$, ^{14}C, $\delta^{34}S$, $^{87}Sr/^{86}Sr$, $\delta^{11}B$, $\delta^{6}Li$, $^{208}Pb/^{206}Pb$, $^{143}Nd/^{144}Nd$, and $^{228}Ra/^{226}Ra$. The results were used to determine how much Mammoth Hot Springs water could be present in thermal waters at La Duke Hot Springs and Bear Creek Warm Springs. In this mass balance approach to calculating possible mixing proportions Mammoth Hot Springs water was chosen as one possible end-member and Chico Hot Springs as the other end-member.

Yellowstone National Park (YNP) is unrivalled for the abundance and diversity of its hydrothermal features, including geysers, fumaroles, mud pots and thermal springs (see White et al., 1988; Smith and Siegel, 2000). These extraordinary features are distributed throughout the entire 9000 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. The Norris-Mammoth corridor (Fig. 4) is a complex north-south subsidence structure, extending ~40 km from the Yellowstone caldera to the Corwin Springs Known Geothermal Resources Area (KGRA) located north of the Park in Montana (Pierce et al., 1991). The corridor contains the only major alignment of volcanic vents and hydrothermally altered areas outside the caldera; the 13 rhyolitic and basaltic vents have ages of 400-80 ka (Hildreth et al., 1991).

The hydrothermal features in YNP are the surface manifestations of very high fluid discharges that include thermal water, water vapour and gases, especially CO_2 (Fournier, 1989; Kharaka et al., 2000, 2002; Werner et al., 2000). Thermal water discharges from YNP have been estimated to average a total of about 3–4 m^3/s (Fournier, 1989; Kharaka et al., 2000). The exceptional hydrothermal features of YNP are the result of a favourable 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 (Wicks et al., 1998), abundant supplies of recharge water primarily from melting snow and frequent seismic activity that creates new fractures and reopens clogged channels for fluid flow (Fournier, 1989; Kharaka et al., 2000). The shallow magmatic heat driving this hydrothermal system is associated with a deep-mantle plume, a hotspot, that is presently centred beneath the Yellowstone caldera and has been responsible, during the last 2.2 Ma, for the huge eruptive volume (~6000 km^3) of rhyolitic ash-flow tuffs and lavas, covering an area of about 17,000 km^2 in and adjacent to YNP (see Wicks et al., 1998; Smith and Siegel, 2000; Christiansen, 2001).

8.1. HYDROTHERMAL FLUID DISCHARGES

Thermal water discharges in YNP have been estimated by totalling the measured rates of individual springs or groups of springs (Allen and Day, 1935) or by using the more accurate river chloride inventory method applied to the four major rivers that drain the Park (Fournier et al., 1976; Norton and Friedman, 1985, 1991; Friedman and Norton, 2000, 2002; Sorey and Colvard, 1997; Ingebritsen et al., 2001). Results show large seasonal and long-term variations, and yield very high total average discharges of 3–4 m^3/s (Fournier, 1989; Kharaka et al., 2000, 2002).

Thermal fluids in the Norris-Mammoth corridor discharge an average of ~0.8 m^3/s from many springs and thermal areas inside YNP, with high fluid discharges obtained from the Norris Geyser Basin and Mammoth Hot Springs system. Norris Geyser Basin, located outside the northwest rim of the 0.6 Ma caldera, contains the widest diversity of hydrothermal activity known in the Park, discharging about 150-250 L/s of water, which attains boiling temperature at surface and 360°C at depth (Fournier et al., 1976; White et al., 1988; Kharaka et al., 2000).

The highest thermal water and gas discharges in the corridor are from Mammoth Hot Springs, where travertine-precipitating thermal water issues from ~100 hot springs scattered over a score of step-like travertine terraces, covering a large area, ~1 km wide and 4 km long. The surface temperatures of the springs (up to 73°C) and the reservoir temperature (~100°C), calculated by chemical geothermometry, are lower than those of boiling springs encountered at Norris. However, the total thermal-water discharges from the Mammoth system, estimated from long-term flow and chloride flux measurements and extensive application of chemical tracers, are very large, averaging 500–600 L/s. The calculated total heat flux from the Mammoth system (220 MW) is comparable to that discharged from the Norris Geyser Basin (Kharaka et al., 1991, 2000; Sorey and Colvard, 1997).

The gas concentration in thermal water from the Mammoth system, dominantly CO_2, is considerable at ~66 mM/L, and equilibrium gas pressures >5 bar are calculated for samples from the Y-10 well (Kharaka et al., 1991). The total CO_2 flux from the Mammoth system amounts to 33-40 M/s. The addition of 17 mM/L of dissolved C, present mainly as HCO_3^- in water samples from the Y-10 well (Kharaka et al., 1991), results in 42-50 M/s calculated total C flux from the Mammoth system.

Extensive tracer tests in 1989-90, using organic and inorganic compounds injected into water in sinkholes, travertine terraces and the Gardner River, established the flow paths, the mixing of thermal and cold surface and groundwaters and the hydraulic connections between the thermal features in the Mammoth area (Kharaka et al., 1991; Sorey et al., 1991; Spall et al., 1992). Extensive flow and chloride and sulphate flux measurements and monitoring were also carried out in 1987-95, especially at Hot River, the Gardner River below Hot River and the Mammoth outflow (Sorey and Colvard, 1997).

Results show that, despite the visual prominence of the Mammoth terraces, approximately 90% of total thermal water discharging from the Mammoth system is obtained from springs and seeps along the banks of the Gardner River, with the bulk emerging at Hot River. Results also indicate a general decrease of ~15% in total thermal water discharge, from ~600 L/s in 1987 to ~500 L/s in 1995. The decrease in discharge for a longer record (1984-2001) calculated by Friedman and Norton (2002) for the Mammoth system, however, was only 5%. The long-term decrease in discharge is probably related to decreases in regional precipitation rather than to tectonic or anthropogenic factors (Sorey and Colvard, 1997; Kharaka et al., 2000; 2002).

8.2. THERMAL WATER AND GAS COMPOSITIONS

The pristine hydrothermal waters at the Norris and other basins in YNP are alkaline sinter-precipitating Na-K-Cl type waters (salinity 1000–2000 mg/L), high in SiO_2, Li and B. Thermal water discharges commonly are modified by boiling, silica precipitation and mixing with local meteoric water (Fournier, 1989; Kharaka et al., 1991, 2002; Ball et al., 1998). The second type of water in the Norris-Mammoth corridor and throughout the Park is acidic and dilute, but with relatively high concentrations of SO_4 and NH_4 and fumarolic gases, especially CO_2 and locally significant H_2S and N_2. The low pH of this water results from high concentrations of CO_2 and oxidation of H_2S to SO_4 (White et al., 1988; Fournier, 1989). The thermal waters from the Mammoth Springs comprise the third water type, being travertine-precipitating Ca-Na-Mg-HCO_3-SO_4-Cl types, with higher salinities of 2000–3000 mg/L. Chemical geothermometry and $\delta^{34}S$ values (21‰) indicate that the high Ca, Mg and SO_4 are obtained from reaction with Palaeozoic carbonates at

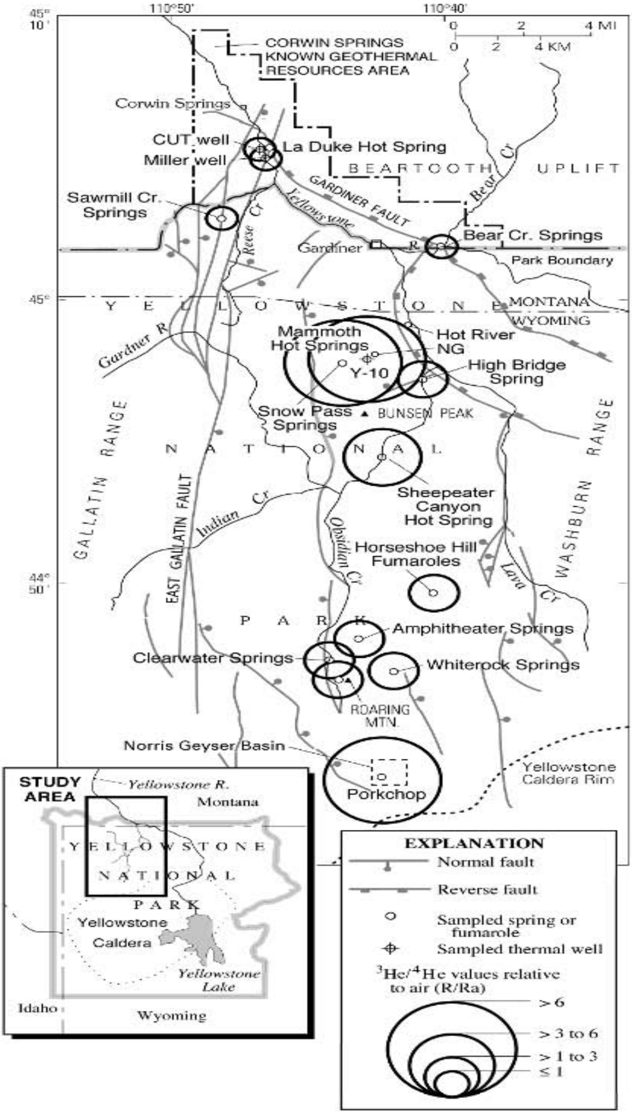

FIG. 4. Distribution of the ^{3}He/^{4}He values relative to air (R/Ra) in thermal fluids from the Norris-Mammoth corridor, Yellowstone National Park, USA. Note the high values for the Mammoth system and Norris Geyser Basin and the relatively low values in the intervening thermal areas (from Kharaka et al., 2000).

~100°C. There are differences in the salinity and chemical composition of water among the terrace springs and other sites (e.g. Hot River) in the Mammoth system, however, these changes result primariy from dilution with local meteoric water and travertine deposition (Kharaka et al., 1991).

Throughout YNP, CO_2 is the dominant gas, comprising 96% to >99% of the total in the Norris-Mammoth corridor, and with locally significant amounts of H_2S and N_2. In the Mammoth area, gas discharges are high and there are >50 mM/L of excess CO_2 relative to Ca and Mg, indicating a source not related to dissolution of carbonates (Kharaka et al., 1991, 2000). The chemical and isotopic compositions of noble gases, especially the $^3He/^4He$ ratios, indicate a mantle origin for the excess CO_2. The molar total $C/^3He$ (~5 x 10^9) and $\delta^{13}C$ values of CO_2 (-3.4 to -5.2‰) are additional support for the conclusion of a mantle origin for the bulk of the CO_2 in the Mammoth system (Kennedy et al., 1985; Kharaka et al., 1991, 2000; Trull et al., 1993).

8.3. ORIGIN AND EVOLUTION OF THERMAL FLUIDS

The δ^2H and $\delta^{18}O$ values of water from 37 thermal springs (some sampled 2-4 times) located mainly in the Norris-Mammoth corridor are plotted in Fig. 5 (Kharaka et al., 2002). These values show significant δ^2H and $\delta^{18}O$ shifts relative to the meteoric water line, with the origin of these shifts being complex and likely being different for these springs and each of the main thermal areas of the Park. Truesdell et al. (1977) and Kharaka et al. (1991, 2002) discussed in detail the isotopic shifts resulting from single-stage or continuous boiling, isotopic exchange between water, dissolved SO_4 and geologic materials and mixing between thermal water and shallow cold meteoric water. Although increases in Cl concentrations are similar in single-stage or continuous steam separation, the H isotopic changes differ significantly. Because Cl behaves conservatively in geothermal systems, and water and steam are the only significant sources of ^1H and ^2H, Cl and SO_4 concentrations coupled with H isotopes of water can be useful interpretive tools (Truesdell et al., 1977; Fournier, 1989; Kharaka et al., 1991).

Kharaka et al. (1991, 2002) showed that the isotopic shifts for the waters from Norris Geyser Basin relative to recharge waters with δ^2H and $\delta^{18}O$ values of about -150 and -20‰, respectively, result mainly from boiling for the δ^2H values and from boiling and isotopic exchange with aquifer minerals for the $\delta^{18}O$ values. In addition to boiling, the isotopes of water from Clearwater Springs are modified by mixing with dilute local meteoric water with a δ^2H value of about -144‰; this mixing is indicated by examination of the Cl vs δ^2H relations of the waters. The samples from Mammoth Hot Springs also show moderate isotopic shifts from the meteoric water line (Kharaka et al., 1991, Table F-2 and Fig. F-5). The sample from the Y-10 well likely is the least modified of the Mammoth sites and the most representative of the upflow thermal water for the Mammoth system. This conclusion is reached because the water in the Y-10 well is at high pressure (~4 bars at ground level), is not affected by precipitation of travertine, and water isotope values are the same for water obtained at ground level and by downhole sampler from a depth of 53 m. The

δ^2H value of water from the Y-10 well (-149‰) is close to a δ^2H value of -151‰ estimated for the recharge waters for the Mammoth system from the Cl vs δ^2H relations of thermal waters. The corresponding δ^{18}O value for the recharge waters is -20.1‰, which would result in a moderate 1.7‰ shift in the δ^{18}O value of water from the Y-10 well.

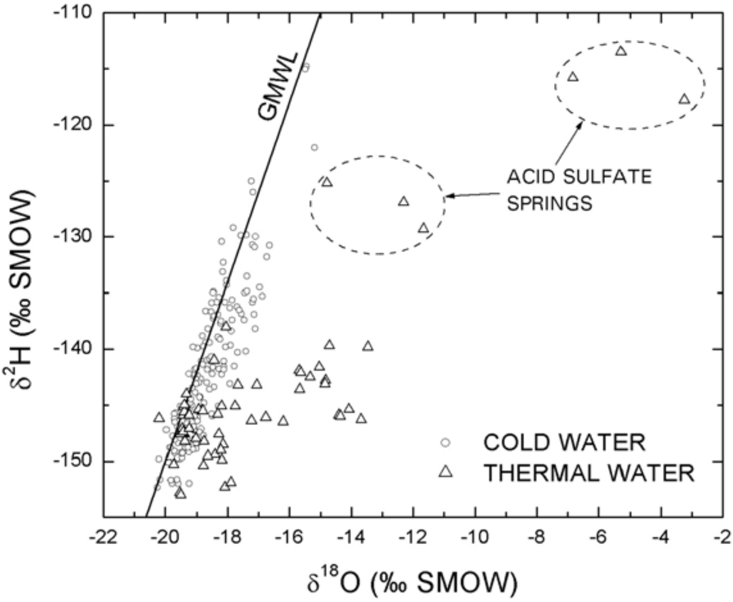

FIG. 5. Scatter plot of δ^2H vs δ^{18}O values for thermal- and cold-water samples from Yellowstone National Park, USA. Samples from acid-sulphate springs controlled by boiling and condensation are delineated (from Kharaka et al., 2002).

There are two possible explanations for the moderate δ ^{18}O shifts for the waters from the Y-10 well and the other sites from Mammoth Hot Springs. The oxygen shift could be the result of isotopic exchange between water and aquifer minerals as the water flows from recharge points in the Gallatin Range to the discharge sites at Mammoth. Oxygen exchange with calcite in Palaeozoic limestone resulting in heavier oxygen isotopes in water is a possible explanation, because isotopic exchange can take place between water and calcite at relatively low (25° to 100°C) temperatures (Clayton et al., 1966; Kharaka and Carothers, 1986; Plummer et al., 1990). Alternatively, the oxygen shift also could result from mixing of a Mammoth meteoric water with the deep and unmodified thermal water from Norris Geyser Basin. The minor δ^2H shifts (from a δ^2H value of about -150‰) can be explained by mixing, as in the case of oxygen isotopes, or they could result from minor evaporation of recharge water before it percolates deep into the subsurface. The isotopic shifts also could result from hydrogen exchange with clay minerals in the sedimentary section (Kharaka and Thordsen, 1992).

Using water isotopes of thermal and meteoric water, Craig et al. (1956) were the first to conclude that deep-percolating meteoric water was the source of all the thermal water in the Yellowstone National Park, with no or minimal magmatic contribution. This conclusion was supported by subsequent detailed investigations combining water isotopes with enthalpies and chemical compositions of thermal water (Truesdell et al., 1977; Fournier, 1989; Kharaka et al., 1991, 2002). Model calculations by Truesdell et al. (1977) indicated that the source meteoric water for Norris, Lower and Shoshone Geyser basins and possibly for all of the other basins in Yellowstone Park has a well constrained δ^2H value of -149‰ and an equivalent δ^{18}O value of -19.9‰.

The isotopic composition of present day precipitation (meteoric water) within and close to the geyser basins in the Park reported by Truesdell et al. (1977), Kharaka et al. (1991, 2002), Thordsen et al. (1992), Rye and Truesdell (1993) and others are generally heavier than that calculated for the recharge water of the hydrothermal system (Truesdell et al., 1977). The spatial distribution of cold-water samples (Thordsen et al., 1992; Kharaka et al., 2002) shows a roughly circular pattern with isotopically lightest waters centred on the mountains and high plateau in the northwest corner of YNP, including the Yellowstone River valley, and becoming heavier in all directions; relatively light water isotopes are also present at high elevations in the southern Absaroka Range, but isotope data for this area are sparse. Results from Thordsen et al., 1992; Kharaka et al., 2002) show that meteoric water with δ^2H and δ^{18}O values lighter than -149‰ and -19.9‰, respectively, are present in the Gallatin and northern Absaroka Ranges at 2.5-3.0 km elevations and higher, and in the Yellowstone River valley at elevations of 1500 m and higher. The total land area (Fig. 6), with δ^2H and δ^{18}O values lighter than -149‰ and -19.9‰, respectively, is relatively small (~200 km^2), and when combined with values for mean annual precipitation (~100 cm/a) and a reasonable value (5-30%) for the recharged portion of precipitation (Sanford, 2002), yields a volume of this recharge water that is not adequate to supply the high total thermal water discharges (3-4 m^3/s) from YNP (Kharaka et al., 2002)

The total land area located in the Gallatin and northern Absaroka Ranges with δ^2H values lighter than -145‰ is about 10,000 km^2, and precipitation over this area may be adequate for recharging the hydrothermal system in YNP (Fig. 6). The value of -149‰ for the δ^2H of recharge water, based on model calculations by Truesdell et al. (1977) is generally accepted (e.g. Kharaka et al., 1991). If a δ^2H value lighter than -145‰ is required for the recharge water, it is possible that the hydrothermal water currently discharging from YNP was recharged during an earlier time when the mean annual temperatures were lower. In northern latitudes the δ^2H values become lighter by 5.6‰ per °C decline in the mean annual temperature (Dansgard, 1964), and a modest lowering of only 0.7°C will change the δ^2H values of precipitation from current values of ≥ -145‰ to the required values of ≥ -149‰.

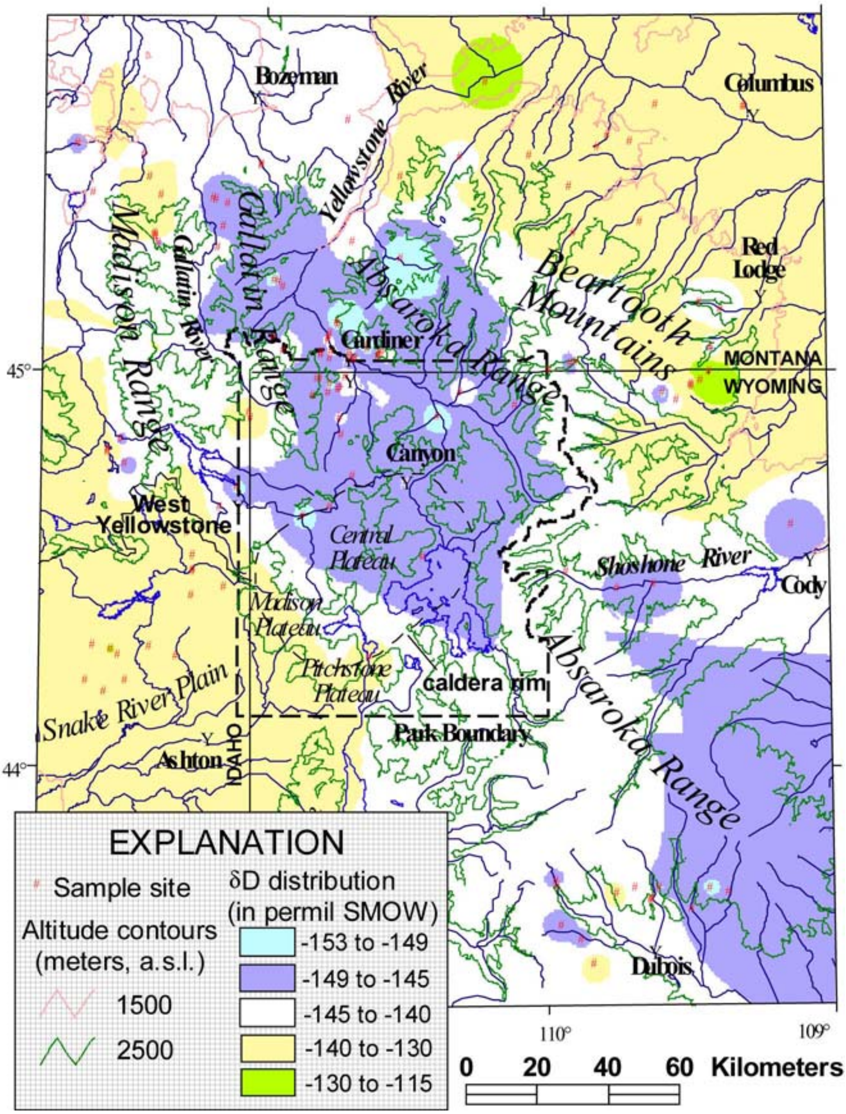

FIG. 6. Spatial distribution of δ^{18}O *values for cold-water samples in the greater Yellowstone National Park region, USA (from Kharaka et al., 2002).*

Climate records for the northern latitudes show significant temperature fluctuations with time (e.g. 1–2ºC lowering during the Little Ice Age) following the Pleistocene, and temperature changes of 5–10ºC are indicated in the last 2 Ma (Bryant, 1997). It is also possible that the hydrothermal water currently discharging from YNP represents a mixture of meteoric water having relatively heavy isotopes similar to present day precipitation with older meteoric water recharged during cooler periods, including during the Pleistocene when the δ^2H values likely were 30–50‰ lighter that current values. A mixture comprised of about 90% water having present-day isotope values with 10% Pleistocene precipitation would be adequate as the source for the hydrothermal water currently discharging from YNP.

A Pleistocene age for even a small portion of the source meteoric water recharging the present hydrothermal system in YNP is probably unlikely, because the high discharge rates (3-4 m^3/s) indicate a relatively short residence time. Radium and radon concentrations in thermal water also indicate that recharge water percolates rapidly (residence time ~500-1000 a) to the heat source at the Norris Geyser basin (Clark and Turekian, 1990). Model calculations using tritium values in thermal water from many geyser basins also yield low (200-1000 a) residence time for the recharge water (Pearson and Truesdell, 1978). Kharaka et al. (2002) conclude that the most logical conclusion from the data discussed above 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).

8.4. HYDROTHERMAL FLUIDS FROM THE MAMMOTH SYSTEM

The pristine water from the Norris Basin has chemical, isotopic and thermal properties similar to those of waters from the caldera basins, which receive their heat and some chemical components from reaction with a relatively shallow magmatic source. The $^3He/^4He$ ratios relative to atmospheric values (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 (Kennedy et al., 1985; Hearn et al., 1990; Kharaka et al., 1992). The chemical and isotopic compositions of water and solutes, especially the $^3He/^4He$ ratios, in the Mammoth Springs indicate that water also derives its heat and some solutes (e.g. Cl, B, ^3He and CO_2) from a magmatic source (Kharaka et al., 1991). White et al. (1988) postulated that the magmatic source for Norris and the entire Norris-Mammoth corridor is located beneath Roaring Mountain. In this model, the lower concentrations of Cl, Br, B and other conservative solutes in the Mammoth water result from mixing 30-40% Norris-type water with 70-60% meteoric water as fluids flow northward to Mammoth; the much higher values for Ca, Mg, SO_4 and HCO_3 in the Mammoth water are obtained from reaction with Palaeozoic carbonates at ~100°C (e.g. Kharaka et al., 2000).

Kharaka et al. (1991) presented an alternative model and postulated that the heat and volatiles for the Mammoth system are provided by a separate magmatic body emplaced near Mammoth ~400 ka. A separate magmatic body is postulated, because (1) gas samples from the Y-10 well and three terrace springs yield R/Ra values of 8.1-8.4, and the sample from Snow Pass gives R/Ra value of 7.5, (2) all the major thermal areas between Norris and Mammoth, including Roaring Mountain, White

Rock Springs, Amphitheater Springs, Clearwater Springs, and Horseshoe Hill, have lower R/Ra values of 2–3 . The emplacement of the magmatic system is constrained by model U/Th ages obtained from the extensive travertine deposits in the Mammoth area that indicate five periods of intermittent, but non-overlapping travertine precipitation from about 400 ka to present. The periods of activity could be related to the thickness of glacial ice in the region and/or magmatic injection at depth (Pierce et al., 1991). The $^{87}Sr/^{86}Sr$ ratios and εNd values of most travertines from the Mammoth system are identical, indicating precipitation from thermal fluids derived from the same hydrothermal system (Bullen and Kharaka, 1992). The exact location of the postulated Mammoth magmatic system is not known, but magnetotelluric and other geophysical surveys conducted indicate partial melt conditions (500–600°C) occur south of Bunsen Peak at depths ≥ 6 km (Stanley et al., 1991). Additional evidence for a separate thermal source for the Mammoth system is obtained from satellite radar interferometry imaging for August 24, 2000 to September 13, 2001, that shows areas of significant inflation and surface uplift between the Norris Geyser Basin and Mammoth Springs that are separated from that imaged for the Norris Geyser Basin (W. C. Wicks, written communication, April, 25, 2002).

9. Concluding summary

Water from thermal springs has been used extensively since prehistoric times for bathing, washing and cooking. More recently geothermal energy – an abundant resource in the Earth's crust – has emerged as an important and clean alternative source of energy for electrical power generation and direct uses, including agriculture, aquaculture and space heating. Electrical power generation using geothermal steam started at Larderello, Italy in 1912, and currently over 8,000 MW of electricity are generated from geothermal power plants in 22 countries.

The δD, $\delta^{18}O$ and tritium values of water, especially when integrated with the concentrations and isotopes of solutes and gases, are powerful geochemical tools for determining the origin, nature, distribution and interactions of fluids in geothermal systems. Water isotopes are powerful tools, because the relations governing their distribution in present-day local meteoric water and their modifications by mixing, boiling, and isotopic exchange with minerals in geothermal systems, are reasonably well known.

The pioneering reports by Craig and his colleagues demonstrated conclusively the meteoric origin of most geothermal fluids, which have deuterium values that are similar to those for local precipitation, regardless of where the geothermal system is located (Craig et al., 1956; Craig, 1963). More recent major advances in the field, including the application of isotope and chemical thermometry, of noble gas data and of high temperature tracers have led to a better understanding of the nature and production characteristics of geothermal systems, the influence of magmatic heat sources, the origins of highly corrosive fluids, scaling and corrosion. Finally, we conclude that a detailed integrated approach is needed to understand fully the behaviour of the major geothermal systems. We employ this integrated approach, using water isotopes and other geochemical and hydrologic parameters to conclude that the recharge to the huge hydrothermal system (3-4 m^3/s) presently discharging from Yellowstone National Park, USA, was recharged in the Gallatin and northern Absaroka Ranges during the Little Ice Age (1350-1870 AD), when the mean annual temperatures were probably 1-2ºC lower.

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17. SALINE WATERS

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1. Introduction

Saline waters often imply natural waters with salinity or total dissolved salts (TDS) above biological tolerance (1–5 g/L), while the term brines is used for waters with salinity greater than that of sea water (35 g/L) or 100 g/L. Brackish waters are detween freshwater (TDS <1 g/L) and sea water. In this article, saline waters are efined as natural waters with salinity greater than that of sea water. Saline waters are currently encountered in diverse geologic settings at the surface and in the upper crust of the Earth; saline lakes in the arid zones, waters in sedimentary basins and crystalline rocks, brines in anoxic marine basins, interstitial waters in marine sediments, hydrothermal waters from mid-ocean ridge and continental geothermal systems. Petrologic evidence, most notably from fluid inclusions, also clearly documents that hot, saline waters have been responsible for large-scale fluid transport, water–rock interactions, and ore depositions in various geologic processes in the past. Among these rather widespread occurrences of saline waters in various geologic settings, both present and past, our main interest here is in those in modern, w-temperature environments (saline lakes, brines in sedimentary basins, crystalline basements, and anoxic marine basins).

