# Isotope hydrology: Applied discipline in Earth sciences

# *Hydrologie isotopique : une discipline des sciences de la Terre*

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**ABSTRACT** – The discipline " isotope hydrology " is being reviewed from the perspective of the Isotope Hydrology Section of the International Atomic Energy Agency in Vienna. The Section was created in the late fifties and is actively involved in the scientific progress of this discipline. The role of the IAEA in the development of isotope hydrology has always been of a dual nature: on one hand, the Section has been and still is heavily engaged in supporting and coordinating further development of isotope methodologies, on the other hand, it serves as an interface between the methodological development in research institutes and the applied work using proven techniques in field projects on water resources assessment and management. The paper provides a brief overview of applications of isotope-based methodologies in hydrology, with emphasis on new trends and challenges related to man's growing impact on the water cycle.
This contribution is a tribute to the memory of the former Head of the Isotope Hydrology Section, Jean-Charles Fontes, to whom we owe so much.

**Keywords** : methodological development, water resources, waste repositories, groundwater pollution, geothermics.

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**RÉSUMÉ** – La discipline nommée « hydrologie isotopique » est considérée du point de vue de la section d'Hydrologie isotopique de l'Agence internationale de l'énergie atomique de Vienne. La section, formée dans les années

cinquante, s'occupe, entre autres, de l'avancement scientifique de cette discipline. Le rôle de l'Agence dans le domaine de l'hydrologie isotopique a toujours été double : d'une part, la section est, comme par le passé, fortement engagée dans le soutien et la coordination des progrès méthodologiques en hydrologie isotopique ; d'autre part, elle agit à l'interface entre les développements méthodologiques dans les instituts de recherche et les applications sur le terrain dans les programmes concernant l'évaluation et la gestion des ressources en eau. Ce mémoire présente une brève revue des applications des méthodes isotopiques en hydrologie, en mettant l'accent sur les nouvelles tendances et les défis occasionnés par les répercussions croissantes des activités humaines sur le cycle de l'eau.
Ce travail constitue un hommage à la mémoire de Jean-Charles Fontes, ancien directeur de la section d'Hydrologie isotopique de l'AIEA, auquel nous tous devons beaucoup.

**Mots clés** : développement méthodologique, ressources en eau, stockage de déchets, pollution des eaux souterraines, géothermie.

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## HISTORICAL OUTLOOK

The discipline "isotope hydrology" was created during the late 1950s and 1960s, beyond the classical hydrological science, by chemists and physicists, many of them working in research centres using artificial radioisotopes. At that time, the main stream of research was directed towards developing and testing new methodologies based on injection of isotope tracers in surface water systems. The relatively small amounts of radioisotopes needed to conduct the experiment and their low detection limit were major advantages of these new techniques.

During the following years, the development of more sensitive detection systems to measure radioactivity and the introduction of mass spectrometric techniques for determination of the atomic ratios of stable isotopes of light elements, led to a progressive increase in the use of environmental isotopes, mainly tritium and carbon-14 as "dating tools" and oxygen-18 and deuterium as indicators of the origin of water bodies. The atmospheric tests of nuclear fusion bombs carried out during the fifties and early sixties released huge amounts of artificial tritium into the atmosphere and consequently the hydrosphere. The observation of this transient tritium pulse in the water cycle led to multiple hydrological studies on a global, regional and local scale.

Among other things, tritium became a powerful indicator of young water in groundwater systems. These tritium studies were complemented by measurements of carbon-14 in total inorganic carbon dissolved in groundwater (TDIC).

In spite of the complexity of the carbon geochemistry in groundwater systems, carbon-14 soon became a widely used tool for assessing groundwater ages. In the seventies and eighties, the number of laboratories capable of measuring environmental isotopes in water samples increased substantially, allowing a wider use of these new methodologies in hydrogeological investigations.

Concerning the stable isotopes of hydrogen and oxygen ($^{2}$H and $^{18}$O), the pioneering work of the early sixties addressed the main factors controlling the concentration of these isotopes in precipitation. Soon it became clear that these natural tracers have a large potential for the identification and characterization of different water bodies in hydrological systems, e.g. hydrograph separation, identification of paleowaters vs. present-day groundwater, mixing processes between groundwater and surface waters.

Isotope and geochemical techniques were initially applied by isotope specialists with limited knowledge of hydrological systems and, consequently, with a different perspective and perception of the problem, to that of hydrologists. While the first group was mainly concerned with the behaviour of isotope tracers in hydrological systems, the second group was more interested in how these systems function. Over the years, the two groups were coming closer in their approach and, as a result, scientists applying isotope methods started to consider in greater detail hydrogeological and climatic frameworks, rather than methodological aspects.

The demand for geochemical and isotope techniques in hydrological projects has been larger in areas where other (conventional) techniques do not provide convincing results. The characterization of groundwater systems in arid regions, the separation of flow components in catchment areas, the interconnection between surface and groundwater or the identification of recharge areas, represent typical problems studied by the combination of isotope and geochemical techniques. Examples of the application of isotope-based tools in hydrology are listed in Table 1.