The first and foremost question regarding the occurrence of saline waters is; what hydrologic regimes and geochemical processes have led to their formations? The sources of salinity can vary widely, including aeolian salts, surficial weathering products, seawater intrusion, subsurface water–rock interactions at elevated mperatures and pressures, and metamorphic–magmatic fluids. However, the fundamental requirement for the formation of saline waters is a closed or semi-osed nature of hydrologic regimes or geochemical systems wherein dissolved solutes, regardless of their sources and geochemical mechanisms, can build up

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within a water body, either subaerial or subsurficial. Otherwise, hydrologic openness either dilutes or flushes dissolved salts out of the water body. Hydrologic and geochemical processes that can produce saline waters are also diverse. Under subaerial conditions, the evaporation of water into the atmosphere from hydrologically restricted water bodies (lakes, marginal seas, etc.) and soil water/groundwater is the primary processes for the build-up of salinity in the arid zone. The formation of ice by freezing in the polar regions can also produce brines subaerially and in soils. Subsurface processes leading to the formation of brines are perhaps even more complex, including boiling and phase separation of water, various water–rock interactions (dissolution of evaporite deposits and other minerals, diagenetic formation of hydrous minerals, etc.), and membrane filtration by shales. A number of geochemical processes at the surface and especially in the subsurface modify the chemical and isotopic compositions of saline waters over prolonged geologic time; compaction and dewatering of formations, redox reactions involving dissolved and gaseous species, maturation and decay of organic matter, and various water–rock interactions (dehydration, hydrolysis, cation exchange, alteration of detrital and igneous/metamorphic rocks, etc.).

2. Isotopic evolution of saline waters

The behaviour of stable oxygen and hydrogen isotopes ($^{18}O/^{16}O$ and $^{2}H/^{1}H$) of water is reasonably well understood for the major hydrologic and geochemical processes that produce saline waters at the surface and in the subsurface. Water molecules evaporating from a surface water body into the atmosphere are invariably depleted in both heavy isotopes, making the remaining water enriched in heavy isotopes. The magnitude of this enrichment depends on many physical (temperature, relative humidity, salinity) and hydrologic (inflow, outflow, the fraction of remaining water) factors. In the $\delta^{2}H$–$\delta^{18}O$ diagram, the trajectory of evaporating water bodies has a slope of 4–6, depending on these factors (Fig. 1). Isotopic enrichments are much more suppressed in evaporative brine bodies than in fresh-water bodies under the same climate condition, due to low activities of water in brines (see discussion for saline lakes). The commonly accepted notion that the trajectory of evaporative brines in the $\delta^{2}H$–$\delta^{18}O$ diagram has slopes smaller than those of freshwater bodies is not correct, however. Evaporation of water from soil water, saturated or undersaturated, also causes the enrichment of heavy waters, but the slope of the trajectory is much smaller (2–3) than that for surface waters, because of an extended diffusion layer at the water-air interface in soil (Allison, 1982). The freezing of water is another mechanism, which also enriches heavy isotopic water in the remaining water. However, the magnitude of this isotopic fractionation is a factor of 3–4 smaller than those for the liquid–vapour transition of water (Lehmann and Siegenthaler, 1991), and the trajectory in the $\delta^{2}H$–$\delta^{18}O$ diagram has a slope of about 7, a value very close to that of the Meteoric Water Line (Fig. 1).

The dissolution of evaporite deposits and other anhydrous minerals does not change the isotopic composition ratio of water, but it does change the isotopic activity ratios (see the section below): the dissolution of hydrated minerals, of course, affects the isotopic composition ratios of water. However, the magnitude of this isotope effect is relatively small (Fig. 1). Various hydrous minerals (clay minerals, gypsum, etc.) are enriched in ^{18}O, but depleted in deuterium compared to water from which they precipitate at isotopic equilibrium (Chacko et al., 2001). Therefore, the remaining water become progressively depleted in ^{18}O and enriched in deuterium during the precipitation of these hydrous minerals from an isolated body of water (Fig. 1). It is also known that light water molecules preferentially pass through a layer of shale under pressure (or water activity) gradients in the subsurface–membrane filtration. This mechanism leaves ^{18}O- and ^{2}H-enriched water and dissolved salts behind (Coplen and Hanshaw, 1973). However, the magnitude of this isotopic effect is an order of magnitude smaller than those of the other isotope fractionations.

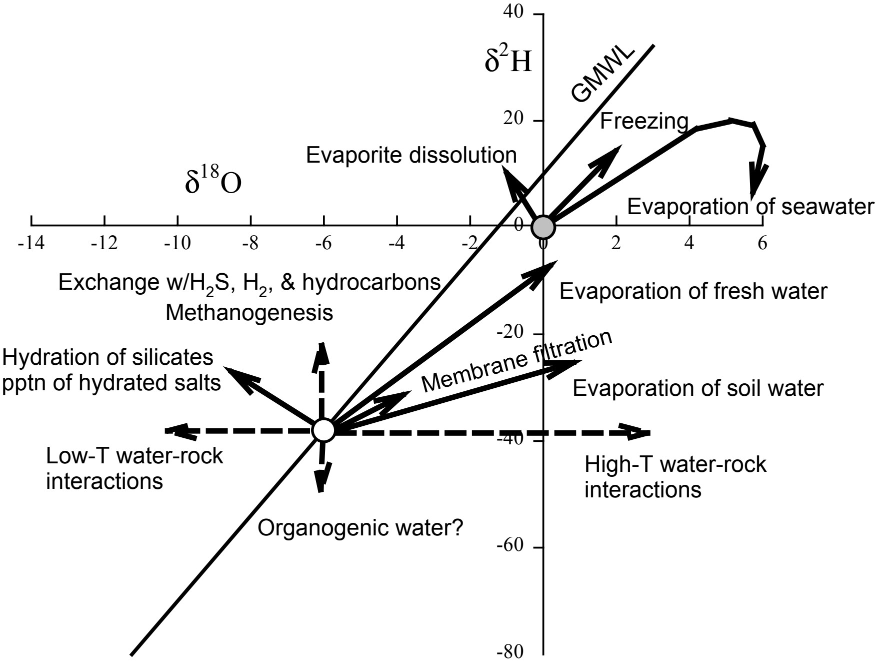

FIG. 1. Schematics for the isotopic evolution of waters in primary, brine-forming processes (solid lines) and secondary, modifying processes (broken lines). The length of the lines reflects the importance of each process. Note that the isotopic ratios are expressed on the activity scale.

There are many secondary geochemical processes which can modify the isotopic composition of saline waters produced by the primary processes discussed above.

These include mixing of different water masses, various diagenetic water–rock interactions (compaction–dehydration, isotopic exchange with minerals caused by mineral alteration or dissolution-precipitation, etc.), isotopic exchange with other aqueous and gaseous/fluid species (H_2S, hydrocarbons), production and consumption of water (redox reactions, methanogenesis, degradation of organic matter, etc.). Among these, various water–rock interactions (alterations and dissolution–precipitation of detrital minerals) at elevated temperatures have profound effects on the isotopic composition of subsurface waters, increasing their $\delta^{18}O$ values - the "^{18}O shift" (Fig. 1). The magnitude of this effect can be significant, controlled by many factors (temperature, water–rock ratio, kinetics of isotopic exchange, etc.). Conversely, water–rock interactions at low-temperatures (<100°C) very likely lead to the depletion of ^{18}O in the fluids because of a large temperature dependency of many mineral–water isotope fractionation factors. Water–rock interactions have relatively small impacts on δ^2H values of subsurface water, due to small hydrogen contents of many rock-forming minerals. Isotopic exchange with H_2S, H_2 and hydrocarbons at low temperatures can increase δ^2H values of waters because of large $^2H/^1H$ fractionation factors between water and these compounds. However, their geochemical significance has never been well documented or understood. The same is true for the contribution of water from organic matter (organogenic water), which is very likely depleted in deuterium.

3. Isotope salt effects and analytical methods for saline waters

The fundamental feature of stable oxygen and hydrogen isotopes ($^{18}O/^{16}O$ and $^2H/^1H$) in saline waters is that the activity ratios of these isotopes differ from their composition ratios, which is known as the "isotope salt effect". Strong interactions between dissolved electrolyte ions and water molecules (e.g. hydration of ions) change the activity of isotopic water molecules. The isotope salt effect was first discovered in the early 1950s (Taube, 1954), but it was not until the 1970s that this effect for geochemically important salts was systematically investigated (Sofer and Gat, 1972, 1975; Stewart and Friedman, 1975). The isotope salt effect can be rigorously defined in terms of thermodynamics (Horita et al., 1993):

$$\Gamma = \frac{R_{activity}}{R_{composition}} = \frac{a({}^1H^2HO)/a(H_2O)}{X({}^1H^2HO)/X(H_2O)} \text{ or } \frac{a(H_2{}^{18}O)/a(H_2{}^{16}O)}{X(H_2{}^{18}O)/X(H_2{}^{16}O)} = \frac{\gamma({}^1H^2HO)}{\gamma(H_2O)} \text{ or } \frac{\gamma(H_2{}^{18}O)}{\gamma(H_2{}^{16}O)} \quad (1)$$

where a, X, and γ denote the activity, mole fraction, and activity coefficient of isotopic water molecules, respectively. The R stands for $^{18}O/^{16}O$ or $^2H/^1H$. From the relation $R = 1 + 10^{-3}\delta$, we obtain,

$$10^3 \ln\Gamma \cong \delta_{activity} - \delta_{composition} \quad (2)$$

The hydrogen and oxygen isotope salt effects of several salts near room temperatures are shown in Fig. 2. At a given temperature, the magnitude of the isotope salt effects is practically linear with the molality (mol/kg H_2O), and the oxygen and hydrogen isotope salt effects in chloride-type brines at 20–25°C can be expressed as a sum of the effects of individual electrolyte components (Sofer and Gat, 1972; 1975, Horita 1989),

$$\begin{aligned} 10^3 \ln \Gamma(^2H/^1H) &= 2.2mNaCl + 2.5mKCl + 5.1mMgCl_2 + 6.1mCaCl_2 \\ 10^3 \ln \Gamma(^{18}O/^{16}O) &= 0.16mKCl - 1.11mMgCl_2 - 0.47mCaCl_2 \end{aligned} \tag{3}$$

where m is the molality (mol/kg H_2O). Horita et al. (1993a, 1995) extended experimental determinations of the isotope salt effects to elevated temperatures, and these studies can be consulted for the isotope salt effects at elevated temperatures.

The isotopic compositions of saline waters have traditionally been determined by the same methods, which have been used for fresh waters; metal- (Zn, U, Cr, etc.) reduction and CO_2–water equilibration methods for δ^2H and $\delta^{18}O$ values, respectively. It should be noted that the former method yields the δ^2H composition values, but that the latter method the $\delta^{18}O$ activity ratio. In addition to this discrepancy in the units between the two analytical methods, several problems are encountered in the isotopic analysis of brines due to dissolved salts; incomplete reduction of water in brines to H_2 and sluggish isotope equilibration between CO_2 and brines (Horita, 1989). The former problem, particularly, resulted in poor δ^2H values of hypersaline brines from the Dead Sea (Fig. 3). Using newly developed analytical methods, the H_2–water equilibration method for the δ^2H activity ratio (Horita, 1988) and the azeotropic distillation method after the removal of alkaline-metal cations for the δ^2H composition ratio (Horita and Gat, 1988), Horita and Gat (1989) determined directly both the δ^2H composition and activity values for a suite of Dead Sea brines (Fig. 3). These results show that δ^2H composition values of Dead Sea brines from the literature are systematically (up to c. 10‰) lower than the new set of data. In addition, the new data of δ^2H activity and composition ratios vary linearly with $\delta^{18}O$ activity values as expected for evaporative water bodies (Fig. 3). The directly measured $^2H/^1H$ isotope salt effects ($10^3\ln\Gamma$) for the Dead Sea brines of salinity $\sigma_{25} = 232.2$ (mNaCl=1.95, mKCl=0.15, mMgCl$_2$=2.00, and mCaCl$_2$=0.49) is +17.8‰, which is in excellent agreement with that (+17.8) calculated from the experimentally determined equation, Eq. (3). A small (+1.2‰) $^2H/^1H$ isotope salt effect was detected even for a suite of sea waters (Shank et al., 1995).

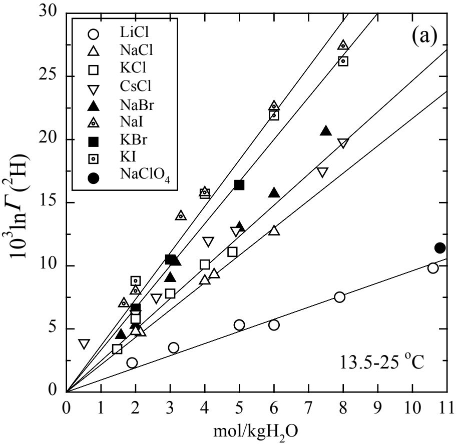

FIG. 2(a). Isotope salt effects of various salts at room temperature:(a) 1:1 salts on $^2H/^1H$ (after Horita et al., 1993a).

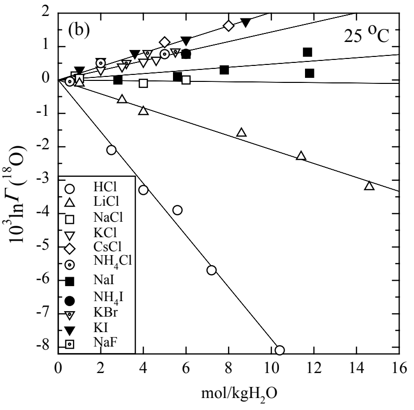

FIG. 2(b). Isotope salt effects of various salts at room temperature: 1:1 salt on $^{18}O/^{16}O$ (after Horita et al., 1993a).

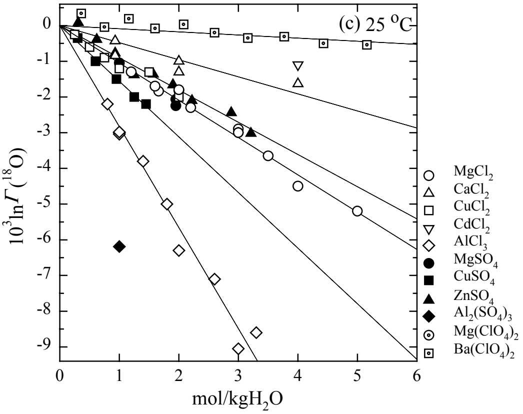

FIG. 2(c). Isotope salt effects of various salts at room temperature: high-valence salts on $^{18}O/^{16}O$(after Horita et al., 1993a).

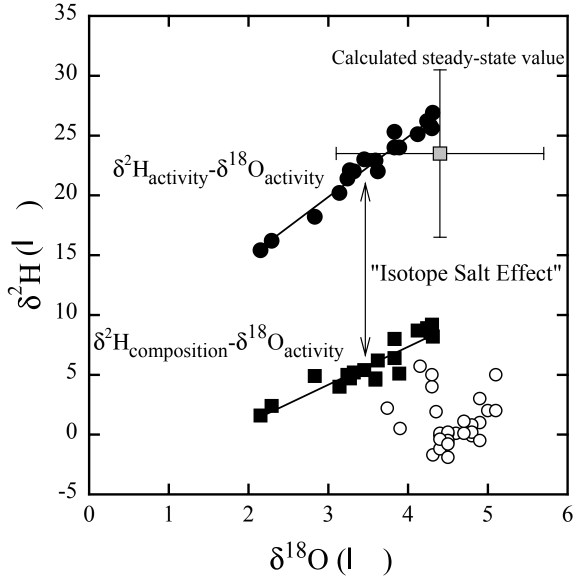

FIG. 3. $\delta^2H - \delta^{18}O$ plot for a suite of Dead Sea brines on the different isotope scales. δ^2H composition values from the literature (open circles, compiled in Gat, 1984) have large systematic errors (after Horita and Gat, 1989).

The H_2–water equilibration method is thus a preferred method for δ^2H measurements of brines because of; (a) high precision and accuracy, (b) yielding the isotope activity ratio, and (c) high throughputs by automation (Horita et al., 1989).

4. Brief history of research on saline waters of various origins

4.1. SALINE LAKES

Saline lakes occur as coastal lagoons in small, restricted marine basins and inland terminal saline lakes (ephemeral shallow playas/salinas and deep perennial lakes). The chemical compositions of inland saline lakes vary widely (Eugster and Hardie, 1978). The two most striking features of the isotopic composition of saline lakes are: (a) the enrichment of heavy isotopes (^2H and ^{18}O) is greatly suppressed compared to freshwater lakes under similar climate and hydrologic conditions (Gonfiantini, 1965) and (b) the behaviour of both δ^2H and $\delta^{18}O$ values of saline waters is complex, first increasing in the early stages, then reaching maxima, and finally decreasing in final desiccation stages (Gonfiantini, 1965; Lloyd, 1966; Fontes and Gonfiantini, 1967). A continuously decreasing activity of water (a_{H_2O}), and thus continuously increasing normalized relative humidity ($h' = h / a_{H_2O} > h$), during the evaporation of saline lakes is the cause of these phenomena, because this value strongly affects steady-state values under a given condition (Gat, 1979; Horita, 1990),

Evaporation pan: $$\delta_{Steady-State} = (h'\delta_{Atm} + \varepsilon)/(h' - \varepsilon) \qquad (4)$$

where $\delta_{Steady-State}$ and δ_{Atm} are the isotopic compositions of an evaporation pan at the steady-state and of atmospheric water vapour, $\varepsilon = \varepsilon^* + (1 - h')C_k$:, $\varepsilon^* = 1000(\alpha - 1)$, α is the equilibrium liquid–vapuor fractionation factor, and C_k the kinetic liquid – vapour isotope fractionation factor. Sofer and Gat (1972; 1975) modelled these complex patterns of isotopic evolution in desiccating bodies of saline waters (Fig. 4); the patterns depend on several physical parameters such as the initial chemical and isotopic compositions, relative humidity, and the isotopic ratios of atmospheric vapour.

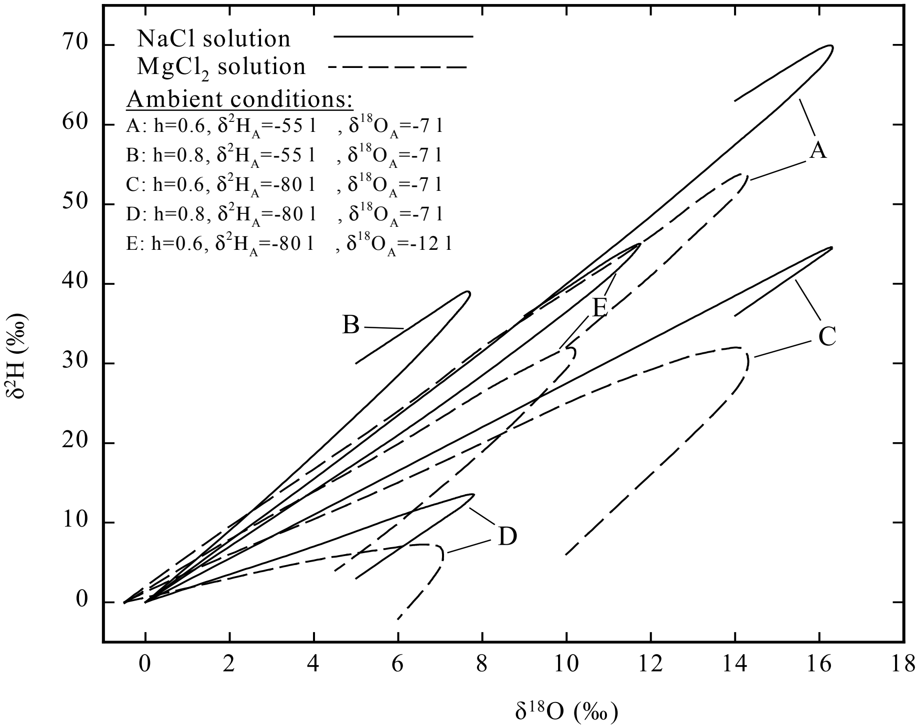

FIG. 4. Computed δ^2H composition and $\delta^{18}O$ activity values for 0.5 molal NaCl or $MgCl_2$ solutions evaporating under different environmental conditions. The "loop" occurs only in the very late stages of desiccation (from Sofer and Gat, 1975).

It should be emphasized that this "loop" or "hook" pattern is unique only to desiccating pans with no inflow, and that saline lakes with continuous inflow show more straightforward, albeit suppressed, enrichments of heavy isotopes. Gat (1984) also modelled seasonal and long-term evolutions of the $\delta^{18}O$ composition of the Dead Sea, a perennial saline lake with constant inflow. Carbonate sediments deposited from the Lake Lisan suggest that this Pleistocene precursor of the Dead Sea is more enriched in ^{18}O than the Dead Sea, despite its lower salinity (about a half) than the Dead Sea. This counterintuitive fact can be readily explained in terms of the steady-state model,

$$\text{Terminal lake: } \delta_{Steady-State} = \alpha\lfloor(\delta_{Atm} - \delta_{Inflow} - C_k)h' + \delta_{Inflow} + \varepsilon^* + C_k\rfloor \qquad (5)$$

where δ_{Inflow} is the isotopic composition of inflow water.

It has often been observed that the slope of the trajectory or evaporation line of saline lakes in the $\delta\,^{2}$H–δ^{18}O diagram is much smaller (3–4) than that for freshwater lakes (4–6) under similar climate conditions. This is to large extent an artifact due to the analytical problems encountered in the δ^{2}H analysis of brines and the isotope salt effects (Fig. 3). Horita and Gat (1989) demonstrated that on the activity scale of both $\delta\,^{2}$H and δ^{18}O values, the trajectory of the Dead Sea brines has a slope of 5.6, instead of 3.8 as previously reported by Gat (1984). This value is very similar to those observed for fresh-water lakes. In fact, isotopic compositions calculated using the steady-state isotope model for terminal lakes (Eq. (5)) agree well, within uncertainties of the environmental parameters (Gat, 1984), with the measured δ^{2}H and δ^{18}O activity values of the Dead Sea (Fig. 3). This clearly demonstrates that the isotopic models developed for saline lakes are of high quality, and that the isotope activity ratios of brines have to be used for the study of saline lakes. For more in-depth discussion and reviews on saline lakes, refer to Gat (1979, 1995).

4.2. SEDIMENTARY BASINS

The occurrence of highly saline brines, generally of a Na-Ca-K-Cl type with salinity up to above 400 g/L, has been reported from many continental sedimentary basins across the world. These brines are often called formation brines or oil-field brines; the latter terminology reflects their close association with petroleum from oil-producing formations. Various ore deposits (e.g. Mississippi-Valley type Pd-Zn ores) are also genetically related to sedimentary brines. The origin of salinity in sedimentary brines has been debated extensively in the literature (see a review by Hanor, 1994), ranging from connate *sea water*s to brines of totally diagenetic or metamorphic origin. Degens et al. (1964) were the first to analyse systematically δ^{18}O values of brines from Palaeozoic, Mesozoic, and Cenozoic formations in Oklahoma, Texas, Colorado, and Utah. They interpreted that mixing of fossil *sea water* (connate waters) with meteoric waters caused the observed positive relationship between the δ^{18}O values and the salinity of the brines.

Clayton et al. (1966) and Graf et al. (1965, 1966) conducted a series of detailed geochemical studies on suites of brines obtained from four major sedimentary basins in North America (Gulf Coast, Illinois, Michigan, and Alberta). Clayton et al. (1966) were the first to report both δ^{2}H and δ^{18}O values of sedimentary brines (Fig. 5).

All sedimentary brines analysed plot on the right side of the Global Meteoric Water Line in the δ^{2}H–δ^{18}O diagram, much like geothermal waters. Each suite of brine samples from the four sedimentary basins show variations in δ^{18}O values much greater than those in δ^{2}H values. Strong positive correlations were also observed between the δ^{18}O values of brines and salinity or recorded temperatures, which were interpreted as progressive oxygen isotope exchange between water and reservoir rocks with depth (and time), particularly with carbonate minerals (Clayton et al., 1966).

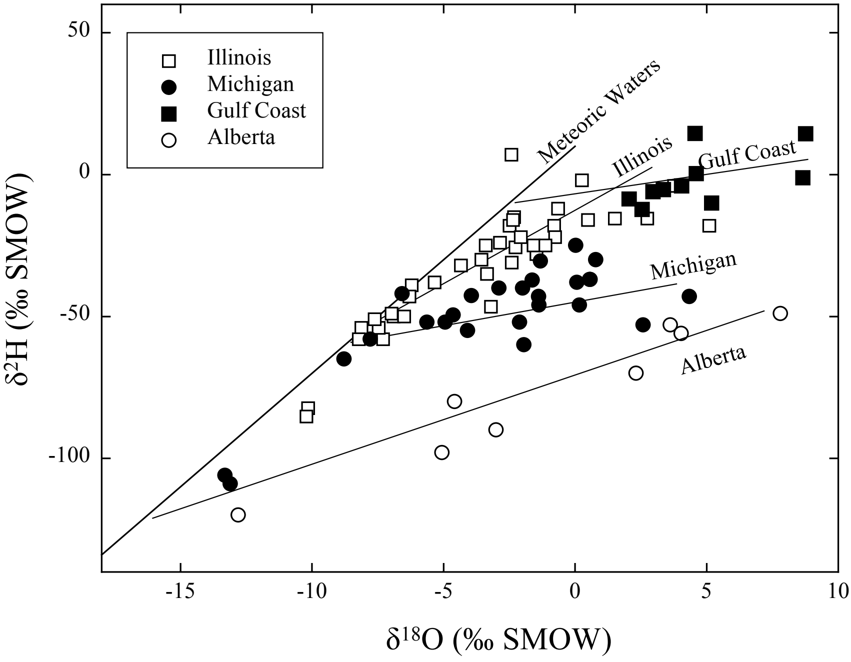

FIG.5. Isotopic composition of brines from the Gulf Coast, Illinois, Michigan, and Alberta sedimentary basins (Clayton et al., 1966). Note that in each basin the isotopic line intersects the Meteoric Water Line at values very close to Recent or Pleistocene meteoric waters.

On the basis of the observation that linear relationships between the δ^2H and δ^{18}O values of brines from each basin extend to Recent or Pleistocene local meteoric waters on the Meteoric Water Line, they concluded that the brines are predominantly of local meteoric origin. In a second study of the three-paper series, Graf et al. (1965) suggested that membrane filtration is also responsible for the observed regular changes in the isotopic compositions. The works by Clayton et al. (1966) and Graf et al. (1965, 1966), which provided a first strong evidence for the meteoric origin of deep sedimentary brines from as old as Early Palaeozoic formations, became classic works in the study of sedimentary brines in the coming years.

In the following years, from the late 1960s through 1980s, many investigators conducted systematic studies on the isotopic compositions of large collections of brines from various sedimentary basins; see reviews by Sheppard (1986), Kharaka and Carothers (1986), and Kharaka and Thordsen (1992). Undoubtedly, sedimentary basins have been undergoing dynamic, complex processes over extended time and space, and no consensus or comprehensive understanding has emerged for a single sedimentary basin. Three major sources of waters have been proposed or recognized to date: (a) recent or old meteoric waters, (b) diagenetically modified connate sea water, and (c) metamorphic waters. Also, mixing of any combinations of these waters. Since Sofer and Gat (1975) demonstrated that a body of extensively evaporated sea water can be depleted in deuterium and moderately enriched in ^{18}O (Fig. 4), several investigators advocated that one of important components in sedimentary brines is evaporated connate sea waters, which is characterized by the highest salinity and isotopic compositions within a suite of brines. Thus, it appears that the pendulum has swung somewhat from the largely meteoric origin (Clayton et al., 1966) back to the connate origin and its mixing with meteoric waters. General similarities observed in the isotopic compositions between sedimentary brines and inclusion brines in halite deposits from the same basins (Knauth and Beeunas, 1986) support the connate (marine or meteoric) origin of some components in sedimentary brines. However, the use of the "loop" phenomenon in Fig. 4 (Sofer and Gat, 1975) for a connate marine origin is somewhat problematic. This is because this phenomenon happens only to late-stage desiccating water bodies; thus their contributions to large masses of sedimentary brines are probably minor. In addition, several investigators extrapolated the "loop" further down on the δ^2H and $\delta^{18}O$ diagram for very late-stage brines. But, such extrapolation has no theoretical basis, and the lowest isotopic compositions that evaporating brines eventually reach are those at isotopic equilibrium with the atmospheric vapour at a given temperature.

During the past two decades, a number of attempts have been made to combine studies on the water isotopes with various other geochemical indicators (major and trace elements, other stable and radiogenic isotopes such as $^{87}Sr/^{86}Sr$, $\delta^{37}Cl$, $\delta^{11}B$, etc.). Radiogenic isotopes, particularly elevated $^{87}Sr/^{86}Sr$ ratios relative to contemporaneous sea waters, suggest extensive water–rock interactions (dissolution of feldspar and carbonates). However, quantitative understanding is still lacking on the influence of such processes on the stable isotope composition of brines. In addition, several other diagenetic processes (mixing, compaction-dehydration, isotopic exchange with H_2S and hydrocarbons, membrane filtration, etc.) probably overprinted the original isotopic signatures. The importance of these secondary processes, particularly those of isotopic exchange with other fluids and membrane filtration, is very poorly understood.

4.3. CRYSTALLINE BASEMENTS

Research in the late 1970s into the disposal of nuclear fuel wastes in stable plutonic rocks lead to the discovery of low-temperature (<30°C), hypersaline (TDS >250 g/L) brines of a Ca-Na-Cl type at great depths (>2000 m) across the Precambrian Canadian Shield (Fig. 6); see a review by Frape and Fritz (1987). Since then, brines of similar chemical compositions have been discovered in many other deep crystalline basements (down to 4 km) in the Scandinavian Shield, and Central and Western Europe, as recently reviewed by Kloppmann et al. (2002). These increasing amounts of data suggest that brines of the Ca-Na-Cl type are rather common, perhaps even a norm, at depths in crystalline basements. In addition to various geochemical processes (connate sea water, migration of sedimentary brines, dissolution of evaporites, hydrothermal/magnetic fluids, brine inclusions in minerals) similar to those for sedimentary brines, the freezing of sea water has been proposed for the source of salinity (Starinsky and Katz, 2003).

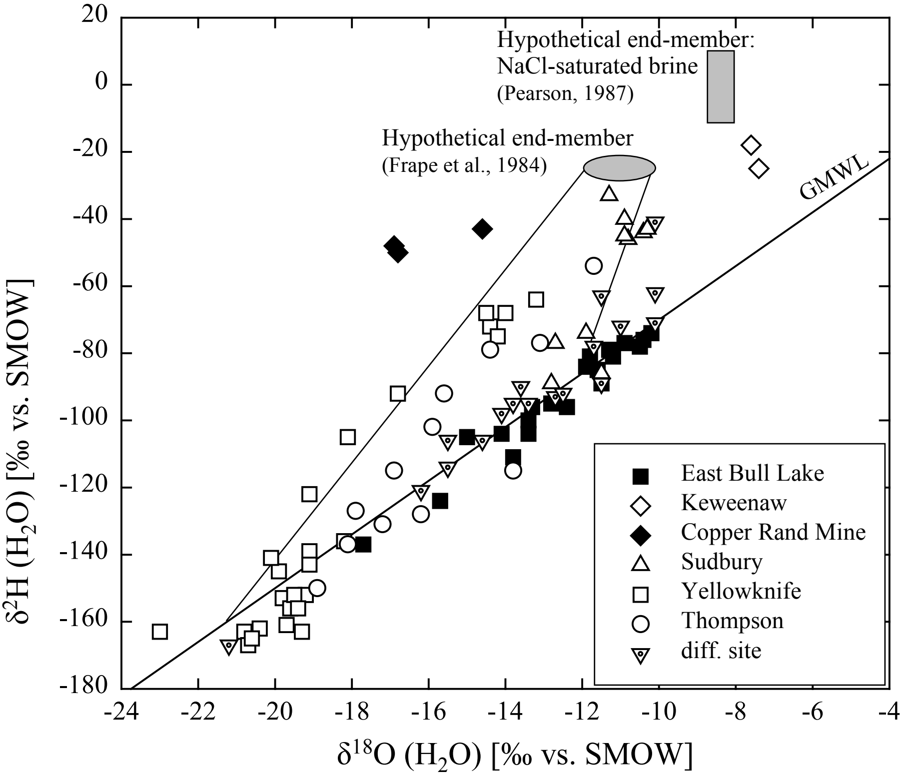

FIG. 6. Isotopic compositions of groundwaters and brines from the Canadian Shield (from Kloppmann, et al., 2002).

These brines from crystalline basements have characteristic stable isotopic signatures. They are plotted above the Meteoric Water Line (Fig. 6) and are distinctly different from brines in saline lakes and sedimentary basins. The magnitude of the departure upward from the Meteoric Water Line is positively correlated with their salinity, and mixing between a hypothetic end-member (δ^2H = 0 to -20‰ and $\delta^{18}O$ = -7 to -10‰) and local meteoric waters was postulated for Canadian Shield brines. A general consensus has emerged on the "exotic" isotopic signatures of hypersaline brines from crystalline basements. Various water–rock interactions under low temperatures (<100°C) and in low water–rock ratio environments can somewhat increase and significantly decrease δ^2H and $\delta^{18}O$ values of waters, respectively. Reactions include alteration of silicate minerals to clay minerals and isotopic exchange (dissolution-precipitation) of carbonate minerals.

4.4. MARINE ANOXIC BASINS

Anoxic hypersaline brine pools have been discovered in the Red Sea, the Mediterranean, and the Gulf of Mexico. These brines were almost certainly formed by the dissolution by sea water of the underlying salt deposits in the basins. Craig (1969) was able to identify a near-surface water in the Red Sea as the source of the brine, based on the isotopic signature of the brines. Since the Red Sea brines are nearly pure NaCl (i.e., no oxygen isotope effect), the CO_2-equilibration method employed for the $\delta^{18}O$ analysis yields the oxygen isotope composition ratios.

An interesting case is that of hypersaline brines discovered in the Tyro and Bannock Basins in the Mediterranean. The Tyro brines are of the Na-Cl type, but the Bannock brines are of the Na-Mg-K-Cl-SO_4 type. Stenni and Longinelli (1990) reported oxygen isotope ratios of the brines, using a CO_2-equilibration method, thus yielding the oxygen isotope activity ratios. They found that $\delta^{18}O$ activity values of the brines from the two basins are very similar (ca. 0.1‰ difference), but slightly (0.3-0.4‰) higher than those of the overlying Mediterranean sea water. On the basis of the similarity in the $\delta^{18}O$ activity values of the two brines, they suggested that the brines of the two basins were coeval. However, $\delta^{18}O$ composition values of the brines calculated from Eq. (3) are ca. 0.5‰ different for the two brines and distinctly (0.5-1.0‰) higher than the calculated $\delta^{18}O$ composition values of the Mediterranean sea water. This suggests that if the two brines had been formed by the dissolution of the underlying Messinian evaporites, waters for the two brines in the Tyro and Bannock Basins would have had different sources. A more systematic study, particularly of $\delta^{2}H$ values of the brines, which are not reported in Stenni and Longinelli (1990), would help identify the relevant geochemical processes for the formation of the two brines.

5. Concluding remarks

Isotopic studies of saline waters, especially those of saline lakes and sedimentary brines, made significant headway in the early 1960s. By the mid-1970s, the oxygen isotopic evolution of saline lakes was very well understood and modelled. However, it was not until the late 1980s that the hydrogen isotope behaviour of saline lakes was properly understood, because of our previous lack of understanding of the isotope salt effects and of proper analytical techniques for the hydrogen isotope ratios in brines. The origins and evolution of sedimentary brines still remain elusive even after almost four decades of active research and the widespread use of radiogenic and other stable isotope techniques. An increasing number of occurrences of brines from crystalline basements and their “exotic” isotope signatures are expected to generate a renewed interest in the study of continental subsurface brines. Our greatly improved understanding of isotope salt effects and the new analytical method (H_2–brine equilibration method) developed during the last decade or so should prove instrumental in these studies.

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HYDROCLIMATIC PROCESSES AND SYSTEMS

18. ISOTOPES IN ATMOSPHERIC MOISTURE

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1. Introduction

The Earth's atmosphere plays an important role in the global hydrologic cycle. It provides a dynamic link between major reservoirs of water on Earth, i.e. the global ocean, large continental ice sheets as well as soil moisture and other water reservoirs on continents such as surface waters, lakes and water in the biosphere (e.g. leafwater). Atmospheric water vapour is the basic vehicle through which this link is accomplished. The amount of water vapour stored in the atmosphere is negligible when compared for instance with the world ocean or continental ice sheets, the corresponding ratios being approximately 10^{-5} and $4x10^{-4}$, respectively (Berner and Berner, 1987). Although being trace constituent of the global atmosphere, responsible for only a tiny fraction of its total mass, atmospheric moisture plays a crucial role in the global ecosystem behaviour. It is a “substrate” from which precipitation is formed. Atmospheric water vapour is the most important greenhouse gas responsible for approximately 60% of the natural greenhouse effect which amounts to ca. 32°C. It is the major source of hydroxyl free radicals vital for efficient “cleaning” of the atmosphere. Finally, atmospheric moisture serves as an important regulator of heat fluxes in the atmosphere, greatly reducing thermal gradients between low and high latitudes.

In contrast to many other atmospheric constituents, distribution of water vapour in the lower atmosphere is highly inhomogeneous. Its concentration expressed as mixing ratio (kg H_2O per kg of dry air) decreases from approximately 10^{-3} in the lower troposphere close to the planetary boundary level to around 3×10^{-6} in the lower stratosphere and then increases again to approximately 10^{-4} at the altitude of 30 km. Close to the Earth's surface, its content varies between approximately 1.5×10^{-2} over tropical oceans to 5×10^{-3} over dry regions in the interior of continents and less than 10^{-3} over ice sheets at high latitudes. While distribution of water vapour in the troposphere is primarily controlled by thermal gradients imposing phase changes (evaporation-condensation-freezing, sublimation-resublimation), both in horizontal and vertical directions, photochemical reactions such as oxidation of

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methane remain the major controlling mechanism responsible for the distribution of water vapour in the stratosphere.

The mass of water vapour in the contemporary atmosphere is estimated to be around 1.3×10^{16} kg, of which about 85% occurs in the lower troposphere, below an altitude of about 5 km. In the past the atmospheric load of moisture most probably fluctuated with changing climate, being lower during glacial periods. The atmosphere is only partially saturated with water, with globally averaged relative humidity of the lower troposphere being around 85%. This apparent lack of saturation results from the existing thermal structure and large-scale circulation patterns of the troposphere.

The mean turnover time of water vapour in the global atmosphere is around 10 days with respect to the net evaporation or precipitation fluxes. If the gross exchange fluxes during the evaporation process are considered, the mean turnover time of water molecules in the atmosphere drops to approximately 2 days. It is therefore evident that the reservoir of atmospheric moisture is very dynamic, quickly responding to changes of external conditions such as the flux of energy reaching the Earth's surface and/or changes of temperature lapse rate in the lower troposphere.

From the overall perspective of the global hydrologic cycle, the isotopes directly incorporated in water molecules (^{2}H, ^{18}O, ^{3}H) are of primary interest. However, the atmosphere is also a space where a number of radioisotopes of other elements, both naturally produced and man-made, are present. The most important for hydrologic applications are ^{14}C, ^{36}Cl , ^{39}Ar, ^{81}Kr and ^{85}Kr. They enter the hydrologic cycle via dissolution in rainfall or in surface water bodies. In the case of ^{14}C, its pathway into the water cycle also includes the biosphere. These radioisotopes serve as time indicators, providing important information about dynamics of water movement in various compartments of the hydrologic cycle.

2. Isotopic composition of atmospheric water vapour and precipitation

Interest in the isotopic composition of atmospheric water vapour goes back to early days of isotope hydrology. In 1965, Craig and Gordon, in their seminal paper devoted to ^{2}H and ^{18}O variations in the ocean and the marine atmosphere (Craig and Gordon, 1965), reported measurements of isotopic composition of atmospheric water vapour over the North Pacific ocean. During the years 1966-67 and 1971-73, a number of vertical profiles of the deuterium and tritium content in the tropospheric water vapour up to the tropopause region over several locations in the continental USA were measured by Ehhalt (Ehhalt 1971, 1974). In 1967 and 1968, Taylor (1972) obtained twenty vertical profiles of the deuterium content in tropospheric water vapour up to an altitude of 5 km over Europe. To date, the sets of measurements by Ehhalt and Taylor remain the major source of information about the vertical distribution of tritium, deuterium and oxygen-18 in water vapour in the lower troposphere, i.e. in the region where most precipitation is formed.

Systematic studies aimed at characterizing the isotopic composition of near-ground water vapour on a regional scale were launched in the early 1980s in Europe. The isotopic composition of daily composite samples of atmospheric moisture was monitored by a network of several sites across the European continent between 1980 and 1984 (Schoch-Fischer et al., 1981). One site (Heidelberg, Germany) is still performing the operation today and has accumulated a unique, high-resolution record of ^{18}O and ^{2}H content of atmospheric water vapour spanning more than two decades (Jacob and Sonntag, 1991). As far as other regions are concerned, a year-long collection programme for daily samples of near-ground water vapour was carried out at Manaus and Belem in Brazil in the early 1980s (Matsui et al., 1983), as well as in Rehovot, Israel, in the 1960s (Tzur, 1971).

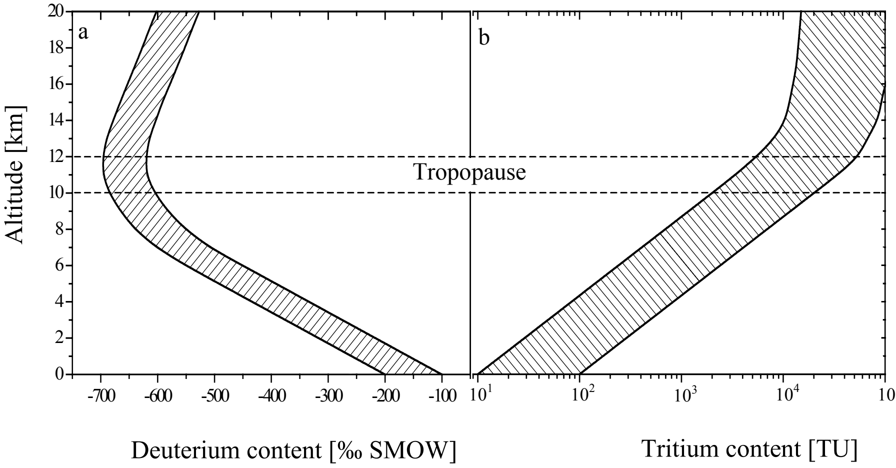

FIG. 1. Schematic representation of vertical distribution of a) deuterium and b) tritium content in atmospheric water vapour in the troposphere and the lower stratosphere. Tritium levels characteristic for the 1990s are shown.

During the 1990s the isotopic composition of atmospheric moisture near the ground was further investigated, although these studies had usually local character and were carried out over a limited time. The past several years have seen a renaissance of interest in isotope studies of near-ground atmospheric moisture. They are stimulated mostly by the need for better understanding of the isotopic signatures of precipitation and the links between the water and carbon cycles within the soil–plant–atmosphere domain.

Already the first attempts to measure the vertical distribution of ^{2}H and ^{18}O contents in tropospheric moisture revealed large variability of the measured isotope ratios, depending on location, season and specific meteorological conditions during sampling. Nevertheless, a common feature observed was a gradual depletion in heavy isotopes with increasing altitude up to the tropopause region, with a reversed trend detected within the stratosphere. In the generalized vertical profile of $\delta^{2}H$ shown in Fig.1 (a), the deuterium content decreases gradually with altitude, from $\delta^{2}H = -150\pm50$ ‰ close to the surface, to $\delta^{2}H = -650\pm30$ ‰ in the tropopause region and then increases again up to δ^2H = -500±50 ‰ at about 40 km altitude (Rozanski and Sonntag, 1982; Johnson et al., 2001). Changes of $\delta^{18}O$ with altitude reveal similar characteristics.

The observed distribution of δ^2H and $\delta^{18}O$ with altitude is thought to derive from the following processes: (i) preferential removal of heavy isotopes from atmospheric moisture, associated with gradual condensation of atmospheric water vapour during cloud formation, (ii) mixing of different air masses containing water vapour with contrasting isotopic composition, (iii) lofting and subsequent evaporation of ice crystals, and (iv) oxidation of methane. Whereas the first two processes are thought to be primary mechanisms controlling the vertical distribution of δ^2H and $\delta^{18}O$ throughout the troposphere, lofting of ice crystals across the tropopause region was suggested as an important phenomenon influencing ^2H and ^{18}O content in the lowermost stratosphere (Keith, 2000). Photochemical oxidation of methane in the mid- and upper stratosphere is responsible for the observed increase of water vapour content with altitude as well as the gradual increase of ^2H and ^{18}O content in this region (Johnson et al., 2001).

The observed vertical distribution of tritium in atmospheric water vapour (Fig.1 (b)) is established as a result of continuous supply of water vapour with low tritium content originating from evaporation of the ocean, and a downward mixing of stratospheric water vapour characterized by elevated tritium levels originating from atmospheric thermonuclear bomb tests in the early 1960s. Isotope fractionation effects play only a minor role in establishing the observed vertical distribution of ^3H. With a shrinking stratospheric reservoir of bomb tritium, the tropospheric levels of this isotope have gradually decreased. In the mid-1990s the observed tritium content varied from approximately 10^2 TU in the lower troposphere to 10^4-10^5 TU in the lower stratosphere (Zahn et al., 1998).

Most observations of the isotopic composition of atmospheric water vapour carried out to date have been performed at ground level, with moisture being sampled within the planetary boundary layer. Some general conclusions are emerging from the data accumulated so far, namely:

- Very large short-term variability of the isotopic composition of near-ground water vapour has been detected: day-to-day variations of ^2H and ^{18}O content recorded at mid-latitude continental sites are often of the same magnitude as seasonal changes, and are tightly linked to weather changes, reflecting the passage of air masses with different rainout histories. This variability is particularly pronounced during the winter months.

- The isotopic composition of atmospheric water vapour recorded near the ground during the summer months in mid-latitude continental regions reflects a significant contribution of transpired moisture, with the isotopic signature reflecting the mixture of summer and winter precipitation. This has a damping effect on the short-term variability induced by synoptic changes during summer.

- The isotopic composition of rainfall appears to be close to isotopic equilibrium with near-ground water vapour. The reason is that raindrops leaving the cloud base continuously re-equilibrate isotopically with the surrounding moisture on their way to the surface, the degree of this re-equilibration being controlled by the size of the raindrops, the actual height of the cloud base and the relative humidity of the atmosphere beneath the cloud. Solid precipitation (snow, hailstone) is usually more depleted in heavy isotopes, reflecting equilibrium conditions at much lower in-cloud temperatures. At sufficiently low condensation temperatures, the isotopic composition of snow is influenced by additional kinetic effect, linked to supersaturation conditions around the forming snow flakes (Jouzel and Merlivat, 1984).

- It seems that the isotopic composition of monthly precipitation, which is the basic type of data being collected worldwide, properly reflects the mean isotope status of the atmospheric water vapour reservoir within the planetary boundary layer. However, whilst this holds for moderate climates, this might not be the case under semi-arid and arid conditions.
- The observed tritium concentration in near-ground atmospheric water vapour may be significantly influenced by surface releases of technogenic tritium. Elevated levels of tritium have been recorded in water vapour and precipitation collected in the vicinity of such technogenic sources (Rozanski et al., 1991).

Since the formation of precipitation is an episodic phenomenon, limited in time and space, the isotopic composition of rainfall should reflect the overall isotope status of the water vapour reservoir at the time when the precipitation was formed. Indeed, numerous isotope studies of single rain events have revealed enhanced isotope variability in relation to monthly means, comparable with changes recorded in the water vapour reservoir.

The reservoir of atmospheric water vapour in the lower troposphere (< 5 km) constitutes a major “substrate” from which precipitation is formed. Applications of the isotopic composition of precipitation in hydrologic studies require that the spatial and temporal variability of this composition be well characterized. The spatial and temporal variability of isotopic composition of precipitation has been monitored on the global scale since the early 1960s, in the framework of the Global Network of Isotopes in Precipitation (GNIP) operated jointly by the IAEA and WMO (http://isohis.iaea.org). Major features of this variability have been extensively discussed in several review papers (e.g. Dansgaard, 1964; Yurtsever and Gat, 1981; Rozanski et al., 1991, Rozanski et al., 1993) and are also addressed briefly elsewhere in this volume. The empirical relationships characterizing links between isotope composition of rainfall and various environmental parameters such as latitude, altitude, distance to the coast, amount of precipitation and surface air temperature have been explored in numerous studies related to the hydrologic cycle. The general dependency of the stable isotope composition of precipitation on temperature has been used to differentiate between recently recharged groundwater and palaeowater.

Figure 2 summarizes major processes and mechanisms controlling the isotopic composition of atmospheric water vapour and precipitation in the lower troposphere. They constitute a physical basis for understanding the observed spatial and temporal variability of heavy isotope ratios in monthly precipitation to which the majority of available data are related.

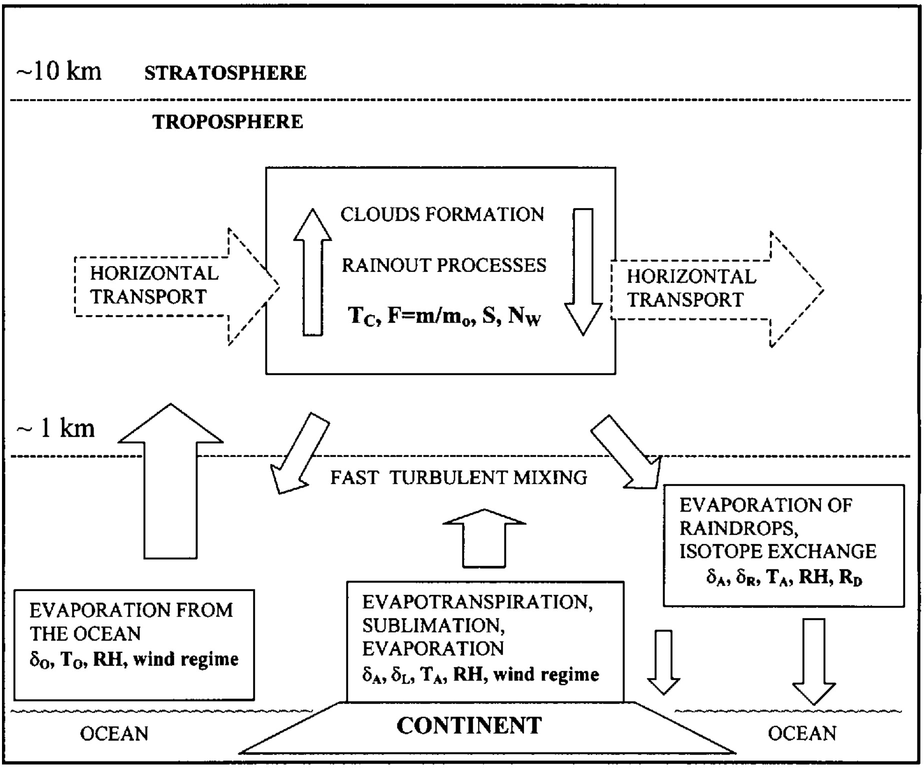

FIG. 2. Schematic representation of the processes controlling isotopic composition of atmospheric water vapour and precipitation. Meaning of symbols: T_O, T_A, T_C - temperature f the ocean surface, temperature in the cloud and temperature within the planetary boundary layer, respectively; RH - relative humidity; δ_A, δ_O, δ_R, δ_L - isotopic composition of atmospheric moisture, of the surface ocean, of the raindrops and of the evaporating water from the continents (surface water bodies, and leaf water) respectively; F - degree of rainout of the given cloud system; S - degree of supersaturation within the cloud; N_W - liquid water content in the cloud; R_D - radius of raindrops.

The first step is the evaporation process from the ocean. This process is well described by the Craig and Gordon mechanistic model which is discussed by Froehlich, Gonfiantini and Rozanski in this volume. The major controlling parameters are: isotopic composition of the surface ocean, sea-surface temperature, relative humidity of the atmosphere and wind regime. Marine moisture is then transported, both vertically and horizontally, until saturation conditions are reached and cloud formation starts.

In-cloud processes may involve fast advective upward transport with entrainment of moist air from below, phase changes with formation of rain drops and/or snow/hail particles, isotope exchange between liquid and gaseous phases in the cloud, kinetic isotope effects during snow formation, removal of precipitation elements at the cloud base and dissipation of dry air with isotopically depleted moisture at cloud tops. The raindrops on their way down to the surface undergo partial evaporation in the unsaturated atmosphere below the cloud base. This process is coupled with isotope exchange between the surrounding moisture and falling raindrops. Both processes modify to some extent the initial isotopic composition of raindrops leaving the cloud base. The isotopic composition of atmospheric moisture within the planetary boundary layer over the continents is modified by backward fluxes of vapour transpired by plants and evaporated from the soil and surface water bodies. The isotopic composition of those fluxes may differ significantly from that of atmospheric moisture of marine origin. Finally, turbulent mixing acts at each step of water vapour transport through the atmosphere, smoothing to some extent the spatial isotope gradients created by the processes outlined above.

First theoretical descriptions of the observed spatial and temporal variations of ^{2}H and ^{18}O content in meteoric waters have their origin in the “isolated air model” based on Rayleigh condensation. The Rayleigh condensation concept has also been used in connection with classical equations of water balance of the atmosphere, applied to model regional isotope fields. Nowadays, two approaches are being mostly pursued: (i) backward trajectory modelling, where the history of precipitating air mass at the given point is being reconstructed from meteorological data, and (ii) regional or global modelling of transport of isotope water molecules in the framework of the global circulation models. The general conclusion emerging from all these models is that the isotopic composition of precipitation recorded at the given location on the continent or over the ocean is a function of rainout and mixing history of the moist air mass from which the precipitation was formed.

Isotope studies of single rain events revealed that isotope composition of successive portions of precipitation within the given event may vary dramatically. The evolution of δ^{18}O or δ^{2}H in time is often V- or W-shaped; a sharp decrease of the δ values was usually observed with a minimum value sometime in the middle of the shower. The most depleted isotope values corresponded usually to the period of most intense rain. The range of observed in-storm variations was quite large, reaching in some cases 10 to 12 per mill for δ^{18}O. The general conclusion of these studies was that the isotopic composition of precipitation from a given rainfall event depends strongly on meteorological history of the air and specific conditions in which the precipitation is produced, as well as isotopic composition of moist air through which it falls.

Precipitation samples collected on the per-event basis also reveal a strong linkage between their isotope signature and the storm's path, structure and evolution (e.g. Gedzelmann and Lawrence, 1990). The fact that isotope fractionation factors for ^{2}H and ^{18}O are sensitive functions of temperature and of the dynamics of phase changes associated with atmospheric moisture (condensation, snow and hail formation) and that the ^{3}H content in atmospheric water vapour is a function of altitude, has been utilized in studying microphysics and the dynamics of in-cloud processes. In particular, with the aid of isotope tracers of water it has been possible to derive information about growth regimes of hailstones, to reconstruct trajectories of hailstones and to investigate the dynamics of individual weather systems (Jouzel, 1986; Smith, 1992).

3. Radioisotopes in the atmosphere

Various radioisotopes permanently present in the atmosphere have long been a subject of interest for hydrology. This interest was stimulated mostly by the fact that, if incorporated in precipitation or dissolved in surface waters, these radioisotopes could be used to derive information on age of groundwater

Table 1. Selected radioisotopes present in the atmosphere, used in hydrologic studies.

Isotope	Half-life	Sources	Specific activity or deposition rate
^{3}H	12.33 a	cosmic rays [b] bomb tests [a] nuclear industry [b]	$0.5 \div 1.3$ Bq/dm^3 H_2O [d] ~ 140 Bq/dm^3 H_2O [e]
^{14}C	5730 a	cosmic rays [a] bomb tests [b] nuclear industry [b]	~ 0.21 Bq/g C [f] ~ 0.36 Bq/g C [g]
^{36}Cl	301,000 a	cosmic rays [a] bomb tests [b] nuclear industry [c]	~ 5 atoms/m^2 ·a [h] ~ 390 atoms/m^2 ·a [i]
^{39}Ar	269 a	cosmic rays [a]	1.87×10^{-3}Bq/dm^3 Ar
^{81}Kr	210,000 a	cosmic rays [a]	1.17×10^{-3}Bq/dm^3
^{85}Kr	10.72 a	cosmic rays [c] nuclear industry [a]	~1400 Bq/dm^3 Kr [j]

a) dominant source; b) source dominating in specific periods and/or regions; c) generally insignificant source; d) range of natural tritium levels in precipitation; e) maximum concentration of tritium in annual precipitation of the northern hemisphere (averaged) in 1963, resulting from atmospheric nuclear bomb tests; f) natural level of ^{14}C in atmospheric CO_2 ; g) maximum annual concentration of ^{14}C in atmospheric CO_2 of the northern hemisphere in 1963, resulting from atmospheric nuclear bomb tests; h) estimated natural deposition (dry and wet) of ^{36}Cl in the northern hemisphere; i) maximum annual deposition of bomb-produced ^{36}Cl in 1957; j) average concentration in the northern hemisphere in the year 2000.