Although the usefulness of these techniques has been clearly recognized by most hydrologists, only a relatively small number of specialized groups are so far integrating isotope techniques as a routine tool in their hydrological investigations.

## INVOLVEMENT OF IAEA

The Isotope Hydrology Section of the International Atomic Energy Agency was created at the time of early developments in isotope hydrology and actively contributes to the scientific progress of the discipline. The Section promotes and co-ordinates research programmes and conducts field applications of these techniques through technical co-operation projects in develo-

TABLE I.

Examples of established and new applications of environmental isotope tools in hydrological studies

*Exemples d'applications classiques et nouvelles de l'outil isotope aux études hydrologiques*

| **Isotope** | **Substance** | **Application** |
|---|---|---|
| $^3H$<br>$^3He/^3H$<br>$^{85}Kr$ | $H_2O$ | – Indication of recent recharge<br>– Infiltration rates in the unsaturated zone<br>– Transport mechanisms: fissure flow, matrix exchange<br>– Delineation of protection zones |
| $^2H/^1H$<br>$^{18}O/^{16}O$ | $H_2O$ | – Identification of recharge areas<br>– Interconnection with surface waters<br>– Aquifer leakage<br>– Salinization mechanisms<br>– Recycling of irrigation water<br>– Identification of paleowaters |
| $^{14}C/^{12}C$<br>$^{13}C/^{12}C$<br>$^{129}I$<br>$^{36}Cl$ | $HCO_3^-$ | – Identification of paleowaters<br>– Groundwater dynamics<br>– Validation of groundwater flow models<br>– Rock-water interaction |
| $^{15}N/^{14}N$<br>$^{18}O/^{16}O$ | $NO_3^-$<br>$NH_4^+$<br>$N_2$ | – Identification of pollution sources<br>– Identification of microbial denitrification |
| $^{11}B/^{10}B$ | $B(OH)_4^-$<br>$B(OH)_3^-$ | – Identification of pollution sources (sewage effluents) |
| $^{13}C/^{12}C$<br>$^2H/^1H$ | $CH_4$ | – Identification of methane source |
| $^{37}Cl/^{35}Cl$ | $Cl^-$<br>Chlorinated hydrocarbons | – Identification of pollution sources<br>– Sources of salinity |
| $^{34}S/^{32}S$<br>$^{18}O/^{16}O$ | $SO_4^=$ | – Pollution processes in groundwater, acidification<br>– Sources of $H_2S$, salinity ; acid mine drainage<br>– Groundwater flow in geothermal systems |

ping countries. Although hydrological problems studied by means of isotope and geochemical methods include mainly the origin and dynamics of groundwater, the possibilities offered by these techniques are being explored also in other fields like geothermics, determination of hydraulic parameters and pollution aspects.

The role of the IAEA in the development of isotope hydrology has always been of a dual nature: on one hand, the Isotope Hydrology Section has been and still is heavily engaged in supporting and coordinating the further development of isotope methodologies, on the other hand, it serves as an interface between the methodological development in research institutes and applied work using proven techniques in field projects on water resources assessment and management. The overall scope of these projects reflects the needs and requirements of Member States in this field. Broadly speaking, it can be divided into the following areas :

- water supply in arid and semi-arid regions ;
- dynamics and protection of groundwater resources ;
- geothermal development ;
- engineering problems in surface waters ;
- soil erosion and sedimentation processes ;
- hydro-climatic changes ;
- analytical support to isotope hydrology laboratories in developing countries.

An important component of the work being done by the Isotope Hydrology Section is the dissemination of information related to the use of isotope-based methodologies in hydrology as well as extensive training activities addressing the needs of developing countries in this field.

## RECENT TRENDS

The above mentioned dual role of IAEA in promoting isotope-based techniques provides a unique perspective with respect to both recent methodological developments and the emerging demand for these techniques in new challenging areas of the water sector. The following paragraphs contain a brief overview of the problems associated with these new areas, in which isotope techniques are already providing or are expected to provide a substantial contribution.

### Assessment of waste repositories

Isotopic and geochemical methods are well suited to study the hydrogeology of potential sites for long-term waste repositories. The list of potential geochemical and isotopic tools to identify the origin of the slowly moving