The presence of radioisotopes in the atmosphere results from natural production by cosmic rays, or is due to anthropogenic releases (nuclear bomb tests, technogenic emissions), or both.

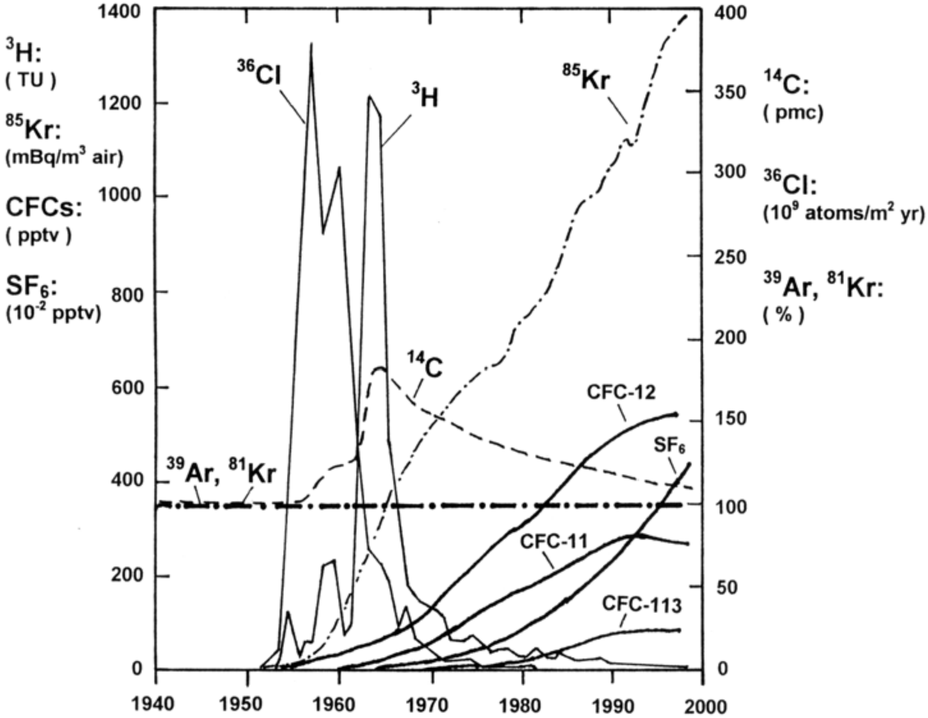

FIG. 3. Time histories of atmospheric concentrations of several radioisotopes during the past 60 years, being used as dating tools in hydrologic studies. For comparison, time histories of some non-radioactive trace substances in the atmosphere (freons; sulphur hexafluoride) are also shown (after Alley et al., 2002 – modified). The tritium curve is considered representative for northern hemispheric precipitation. The radiocarbon content in atmospheric CO_2 is reported in Per cent of Modern Carbon (pmc). Current concentrations of ^{39}Ar and ^{81}Kr in the atmosphere (cf. Table 1) are reported as 100 %. For ^{36}Cl the total deposition rate is reported. For comparison, time histories of some non-radioactive, anthropogenic trace constituents in the atmosphere (CFC-11, CFC-12, CFC-113, SF_6) are also shown in Fig.3.

Table 1 summarizes basic data for several atmospheric radioisotopes employed in studies of global hydrologic cycle. Those which have only natural sources are ^{39}A and ^{81}Kr – their specific activity in the atmosphere is practically constant. Others have very low natural background and their concentration is determined exclusively by anthropogenic releases (^{85}Kr).

A special category is formed by radioisotopes which were produced in large amounts during atmospheric nuclear bomb tests in late 1950s and early 1960s. The most prominent example of this group is tritium. It reveals a distinct maximum of concentration in the global rainfall in 1962-63, when the major tests were performed. Similar behaviour is seen for ^{36}Cl, although the maximum concentration of this isotope in atmosphere was observed already in the late 1950s (cf. Fig. 3). The tritium concentration in precipitation is nowadays close to natural levels in most parts of the world. Chlorine-36 concentration returned to natural levels in the 1980s.

The "time histories" of different radioisotopes in the atmosphere are shown in Fig. 3. They represent the input functions to hydrologic systems (ocean, lakes, groundwater bodies) and thus determine the mean residence time of water in such systems. The interpretation of specific activities of radioisotopes measured in groundwater is done mostly in the framework of so-called lumped-parameter box models. In recent years, radioisotope data have been used more and more as a calibration and validation tool for numerical flow and transport models.

4. Outlook

Despite the fact that the isotopic composition of atmospheric water vapour has been investigated for more than four decades, our knowledge of isotopic variability in this reservoir on different temporal and spatial scales is still far from satisfactory. Most of the existing data has been gathered at ground level on continents, where the atmospheric vapour reservoir is strongly influenced by backward water fluxes from the biosphere and the soil. On the other hand, future global circulation models focused on simulating the response of the global hydrologic cycle to climate change would greatly benefit from the availability of reliable, high-quality systematic data on the isotopic composition of atmospheric water vapour, both over the ocean and the continents. Of particular value in this respect would be systematic measurements of vertical profiles of δ^2H and δ^{18}O in atmospheric moisture over the oceans and the continents.

More measurements of the isotopic composition of atmospheric moisture close to the ground are also needed, in the context of growing interest in better understanding of the interactions between the carbon and water cycle within different ecosystems. This specific application requires high-resolution sampling of water vapour in combination with measurements of isotopic composition of plant and soil water, as well as isotope characterization of different components of the carbon cycle (atmospheric CO_2, soil CO_2, plant carbon, organic matter in the soil, etc.).

The major challenge in studying the isotopic composition of atmospheric water vapour has always been adequate sampling technique, allowing collection of water vapour without isotope effects. Historically, first determinations of the isotopic composition of atmospheric water vapour in the 1960s were performed with the aid of a cryogenic method utilizing low temperatures. The vapour was removed quantitatively from the stream of air by passing it through specially designed collection traps immersed in a mixture of dry ice and alcohol. Despite numerous attempts to introduce another collection techniques (e.g. absorption on activated charcoal or on a molecular sieve), this method remains the most frequently used up to now. Emerging new applications would greatly benefit from in situ spectroscopic measurements of ^{18}O and ^{2}H contents in atmospheric water vapour. It is hoped that such techniques will soon become available.

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19. HOW MUCH CLIMATIC INFORMATION DO WATER ISOTOPES CONTAIN?

A systematic comparison between the IAEA/GNIP isotope network and the ECHAM 4 atmospheric general circulation model

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1. Introduction

In the last 50 years, the $^{18}O/^{16}O$ signature of meteoric water (in the following, $\delta^{18}O_{prec}$) has become a key tracer intensively used both in hydrology and in palaeoclimatology. In palaeoclimatology, the original atmospheric signal, i.e. $\delta^{18}O_{prec}$, is reconstructed by means of a variety of palaeo-archives such as ice cores, lacustrine sediments, tree ring cellulose or speleothems. In both research fields, the understanding of the original isotope signal, before entering a hydrologic system or before being archived, is essential.

To this end, a powerful modelling tool was developed about 20 years ago: Atmospheric General Circulation Models (AGCMs) fitted with water isotope diagnostics (Hoffmann et al., 1998; Joussaume et al., 1984; Jouzel et al., 1987). The fitting procedure is a relatively straightforward, although technically difficult process. The hydrologic cycle as described in these three-dimensional AGCMs has

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Table 1. List of AGCMs which are equipped with a water isotope module. Publications are given in order of the relevant time-scale.

AGCM	Annual and seasonal time scale	Interannual time scale	Palaeo i.e. >1000 years time scale
LMD, Paris	Joussaume et al., 1984		Joussaume and Jouzel, 1993
GISS, New York	Jouzel et al., 1991; Jouzel et al., 1987	Cole et al., 1999; Cole et al., 1993; Vuille et al., 2003a; 2003b	Charles et al., 1994; Delaygue et al., 2000a; Delaygue et al., 1999; Delaygue et al., 2000b; Jouzel et al., 2000; Jouzel et al., 1994
ECHAM, Hamburg	Hoffmann et al., 1998	Werner and Heimann, 2002; This paper.	Hoffmann and Heimann, 1997; Hoffmann et al., 2000; Werner et al., 2000a; Werner et al., 2000b; Werner et al., 2000c
GENESIS, Boulder	Mathieu et al., 2002		
MUC, Melbourne	Noon and Simmonds, 2002a; Noon and Simmonds, 2003	Noon and Simmonds, 2002b	

to be replicated, and each time a phase transition is calculated in the model the corresponding fractionation process has to be taken into account to estimate the isotopic composition of the various water fractions. In this way, the water isotopes are computed solely depending on climate, with their variability simulated by the AGCM. The AGCM itself is constrained, depending on the time scale considered, by observed or reconstructed sea surface temperatures (SSTs), atmospheric greenhouse gas concentrations and solar insolation. To date, at least half a dozen modelling groups have followed this approach (see Table 1) and additional modelling groups are expected to build such an isotope module into their GCMs.

The focus of interest of the various scientists using the results of three-dimensional water isotope models is different, according to their main working field and speciality.

GCM modellers, for example, are interested in an independent test of the parameterization of the model's water cycle. A variety of basically unobserved variables such as condensation temperatures, cloud thickness, evaporation rates, etc. influence the $\delta^{18}O_{prec}$ signal. Therefore, comparison of modelled and observed water isotope signals presents a valuable test for this important part of the physics of AGCMs. Hydrologists, on the other hand, are increasingly applying their models to larger spatial scales. This typically involves the need to apply new and uncertain parameterization techniques and again calls for an independent and sensitive test procedure, as provided by water isotopes. Spatial scales of AGCMs and some hydrologic models are now sufficiently close to each other that a physical coupling will be feasible soon.

Finally, palaeoclimatologists certainly have the most vivid interest in a water isotope modelling tool that allows the interpretation of $\delta^{18}O_{prec}$ not only in terms of local temperatures or precipitation rates but also in terms of atmospheric circulation and source region changes, for example.

Classically, palaeoclimatologists do the necessary calibration of an isotope palaeo-record using a modern analogue technique. They establish a relationship between regional $\delta^{18}O_{prec}$ and climate parameter (for example annual $T_{surface}$) and subsequently apply this modern spatial relationship to the temporal $\delta^{18}O_{prec}$ series they have measured. However, it is well known that such modern analogue methods involve many uncertainties. The most important example of its failure is probably the application of the modern spatial $\delta^{18}O_{prec}$/temperature relationship in interpreting the ice core records in Central Greenland. Here, a number of independent studies have shown that, at least on a glacial/interglacial time-scale, the real temporal $\delta^{18}O_{prec}$/temperature slope is about half the modern spatial slope (Cuffey et al., 1995; Dahl-Jensen and Johnsen, 1986; Severinghaus et al., 1998). It is certainly one of the major successes of "isotopic AGCMs" that they were able to give a sound explanation for this de-calibration of the isotopic thermometer by simulating a strong shift in the seasonal distribution of precipitation under full glacial conditions (Werner et al., 2000c).

This Paper reports on advances in modelling water isotopes by means of GCMs during the last five years. After briefly summarizing the fractionation physics built into AGCMs (Section 2), we present results of the ECHAM "isotopic AGCM" integrated under boundary conditions corresponding to the 20th century. In Section 3, we present a model/data comparison for the most recent version of the ECHAM

AGCM, the cycle 4 version of the climate model of the Max-Planck Institut für Meteorologie, Hamburg. In an earlier paper (Hoffmann et al., 1998), results of the cycle 3 version of the ECHAM model were compared with observations of the IAEA/GNIP network. Here, we did a systematic model evaluation of the ECHAM 4 version in T30 resolution on a seasonal to interannual scale. The model/data comparison presented here is designed to include "palaeo-isotope" series in the future and to extend this kind of study to the interdecadal and centennial time-scale.

2. Model physics

The ECHAM 4 model is documented in detail in Roeckner et al., 1996. Isotope physics was described in Hoffmann, 1995 and Hoffmann et al, 1998,and further results with the actual ECHAM 4 model are documented in Werner and Heimann, 2001and Werner et al., 2000b, 2000c. Here we summarize briefly the way how the physics of water isotopes is, in principle, built into all existing "isotopic AGCMs".

According to Merlivat and Jouzel, 1979, isotopic fractionation at the ocean surface combines effects of equilibrium and kinetic fractionation. The scaled difference between δD and δ^{18}O in meteoric water, d=δD-8*δ^{18}O, the deuterium excess, sensitively depends on the non-equilibrium, kinetic fractionation at the ocean–atmosphere interphase.

This quantity is not discussed here, but in first order the above approach gives satisfying results for the deuterium excess simulated by AGCMs, (Jouzel et al., 1987, Delaygue et al., 2000b; Hoffmann et al., 1998; Werner et al., 2000a). Cloud-internal processes (condensation, evaporation) take place in isotopic equilibrium, and a fraction of falling raindrops is assumed to be in equilibrium with the surrounding water vapour, depending on the type of precipitation: 95% is in equilibrium for large-scale (typically extra-tropical) precipitation due to the comparably small droplet size and only 50% of the precipitation is in equilibrium if the precipitation is formed in convective events.

Though it is reasonable to assume that isotopic equilibrium is less complete in convective systems than in large-scale cloud systems, the actual values of the equilibration are not based on observations. In nature, equilibration might vary a lot between individual precipitation events. Further kinetic (non-equilibrium) processes take place during the formation of ice crystals at very cold temperatures (Jouzel and Merlivat, 1984) and during the fall of raindrops below the cloud base through a very dry atmosphere (Jouzel et al., 1987). In the ECHAM model, no fractionation takes place during evapotranspiration from the continental surface. Though certainly justified for plants this is a strong assumption for evaporation from bare soils and snow surfaces. The water isotopes were tracked in the model's soil hydrology and runoff. For further details on the incorporation of the water isotopes into AGCMs we refer to the original publications (Hoffmann, 1995; Joussaume, 1983; Jouzel et al., 1987).

3. Results

3.1. GLOBAL RELATIONSHIPS

Comparing results of a GCM with observations is always a difficult task, as a spatially very heterogeneous data set can be compared in several different ways with gridded model results. Thus it is sometimes difficult to ascribe the differences between observations and model results clearly to model deficiencies or to the chosen method of comparison. Here we perform the data/model comparison strictly on the basis of the existing observational IAEA/GNIP network.

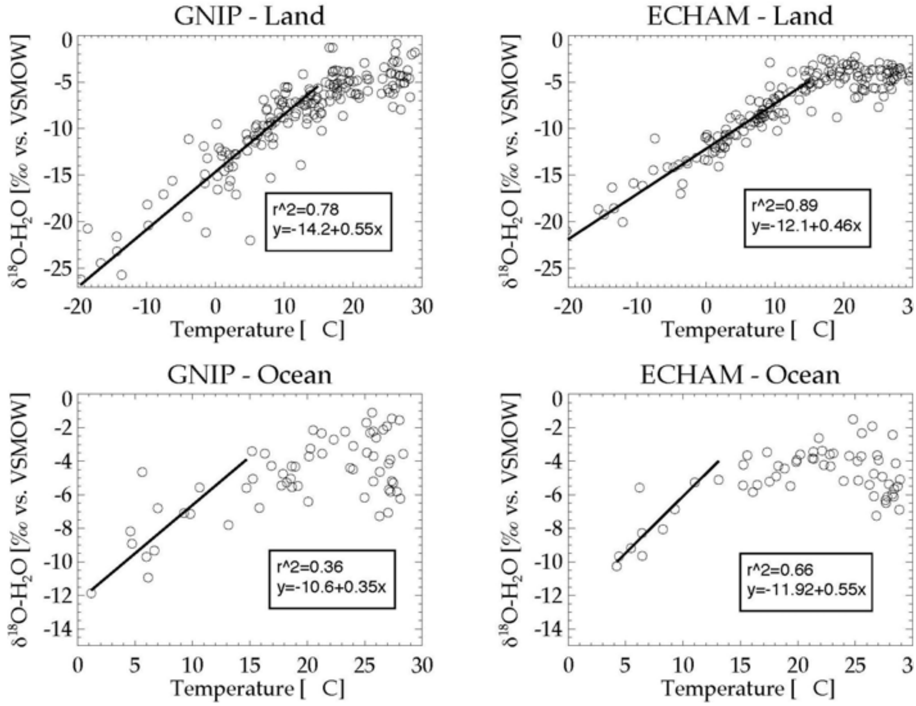


FIG. 1. Comparison of the simulated and observed temperature/$d^{18}O$ relationship (annual mean) over land and over the ocean, respectively. The simulation of the ECHAM 4 model was forced with observed SSTs for the period 1903-1993. The observations are exclusively from the GNIP/IAEA networks functioning since 1961 (http://isohis.iaea.org). Annual and monthly means of the model and of the observations were computed for the same time period, respecting gaps in the observations. The linear correlations are calculated for a mean temperature < 15°C.

The ECHAM model was integrated in T30 spectral resolution (corresponding to a spatial resolution of 3.75° x 3.75° and a model time step of 30 minutes) and monthly observations of the isotopes and the concurrent meteorological data were superimposed on the spatial grid of the model. If several observations existed within one grid cell we simply calculated the precipitation weighted arithmetic mean of the existing data. Monthly anomalies were only considered when at least four measurements per month existed. A 20th century simulation with the cycle version 4 of the ECHAM model was performed using realistic SST (SST data set provided by the United Kingdom Meteorological Office (Hurrell and Trenberth, 1999) and greenhouse gas forcing from 1903-1993 (IPCC, 1995). Model results were treated in the same way as the observations using exactly the months when observations were available.

Global spatial relationships between the water isotopes and near-surface temperature are calculated separately over the continents and over the oceans, respectively (Fig. 1, upper and lower panel). In contrast to the cycle 3 version (which overestimates the $\delta^{18}O_{prec}/T$ relation (Hoffmann et al., 1998) the model underestimates by about 15% the spatial isotope/temperature relation over land. It is possible that this difference between the cycle 3 and 4 version of the ECHAM model is due to the fact that in this study we compare the results on the GNIP/IAEA observational grid.

The correlation ($r^2_{obs}=0.78$; $r^2_{model}=0.89$) and the point where the temperature control on the isotopes breaks down (at about 15°C) are in good agreement with the observations. Over the ocean, continuous vapour recharge of air masses leads to the weakening of the isotope/temperature relationship, which is correctly captured by the model.

The temperature threshold of about 15°C in the case of the “temperature effect” geographically corresponds to the boundary between mid- and low latitudes. This termination is probably triggered by the growing importance of convective precipitation. The intensity of convective events is only spuriously affected by surface temperature and, rather, is controlled by large-scale moisture confluence. In a simple Rayleigh distillation model, rainout intensity controls the isotopic signal and, consequently, it was suggested that in convective events the precipitation amount itself is inversely related to the water isotopic composition of the rain (Dansgaard, 1964). This inverse $\delta^{18}O_{prec}$ /prec. relation, or “amount effect”, appears only weakly when comparing annual means of precipitation amount and of the water isotope signal $\delta^{18}O_{prec}$ for the GNIP stations (see Fig. 2): it is rather overestimated by the model.

Though the “amount effect” is clearly seen for selected stations and regions (for example, Rozanski et al., 1992; Rozanski et al., 1993) globally the precipitation–water isotope relationship is very noisy (in the observations and in the model). One could expect the amount effect to appear more clearly over the tropical ocean, since terrestrial stations are more influenced by atmospheric circulation, which occasionally brings a station under the influence of continental, and thus depleted, air masses. However, even when restricting our analysis to ocean stations with a mean temperature greater than 15°C, the amount effect still shows up only weakly

(Fig. 2). Even when computing the same $\delta^{18}O_{prec}$/prec. correlation on a monthly basis (not shown here) the amount effect does not appear much clearer on the global scale.

In a next step we compare monthly means of the water isotopes and temperature to validate the simulated seasonal cycle (Fig. 3). The modelled seasonal $\delta^{18}O_{prec}$/temperature relation is in good agreement with the observations. However, as for the spatial $\delta^{18}O_{prec}$/prec. relation (Fig. 2) the model underestimates the noise in the seasonal relation over the ocean.

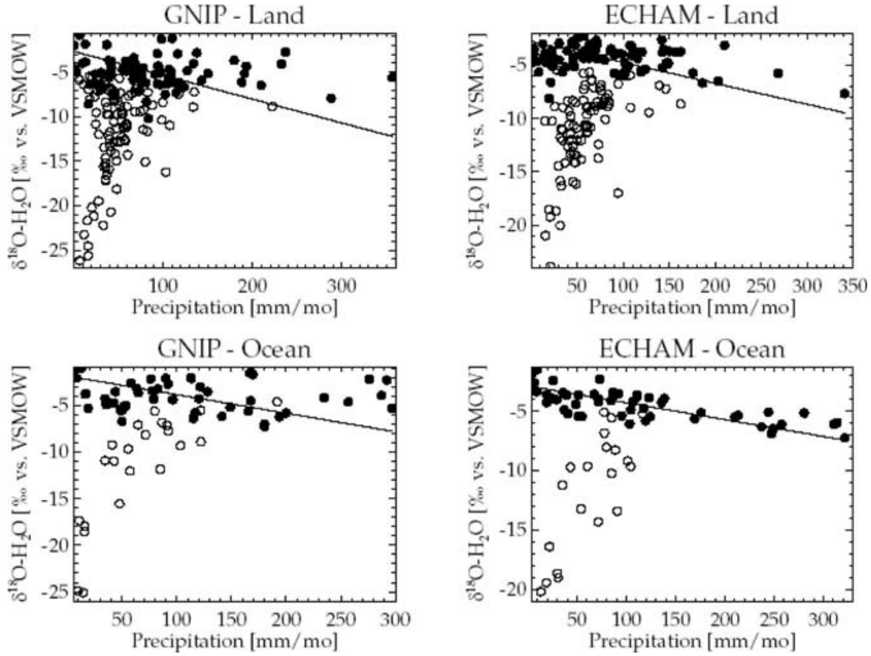


FIG. 2. Same as for Fig.1 for the Precipitation/δ^{18}O relationship. This time, the correlations were computed for all stations/grid points with a mean temperature >15°C (full circles).

3.2 ANNUAL AND SEASONAL SCALE

In order to identify regions and climatic zones where model results deviate significantly from the observed seasonal cycle we calculated phasing and amplitude of the simulated water isotope signal and compared them to observations (see Fig. 4). The phasing is evaluated by computing the correlation between simulated and observed monthly mean values. A correlation of 1 therefore means a perfect phasing of the simulated isotope cycle. In high northern and southern latitudes the

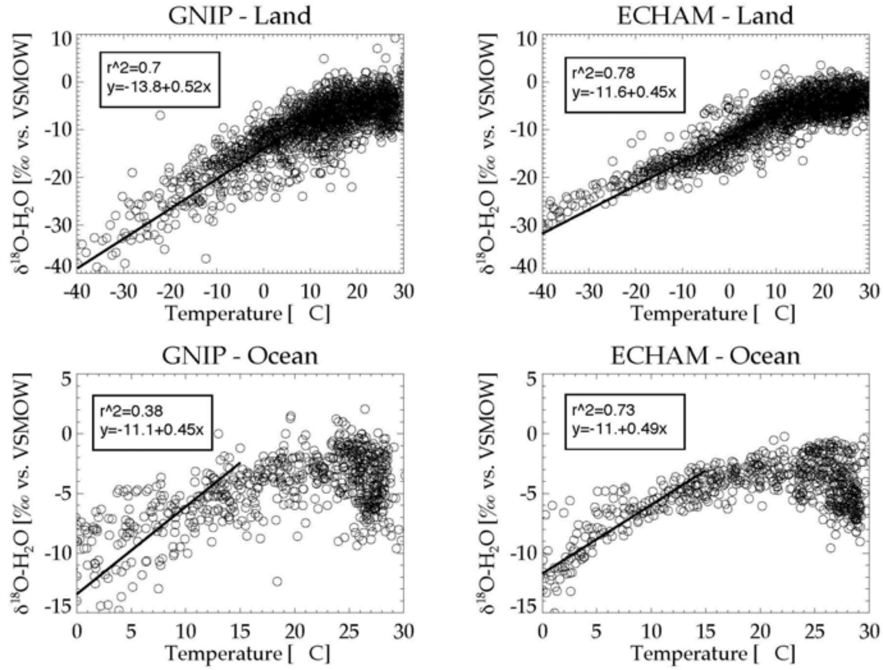


FIG. 3. The temperature/$\delta^{18}O$ relationship for monthly means. Correlations are computed for stations with a mean temperature < 15°C.

model quite accurately simulates the seasonal cycle (r>0.7). In low latitudes the model occasionally does not reproduce the correct spatial extension and/or onset of monsoon precipitation (China). Generally, poor statistics (i.e. rare rain events) most probably is responsible for a comparably small correlation in some dry areas (Sahel and the Mediterranean region). Equally the model has problems to simulate the precise position of the Inter-Tropical Convergence Zone, as is evident over the tropical Pacific and South America (r sometimes <0.3). The strong rainfall within the ITCZ is typically associated with relatively depleted isotope values, which is why small shifts in its simulated position relative to the observations lead to a drastic worsening of the correlation. The amplitude of the seasonal cycle is evaluated in Fig. 4(b), which shows the relative deviation of the simulated from the observed seasonal amplitude:

$$\text{Amplitude} = ((\text{Max}^{\text{GNIP}}-\text{Min}^{\text{GNIP}})/(\text{Max}^{\text{ECHAM}}-\text{Min}^{\text{ECHAM}}) - 1) * 100. \qquad (1)$$

where Max and Min refer to the maximum and minimum δ^{18}O values of the long-term monthly means in the GNIP network and in the ECHAM simulation respectively.

Ideally the relative deviation of the simulated amplitude (Eq. (1)) would always be zero. In fact, at most GNIP stations the model indeed reproduces the observed amplitude within 20%, and larger deviations can only be identified in regions with small seasonal amplitudes (Atlantic ocean sites). Clear spatial patterns can be found, for example, over Europe, where the model underestimates the seasonality in southern Europe and overestimates it in northern Europe.

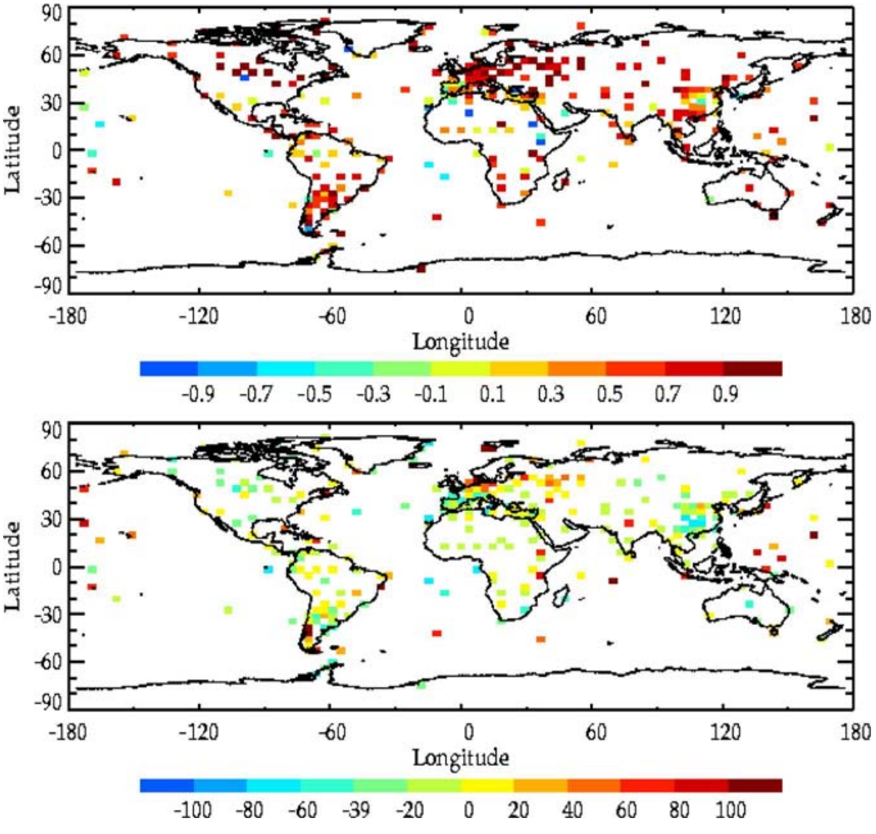


FIG. 4. Phasing and amplitude of the simulated water isotope signal relative to the GNIP/IAEA observations. The upper panel shows the non-normalized correlation between simulated and observed isotope signals (ideally based on 12 values). Perfect agreement between model and observations corresponds to r=1. The lower panel shows the reproduction of the seasonal amplitude (Eq. (1)). 100% corresponds to a perfect agreement between the model and the observations.