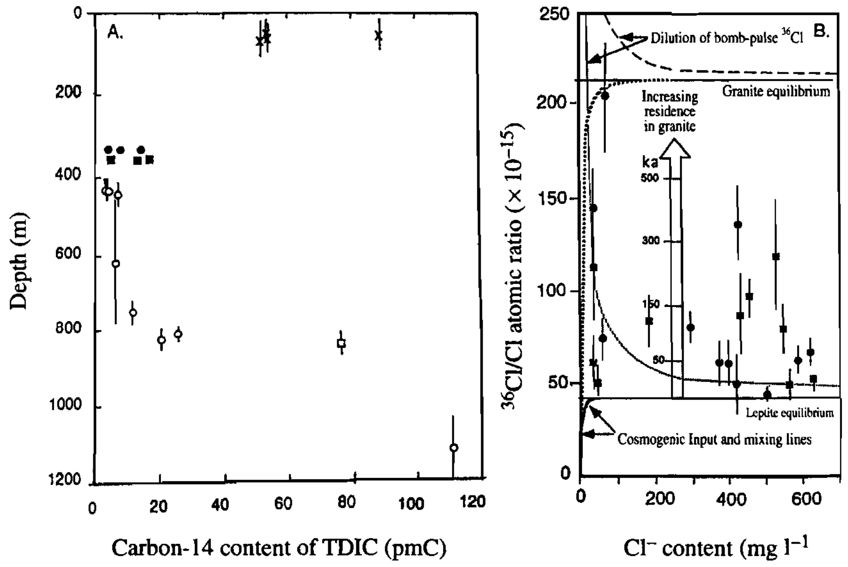


FIGURE 1.

A. Radiocarbon content of the TDIC in the Stripa mine waters (central Sweden) sampled at various depths (Fontes, 1994).

B. $^{36}$Cl/Cl ratio versus Cl$^-$ content in Stripa deep groundwaters. The distance between equilibrium $^{36}$Cl/Cl ratios for leptite and granite, respectively, can be interpreted in terms of time elapsed since the saline waters entered the pluton intrusion (Fontes, 1994).

*A. Teneur en radiocarbone du CITD dans les eaux de la mine de Stripa (Suède centrale) échantillonnée à différentes profondeurs (Fontes, 1994).*

*B. Rapport $^{36}$Cl/Cl en fonction de la teneur en Cl$^-$ dans les eaux souterraines profondes de Stripa. La distance entre les rapports à l'équilibre $^{36}$Cl/Cl pour la leptite et le granite respectivement peut être interprétée comme le temps écoulé depuis que les eaux salées ont pénétré l'intrusion plutonique (Fontes, 1994).*

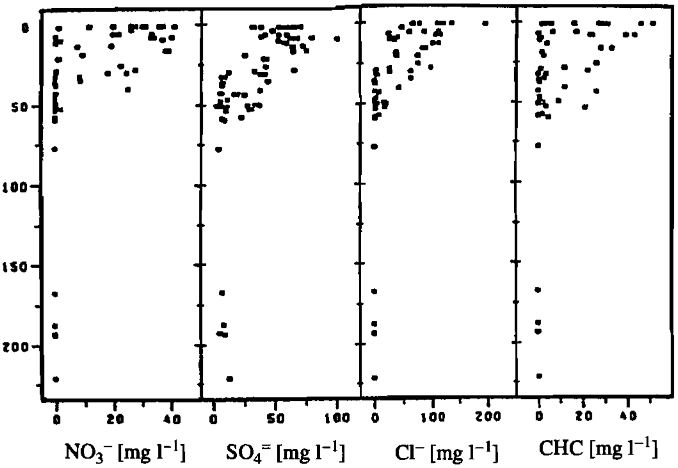
groundwaters and solutes, and to estimate their possible age is relatively large. The complexity of the contaminant behaviour in underground systems calls for the use of different approaches and methodologies. The list of potential tools include many isotopes or chemical species; from the commonly used major ionic components and the stable isotopes of the water molecule to some specific isotopes like $^{81}Kr$, $^{37}Cl$ or $^{36}Cl$, or trace elements, boron, or noble gases. Under special circumstances, several isotopes can be used to infer past hydrological circulation patterns that can serve as a constraint for the validation of predictive transport models of toxic substances being released from the repository.

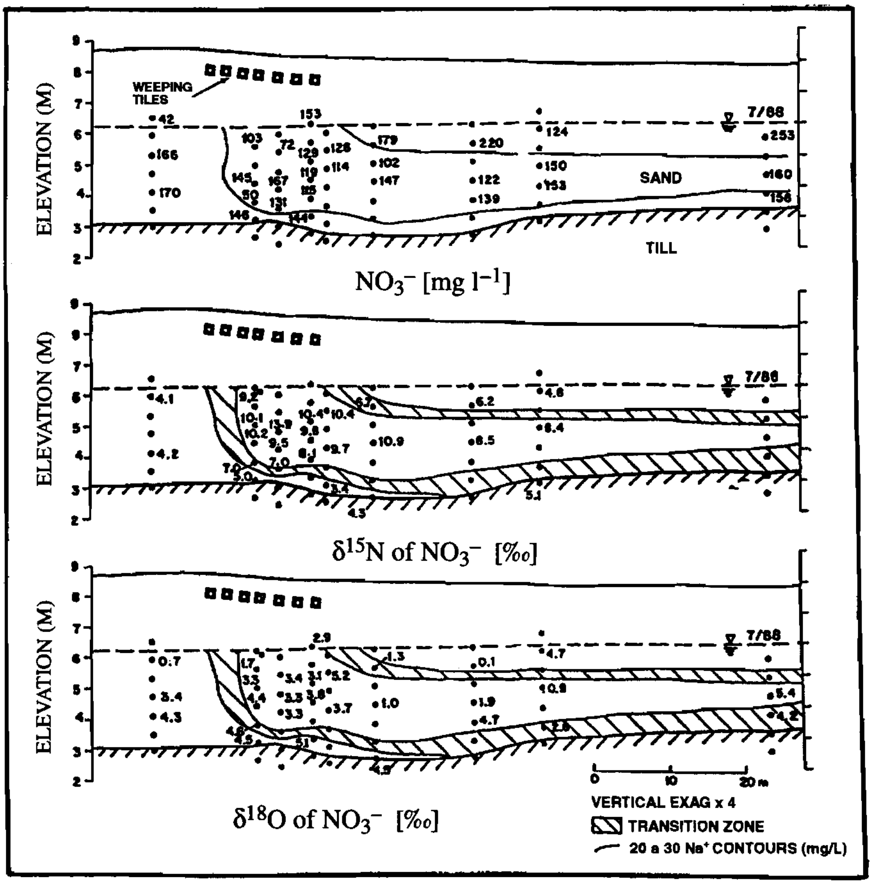
Figure 1 illustrates the use of isotopes in a feasibility study aimed at assessing the potential of old mines located in crystalline environments as repository sites. The study was performed at Stripa Mine, central Sweden. Both carbon-14 and tritium content (the latter is not shown in Fig.1) in mine waters collected at various levels clearly point to the occurrence of fast groundwater circulation at depth. Figure 1B shows the $^{36}Cl/Cl$ ratio versus $Cl^-$ content in Stripa deep groundwaters. Due to the contrast in the equilibrium concentration of the *in situ* produced $^{36}Cl$ in the metamorphic rocks (leptites) and the pluton of granite, it was possible to estimate the time elapsed since the saline solutions migrated into the granite intrusion from the surrounding metamorphic rocks (Fontes, 1994).

Deep unsaturated zones are considered as another potential environment for the disposal of radioactive wastes. Such zones, with a depth exceeding 200 metres, exist at present in several parts of the world. In a study carried out recently in southern Nevada, USA (Tyler *et al.*, 1995), the distribution of $^{36}Cl$, $Cl^-$, deuterium and oxygen-18 in the soil water was studied across the unsaturated zone extending over 250 m. Apart from conclusions on the usefulness as a site for waste disposal, the study manifested that isotopic tracers in the vadose zone allow the reconstruction of palaeoclimatic and palaeohydrological conditions in arid regions. The potential of deep unsaturated zones in arid regions as archives of past climatic and hydrological changes needs to be further explored.

### Groundwater pollution

Pollution of shallow aquifers by anthropogenic contaminants is becoming one of the central problems in the management of water resources. Figure 2 (upper panel) shows depth profiles of characteristic anthropogenic contaminants (nitrate, sulfate, choride, chlorinated hydrocarbons) in Quaternary and Tertiary aquifer systems in the area of Munich, Germany (Rauert *et al.*, 1993). The substantial contamination observed in the Quaternary aquifers of this region is typical not only for highly industrialized regions of temperate zones,


0
50
100
150
200
0 20 40
0 50 100
0 100 200
0 20 40
NO3− [mg l−1]
SO4= [mg l−1]
Cl− [mg l−1]
CHC [mg l−1]


ELEVATION (M)
WEEPING TILES
7/88
SAND
TILL
NO3− [mg l−1]
δ15N of NO3− [‰]
δ18O of NO3− [‰]
0 10 20 m
VERTICAL EXAG x 4
TRANSITION ZONE
20 a 30 Na+ CONTOURS (mg/L)

but is becoming apparent also in developing countries. Perhaps the most common pollution is the one caused by nitrate originating from agriculture and sewage systems.

Until recently, only $^{15}N$ was measured in dissolved nitrate or ammonia. The ambiguity in the interpretation of the $^{15}N$ results led to the publication of many papers defending or criticizing the usefulness of this isotope as the source indicator of nitrate and as a tracer of transformation processes which nitrogen compounds undergo in the environment. Recent analytical developments enabled also oxygen-18 to be measured effectively in nitrates (e.g. Böttcher *et al.*, 1990 ; Aravena *et al.*, 1993 ; Durka *et al.*, 1994, Kendall *et al.*, 1996 [see references]). The combined use of these two tracers offers new possibilities to resolve the ambiguity discussed above. This new approach has been applied in several field studies aimed at distinguishing between the possible sources of nitrate in shallow groundwater, studying nitrogen dynamics in shallow groundwater systems (Böttcher *et al.*, 1990) and investigating dynamics of soil organic matter in forest areas. Figure 2 (lower panel) illustrates the combined use of $^{15}N$ and $^{18}O$ as tracers to delineate a nitrate plume originating from a domestic septic system. The aquifer is characterized by high nitrate content outside and inside the contaminant plume (Aravena *et al.*, 1993).

Kendall *et al.* (1996) used a similar approach to study the sources of nitrate in catchment areas during spring (snow melt season). In many of the catchment areas it was observed that the nitrate concentration increases in the early spring.

◀ FIGURE 2.