3.3. INTERANNUAL TIME-SCALE

As mentioned above, we restrict our analysis of interannual isotope/climate parameter relationships to the time period common to IAEA/GNIP measurements (i.e. excluding also all sampling gaps at individual GNIP stations) and model simulation, that is the period from 1961-1993. In Figs 5-8 correlations and slopes are presented between monthly anomalies of $\delta^{18}O_{prec}$ and temperature or precipitation, respectively. Observed correlations between monthly anomalies of $\delta^{18}O_{prec}$ and temperature are spurious, even in regions where long-term high-quality records exist, e.g. over Europe. Only locally does the correlation exceed $r > 0.4$; this value does not improve even when we take into account the full GNIP/IAEA sampling period (and not just the period 1961-1993).

The result implies that typically more than 80% of the interannual isotope variability is controlled by factors other than local temperature variations. Important factors that might strongly affect the $\delta^{18}O$ signal are changing moisture source regions and continental recycling rates, both known to mask a simple control of $\delta^{18}O_{prec}$ by local climate parameters. This result has already been mentioned in several studies analysing interannual variability in isotopic models and in the GNIP observational network (Cole et al., 1999; Vuille et al., 2003b).

In summary we are faced with a variety of locally and temporally highly variable factors influencing the $\delta^{18}O$ signal and thus, a single dominating factor, at least on the interannual scale discussed here, is difficult to identify. Though most $\delta^{18}O_{prec}$ /temperature correlations are positive, in low latitudes (Southeast Asian monsoon system) sometimes they become negative. Such unphysical relations are caused by an overshadowing amount effect, i.e. strongest rainfall at warm summer temperatures creates rainout conditions which give rise to more negative isotope signals. Observed $\delta^{18}O_{prec}$/temperature slopes vary also quite substantially, between 0.1‰ per °C and 0.6% per °C over Europe and North America for example. A reasonable calibration for palaeostudies based on these findings is not feasible.

3.4. PREC./TEMPERATURE

The ECHAM model (Fig. 6) overestimates the influence of interannual temperature variations on the water isotopes by at least a factor of 2 (Figs. 5 and 6). Simulated $\delta^{18}O$ correlations are spatially more homogeneous, and a much clearer land/sea contrast can be found in the model results compared to the GNIP observations. Over Europe and North America, correlations vary between 0.4 and 0.6 whereas over the oceans correlations are close to 0. The simulated $\delta^{18}O_{prec}$ /temperature slopes spread around the simulated global spatial slope of 0.5‰ per °C. Basically the model comes much closer to the ideal case of a constant isotope/local temperature relationship, spatially as well as on various time-scales. Different possible explanations are at hand for this deviation of the model from the GNIP observations on the interannual time scale. First, it is of course possible that the way we parameterized temperature control on the water isotopes in the model is incorrect.

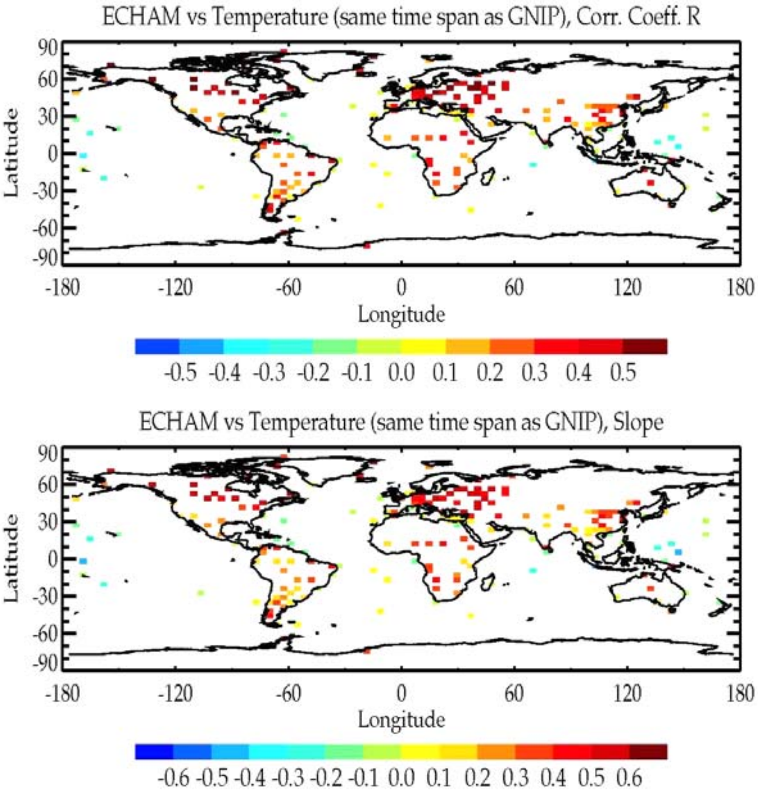
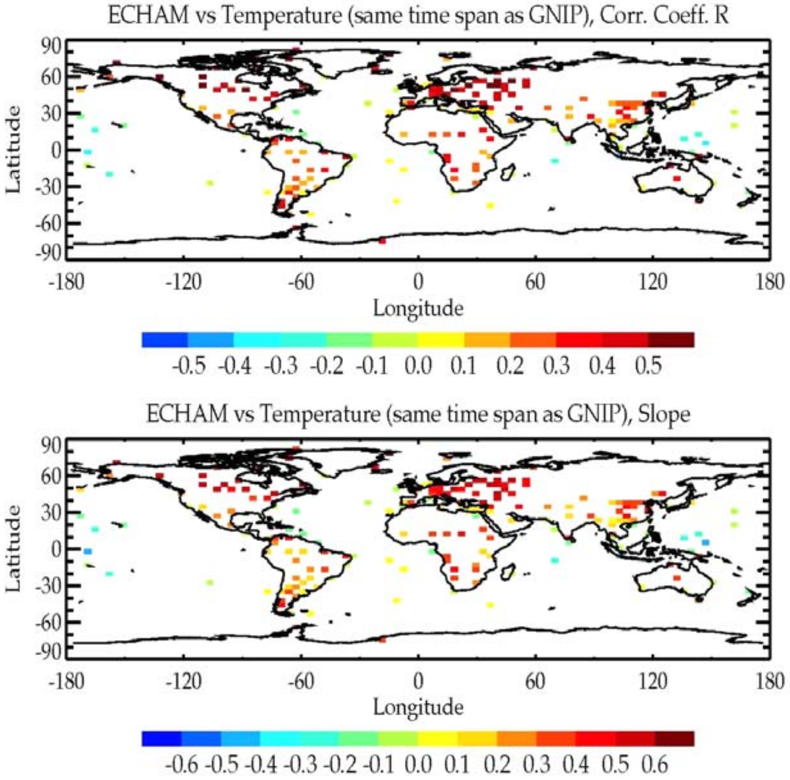


FIG. 5. Correlation between temperature and $\delta^{18}O$ and the corresponding slope for the GNIP/IAEA data for the period 1961-1994.

However, we then have to explain how it is possible that the model is adequate on the annual and seasonal time scale but fails on the interannual scale. An alternative explanation has to do with the GNIP observational network. Besides possible problems with the quality of the isotope measurements, there is also the issue of how we treat several stations within one grid point. Over Europe in particular, we merge monthly anomalies of stations with considerably different meteorological regimes (e.g. north and south of the Alps) into one grid point record. Moreover, the quality and length of GNIP data records differ significantly (IAEA, 1992). In fact, single long-term stations or even several stations from one region under a similar atmospheric influence (e.g. the Swiss stations discussed in Rozanski et al., 1993) show stronger interannual correlations between the isotopes and temperature than we calculate here for the GNIP network (Fig. 5).

Figures 7 and 8 show the same analysis as in Figs 5 and 6 but for the relation between the water isotopes and precipitation amount ("interannual amount effect"). In the observations (Fig. 7) and in the ECHAM simulation (Fig. 8), the $\delta^{18}O_{prec}$ /Prec. correlation is nearly everywhere negative.

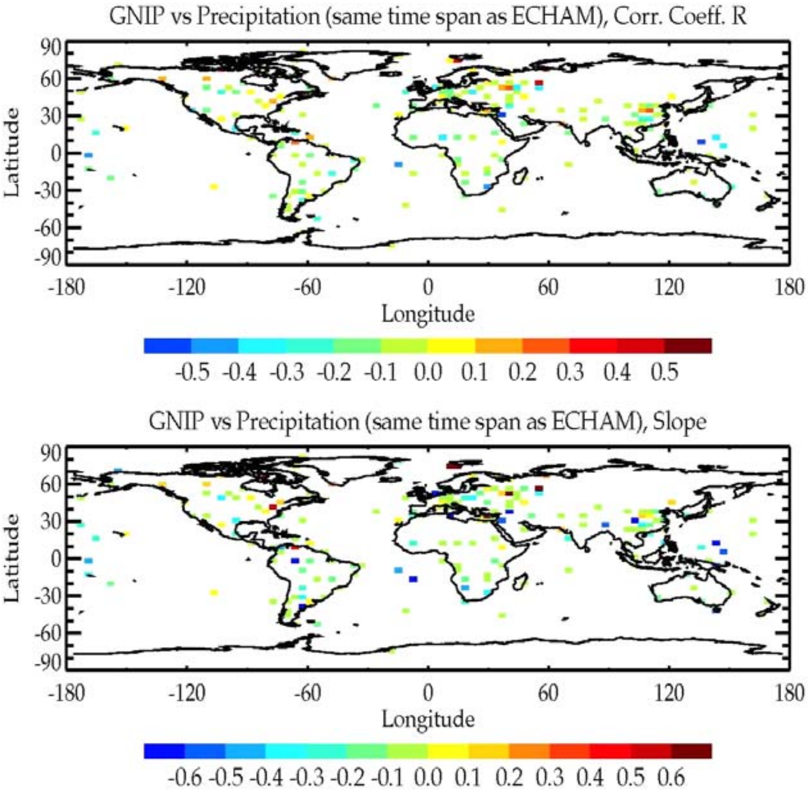


ECHAM vs Temperature (same time span as GNIP), Corr. Coeff. R

ECHAM vs Temperature (same time span as GNIP), Slope

FIG. 6. Same as Fig. 5 for the ECHAM 4 model.

At least in the model, but to some extent also in the observations, the tropics show a stronger influence of precipitation on the isotope signal. In high latitudes, this anti-correlation is an artefact of the (weak) anti-correlation between temperature and precipitation amount which is caused thermodynamically. Anomalously warm (cold) years tend to be slightly wetter (dryer). At the same time, warm (cold) temperature anomalies are responsible for higher (lower) isotope values (Figs 5 and 6). The anti-correlation is thus a sort of artefact of the temperature effect on the one hand and a weak control of temperature on the amount of precipitation on the other hand. In low latitudes, however, the anti-correlation between the isotopes and precipitation is a direct consequence of the amount effect. The model again overestimates the anti-correlation and shows more clearly than the observation regions where precipitation variability leads to comparably strong isotope signals. For example, precipitation anomalies linked with the ENSO phenomenon (over the West-Pacific warm pool, the Central Pacific and over South America) are nicely anti-correlated with isotope anomalies (r <-0.6).


GNIP vs Precipitation (same time span as ECHAM), Corr. Coeff. R

GNIP vs Precipitation (same time span as ECHAM), Slope

FIG. 7. Correlation between precipitation and $\delta^{18}O$ and the corresponding slope for the GNIP/IAEA data for the period 1961-1994.

4. Discussion and conclusion

As was already shown in previous publications, “isotopic AGCMs” are able to simulate reasonably well the seasonal cycle and the spatial distribution of water isotopes. On this time scale, deviations between the model and the GNIP observations are typically less than 20% of the phasing and the amplitude of the seasonal cycle. On an interannual scale, however, the water isotopes are only weakly controlled by local temperature/precipitation changes in most regions of the world. Computed correlations between the isotopes and local climate are overestimated by the ECHAM 4 model, and, moreover, the simulated spatial coherency of these correlations is greater than in the IAEA/GNIP network: the model appears to define more clearly than the observations whether in a given region the temperature effect or the amount effect governs the isotope variations in precipitation. It is certainly an objective for future work to explain this finding. One could imagine that with higher spatial resolution the model becomes spatially more incoherent. To test this hypothesis we need long-term integrations in high resolution (T106, corresponding to a 1° resolution). Furthermore, such a response of the AGCM might be model-dependent, and similar simulations should be performed with other existing "isotopic" AGCMs to test this possibility (see Table 1).

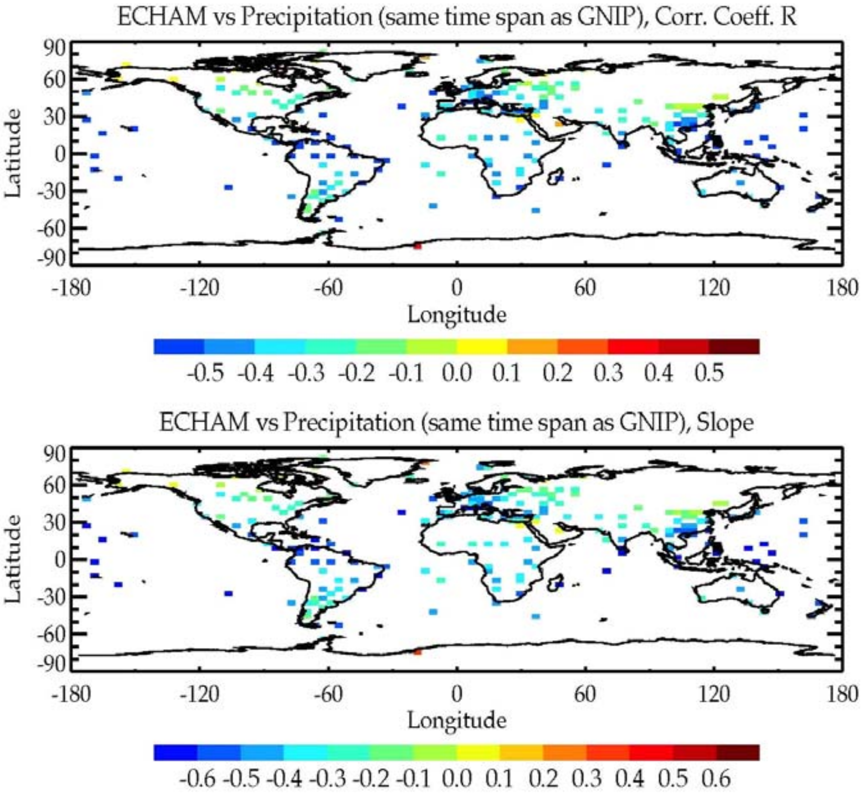


FIG. 8. Same as Fig. 5 for the ECHAM 4 model.

However, there are hints that various factors controlling the water isotopes on an interannual time scale (source and trajectory changes, recycling rate, etc.) cancel each other out to some extent when changing to the decadal and inter-decadal scale. This cancelling then leads to a clearer relation of $\delta^{18}O_{prec}$ to local climate parameters. For example, the decadal signal-to-noise ratio of Andean isotope records was shown to be extremely favourable, and the resulting mean Andean isotope signal was demonstrated to be controlled by large-scale displacements of the Hadley-Walker circulation, probably triggered by ENSO variability in the Central Pacific (Bradley et al., 2003; Hoffmann, 2003; Hoffmann et al., 2003).

Another example of an successful interpretation of high resolution isotope series in terms of climate parameters stems from Greenland. White et al., 1997, demonstrated that one needs several ice core isotope records from the same spot to reduce post-depositional noise and to construct a representative isotope signal for Central Greenland. This signal is still influenced by several factors including local temperature, North Atlantic SST and pressure gradients, notably those associated with the North Atlantic Oscillation (NAO). Moreover, when dealing even more carefully with seasonality in these Central Greenland isotope records, Vinther et al., 2003, was even able to establish an excellent relationship between the mean Greenland isotope signal and the NAO, which itself of course already combines a number of atmospheric processes (not only temperature, but also precipitation and circulation changes).

The latter two examples aim to demonstrate that a reasonable interpretation of long-term changes (which means in the context of this discussion an interannual to centennial scale) is feasible given two key conditions are fulfilled.

- A mean regional isotope signal must be established. The aim is to reduce several noise factors in the isotope series, such as archive effects (for example post-depositional effects in ice core records) or small-scale variance (the leading pattern of the different isotope records in the Andes or in Central Greenland was shown to be more representative than each individual series). Even for the GNIP isotope data, as was mentioned above, more attention should be given to this point than was the case in this work. For example, we averaged the existing GNIP data into one grid point record, though there are considerable differences in terms of station length and quality as well as microclimatic differences (Alpine stations north and south of the Alps from high and low altitude were merged into one record).
- The full complexity of the isotope signal must be taken into account , e.g. the influence of source region and trajectory changes. This can be achieved by using “isotopic” AGCMs. The weak relation between interannual climate and isotope variations is the reason why there are no palaeo-isotope series in the databases used to reconstruct millennial temperature trends (Jones et al., 2001; Mann et al., 1998). These studies are based on the assumption that a specific proxy, typically tree ring width and density series, project significantly on observed interannual temperature variability over the period where direct meteorological observations exist (end of the 19th and the 20th century). In the next step the established (non-linear) transfer functions are used to deduce, for example, northern-hemisphere temperature trends since about 1000 A.D. from the entire proxy time series. These works lead to the important conclusion that the 20th century is probably the warmest since at least 1000 years, due to anthropogenic greenhouse gas emission (Mann et al., 1998). A critical point in

these studies is the applicability of the computed transfer functions within a longer time frame than the interannual scale on which the calibration has been established, i.e. it essentially raises the question of the stability of atmospheric tele-connections. For tree ring analysis, there is also a non-trivial problem arising from the aging of trees, for which a reasonable correction has to be applied. Finally, the calibration period, basically the 20th century, is already influenced by a changing climate and changing atmospheric CO_2 concentrations (Briffa et al., 1998). The latter factor is obviously of major importance for living trees and might also influence their sensitivity to temperature changes.

An estimation of inter-decadal to centennial climate variability in the last millennium, independent of the Mann-approach through water isotope analyses, seems possible in the future We suggest that long (~millenial) palaeo-isotope records are introduced into the same model/data framework as has been done here for the IAEA/GNIP network. This means that long-term integrations of "isotopic ocean-atmosphere" GCMs have to be carried out with realistic boundary conditions of the last millennium (solar insolation, volcanic eruption, etc.). Variability and trends of observed and simulated isotope signals on an inter-decadal to centennial time scale will then provide us with an independent estimate of climate variability during the last millennium.

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20. STABLE ISOTOPES THROUGH THE HOLOCENE AS RECORDED IN LOW-LATITUDE, HIGH-ALTITUDE ICE CORES

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1. Introduction

Quantitative use of stable isotopes as proxies for the air temperature at the time of precipitation formation requires establishing relevant transfer functions. Unfortunately, in remote areas where most ice cores are recovered the requisite in situ meteorological observations and contemporaneous precipitation collections are sparse or absent. The processes that determine the values of oxygen and hydrogen isotopic ratios ($\delta^{18}O$ and δD (or ^{2}H), respectively) in snowfall are complex and so far there is no reasonable model linking the ratios with any single meteorological or hydrologic factor. This is particularly the case for high-elevation, low-latitude glaciers and ice caps, where continental and altitude effects are additional considerations.

Thompson et al. (2003) compared the $\delta^{18}O$ ice histories back to the Last Glacial Stage (LGS) from three low-latitude ice fields in South America and the Tibetan Plateau with similar histories from three polar ice cores. Although these records show large-scale similarities as well as important regional differences, they strongly suggest that, on millennial time scales, changes in $\delta^{18}O$ ice in the tropics represent large-scale climatic variations, including temperature, just as they do in the polar regions. The $\delta^{18}O$ ice records from seven low-latitude, high-altitude glaciers form the basis for this review of how faithfully non-polar ice cores record air temperatures from the end of the LGS through the Holocene.

P.K. Aggarwal, J.R. Gat and K.F.O. Froehlich (eds), Isotopes in the Water Cycle: Past, Present and Future of a Developing Science, 321-339.

The low and mid-latitude ice core recovery sites (Fig. 1) include three from the Tibetan Plateau [Dunde ice cap, (38°N, 5325 m asl), Guliya ice cap, (35°N, 6200 m asl) and Dasuopu Glacier in the Chinese Himalayas (28°N, 7200 m asl)], three from the Andes of South America [Huascarán (Peru, 9°S, 6050 m asl), Quelccaya ice cap (Peru, 14°S, 5670 m asl) and Sajama (Bolivia, 18°S, 6550 m asl) and from Kilimanjaro (Tanzania, 3°S, 5895 m asl)]. The cores from these sites are compared with three polar records, including the Renland (Johnsen et al., 1992) and GISP2 (Grootes et al., 1993) ice cores from Greenland, and the Vostok core from East Antarctica (Jouzel et al., 1987; Petit et al., 1999).

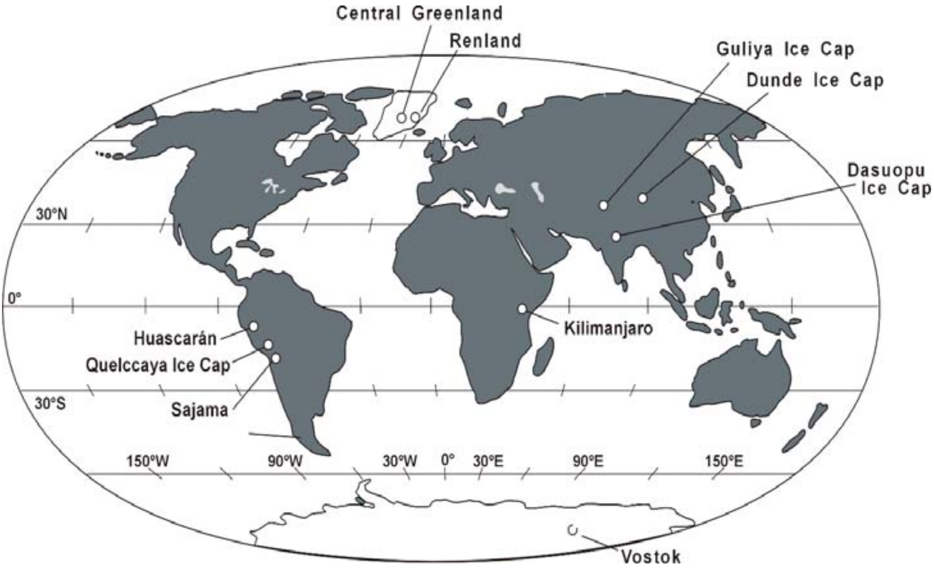


FIG. 1. Locations of ice coring sites discussed in this Paper.

Precipitation is essential for glacier development on high elevation, low and mid-latitude mountain ranges. In these ice core sites the precipitation is highly seasonal. Figure 2 illustrates the modern average monthly precipitation distribution along the tropical Andes of South America, while Fig. 3 illustrates the precipitation across the Tibetan Plateau. Seventy to eighty per cent of the annual precipitation falls in the austral summer (DJF) in the Andes and in the boreal summer (JJA) on the Tibetan Plateau. Along the Andes annual precipitation decreases from north to south while over the Tibetan Plateau both the total annual precipitation and the seasonality decreases abruptly from south to north. This pattern reflects the seasonal cycle in the general circulation of the tropical atmosphere, and more specifically of the Hadley cell with deep convection and associated precipitation on land, warmest sea surface temperatures in the summer hemisphere tropics, and general subsiding motion and dry conditions in the winter hemisphere tropics.

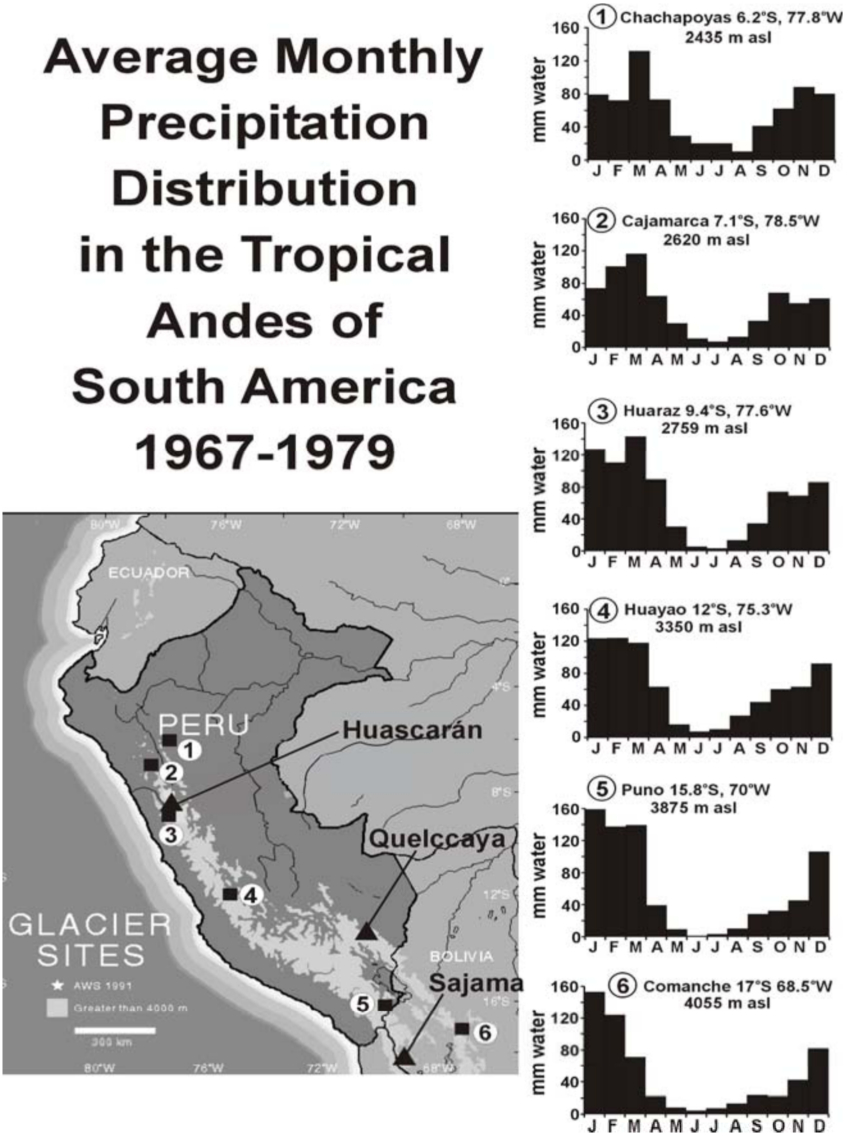


FIG. 2. Meteorological station precipitation records showing the monthly distribution of precipitation under current climate conditions where 70 to 80% of precipitation falls in austral summer (DJF) in the tropical Andes. The locations of the Huascarán, Quelccaya,and Sajama ice core sites are also shown. Holocene ice core $\delta^{18}O$ records and their relation to temperature.