**Upper panel.** Depth profiles of $NO_3^-$, $SO_3^{2-}$, $Cl^-$ and chlorinated hydrocarbons (CHC) in the shallow (Quaternary) and the deep (Tertiary) aquifer systems in the area of Munich, Germany (Rauert *et al.*, 1993).

**Lower panel.** Distribution of $NO_3^-$, $\delta^{15}N$ of $NO_3^-$ and $\delta^{18}O$ of $NO_3^-$ in shallow groundwater system in Ontario, Canada, affected by a contaminant plume originating from a domestic septic system (Aravena *et al.*, 1993). High concentrations of $NO_3^-$ in the aquifer make the delineation of the plume based only on $NO_3^-$ concentration practically impossible. The apparent enrichment in $^{15}N$ and $^{18}O$ of the nitrate originating from the septic tanks makes such a distinction feasible.

***Panneau supérieur.*** *Profils de $NO_3^-$, $SO_4^{2-}$, $Cl^-$ et carbones hydrogénés chlorurés (CHC) en fonction de la profondeur dans les systèmes aquifères superficiels (quaternaires) et profonds (tertiaires) de la région de Munich (Rauert et al., 1993).*

***Panneau inférieur.*** *Distribution de $NO_3^-$, $\delta^{15}N$ de $NO_3^-$, et $\delta^{18}O$ de $NO_3^-$ dans un système aquifère superficiel de l'Ontario (Canada), contaminé par un système de fosses septiques domestiques (Araneva* et al., *1993). Les concentrations élevées en $NO_3^-$ dans l'aquifère ne permettent pas de délimiter le panache des eaux contaminées par la seule mesure des concentrations en $NO_3^-$. Cette délimitation est possible en raison de l'enrichissement apparent en $^{15}N$ et $^{18}O$ des nitrates provenant des fosses septiques.*

The isotope data provided evidence that soil nitrate is the major source of the observed increase rather than atmospheric deposition, as previously assumed.

## Geothermal development

Isotope methods are considered a well established tool in most geothermal development projects. They provide basic information in the early stages of the exploration phase for the selection of potential drilling sites and are also useful in the elaboration of the conceptual models on the flow pattern in the area as well as in the location of reinjection wells for geothermal fluid. During the production phase, the reservoir is regularly monitored for physicochemical changes in the fluids in order to predict the evolution of the system. Apart from being used as additional geothermometers, the properties of isotope species are used to investigate the recharge area, the flow patterns, processes linked to water-rock interaction or steam separation, dilution or mixing with other water bodies.

Isotopes have produced strong evidence that geothermal waters are meteoric in origin (Craig, 1963), that they have been heated up and interacted with the rocks. Recent evidence suggests that in high temperature volcanic systems tapped by deep wells, geothermal waters are enriched both in $^{18}O$ and $^{2}H$, not only due to water-rock interaction but mainly because of mixing between meteoric and magmatic waters (Giggenbach, 1992; Mizutani *et al.*, 1986; D'Amore and Bolognesi, 1994; Gerardo *et al.*, 1993; Seki, 1991; Yoshida, 1991). Figure 3 illustrates major isotopic characteristics of different geothermal systems in the world.

Most of the high temperature geothermal areas are situated in volcanoes. These environments produce acidic fluids that are corrosive and cause fast deterioration of wells, as well as pipelines. Their commonly postulated origins are: (i) condensation of $H_2S$-rich steam into groundwater to form acid-sulfate waters, (ii) direct input of sulfur dioxide and other volcanic gases, and (iii) remobilization of sulfur deposits at depth. The understanding of their actual origin and occurrence enables better development strategies, specifically, drilling targets can be better defined. Recent studies indicate that the actual origin and the processes undergone by acidic fluids can be understood through the correlation of $^{34}S$ and $^{18}O$ in $SO_4^=$ as well as with other geochemical parameters. The usefulness of this technique was demonstrated in some New Zealand, Philippine and American fields (Robinson *et al.*, 1987).

## Engineering applications in surface waters

A number of hydraulic projects related to the utilization of surface waters demand the use of tracer methods to identify the relationship between different water types or to characterize the hydraulic parameters related to water

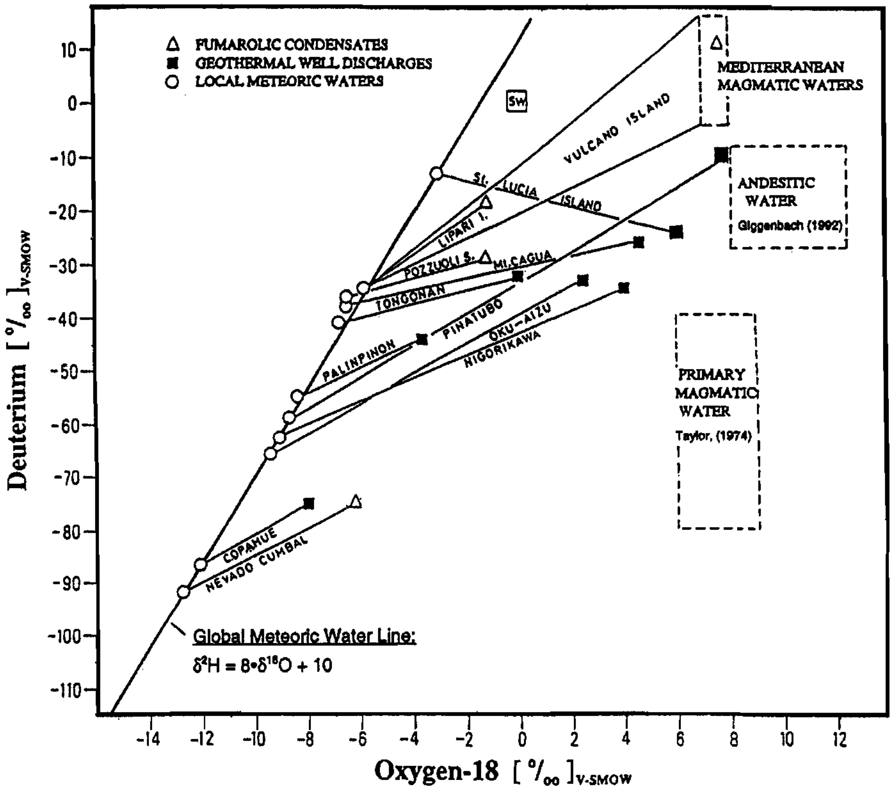


FIGURE 3.

Isotope characteristics of major geothermal systems of the world. Modified after D'Amore and Bolognesi, 1994; Giggenbach, 1992.

*Caractéristiques isotopiques des principaux systèmes géothermiques du monde. Modifié d'après D'Amore et Bolognesi, 1994 ; Giggenbach, 1992.*

and solute transport. The classical examples of these engineering problems are related to the identification of the flow patterns of subsurface flow emerging as leakage at the bottom of dams. These leakages in some cases can affect the stability of the dam and require a careful diagnosis before a costly remediation programme is implemented. Tracer methods are of primary importance here.

The modification of natural flow patterns as a consequence of the construction of a surface reservoir leads to changes in the discharge patterns of local groundwater and, in some cases, to the development of leakage through the contact between the embankment and the surrounding rocks or the bottom of the reservoir. Due to the chemical and isotopic contrast between the different types of water contributing to leakages (reservoir water, groundwater), the contribution of each type can be easily assessed by geochemical and isotopic methods. Furthermore, the transport dynamics of water from the reservoir to the leakage outlet can be studied through interconnection experiments using artificial tracers.

Another growing field of application of tracers, both in developed and developing countries, is the validation of mathematical models created to predict the transport of pollutants in surface waters and adjacent groundwater systems released in accidental spills (Stichler *et al.*, 1986; Plata Bedmar *et al.*, 1992; Adler *et al.*, 1993; Aoki *et al.*, 1996).

## NEW ISOTOPIC TOOLS AND APPROACHES

### Isotopic fingerprints

Boron isotopes have recently been applied to identify sources of anthropogenic pollution in groundwater, particurlary of sewage effluents (Vengosh *et al.*, 1994). The distinct isotopic signature of boron in anthropogenic boron compounds (especially sodium perborate used as a bleaching agent in detergents) makes the $^{11}B/^{10}B$ ratio a useful tool in tracing the origin of dissolved constituents and, hence, sources of contamination in groundwater.

Chlorine-37 and $^{13}C$ have been used to identify the source of pollution of shallow groundwater by organic contaminants, particularly chlorinated solvents (Aravena *et al.*, 1996). This issue has legal implications because of the high costs of remedial measures which should be charged to the institution/company responsible for the pollution. The preliminary data suggest that it will be possible to identify the producer of the given chemical compound through its characteristic isotopic signature.

Recently, it has been demonstrated (Rank *et al.*, 1992; Maloszewski *et al.*, 1995) that rainfall infiltrating through sanitary landfills often acquires a specific isotope signature which can be used to delineate the contaminant plume caused by the given waste disposal site in the groundwater system. Elevated concentrations of tritium in water percolating through the landfill were recorded, most probably originating from disposed leaking watches where tritium is widely used in dials. In addition, it was found that percolating water can be enriched in deuterium by up to 40 ‰, when compared to local rainfall. This enrichment stems from isotope effects during the anaerobic decomposition of organic wastes and can be used as a «natural» tracer for the water circulating through a landfill.

### Isotope mapping

In major urban centers and in areas of intense agricultural activities connected with irrigation, local groundwater systems are under heavy stress. Irrigation return flow, modification of the natural flow patterns and the recharge/discharge regime, leakages from distribution and sewage systems, are all factors which make sound management of water resources in these areas extremely difficult. Recently, it was demonstrated (Davisson and Criss, 1996) that a widespread isotope mapping of the aquifers exploited under such conditions, using classical isotopic indicators (deuterium, oxygen-18, tritium, carbon-14, carbon-13), can provide new insight into the effects of exploitation and disturbance of the natural flow pattern in such systems, and can help to design adequate management strategies.