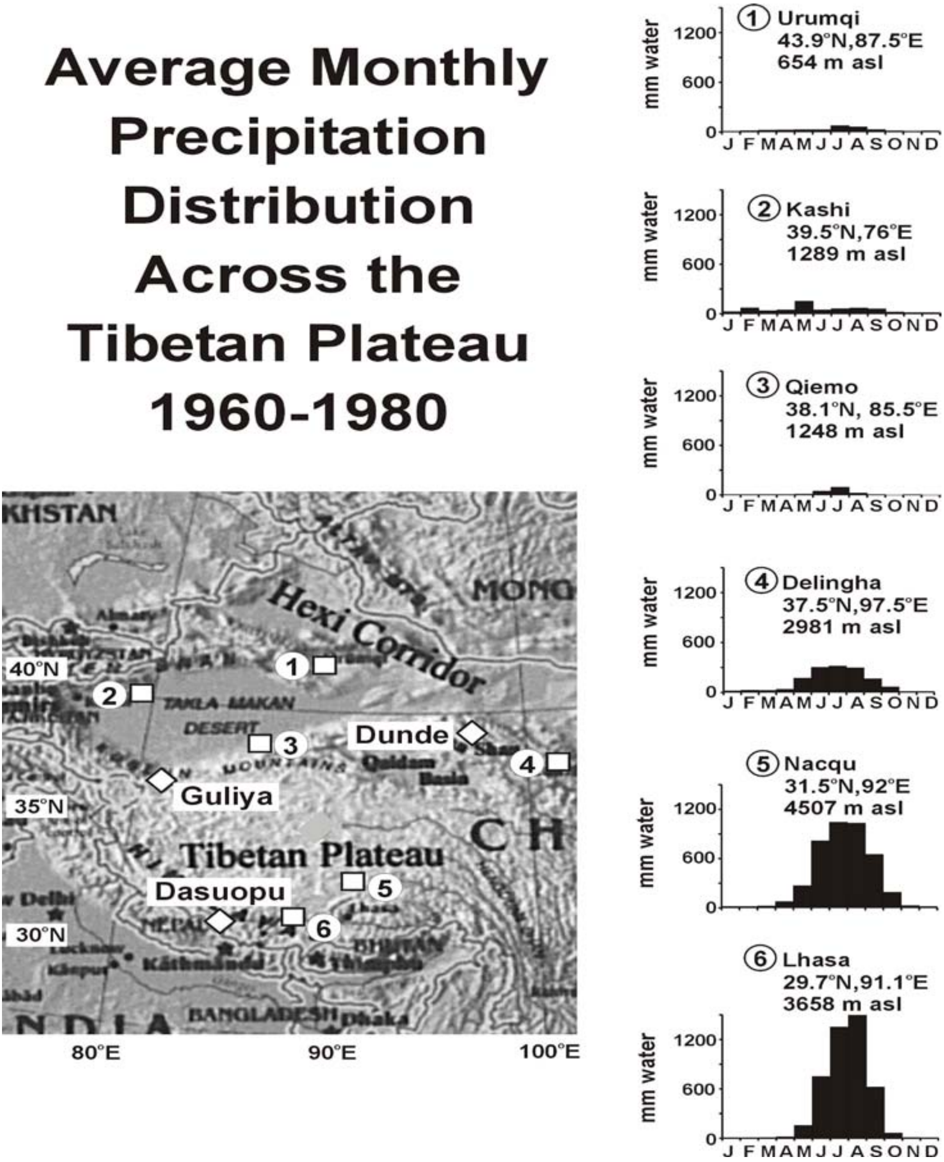


FIG. 3. Meteorological station precipitation records showing the monthly distribution of precipitation under current climate conditions where 70 to 80% of the precipitation falls in the boreal summer (JJA) on the Tibetan Plateau. The locations of the Dunde, Guliya, and Dasuopu ice core sites are also shown.

2. Holocene ice core δ^{18}O records and their relation to temperature

The δ^{18}O profiles of the longest low-latitude ice cores (Guliya, Huascarán, Sajama) were presented together in Thompson et al. (2003). The δ^{18}O-proxy temperature difference between the Last Glacial Maximum (LGM) and the Early Holocene (EH) in these cores is similar not only to polar cores, but to other climate histories from other archives such as corals (Guilderson et al., 1994; Beck et al., 1997), noble gases from groundwater (Stute et al., 1995), marine sediment pore fluids (Schrag et al., 1996), snowline depression (Broecker and Denton 1990; Herd and Naeser, 1974; Klein et al., 1995; Osmaston 1965; Porter 1979; Rodbell1992), and pollen studies (Colinvaux et al., 1996). All these records together suggest that the LGM cooling was global.

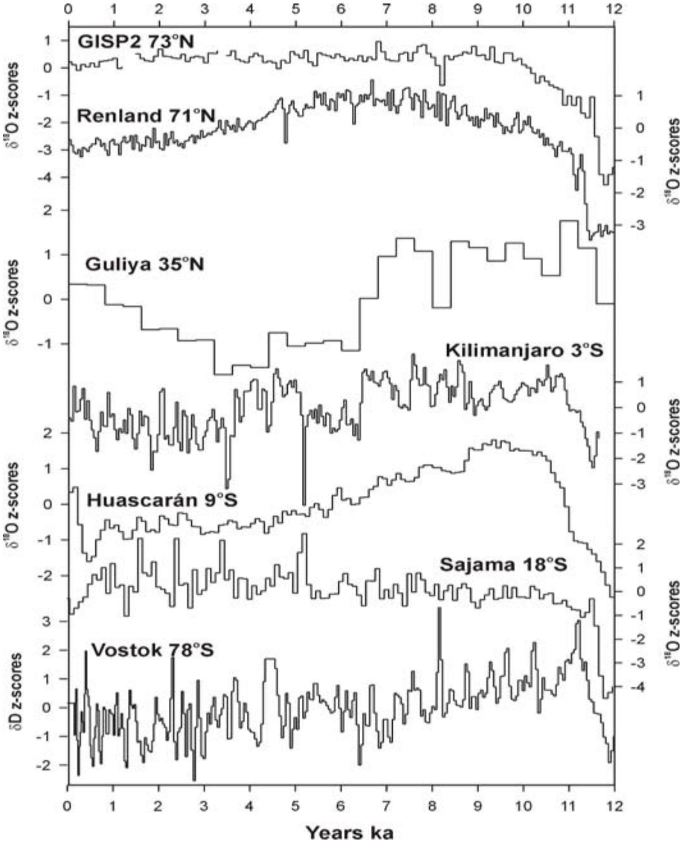


FIG. 4. The δ^{18}O ice histories for the last 12,000 years from seven cores from the northern polar latitudes through the tropics to the southern polar latitudes. From top to bottom the records are from: GISP2, Greenland (Grootes et al., 1993), Renland, Greenland (Johnsen et al., 1992),Guliya, Tibet (Thompson et al., 1997), Kilimanjaro, Tanzania (Thompson et al., 2002),Huascarán, Peru (Thompson, 2000), Sajama, Bolivia (Thompson et al., 2000), and Vostok, Antarctica (Petit et al., 1999).

Of all ice cores sites throughout the world, Kilimanjaro at 3°S is closest to the equator and thus provides deep tropical records of variations in δ^{18}O, δD, and deuterium (d) excess (Fig. 5). On a global scale, fractionation of oxygen and hydrogen during evaporation and precipitation processes approximates a well-defined relationship, whereby $\delta D = 8\delta O + 10$. This meteoric water line as defined by Craig (1961) is very nearly identical to that illustrated in Fig. 5 for this most equatorial of the world's ice core records. This would suggest that the stable isotopic ratios in these ice fields have not been altered by post-depositional melting or sublimation.

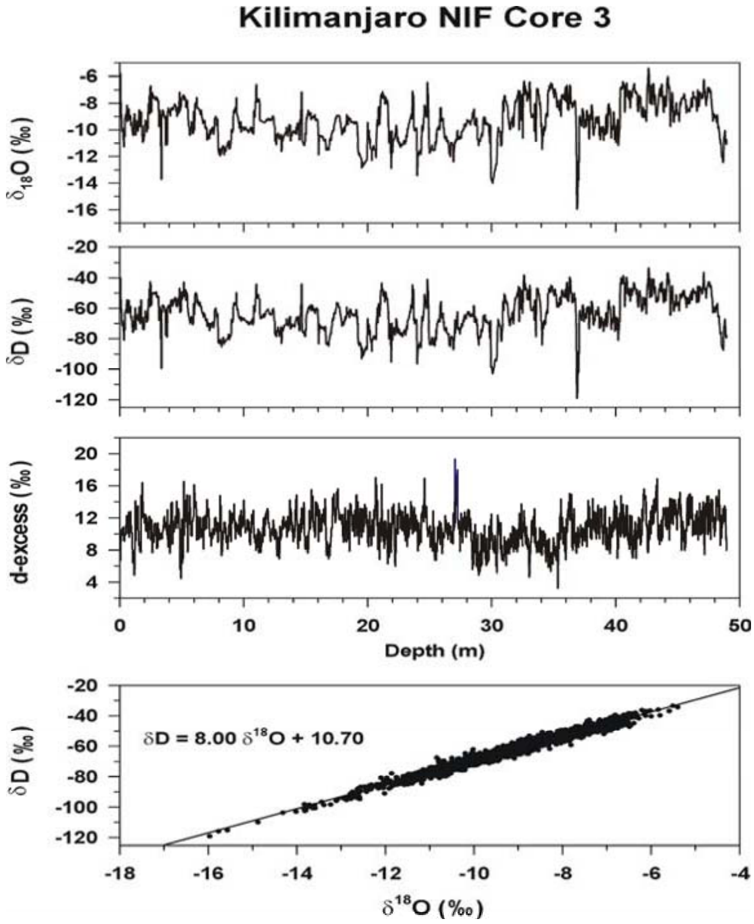


FIG. 5. The δ^{18}O ice, δD and deuterium excess for Core 3 from the Northern Ice Field (NIF) of Kilimanjaro plotted with depth.

Five of the isotopic records in Fig. 4 (Renland, Guliya, Kilimanjaro, Huascarán, and Vostok) show an Early Holocene “Hypsithermal” warm period (i.e. isotopically enriched) and a Late Holocene “Neoglacial” one (i.e. isotopically depleted). Paradoxically, the two records that do not follow this trend are located relatively close to others that do. The GISP2 ice core record from the summit of Greenland lacks the EH warming, although the drill site is only ~400 km to the east of Renland (which is on the east coast) and at the same latitude (~71°N). The Holocene $\delta^{18}O$ record in Sajama (at 18°S in Bolivia) shows no large-scale variation, which is very different from Huascarán, located 1350 km to the NE along the Andes range.

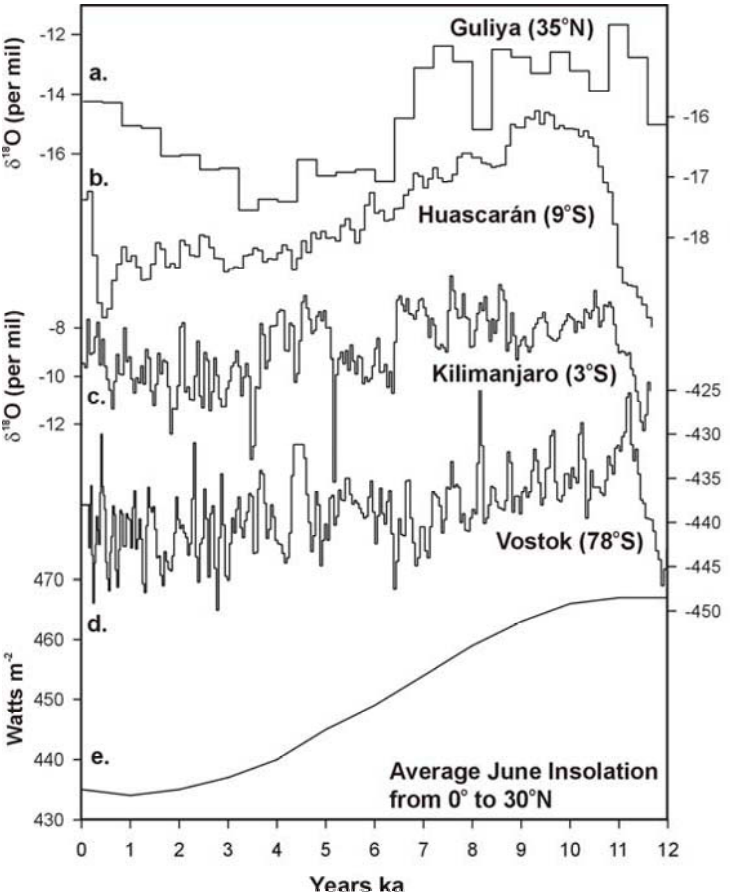


FIG.6. The $\delta^{18}O$ or δD(or ^2H) ice plotted for (a) Renland (Johnsen et al., 1992), (b) Kilimanjaro (Thompson et al., 2002), (c) Huascarán, (Thompson, 2000) and (d) Vostok (Petit et al., 1999) over the last12 thousand years, along with (e) the tropical northern hemisphere (average of 0 to 30^{o}N) insolation changes (Berger and Loutre, 1991).

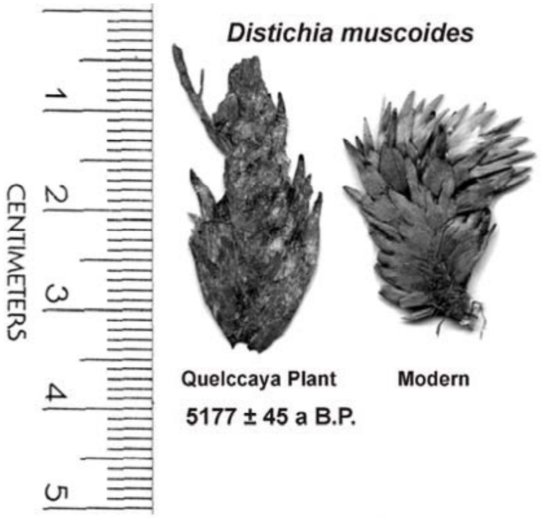
These differences in climate histories between ice cores sites located in close proximity to each other suggest the importance of regional controls on the isotopic record (e.g. the presence of large lakes upwind in the case of Sajama). This is at odds with the idea argued in the literature (e.g. Baker et al., 2001) that tropical $\delta^{18}O$ ice records the regional precipitation, while polar $\delta^{18}O$ ice primarily reflects temperature (Dansgaard, 1964; Dansgaard and Oeschger, 1989). In light of the climatological differences between Huascarán (warm, wet Holocene, Thompson et al., 1995a; 2000a;Thompson, 2000) and Sajama (warm and dry Holocene, Thompson et al., 1998, 2000a; Thompson, 2000) and their similar Holocene $\delta^{18}O$ ice averages, we argue that decadal to century variations in $\delta^{18}O$ ice principally reflect temperature and not precipitation.

The $\delta^{18}O$ or δD records from Renland, Kilimanjaro, Huascarán and Vostok are shown in Fig.6 (a-d). There are similarities between the polar and the tropical isotopic records, suggesting that they are recording the same large-scale variations in the global climate system. All of these isotopic curves mimic the average tropical insulation curve between 0°and 30°N (Fig. 6e), suggesting that the higher temperatures of the EH may have been largely precession-driven. An independent confirmation of the temperature interpretation of the tropical isotopic record was made with the discovery of a plant at the base of the Quelccaya ice cap, located ~800km to the southwest of Huascarán. This plant, shown in Fig. 7, was identified as *Distichia muscoides (Juncaceae*), and was exposed by the receding ice between the austral winter of 2001and its discovery the following year. Interestingly, the altitude where it was found (~5200 m asl) is much higher than the altitude range at which it currently grows (4400 - 4800 m asl). Six samples were recovered and ^{14}C AMS-dated at two laboratories, both of which placed its age at 5177± 45a BP (Fig 7). This date, along with the plant's location, suggests that the climate at this altitude in the Andes was much warmer before ~5.2 ka, which is consistent with the $\delta^{18}O$ records from both Kilimanjaro and Huascarán.

In the longer Huascarán record (Fig. 6c), the early Holocene period was more ^{18}O-enriched than today, indicating warmer conditions which allowed plants to grow at higher elevations than they do under the modern climate. The Kilimanjaro $\delta^{18}O$ record (Fig. 6b) also illustrates this "Hypsithermal" warm period, although the aerosol data also indicate that the climate, while variable, was generally much wetter (Thompson et al., 2002). In fact, the period of ^{18}O enrichment in the Kilimanjaro record corresponds to the well documented "African Humid Period" (e.g. deMenocal et al., 2000). These higher tropical temperatures during the EH may have also determined the mean stable isotopic composition of water vapour in the global atmosphere, which was (and still is) likely dominated by the tropical hydrological system.

3. Controls on isotopic fractionation on precipitation on low-latitude mountains

Two models, which were discussed in some detail in Thompson et al. (2003), have been developed to explain the mechanisms responsible for the $\delta^{18}O$ ice composition found in the Andean ice cores under modern (Holocene) conditions. Grootes et al. (1989) developed a hydrological model of moisture transport which explains the large seasonal difference in $\delta^{18}O$ ice for a region that experiences an annual temperature range of only a few degrees Centigrade. The isotopic composition of ocean water at the source (i.e. the tropical North Atlantic) is modified as the vapour moves across the Amazon Basin and is recycled within thunderstorms when the heavier isotopes are preferentially removed. During the wet season most of the isotopically enriched surface water is transported out of the Amazon Basin by the river system, but in the dry season most of the precipitation that falls in the Amazon is re-evaporated. The ^{18}O-depleted wet season precipitation, which comprises 70 to 80% of the snowfall in the Andes, is further depleted as the air masses are forced to rise over the Andes.



Radiocarbon dates of plants from base of Quelccaya Ice Cap

	^{14}C age	Error (+/-)	Calibrated age (Before 1950 A.D.)	Relative area under probability distribution
Lawrence Livermore National Laboratory				
Sample 1 First run	4470	60	5284-5161 (1σ) 5302-4961 (2σ)	.534 .926
Sample 1 Second run	4525	40	5186-5121 (1σ) 5311-5047 (2σ)	.413 1.000
Sample 2 First run	4530	45	5186-5120 (1σ) 5317-5040 (2σ)	.396 .993
Sample 2 Second run	4465	40	5278-5171 (1σ) 5295-4967 (2σ)	.580 .984
National Ocean Sciences AMS Facility at Woods Hole Oceanographic Institution				
Sample 1	4530	45	5186-5120 (1σ) 5317-5040 (2σ)	.396 .993
Sample 2	4510	40	5188-5119 (1σ) 5307-5040 (2σ)	.404 .988

FIG. 7. The plant Distichia muscoides (5177± 45 a BP) collected at the retreating margin of the Quelccaya ice cap in August of 2002 compared to the modern plant.

An alternative explanation for the δ^{18}O ice in Andean precipitation includes the important consideration that in tropical mountainous regions snowfall generally originates from thunderstorms with convective cells that extend to great heights such that the mean level of condensation in these storms would be much higher than the condensation level for polar precipitation. More importantly, in the tropics both the geographic location and elevation of the zone of maximum condensation changes from the wet to the dry season. During the height of the wet season, the condensation level is about 2 km higher, where temperatures are cooler and, conversely, in the dry season condensation takes place at a lower, warmer level in the atmosphere.

Thus, the more depleted δ^{18}O ice values arrive in the wet season snow and could be interpreted as either an ‘amount effect’ or a temperature signal reflecting changes in the height of the zone of maximum condensation, or some combination of the two (Thompson et al., 2000a). One of the most important questions concerning ice core $^{\delta 18}$O ice records is whether they are a realistic proxy indicator of lower tropospheric temperatures. Observations made by Yao et al. (1996) suggest that on short time scales δ^{18}O ice trends in precipitation provide a record of temperature trends along the northern part of the Tibetan Plateau. Further to the south, where monsoonal precipitation is more dominant, the δ^{18}O-temperature relationship reverses, so that the most isotopically depleted snow arrives during the summer monsoon (Thompson et al., 2000a). However, as discussed later, intensified atmospheric convection leads to colder condensation temperatures that may be interpreted erroneously as an “amount effect”. On annual time scales this δ^{18}O-temperature relationship (e.g., depleted δ^{18}O ice in the warm, wet season) reflects atmospheric dynamical processes, but over many decades to centuries, atmospheric temperature becomes the dominant process controlling average δ^{18}O ice.

4. δ^{18}O history of the tropical Andes over the last millennium

Quelccaya’s decadally averaged δ^{18}O history for the last millennium (Fig. 8(a)) records the “Medieval Warm Period”, characterized by more enriched isotopes from A.D. 1100 to 1375, and the “Little Ice Age” characterized by more negative δ^{18}O lasting until A.D. 1880 (Thompson et al, 1985; 1986). However, the accumulation (An) reconstruction for Quelccaya since 1000 A.D. (Fig. 8(b)) shows little similarity to the isotope record (R2=0.02). The first part of the Little Ice Age, or LIA (1500 to 1720 A.D.) experienced a 30% increase in precipitation, while there was a 20% decrease during the latter part (1720 to 1880 A.D.), but the ^{18}O depletion of 0.9 ‰ occurred consistently through the entire LIA. The lack of similarity between the δ^{18}O and the An through the last millennium indicates that isotopic ratio of snowfall on Quelccaya is not precipitation-dependent. The decadal averages of δ^{18}O since 1000 A.D. for the other Andean ice cores, Huascarán and Sajama, were presented individually along with Quelccaya in Thompson et al. (2003).

The composite of these three records is shown in Fig. 9(a), which clearly illustrates the expression in the Andes of the ‘Mediaeval Warming’ from 1000 to ~1400 A.D., followed by the LIA from~1450 to ~1850 A.D. The recent warming since 1900 A.D. is also very apparent, and the composite in Fig. 9(a) shows that the amount of ^{18}O-enrichment of the last century is the greatest of the last millennium.

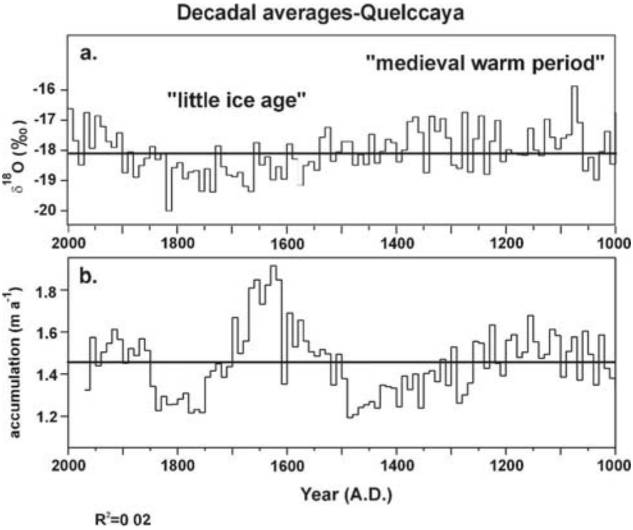


FIG. 8. Decadal averages of (a) δ^{18}O and (b) accumulation in water equivalent since 1000 A.D. from the Quelccaya ice cap summit core.

5. δ^{18}O history of the Tibetan Plateau over the last millennium

The Dunde ice cap (5325 m asl) on the northeast side of the Tibetan Plateau, the Guliya ice cap(6200 m asl) on the northwest side and Dasuopu Glacier (7200 m asl) on the southern margin form a regional triangular pattern with elevations decreasing from south to north (Fig. 3). The averages of their δ^{18}O ice values since 1000 A.D. (Dasuopu: -20.32‰; Guliya: -14.23 ‰; Dunde: -10.81‰) decrease with increasing altitude (Thompson et al., 2003).

All these glaciers are affected primarily by the Asian Monsoon System in the boreal summer, with minor precipitation in the winter from prevailing westerlies. As was the case for Quelccaya in the Andes, the oxygen isotopic records from these three ice cores bear little resemblance to their corresponding accumulation (An) records. For instance, for the period since 1860 A.D. the R2 between the 5-year averages of δ^{18}O ice and An on Dasuopu is only 0.19, while there is a much stronger statistical relationship between δ^{18}O ice and northern hemisphere temperature anomalies (R2 = 0.37) (Thompson et al., 2000b, their Fig. 6 and Thompson et al., 2003). Visual scrutiny of the δ^{18}Oand An records from the Dunde ice cap since

~1600 A.D. and the Guliya ice cap since 1000 A.D. also show little similarity (Thompson, 1992; Thompson et al., 1995b). These data provide qualitative evidence that temperature, and not the amount of precipitation (or amount effect), is the dominant process controlling δ^{18}O ice over at least this part of the Tibetan Plateau.

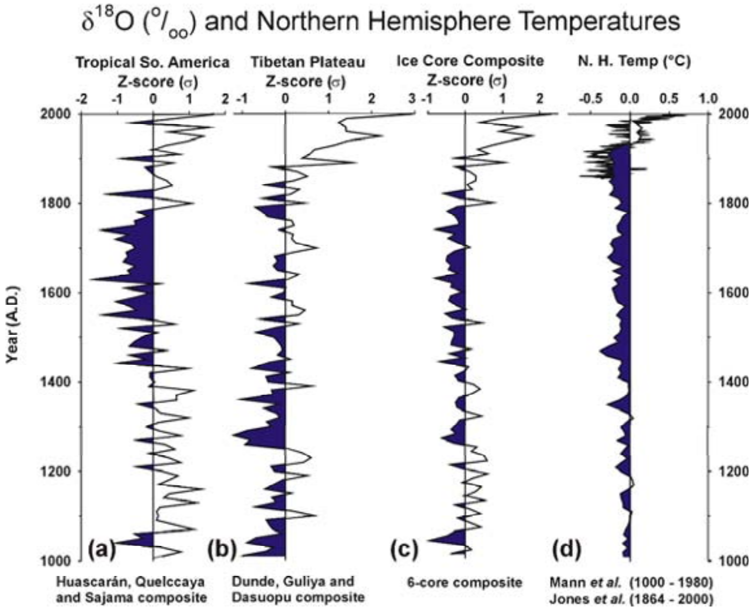


FIG. 9. Regional composites, shown as z-scores, for the last millennium constructed from the decadal averages of δ^{18}O ice from three Tibetan ice cores (a) and three Andean ice cores (b). The composite of all six low latitude cores is shown in (c). The measured (Jones et al., 1999) and reconstructed (Mann et al., 1999) northern hemisphere temperatures are shown in (d) and are plotted as deviations (°C) from their respective 1961-1990 means. Note that the average of δ^{18}O ice for the 1991 to 2000 decade is based on the 1991 to 1997 annual values for the Dasuopu core drilled in 1997 and on the1991-1997 annual values for the Sajama drilled in 1997. The Quelccaya δ^{18}O ice history has been updated to 2000 by drilling new shallow cores.

6. The decadal averages of δ^{18}O ice from the three Tibetan ice cores

The individual δ^{18}O profiles from the Dunde, Guliya, and Dasuopu ice cores display some major differences on both decadal and centennial scales (Thompson et al., 2003). This is not surprising given the diverse regional settings that contribute to differences in precipitation source and post-depositional processes. However, since 1800 all three $^{\delta 18}$O ice histories show a consistent trend of enrichment, suggesting that a large spatial-scale warming has affected the region. As with the Andean cores, these three Tibetan cores were combined and their composite is shown in Fig. 9(b). Although the Tibetan Plateau composite shows major differences to the tropical South American composite (Fig. 9(a)), both show an enrichment (warming) trend since 1900 A.D. that is unprecedented in the last millennium. This warming is even more pronounced in Tibet than in the Andes, an observation that is discussed in detail below.

7. 20th century warming

Evidence is accumulating for a strong warming in the tropics in the second half of the 20th century. Although cause and effect are difficult to confirm, it is likely that this warming is the principal driver of the rapid retreat and, in some cases, the disappearance, of ice caps and glaciers at high elevations in the tropics and subtropics. The six cores discussed above provide an opportunity to examine the changes over the last millennium in $\delta^{18}O$ ice at low latitudes in both hemispheres. By their nature, ice cores record fluctuations in the local, regional and larger-scale environment. Thus, they contain local signals that are superimposed upon more regional to global forcings. Unravelling these signals is challenging, given there are only seven low latitude ice cores, including Kilimanjaro, that extend over the last millennium. Integrating the ice core histories with other local proxy records helps in deciphering the local to regional events.

To capture changes at the large spatial scales, we created a tropical composite of the decadal averages of $\delta^{18}O$ ice for the three Tibetan Plateau and the three tropical South American Andes ice cores (Fig. 9(c)). Moreover, since 70 to 80% of the snow in the tropical Andes of South America falls during the wet season (November to April) and on the Tibetan Plateau 70 to 80% of the snow falls in the monsoon season (May to August) (see Figures 2 and 3), combining all six of these records should give a more representative annual, and thus decadal, average $\delta^{18}O$ ice for high elevations in the low latitudes. This composite $\delta^{18}O$ ice record shows enriched $\delta^{18}O$ ice from 1140 to1250 A.D., possibly reflecting the ‘Mediaeval Warm Period’, and more depleted $\delta^{18}O$ ice from ~1300 to 1850 A.D. correlative with the LIA (Bradley, 2000). However, the most dominant signal in the$\delta^{18}O$ ice composite is the isotopic enrichment in the 20th century.

Figure 9(d) presents the millennial record of decadal temperature variations reconstructed for the last millennium from different types of proxy data primarily from northern hemisphere (NH) locations (Mann et al., 1999). The annual average NH instrumental temperature history from 1864 to 2000 (Jones et al., 1999 and updated from their web site) is also plotted in Fig. 9(d). Both records are presented as deviations from their respective 1961 to 1990 mean values. The similarities between the ice core $\delta^{18}O$ ice composite and the best NH temperature record over the last millennium provide strong evidence that over large distances and decadal and longer time scales, the dominant control on the ice core $\delta^{18}O$ ice record is temperature. The composites illustrate that the 20th century $\delta^{18}O$ ice enrichment is the dominant longer-term (e.g. century-scale) feature common to these regions that are geographically quite separated. The ice core results support meteorological evidence (Jones et al, 1999; Hansen et al., 2001) of a significant 20th century warming, but they have the added value of placing the observations within a longer-term perspective that seems to be signalling a large and unusual warming that is under way at high elevations in the tropics. This is significant as seasonal and annual temperature variations are rather small in the tropics. The average δ^{18}O ice in Dunde ice deposited since 1950 is enriched by 0.99‰ relative to the millennial mean and similar enrichments on Guliya and Dasuopu are 1.05‰ and 1.84‰, respectively (Thompson et al., 2003). This recent warming is most pronounced at the highest elevation site, Dasuopu, along the southern edge of the Tibetan Plateau. This suggests an amplification of warming at higher elevations in the tropics, as might be expected from the atmospheric thermodynamic considerations discussed above. A recent study (Liu and Chen, 2000) on the Plateau reports a linearly increasing temperature trend of ~0.16°C per decade from 1955 to 1996 and an increasing winter trend of ~0.32°C per decade. Records from 178 stations across the Plateau reveal that the greatest rate of warming (~0.35°C per decade) from 1960 to 1990 occurred at the highest elevation sites. Although these meteorological observations on the Plateau are sparse, they do support the ice core evidence of the enhancement of warming at higher elevations.

Meteorological observations in the tropical Andes are relatively few and of short duration, and there is a similar dearth of data for Tibet. Vuille and Bradley (2000) found that temperature in the tropical Andes has increased by 0.10°C to 0.11°C per decade since 1939. Further, their data indicate that the rate of warming has more than tripled over the last 25 years (0.32°C-0.34°C/decade) and that the last two years of their data series, associated with the 1997/98 El Niño, were the warmest of the last six decades. However, contrary to the findings of Liu and Chen(2000) in Tibet, the rate of warming tends to diminish with increasing elevation. Since 1950 the average $^{\delta 18}$O ice values on Huascarán, the most equatorial site, and Quelccaya have enriched by +1.31‰ and +0.51‰, respectively, over their millennial means. On Sajama, the highest and most southerly site (18°S), the average $^{\delta 18}$O ice in the last 50 years is depleted by 0.20‰ relative to its millennial mean. Clearly, understanding the controls on $^{\delta 18}$O ice in Sajama snowfall warrants additional investigation. A more detailed discussion of some of these controls for recent (since1980) snowfall on Sajama, Quelccaya and Huascarán can be found in Vuille et al. (2003) and Bradley et al. (2003).Other evidence of this high elevation warming is provided by the alpine ice masses that are particularly sensitive to small changes in ambient temperatures as they exist very close to the melting point. Six shallow cores retrieved from the summit of Quelccaya since 1976 document the impact of the recent warming and associated meltwater percolation on the quality of the isotopic signal now preserved in the ice cap's accumulating snow. The sequence of isotopic records from shallow cores taken at the Summit between 1976 and 2002 (Fig. 10) reveals how distinct annual cycles in δ^{18}O that helped date the upper 600 years in the 1983 cores have not been well preserved at depth since 1991.

Figure 10 also illustrates that the average δ^{18}O value for the upper 6 to 15 metres of firn has enriched ~3‰ and ~3.5‰ for the upper 6 metres in all cores from 1976 to 2000, contemporaneous with a strong warming in this region (Vuille et al. 2000) that is at least partially responsible for the accelerating rate of glacier retreat. The 2002 summit core shows a better preserved δ^{18}O and ~2.3‰ depletion since 2000, reflecting a short term fluctuation around the longer-term regional warming trend.

These data suggest that both the oxygen isotopes and the glacier extent are extremely sensitive to large-scale and regional climate changes, but the long-term trend since 1963 remains one of $\delta^{18}O$ enrichment and pronounced, accelerating glacier retreat.

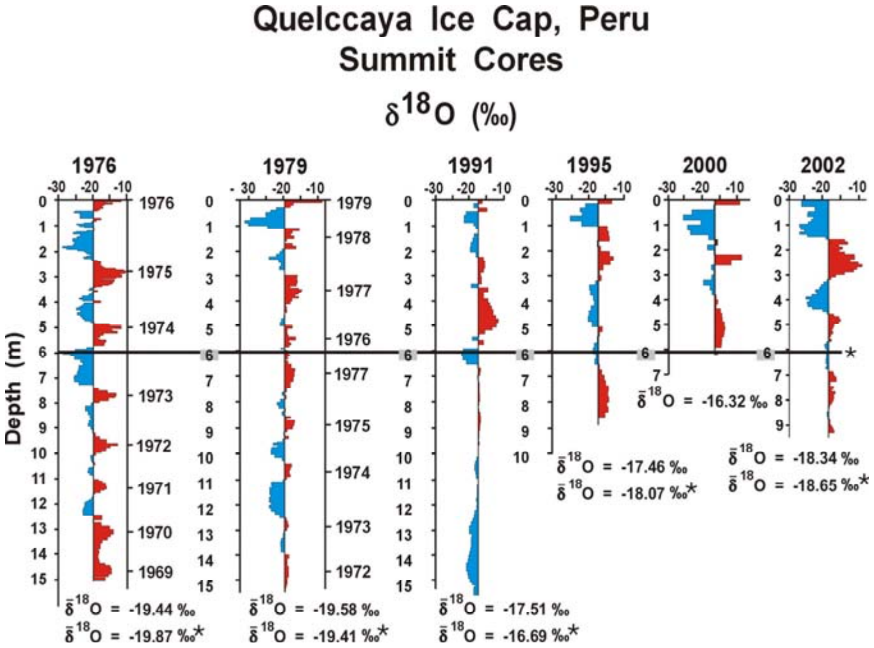


FIG. 10. $\delta^{18}O$ profiles from six shallow cores drilled from the summit of the Quelccaya ice cap from 1976 to 2002, showing the increasing isotopic enrichment and homogenization of the climate signal toward the present. The mean values for each core are shown at the bottom; those marked by an asterisk are the averages from the top of each core to the line at 6 m depth.

The retreat of the Quelccaya ice cap (Peru) is now well documented (Brecher and Thompson, 1993; Thompson et al., 2000a). The observations of the Qori Kalis outlet glacier highlight the sensitivity of these ice fields to ambient air temperatures. These observations document a rapid retreat that has accelerated over the 37-year period from 1963 to 2000. If one takes the 1963 to 1983 rate as a benchmark, Qori Kalis ablated five times faster from 1993 to 1995, eight times faster from 1995 to 1998, and thirty-two times faster from 1998 to 2000. The retreating outlet glacier essentially ‘stopped dead in its tracks’ from 1991 to 1993 due to the cooling effect of the eruption of Mt. Pinatubo in 1991, but by 1995 it had resumed its rapid retreat. Additional glaciological evidence exists for tropical warming and related ice loss. Hastenrath and Kruss (1992) reported that the total ice cover on Mount Kenya decreased by 40% between 1963 and 1987 and today it continues to diminish.

The Speke glacier in the Ruwenzori Range of Uganda has retreated substantially since it was first observed in 1958 (Kaser and Noggler, 1991). The ice fields on

Kilimanjaro lost 73% of their area between 1912 and 1989 (Hastenrath and Greischar, 1997). During the drilling of Kilimanjaro in 2000, OSU commissioned a new aerial photograph of the summit area, and from that the updated calculation reveals that Kilimanjaro has now lost ~80% of its ice coverage since 1912 (Thompson et al. 2002).

8. Conclusions

Tropical and subtropical ice core records have the potential to provide annual to millennial-scale records of El Niño-Southern Oscillation events and monsoon variability and will continue to provide additional insight to the magnitude and frequency of change in these and other large-scale climate phenomena. The composite low latitude record clearly shows unique changes underway in the 20th century in the low latitudes when viewed from the perspective of the last one-thousand years. The ice cores also contain archives of decadal- to millennial-scale climatic and environmental variability and provide unique insight to both regional and global scale events ranging from the Early Holocene Hypsithermal and the Late Holocene Neoglacial to the Little Ice Age to the recent warming. The data presented here clearly demonstrate that some, if not all, of these unique archives are in imminent danger of being lost if the current warming persists. The urgent need to understand the nature of climate variability in the tropics is illustrated by the geography and demographics of the tropics (± 30° from the equator), which account for 50% of the Earth's surface area, are home to ~70% of the current population of 6.2 billion, produces only ~20% of the world's agricultural goods and accounts for ~80% of the world's births.

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21. GROUNDWATER AS AN ARCHIVE OF CLIMATIC AND ENVIRONMENTAL CHANGE

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1. Introduction

Groundwater contained in large sedimentary basins is emerging as a direct archive of past climatic and hydrological change at both low and mid-latitudes, which may be used alongside other proxy data. Indirect evidence of the palaeohydrology in the Late Pleistocene and Holocene has been deduced from various sources especially dated lake sediments (Fontes and Gasse, 1991; Gasse, 2000; Hoelzmann et al., 2000) and speleothems (Bar-Matthews et al., 1997). In contrast to other archives such as ice cores or tree rings, which contain high-resolution information, data available in large groundwater bodies are of low resolution (typically ± 1000 a). This is due to the advection or dispersion of any climatic input signal in the water body; many groundwater data are obtained from pumped samples where sample intervals may extend over tens of metres. Nevertheless, specific indications of palaeo-temperature, air mass circulation and vegetation history may be retained in a range of different chemical and isotopic signals (Fontes et al., 1993; Stute and Schlosser, 1993), notably in confined aquifers where sequential changes may be recorded in groundwater as it moves along flow lines in confined aquifers, or in the stratification of phreatic aquifers. Dated groundwaters are important since these contain the direct evidence of discrete, prolonged wet episodes. Even the *absence* of dated waters over some time interval may indicate periods of drought (Sonntag et al., 1978) or ice cover (Bath et al., 1978; Edmunds et al., 2001). The correlation between groundwater records and aeolian deposition in semi-arid/arid regions (Edmunds et al., 1999, Swezy, 2001) can also provide complimentary evidence of wet and dry intervals.

The unsaturated zone may also, under favourable circumstances, contain records of past environment and climate at decadal to millennial scale resolution, mainly as variations in salinity and in stable isotope enrichments in percolating waters (Edmunds and Tyler, 2002). Such records are particularly found in porous media in areas of low moisture flux, notably beneath modern arid or semi-arid areas. The resolution of unsaturated (vadose) zone records will depend on the dispersion of the

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signal (Cook et al., 1992) but decadal scale records may be retained, as in west Africa, over one or two hundred years (Edmunds and Gaye, 1997), or at the millennial scale over the Late Pleistocene (Tyler et al., 1996). The current knowledge on the potential of large sedimentary basins to serve as climatic archives is here briefly reviewed, focusing on Africa. A more detailed review of the topic is given by Edmunds et al. (2003).

2. Tools for groundwater archive studies

The prerequisite for using groundwaters for palaeoclimatic archive studies is a reliable recharge chronology. Radiocarbon remains the only practical tool for this purpose, being suited also to the turnover times of most groundwaters. It has been used as the time line in all published aquifer archive studies. Despite improved analytical precision of radiocarbon dating to within a few decades using AMS measurements, the dating resolution for groundwaters is limited by water–rock interaction and requires knowledge of the carbonate hydrogeochemistry aided by understanding of the $\delta^{13}C$ evolution. Interpretation of radiocarbon activities to provide absolute ages may also be facilitated using geochemical models (Clark and Fritz, 1997). For some applications where lower resolution is required (e.g. the separation of Holocene from Late Pleistocene waters) uncorrected activities may suffice. In fact, the sources of solid carbonate which give rise to the bicarbonate ^{14}C composition, according to the reaction stoichiometrics, may be from *active* soil carbonate deposited from immediately antecedent drying cycles; in such circumstances no ^{14}C correction may be required. Most, if not all, published studies are derived from non-carbonate aquifers, where water–rock interaction affecting ^{14}C is minimal (Darling et al., 1997). Additional tools such as ^{81}Kr, uranium series and chemical trends may be used to verify the timescales or to extend the dating range in large aquifers (Loosli et al., 1999).

Noble gas ratios in groundwater (corrected for excess atmospheric air) preserved under closed system conditions offer an important technique for reconstructing the palaeotemperature at the time of recharge. The palaeoclimatic significance of noble gas ratios was first recognized by Mazor (1972) and the first palaeotemperature record established in the East Midlands Triassic sandstone aquifer (Andrews and Lee, 1979). The systematics of the noble gas palaeothermometer has been described most recently and in detail by Stute and Schlosser (1999).

The characteristic values in oxygen-18 and deuterium observed in precipitation at the present day may be used as sensitive indicators of change and complexity in past temperature, precipitation patterns and air mass circulation. Past rainfall stored as palaeogroundwater, together with other hydrological archives including ice, provide evidence of former climatic conditions (Rozanski et al., 1997). Climatic changes are expressed primarily as, (i) isotopic depletion relative to modern groundwaters with reference to the meteoric water line; (ii) change in the deuterium excess, signifying changes in humidity in the air mass as it detaches from its primary oceanic source moving over arid regions; and (iii) local condensation and evaporation effects within clouds or in falling rain. Oxygen isotopic

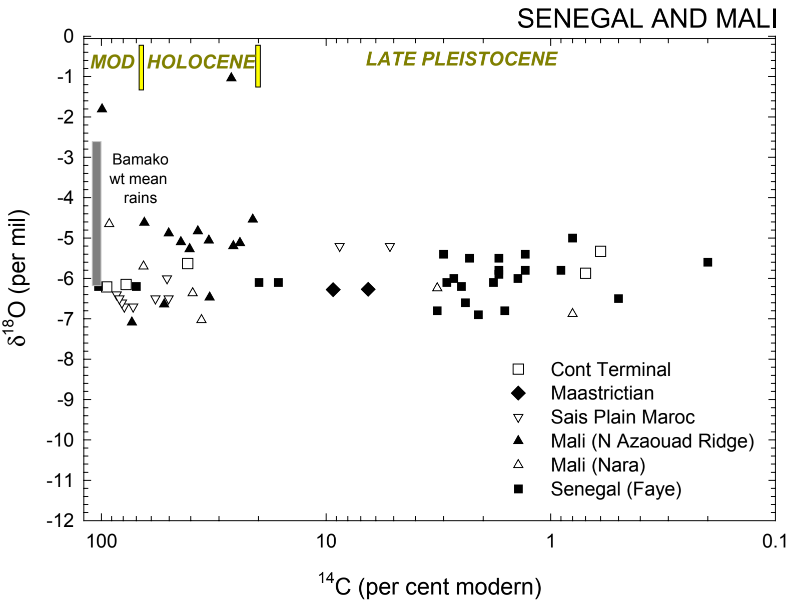

FIG. 1. The change in $\delta^{18}O$ during the Late Pleistocene and Holocene in Senegal, Mali and Morocco as shown by dated groundwaters (^{14}C as percent modern carbon).

enrichment due to near-surface evaporation is also found in many groundwaters, signifying aridity and that rates of aquifer recharge are likely to be low. Recent comparative studies with noble gases have shown that changes in the stable isotope ratios between modern and palaeowaters are not simply related to temperature (Andrews, 1993; Andrews et al., 1994; Stute and Schlosser, 1993; Stute and Talma, 1998).

The combined use of chloride and the stable isotopes of water ($\delta^{18}O$, $\delta^{2}H$), moreover, provide a powerful technique for studying past rainfall and evaporation cycles in groundwaters. Over continental areas groundwater solutes are dominantly of atmospheric origin and are concentrated in proportion to evaporation during recharge. The large freshwater reserves in some basins of modern arid zones are therefore a priori indicators of wetter climates. In many shallow aquifers higher salinity is mainly a legacy of the onset of more arid conditions during the past 4000 years.

3. Dated groundwaters in large sedimentary basins in Africa

Groundwater climatic archives are now available in many of the large sedimentary basins across the world. There is in particular an extensive literature on the isotopic characteristics of groundwaters in northern Africa obtained over the past 30 years which may be compared with records from Europe. This work has formed a contribution to the Pole–Equator–Pole (PEP-3) study and is used here to illustrate the contrasting palaeoclimatic evolution across continents. Groundwaters containing radiocarbon as well as oxygen and hydrogen stable isotope compositions have been compiled and reviewed for Africa by Edmunds et al. (2003); age corrections were not used for the main analysis in view of the uncertainties that may be introduced. Plots of radiocarbon activities expressed as per cent modern carbon (pmc) were used to provide a relative timescale to evaluate the significance of the stable isotope ($\delta^{18}O$) compositions. In these plots three timescales, Modern, Holocene and Late Pleistocene are recognized.

A comparison of two areas (NW Africa and NE Africa) taken from the wider study and illustrating the east to west groundwater evolution is shown in Figures 1 and 2. The Saïs Plain, northern Morocco, contains records of dated groundwaters from a Quaternary lacustrine carbonate sequence (Kabbaj et al., 1978) with $\delta^{13}C$ values (-13 to -17‰) indicating little or no reaction with the carbonate matrix (Fig.1). In Senegal, data are from the Cretaceous Maastrichtian aquifer with a few results also from the overlying Oligo-Miocene (Faye, 1994; Faye et al., 1993). For Mali, results from Fontes et al. (1991) contain a transect from the Niger river near Toumbouctou northwards. Only those data from north of the Azaouad Ridge are included here since those to the south are considered to have recharged from northwards (Holocene) flooding of the Niger. Also included are data from western Mali on the line from Koulikoro north to Nara (Dinçer et al., 1984) where the aquifers are mainly found in sandstones and schists of Cambrian age; the $\delta^{13}C$ values are all more negative than -10‰.

The northeast Africa region is dominated by the vast Nubian Cretaceous Sandstone aquifer (Fig. 2) in the Kufra Basin, northern Sudan and the Western Desert of Egypt. The Nubian system is then overstepped in Libya by Tertiary sedimentary basins, which, like the Nubian system, are mainly continental in origin but with marine facies (containing brackish water) nearer to the coast. Data used here (Fig. 2) are from freshwaters from the continental aquifers, which preserve mainly initial carbon isotope inputs with little or no modification by water–rock interaction, although some Holocene waters (Edmunds and Wright, 1979) may (as described above) have reacted with active calcretes, affecting age correction. Data from northern Libya are from the Sirt Basin (Edmunds and Wright, 1979), and from the Murzuq and other basins in western and central Libya (Srdoč et al., 1980; Salem et al., 1980). Data from Egypt (Thorweihe, 1982) are from the phreatic or semi-confined aquifers feeding the major oases of the Western Desert in the Nubian sandstone, which may be compared with data from southern Libya (Kufra) in Edmunds and Wright (1979). Data from the same aquifer in northern Sudan (Fig. 3f) are from Darling et al. (1987) (Butana), as well as from Darfur and Kordofan (Groening et al., 1993).

These plots illustrate the significant differences in climate and recharge characteristics.

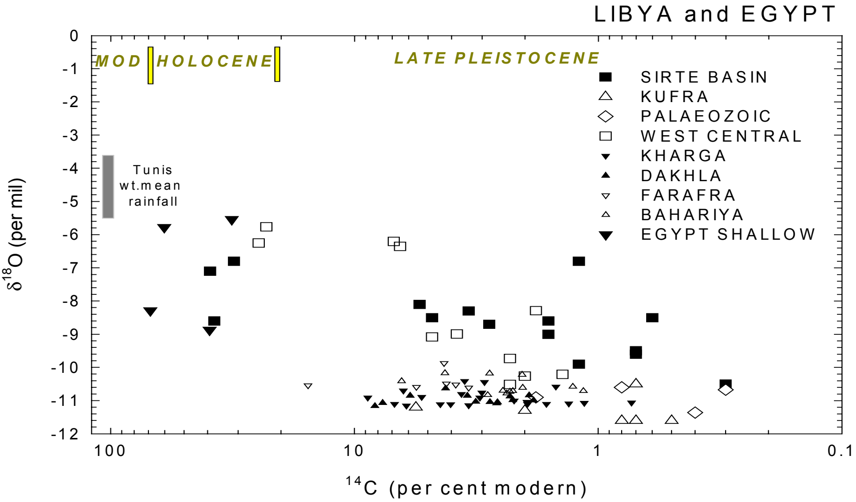

FIG. 2. The change in δ^{18}O during the Late Pleistocene and Holocene in Libya and Egypt as shown by dated groundwaters (^{14}C as percent modern carbon).

An overall trend is found in Late Pleistocene palaeowater δ^{18}O composition from west to east from around -6‰ to -10.5‰, first observed by Sonntag et al. (1978). This describes an overall *continental effect* with an Atlantic moisture source moving from west to east, the air mass having evolved according to Rayleigh (closed system) fractionation with residual isotopically lighter rains further to the east. The former widespread extent of these rains recorded in groundwaters beneath the present Sahara points to the shift of the Atlantic jet stream well to the south during most of the Late Pleistocene, as well as a weakening of the southwest monsoon. The more enriched isotopic signatures of groundwaters in Nigeria/Cameroon, compared with waters to the north suggests that, during part of the Late Pleistocene, monsoon rains derived from the Gulf of Guinea still prevailed south of 16°N. In Senegal, the similarities of the isotopic compositions reflect the continuity of the maritime influence but with recharge derived from the southwest monsoon activity of variable strength.

Late Pleistocene palaeowaters of northeast Africa show trends on a north to south basis, seen most clearly in the groundwaters in Libya and Egypt. All these waters are also isotopically much lighter than in western Africa. Groundwater in the Kufra Basin (Nubian Sandstone) is isotopically the lightest in north Africa (-11.5‰) and this compares with the Sirte Basin to the north where the palaeowaters are some 3‰ more enriched in δ^{18}O (Edmunds and Wright, 1979). Groundwaters from the Egyptian oases also show distinctive compositions (Thorweihe, 1982) lying within the range -10 to -11‰. Thus each sedimentary basin seems to have a distinctive composition, which supports the likelihood of local evolution of groundwater within each basin, forming at the extreme of the evolution of the

Atlantic air mass source. The effects of runoff from the central Saharan mountains may also have contributed to isotopically light runoff.

A gap in the record exists in most of the data-sets for groundwaters with ^{14}C of approximately 5-15 pmc. This was first noticed for north African ^{14}C data-sets by Geyh and Jäkel (1974) and demonstrated for groundwaters by Sonntag et al. (1978, 1980). This is interpreted as an arid interlude, coinciding with the Last Glacial Maximum (LGM) in Europe.

Holocene groundwaters show markedly different properties across the continent both in relation to those from the Late Pleistocene, as well as trends during the Holocene itself. In Morocco, the Holocene groundwaters are isotopically lighter (around 1-2‰ in $\delta^{18}O$) relative to those from humid periods of the Late Pleistocene. In Senegal there is a similar if subdued tendency less marked than to the north. This may be explained by the maritime situation of both countries, where the influence of the Atlantic moisture (and sea-surface temperature effects) is felt directly. The relative isotopic enrichment during the Late Pleistocene may be the result of the change in the ocean composition due to the lighter isotopes being enriched in the ice caps. This is the only noticeable effect over the past 30 ka in the coastal areas and the otherwise similar isotope compositions demonstrate the constancy of the westerly Atlantic air masses, and the south westerly monsoons (which varied in intensity), over the whole period.

Elsewhere in northern Africa, modern and most Holocene groundwaters have isotopic compositions which are significantly enriched relative to the Late Pleistocene pluvial periods. However the compositions of the Early Holocene groundwaters are depleted when compared to the modern rains. The Holocene, on the basis of extensive evidence from other proxy data, was a period with short (millennial scale) duration, but intense wet phases, which were not synchronous across the continent, from 11.4 to 5.4 ka BP (Gasse, 2000), prior to the desiccation that led to the present day conditions commencing around 4.5 ka BP. The groundwater isotopic composition therefore suggests the greater intensity of the rainfall in the Holocene as compared with the present-day rainfall, due to a greater strength and northward movement of the African monsoon.

4. Noble gas recharge temperatures on a global scale

Palaeotemperature measurements using noble gases have now been carried out particularly in Africa, Europe and America where large sedimentary basins occur and where samples of groundwater from pumped boreholes may be obtained (preserving pressures sufficient to avoid loss of gases). Earlier results were reviewed by Stute and Schlosser (1993). Some of the main results worldwide are summarized in Table 1, obtained from Niger (Le Gal La Salle, 1992), Senegal (Faye, 1992), Algeria (Guendouz et al., 1998), Nigeria (Edmunds et al., 1999), Namibia (Stute and Talma, 1998), Oman (Weyhenmeyer et al., 2000), Portugal (Carreira et al., 1996); Hungary (Stute and Deak, 1989), NE Brazil (Stute et al., 1995). These have been calculated relative to the mean annual ground temperature as represented by present day near-surface groundwater temperatures. It is found that the average global cooling at and immediately prior to the last glacial maximum (samples measured over the range approximately 30 to 20ka BP) was between 5–6°C. However there is evidence from continental areas such as northern Nigeria as well as Niger that the cooling was 1–2°C degrees cooler (6–7°C).

In the Great Hungarian Plain a distinction may be drawn between recharge dating between 10–20 ka and older waters in excess of 20 ka BP. The former have much cooler recharge temperatures (Stute and Deak, 1989; Stute and Schlosser, 1999) around 8.6°C lower than the present as compared with a 5°C drop in the older group. These results suggest continuous recharge during the LGM and stable isotope data indicating that melting ice may account for the lower signatures. Continuous recharge beneath the ice sheets at temperatures around zero was also indicated from Estonia (Vaikmae et al., 2001; Loosli et al., 2001) although here the noble gas data are difficult to interpret due to the high excess air amounts. These two European results contrast with those from UK, Portugal and Africa – Libya and Nigeria (Fig. 3) where different climatic or hydrological conditions are recorded, especially a cessation of recharge caused by aridity or permafrost.

Table 1. Summary of noble gas recharge temperature (NGRT) results for northern Africa

	Mean NGRT and range	Modern annual mean air temperature	ΔT (LGM)
Illumeden (Niger)	19.6 (16–22)		>7
Algeria	16.9 (12–24)	21.0	2–3
Nigeria (Chad Formation)	22.0 (20.3–27.5)	28.5	6–7°C
Egypt	23.7 (21.8–25.6)	21.8–23.5	2–3
Oman	26.6 (26-27)	33.0	6.5 ±0.6
Namibia	21.4 (20.5–21.7)	26.7	5.3
Portugal	7.9–10.0	15.0	5–6
Hungary	8.6 (2.0–7.9)	11.4	5*
United Kingdom	3.5 (2.0-4.3)	9.5	6

*See discussion

5. Continental intercomparisons

The African results may be compared more closely with those from Europe. The Late Pleistocene groundwaters in northern Africa record evidence of cooler climates and significant recharge prior to the LGM. Air mass circulation over Africa during the Late Pleistocene was significantly different from the present day with evidence, shown clearly in the groundwater archive, of a reinforcement and southward shift of the Atlantic westerly flow across the present Sahara during the period. A corresponding decline of monsoon rains occurred at this time with the onset of a period of aridity. Evidence then is found for a northward extension of the African monsoon, with increased intensity notably during the Early to Mid-Holocene coinciding with a retreat of the Atlantic system to the north. The extent of cooling at the LGM recorded in the noble gas ratios was up to 7°C. The groundwater isotopic evidence in different places records strong variations in humidity of the air masses supplying moisture across the continent at different times over the past 30,000 years.