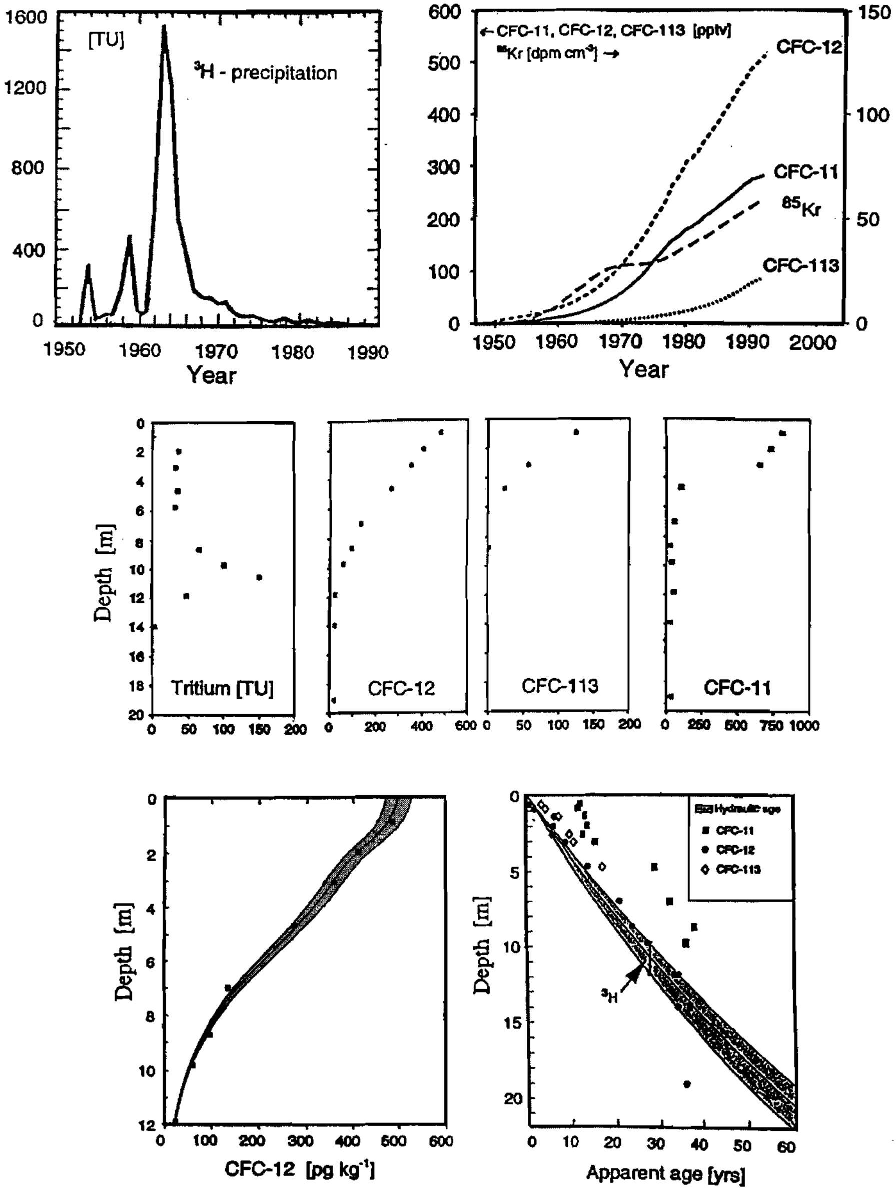
### New tracers for young groundwater

In most parts of the world the concentration of tritium in precipitation is approaching the natural level. This makes the use of bomb-tritium as a tracer for groundwater more and more problematic. The results of lumped parameter modelling of groundwater systems suggest that by the end of the present decade the quantitative estimates of the mean residence time of water using bomb-tritium will no longer be possible. On the other hand, there is a growing demand for quantitative assessment of the dynamics of shallow groundwater systems in connection with pollutant transport and protection of water resources.

Attempts have been made to use both radioactive ($^{85}$Kr) and non-radioactive substances (tritiogenic $^{3}$He, chlorofluorocarbons) as tracers for young groundwaters. In several recent studies the applicability of the above mentioned tracers in shallow groundwater systems has been examined in some detail (e.g. Schlosser *et al.*, 1989, Smethie *et al.*, 1992; Ekwurzel *et al.*, 1994; Cook *et al.*, 1995, Cook and Solomon, 1995). Figure 4 illustrates the use of CFC-11, CFC-12 and CFC-113 to derive apparent ages of groundwater in a well-characterized field site in central Ontario, Canada, where a detailed tritium investigation was performed earlier (Robertson and Cherry, 1989). The experience gathered so far with these new tracers is encouraging in spite of problems with sampling ($^{85}$Kr, $^{3}$He) and with sorption and degradation of CFCs.