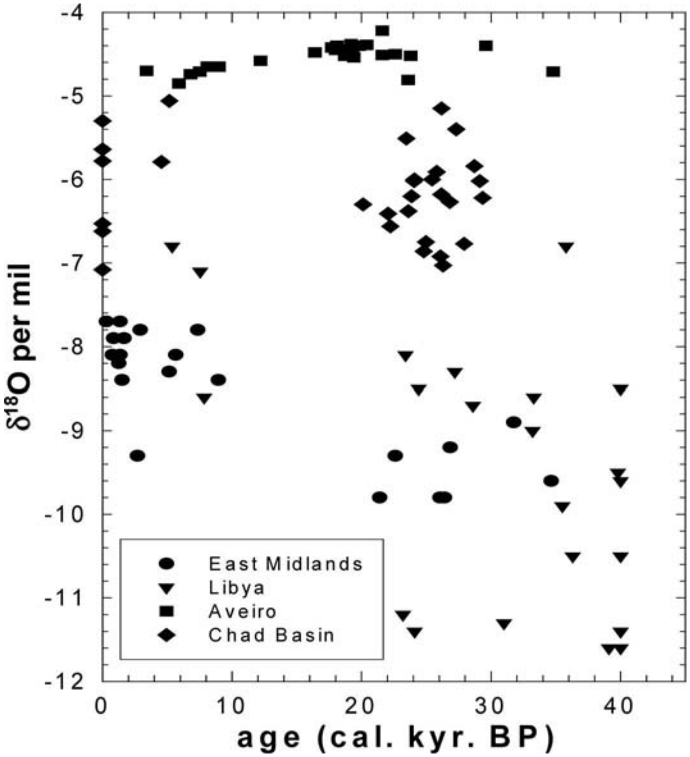

FIG. 3. Plot of $\delta^{18}O$ against corrected radiocarbon activities to show the comparative recharge situations in Africa and Europe during the last 30,000 years.

The Late Pleistocene and Holocene climate and hydrology in Africa is also consistent palaeo-groundwater archives in Europe, where significant replenishment of aquifers took place during the pluvial periods and where general cooling of around 5-6°C is recorded in the noble gas recharge temperatures. In coastal Portugal, as in Morocco, however the lack of any stable isotope depletion indicates the constancy of the southwest Atlantic air circulation at medium latitudes over the whole of the Late Pleistocene and Holocene, as well as proximity to the oceans.

This is shown in Fig. 3, where some isotopic data for dated African and European aquifers are compared. The aridity of Africa during the LGM, shown here by records from the Chad Basin (Edmunds et al., 1998), is balanced by recharge continuity in Portugal and then by a recharge gap in the UK corresponding to permafrost cover ahead of the continental ice sheet. The gradients of noble gas recharge temperature versus $\delta^{18}O$ from several different European aquifers have sub-parallel trends (Fig 4) and help to summarize the palaeoclimatic evolution from the Late Pleistocene to the present (Loosli et al., 2001), emphasising especially that $\delta^{18}O$ trends may not simply be used as a palaeothermometer. The gradients from Portugal and Belgium are almost flat and negative respectively, reflecting the influence of the oceanic $\delta^{18}O$ on the air mass.

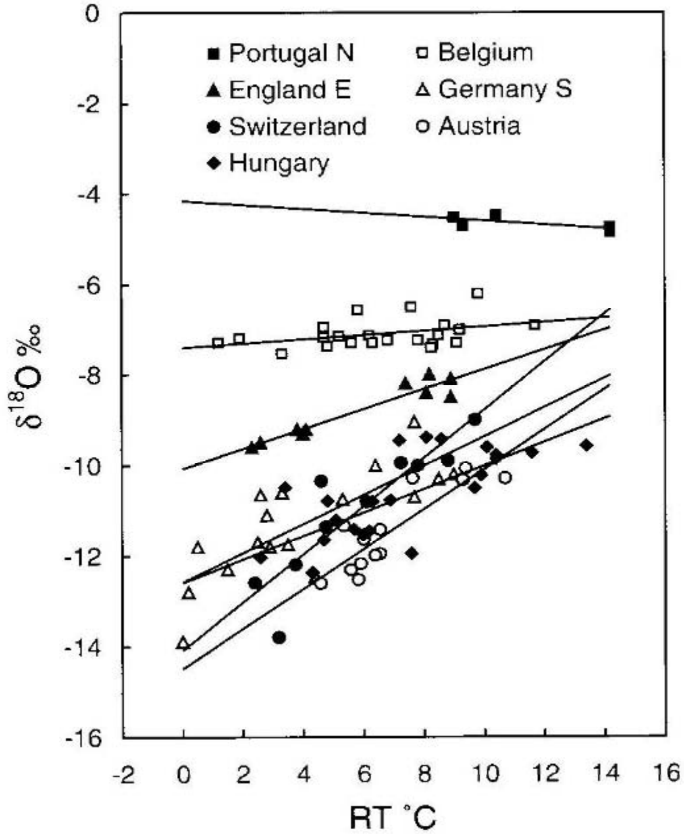

FIG. 4. Plot of $\delta^{18}O$ against recharge temperature showing the gradients between the Late Pleistocene and the present day for various European areas. Data sources are given *in Loosli et al., 2001.*

6. Summary

Groundwaters of known age contained in major aquifer systems in sedimentary basins are of specific value in determining low resolution (±1000 a) characteristics of past climates, specifically palaeotemperature, air mass origins, humid/arid transitions, rainfall intensity. Results from northern Africa indicate the predominance of westerly air flow during the Late Pleistocene, characterized also by a continental effect of about 4.5‰ $\delta^{18}O$. Greater aridity is recorded by the absence of dated groundwaters over most of northern Africa during the LGM. An intensification of the African monsoon during the Early Holocene is apparent from isotopically light groundwaters found especially over Sudan; however, over the past 6000 years there was a shift to the more enriched composition of modern times.

Maximum cooling around the LGM of 5-7°C is recorded in the noble gas recharge temperatures. Evidence in African groundwaters is matched by complementary data from northern Europe, where a recharge gap is found corresponding to permafrost conditions.

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22. ISOTOPIC PALAEOLIMNOLOGY

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1. Introduction

Much of our knowledge of past global climate change has been gained in the past 40 years from isotope records in ice sheets and deep-sea sediments, with $\delta^{18}O$ as the main palaeoclimate indicator. However, many specific questions remain to be answered before we can understand the ocean–atmosphere–land interactions within the climate system and reduce uncertainties in changes relevant to human societies. Indeed, the regional responses to global climate change are still poorly known owing to geographical gaps in data coverage and to the scarcity of high-resolution records over large areas such as central Asia or the southern tropics. How does the continental hydrologic cycle responds to global climate change and how does the latter affect the Earth's climate system? How are decadal to century-scale climate events, such as drastic droughts in the tropics or the "Little Ice Age" in medium latitudes, related to global change? What is the response time of a given water body to mean annual or seasonal climate changes?

Lake deposits represent a powerful proxy source for continental palaeoclimatology because (i) lakes are present at all latitudes; (ii) the reservoirs are small compared to the oceans, so that geochemical perturbations are large; (iii) their response time to external perturbations is relatively short; (iv) a great range of "proxy" signatures is decipherable from lake sediments using stable isotope analysis combined with microfossil, sedimentological, and geochemical studies; (v) sedimentation rates are high and thus high-resolution signals are possible. Even seasonal hydrologic changes can be analysed in the case of annually laminated sediments.

Isotope methods have considerably contributed to the study of lake sediments as palaeoclimatic indicators, in both the establishment of absolute chronologies and environmental reconstructions.

P.K. Aggarwal, J.R. Gat and K.F.O. Froehlich (eds), Isotopes in the Water Cycle: Past, Present and Future of a Developing Science, 353-358.

2. Nuclear methods of dating

Understanding the driving force behind climatically induced changes in lake systems first requires a reliable chronology. In the 1950s, ^{14}C-dating radically altered our view of the timing and mechanisms of climate changes as inferred from lake sediments. For example, we knew that the Sahara desert had been occupied by extensive lakes, but little else. It was firmly believed (e.g. Nillson, 1931) that the wetting of northern Africa coincided with glacial periods and ice sheet development in more northerly latitudes: the storm tracks of the northern latitudes would be pushed southward, there would be less evaporation because of lower temperature, and thus the subtropical desert would be wetter. This “pluvial theory” began to crumble with the first ^{14}C-dates from the Sahara (Libby, 1955; Delibrias et al., 1957), and was finally abandoned in the last 30 years in the view of the overwhelming ^{14}C-dated evidence which demonstrated the Early Holocene age of the last wet phase in the Sahara (Servant, 1973). A further important step has been to discover that the amount of ^{14}C in the atmosphere has varied through time. But it took more than two decades after the first calibration curve (Suess, 1970) to develop programs easily accessible to palaeolimnologists to translate ^{14}C-ages into calibrated ages (Stuiver et al., 1993, 1998; Bard, 1998). Correlations of lake records with other types of palaeoclimate series as well as with changes in orbital Earth’s parameters then became possible. Numerous factors can bias ^{14}C-ages of lacustrine materials, e.g. reworking or inputs of dissolved dead carbon into lake water. The risk of distortion is attenuated through a careful selection of the best appropriate material, such as aerial macrophyte or insect fragments entrapped in lake sediments occurring in very low amounts, that ^{14}C-AMS techniques now allow us to date.

Several other nuclear dating methods can now be applied, depending on the material and the time-scale under investigation. For example, the ^{210}Pb method (Appleby and Oldfield, 1978, 1983) is now widely used for dating lake sediments spanning the last 150-200 years, an important interval for disentangling the impacts of climatic and anthropogenic factors on lake systems. The method is complex, as ^{210}Pb measured at intervals within a core includes a fraction supported by the radioactive decay of ^{220}Ra/^{222}Rn located within the sediment, and an unsupported fraction which is primarily derived from atmospheric fallout. Dating models (age-depth point transformations), e.g. the “Constant Initial Concentration” (CIC) or the “Constant Rate of Supply” (CRS) (Appleby and Oldfield, 1978) should be applied to derive ages. The model reliability should be tested using other time indicators, e.g. the 1963 peak of weapon test tracers (^{137}Cs) or varve counting. Dating lake sediments beyond the limit of the ^{14}C method often remains difficult, although K-Ar and ^{39}Ar/^{40}Ar in volcanic interbedded materials, U/Th disequilibrium or luminescence techniques can sometimes provide reliable chronologies of long-term lake sediment series of utmost interest for comparison with the long marine and ice core records. Cosmogenic isotopes, e.g. ^{10}Be, are now starting to be used to date lacustrine terraces or palaeoshorelines.

3. Stable isotope analyses in lake sediments

Over the past decades, many laboratories have produced isotopic records of palaeoclimate mainly based on authigenic carbonates from fresh to hypersaline palaeolakes (e.g. Stuiver, 1970; Gasse et al., 1974; Eicher and Siegenthaler, 1976), but without the same co-ordination effort as in the field of palaeo-oceanography. Perhaps, this is due to the complexity of lake systems compared to the globally interconnected system of the world's oceans, and to the diversity of lacustrine materials. Developments in concepts and techniques (Fritz and Fontes, 1980, 1986) led to considerable progress in environmental isotope geochemistry in the 1980s. It is now recognized that isotope palaeolimnology can undoubtedly improve our knowledge of past continental climates (Swart et al., 1993; Gat, 1995; Last and Smol, 2001)

The oxygen isotopic composition of inorganic or biogenic carbonates has been and is the most widely used proxy for evaluation of changes in temperature and the hydrologic cycle. $\delta^{18}O$ records from diatom silica are currently increasing in number, and aquatic cellulose $\delta^{18}O$ in arctic lakes has recently been shown to be a good hydroclimatic indicator (Wolfe et al., 2001) Assuming that diagenetic processes have not altered the signal, the oxygen isotopic composition of a carbonate or of biogenic silica precipitated in equilibrium with its environment depends primarily on (i) ambient temperature and (ii) the isotopic composition of local water. If one of these variables can be estimated using independent methods, for example water temperature inferred from biological remains, the "unknown" (water composition) can be calculated taking into account the isotopic fractionation between the water and the mineral concerned. Isotopic analyses can also be performed on interstitial waters or in water inclusions trapped during crystal growth, with the advantage of providing both water isotopes ($\delta^{18}O$ and $\delta^{2}H$). Climatic and non-climatic factors that dominate or contribute to the isotopic composition of lake water – rainfall amount, isotopic composition and seasonality, evaporation processes, residence time – are numerous and site-specific. That is why most records are still qualitative. Indeed, any quantitative interpretation of oxygen isotope records requires that the hydrology of the investigated lake is well understood, including the effect of processes in the watershed which provide the inflowing water (Gat and Lister, 1995), and that the analysed material is calibrated. In particular, monitoring over at least one annual hydrologic cycle is crucial to understand seasonal changes. $\delta^{18}O$ records from lake sediments then potentially allow estimates of past rainfall isotopic composition. Several authors have recently related $\delta^{18}O$ records to changes in the isotopic composition of local precipitation, in moisture source region and in atmospheric circulation patterns in the monsoon domain of China (Wei and Gasse, 1999), western Europe (von Grafenstein et al., 1999) or East Africa (Barker et al., 2001) Hydrologic-isotopic-balance models currently developed on widely differing spatial and temporal scales (e.g. Gibson et al., 2002; Benson and Paillet, 2002) and applied to palaeolake systems will certainly favour such approaches. Quantified $\delta^{18}O$ records will provide crucial data for evaluating and refining global climate models.

Palaeoclimate information can be provided by the carbon isotopic composition of authigenic carbonates, which also involves a number of factors – the source of dissolved inorganic carbon in the lake, mixing and stratification, residence time, biological activity. For example, the covariance of $\delta^{13}C$ and $\delta^{18}O$, or the lack of it, indicates whether the lake was an open or closed system. Isotopic composition of sedimentary organic matter also became a powerful indicator of ecological and climatic change, when combined with its component analysis and with other geochemical data. Fluctuations in $\delta^{13}C$ of the allochthonous organic fraction are now routinely interpreted as changes in the vegetal cover in the basin (shifts from C3 to C4 vegetation), and $\delta^{13}C$ of the autochthonous organic matter can be related to climatically induced changes in a lake's trophic status. N-itrogen isotopic isotope analysis is gaining increasing usage for understanding nutrient sources, nutrient cycling, mixing regime and sediment provenance in paleolakes (Talbot, 2001).values

Many others environmental isotopes from lake deposits can be used to infer changes in the source of water and in the hydrologic network. For example, Talbot et al. (2000) resolved the timing (11.5 ^{14}C ka) of Lake Victoria's overflow to the Nile river by using strontium isotopes as tracers for water from the principal lakes and river of the Upper Nile.

4. Perspectives

Developing dating techniques remains a priority to obtain reliable and accurate chronology.

Stable isotope records developed from well-dated lacustrine sequences can contain critical information on climate changes that will become increasingly important as we strive to understand the past and predict future climates.

However, several aspects should be developed to use the full potential of lake sediments. In particular, the study of seasonal changes in the hydrologic cycle is, in most cases, not sufficiently investigated. Although some studies have shown that the seasonal distribution of palaeorainfall and seasonal hydrologic contrasts can be identified using the carbonate isotope composition of laminated bottom sediments, mollusc shells or stromatolites, these data are usually not quantified.

We can expect that the spreading of recently developed techniques, such as laser ablation coupled with mass spectrometry, or molecular-isotopic stratigraphy will considerably refine the time-resolution and accuracy of the isotope records.

The PAGES-ISOMAP initiative (www.pages-igbp.org) is dedicated to continental isotope palaeoclimatology, and especially to the mapping and modelling of water isotope data from precipitation. Oxygen isotope records should be largely integrated within this co-ordination effort. However, the reconstruction of past rainfall isotope composition from lakes requires model calibration and validation based on modern meteorological, hydrologic, and isotopic time-series. While such series are available across reasonable time intervals in most northern countries, that is not the case in many areas of the world. The development of the GNIP network remains a challenge for correctly widening the geographical coverage of lacustrine isotope records.

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APPENDICES

A. LIST OF SEMINAL PAPERS ON ISOTOPE HYDROLOGY (THE ISOTOPES OF HYDROGEN AND OXYGEN)

In chronological order, up to 1970

Lord Rayleigh (1902) On the distillation of binary mixtures.*Phil. Mag. 4* (series 6) 521-537.

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B. LIST OF PAPERS PRESENTED AT THE 1st IAEA SYMPOSIUM ON ISOTOPE HYDROLOGY (TOKYO, 1963)

A comparison of radioisotope methods for river flow measurement
C.G. Clayton, D B. Smith

Appareil pour la mesure des vitesses relatives des eaux souterraines par la méthode de dilution ponctuelle
J. Guizerix. G. Grandclément, B. Gaillard, P. Ruby

Use of radioisotopes for open-channel flow measurements
L.O. Timblin, Jr., A.J. Peterka

Determination par détection nucléaire des coefficients de diffusion et des courants clans les eaux naturelles. Evolution de la surface de collection d'un grand lac alpin pour les retombées radioactives
R. Chesselet, B. Dussart , D. Nordemann

An investigation of the hydraulics of an underground pool with iodine-131
D.B. Smith, W. E. Clark

A study in river engineering based on the results of field measurements of flow velocities with radioisotopes in the Sorachi River, Japan
M. Kato, Y. Morita, M. Kohama, N. Hayashi, O. Sato

Methods for measuring sand transport using radioactive tracers
G.H. Lean, M J. Crickmore

Etude du débit solide de charriage dans les riviéres alluviales au moyen detraceurs radioactifs
J E. Chabert, P. Jaffry, G. Courtois, R. Hours

Radiotracer experiments on littoral drift in Japan
M. Kato, M. Homma, S. Sato,S. Sakagishi

The place of isotope methods in groundwater research
Y. Harpaz, S. Mandel, J.R. Gat, A. Nir

Hydrologic phenomena affecting the use of tracers in timing groundwater flow
C.V. Theis

Application of radioactive tracers in scientific groundwater hydrology
R.W. Nelson, A.E. Reisenauer

Note sur l'utilisation éventuelle des complexes de nitronitrosylruthénium comme traceurs en hydrologie
C. Gailledreau

Measurement of river-bed variations during a flood
A. Ariizumi, O. Kondo

Les mesures de débits effectuées en France a l'aide de traceurs radioactifs par la méthode d'intégration
J. Guizerix, G. Grandclément, R. Hours, H. André, R. Wolf, R. Perez

New experiences with the use of radioactive isotopes in hydrology
H. Moser, F. Neumaier, W. Rauert

A method for the estimation of groundwater stratification
S. Iwai, Y. Inoue

The use of tritium in tracing karst groundwater in Greece
D. J. Burdon, E. Eriksson, T. Papadimitropoulos, N. Papakis, B. R. Payne

Deux utilisations du brome-82 en hydrodynamique souterraine
B. Degot, P.Ch. Leveque, G. Courtois, M. Gasnier, S. Godar

Field and laboratory tests of chromium-5l-EDTA and tritium water as a double tracer for groundwater flow
G. Knutsson, K. Ljunggren, H.G. Forsberg

Investigation of the movement of infiltrating acidic hot-spring water in the ground by means of radioisotopes
A. Arlizumi, O. Kondo

The use of the carbon isotopes in groundwater studies
J.C. Vogel, D. Ehhalt

A comparison of carbon-14 and tritium ages of groundwater
K.O. Münnich, W. Roether

A survey of the natural isotopes of water in South Africa
J.C. Vogel, D. Ehhalt, W. Roether

The runoff of fall-out radiostrontium from a river and its applications in hydrology
N. Yamagata, T. Okita, K. Kodaira

Estimation of the direct contribution of meteoric water to river waters by means of fall-out radiocaesium and radiostrontium

Y. Miyake, H. Tsubota

Measurement of river dilution and flow by means of radioactive tracers and activation analysis

M. Kobayashi, A. Nukazawa

C. EXCERPTS FROM REPORT OF 1st IAEA PANEL ON THE APPLICATION OF ISOTOPE TECHNIQUES IN HYDROLOGY

Vienna, 6 to 9 November 1961

List of participants

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H.G. Forsberg	
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Report Summary

ISOTOPE TRACERS OF WATER

1.) The Panel considered that the effectiveness of a tracer depends upon the degree of adsorption and also on the suitability of half-life dictated by the duration of the experiment.

a. Reasonably adequate tracers having either a relatively short half-life or one of the order of a number of years have been successfully employed, while in the intermediate range no reasonably successful labelled tracer has so far been found. Intensive chemical screening tests are required on radioisotopes having half-lives in the intermediate range, i.e. from about 1 week to a few years.

b. Adsorption of tracers at low concentration was recognized to constitute a limitation of tracer methods. These difficulties could only be overcome by using carrier material, the quantities of which would be prohibitive when experiments over both a long distance and involving large volumes were carried out.

c. For specific applications (i.e. discharge and leakage measurements) the possibility should be developed of using radioisotopes having a half -life between a few minutes and a few days, produced in the field both by neutron generators and milking of daughter products from longer-lived parents. Currently, production by the latter method is possible, but in general the fluxes of neutron generators are still too small to permit the production of appreciable amounts of short-lived isotopes in the field.

2.) Concern was expressed about the use of artificially injected tritium for large-scale groundwater experiments in areas where the use of natural tritium for the solution of hydrologic problems might be preferable. It was agreed that every individual case should be examined very carefully by weighing the additional advantages arising out of the use of injected tritium as against the usefulness of atmospheric tritium.

3.) Stable isotopes might be applicable to particular problems especially where large differences in isotopic abundance are expected, due for example to significant differences in altitude, temperature, origin and other parameters. The Panel recommended to continue surveying the significance of such abundances.

4.) The possibility was also discussed of the radioactivation by neutrons of the natural constituents of groundwater.This technique shows some promise for problems of mixing of water of different origins. Further survey work is necessary before its usefulness can be evaluated.

5.) The usefulness of the addition of stable tracers and their detection by radiactivation has been considered but does not yet look promising, although there may be some specific cases where it might be applied.

DATING OF WATER

6.) As possible methods of dating of groundwater the use was discussed of tritium (both natural and man-made), C^{14} and naturally occurring radioisotopes of the uranium and thorium decay series.

7.) Tritium was considered a suitable isotope for the dating of relatively young aquifers (with an age not exceeding 100 years) while members of the uranium and thorium decay series might be useful for dating very old aquifers.

a. In the case of natural tritium, it was realized that proper dating of groundwater is possible if an amount of “man-made tritium” is added. However, in order to arrive at an average age of a water formation, due consideration should be given to the representatives of the samples regarding age and to the distortion arising out of possible stratification of water according to age.

b. Man-made tritium has been added mainly in pulses which are possible to detect in groundwater and which can be utilized both for dating and tracing in order to arrive at groundwater reservoir characteristics; however, this tritium has introduced an additional complication in the evaluation of ages of water. However, whatever the distortion, the results so obtained would at least give an indication of the minimum age of the water; in due time, by extended sampling and analysis it might still be possible to arrive at quantitatively significant results.

8.) The possibility of using C^{14} may hold some promise for the dating of old groundwater, but the members of the Panel had insufficient data on work already done in this field to arrive at any specific conclusion.

9.) As to using members of the uranium or thorium series for dating of old groundwater and formations, no significant experience is available but this idea was felt worthwhile pursuing.

PROBLEMS OF HYDROLOGY AND HYDRAULIC ENGINEERING

10.) A number of typical groundwater and surface water problems were discussed to which isotope techniques might be applicable.

11.) The groundwater problems discussed included mainly: determination of the age of water in isolated or trapped aquifers, the ratio of replenishments to withdrawals of water in aquifers under exploitation, natural recharge into stream bed formations from rivers, natural and artificial recharge into groundwater bodies, problems of underground storage of fresh water in brackish aquifer – or vice versa, of brackish water in fresh aquifers, the contamination of aquifers by sea water and generally the determination of the hydrologic parameters of groundwater reservoirs.

a. Among specific groundwater applications, the Panel discussed the importance of a more detailed knowledge of the variation of age of water with depth and of the degree of lack of representativeness resulting from such variations, as far as age is concerned, of samples of water obtained by pumping from wells. The Panel arrived at the conclusion that more data on these problems would have to be collected before attempting dating procedures.

b. Another specific application discussed concerned the suspected contamination of fresh water by sea water; this might be amenable to solution by studying the change in S^{32}/S^{34} ratios and possibly also using radioactivation of trace constituents present in sea water but not present in groundwater.

12.) The question of evaporation from free water areas, from shallow groundwater bodies and from soils was also discussed and the Panel found that this subject would require additional basic and applied research before any practical application could be made available.

13.) On the other hand, regarding the measurement of soil moisture by nuclear techniques, the Panel found that available techniques are now sufficiently developed for immediate application.

14.) The application of isotope techniques to problems of hydraulic engineering was discussed, covering especially the determination of discharges, location of leakages and sediment problems.

a. The Panel arrived at the conclusion that, regarding the measurement of the discharge by the two-peak, total count and dilution methods in those cases where occasional spot measurements are sufficient and good accuracy is required, the use of isotopes can now be considered to be an adequate technique ready for application.

b. In addition, the application of radioisotope techniques shows promise in the study of other problems of hydraulic engineering, such as seepage of water under and around hydraulic structures, determination of seepage losses from canals and other conduits, and the investigation of currents and turbulent diffusion in water bodies.

c. The Panel also discussed briefly the application of isotope techniques to sediment problems encountered in hydraulic engineering such as bedload movement in natural water courses, river bed erosion, degradation and silting up of river stretches, silting up of reservoirs, sandbar formation and movement, coastal erosion, sediment problems of river mouths, sediment problems of ports, vertical distribution of suspended material, and hydraulics of settling basins.

15.) It was realized that a lot of additional study on isotope applications in hydraulic engineering would be needed in cases where quantitative results are required. Where a qualitative answer is sufficient, isotope techniques can already now be applied to many of the problems enumerated.

CONCLUSIONS AND RECOMMENDATIONS

16.) Considering the present status of isotope applications and the growing urgency for solving acute hydrologic problems in many parts of the world, the Panel felt that, in order to improve the application of isotope techniques, certain basic research work and investigations should be undertaken at the earliest possible date. This would include the following:

a. Screening tests for suitable water tracers, including radioactive inert gases, for different time scales, especially for the intermediate time scale requiring radioisotopes having a half-life between one week and a few years: laboratory experiments should be coupled with field experiments;

b. Continuation of collection of stable isotope data of natural waters including shallow groundwater;

c. In addition to the existing world-wide sampling of rainwater a world-wide collection of river and groundwater samples should be undertaken in order to utilize the unique situation of tritium in the atmosphere, as a consequence of the introduction of man-made tritium into nature, with a view to later analysis in connection with the solution of local hydrologic problems; standardized sampling techniques should be established as early as possible.

d. Improvement of sensitivity of scintillation counting of tritium;

e. Further examination of the possible use of C^{14} and suitable members of the uranium and thorium decay series for the age determination of groundwater;

f. Study of the age stratification of groundwater and connected variations of horizontal movement with depth (standardized sampling techniques to be established, in order to ensure adequate representativeness regarding age of samples).

g. The calibration of isotope techniques by applying them to hydrologic problems where all reservoir parameters have been ascertained by standard hydrologic methods; on the other hand, in hydraulic engineering, isotope techniques could sometimes be used to calibrate existing hydraulic methods.

17.) It is the opinion of the Panel that while the project approach should be primarily the responsibility of individual countries, (sometimes assisted by international organizations), basic research should preferably be carried out with the assistance of the Agency. The Panel therefore recommends the Agency to promote work outlined under items (i) to (vii) in paragraph 16.

18.) The Panel is of the opinion that the Agency should pass on to the Member States the following recommendations:

a. Projects connected with the application of isotope techniques to problems of hydrology and hydraulic engineering would have a better chance of success if undertaken by a combined team including a hydrologist (or hydraulic engineer in hydraulic problems), an isotope specialist, a groundwater geologist, a geochemist, and other specialists for special subjects (if required).

b. When considering large-scale experimental introduction of tritium into groundwater, due consideration should be given to possible interference with dating and tracing techniques based on tritium already contained in the water.

c. The application of isotope techniques and especially those using tritium are conditional upon the availability of adequate laboratory facilities and trained personnel.

19.) The Panel also recognized the importance of a rapid circulation of up-to-date information on isotope techniques applied to hydrologic and hydraulic problems. It therefore recommends the Agency to act as an information centre with the following terms of reference:

a. collect information, interim and other, on the results of isotope applications in hydrology and hydraulic engineering;

b. disseminate summarized information to Member States, specialized agencies and other interested organizations; and

c. supply detailed information on request.

20.) Recognizing also the importance of the project approach the Panel recommends the Agency to set up a Board of Review to be available upon request to Member States, with the following terms of reference:

a. to advise on the application of isotope techniques in hydrologic and hydraulic projects; and

b. to evaluate results from projects with a view to ascertaining the value of applied isotope techniques.

The chairman of the Board should be a staff member of the Agency, the other members being invited specialists from fields according to the requirements of each proposed project.