## CONCLUDING REMARKS

Over the last decade, a major shift from the assessment towards the management of water resources has been observed. The problems related to pollution of both surface and groundwater systems are becoming central target areas for many institutions working in the water sector. The problems being tackled involve identification of pollutants, their transport in an underground


1600
1200
800
400
0
[TU]
³H - precipitation
1950
1960
1970
1980
1990
Year
600
500
400
300
200
100
0
150
100
50
0
← CFC-11, CFC-12, CFC-113 [pptv]
⁸⁵Kr [dpm cm⁻³] →
CFC-12
CFC-11
⁸⁵Kr
CFC-113
1950
1960
1970
1980
1990
2000
Year
Depth [m]
0
2
4
6
8
10
12
14
16
18
20
Tritium [TU]
0 50 100 150 200
CFC-12
0 200 400 600
CFC-113
0 50 100 150 200
CFC-11
0 250 500 750 1000
Depth [m]
0
2
4
6
8
10
12
0 100 200 300 400 500 600
CFC-12 [pg kg⁻¹]
Depth [m]
0
5
10
15
20
Hydraulic age
CFC-11
CFC-12
CFC-113
³H
0 10 20 30 40 50 60
Apparent age [yrs]

environment and the development of adequate remediation strategies. A better understanding of the processes taking place in the unsaturated zone is seen as one of the key elements of sound management of groundwater resources. The growing need for quantification of contaminant transport in both surface and underground environment calls for the development of realistic models of flow and mass transport in various geological media. This in turn requires adequate calibration and validation methodologies to be used.

The anthropogenic impact on climate and related short-term evolution of the hydrological cycle is already a major challenge and will necessarily become one of the most important tasks for the scientists of the next century. Better quantification of response of the hydrological cycle to short-term climate variability, in particular in the inter-tropical zone, is crucial. This region, occu-

◀ FIGURE 4.

**Top panel.** Long-term variations of atmospheric tritium, $^{85}$Kr and chlorofluorocarbon (CFC-11, CFC-12, CFC-113) concentrations in the northern hemisphere, between 1950 and 1990 (after Ekwurzel *et al.*, 1994; Cook and Solomon, 1995).

**Middle panel.** Depth profiles of tritium, CFC-11, CFC-12 and CFC-113 measured in 1991 in the shallow aquifer located in central Ontario, Canada (Cook *et al.*, 1995).

**Bottom panel** (left). Comparison of measured depth profile of CFC-12 concentration in the above mentioned shallow aquifer with model profiles simulated, using the two-dimensional flow model. The shaded region depicts the profiles simulated under a recharge rate of 130 mm yr$^{-1}$ for recharge temperatures between 2 °C and 4 °C (Cook *et al.*, 1995).

**Bottom panel** (right). Apparent groundwater age profiles estimated using tritium and chlorofluorocarbons, for the above mentioned shallow aquifer. The error bar depicts the position of the $^{3}$H peak in 1991. The shaded region depicts the hydraulic age profile calculated using the two-dimensional flow model, using the recharge rate obtained from the position of the tritium peak (Cook *et al.*, 1995).

***Panneau supérieur.*** *Variations à long terme des concentrations dans l'atmosphère en tritium, $^{85}$Kr et chlorofluorocarbones (CFC-11, CFC-12, CFC-113) de l'hémipshère nord, entre 1950 et 1990 (d'après Ekwurzel* et al., *1994; Cook et Solomon, 1995).*

***Panneau central.*** *Profils des concentrations en tritium, CFC-11, CFC-12, CFC-113 mesurés en 1991 en fonction de la profondeur, dans l'aquifère superficiel de l'Ontario central, Canada (Cook* et al., *1995).*

***Panneau inférieur gauche.*** *Comparaison du profil vertical des concentrations en CFC-12 dans l'aquifère précité avec les profils simulés par un modèle de circulation à deux dimensions. La zone ombrée indique les profils simulés avec un taux de recharge de 130 mm a$^{-1}$, et des températures de recharge comprises entre 2 °C et 4 °C (Cook* et al., *1995).*

***Panneau inférieur droit.*** *Âges apparents des eaux souterraines du même aquifère superficiel en fonction de la profondeur, estimés à partir des concentrations en tritium et en chlorofluorocarbone. La barre d'erreur représente la position du pic de $^{3}$H en 1991. La zone ombrée indique l'âge hydraulique du profil, calculé à partir d'un modèle de circulation à 2 dimensions, et le taux de recharge déduit de la position du pic de tritium (Cook* et al., *1995).*

pied mostly by developing countries, is subject to extreme hydroclimatic variations (droughts and floods). The short-term predictions of such events are therefore a major requirement for sustainable development of the region.

These new challenges require an integrated approach combining conventional and non-conventional methodologies. Isotope tools, although still considered "non-conventional" by the majority of the hydrological community, can make important contributions in these new target areas. Links should be explored between isotope/geochemical methods and techniques which provide spatially averaged information, such as remote sensing. An important prerequisite for success in this new endeavour is a broad education programme for hydrologists and hydrogeologists at university level, which should cover modern physical and chemical methods, including isotope-based methodologies, for a better understanding of the structure and dynamics of the water cycle at various spatial and temporal scales.

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