Isotopes in climatological studies

Environmental isotopes are helping us understand the world's climate

by Kazimierz Rozanski and Roberto Gonfiantini

The fundamental motivation for the recent explosion of interest in climate studies is the growing scientific concern that rapidly expanding human impact on the global ecosystem may significantly alter the world's climate in the near future. The major source for this concern is the observed change in the earth's atmosphere, probably the most vulnerable component of the entire ecosphere.

Observation data clearly show that the concentration in air of some trace constituents such as carbon dioxide, methane, carbon monoxide, ozone, chlorofluoro-hydrocarbons (CFCs), nitrogen and sulphur oxides, is changing as a result of anthropogenic emissions. These changes may have harmful, far-reaching consequences in the near future via direct effects on the biosphere — including human beings—and, indirectly, via the alteration of the life-supporting conditions. Global warming as a result of the rapidly increasing concentration of some atmospheric components — known as the "greenhouse effect" — may serve as a prominent example of such consequences.

As a matter of fact, the global average surface air temperature has been rising for a century, probably because the earth is going through one of its minor climatic oscillations, which have been frequent in the past. But in the near future the rate of warming of the earth's atmosphere—which has been approximately half a degree Celsius in the last 100 years—is expected to increase drastically, with consequences which have been announced as dramatic, such as the reduction of the polar ice caps with rise of the sea level and flooding of low coastal lands, changes in precipitation distribution patterns and river regimes, and expansion of arid lands.

The reason for the predicted increase of the global mean warming rate of the lower layers of the atmosphere lies in the additional energy trapped by some atmosphere trace gases intercepting the earth's infrared radiation, which otherwise would escape into space. Carbon dioxide and methane are the most important greenhouse gases, the concentration of which in the air has been increasing since the middle of last century, mainly — but not only — due to the growing consumption of fossil fuels. *(See Table 1.)*

The predictions on the onset and extent of the greenhouse effect are, however, admittedly imprecise due to the complexity of environmental interactions, and the still incomplete knowledge of global meteorological and climatological mechanisms. For instance, we are still far from achieving a thorough understanding of the processes regulating the composition of the atmosphere and the feedback mechanisms that operate between the major compartments (atmosphere, hydrosphere, biosphere, geosphere) of the global ecosystem, and determine its climatic response to internal and external forcing. In recent years, it has become apparent that a deeper insight into the dynamics of this extremely complex, non-linear system can be gained only by an integrated approach which combines two general directions of research aimed at:

- ***Understanding of the present climate.*** This includes evaluation of trends in observation data; refinement and improvement of the atmospheric general circulation models (GCMs); deeper understanding of the role of oceanic circulation on climate; identification and evaluation of important feed-back mechanisms; evaluation of sources and sinks of greenhouse gases;
- ***Understanding of the past climate.*** This includes better characterization of past climatic fluctuations, with a better definition of causes, timing and amplitude; detailed reconstruction of the global ecosystem behaviour during major glacial/interglacial transitions; elaboration of models directed to meaningful projections of past climatic fluctuations into the future.

Environmental isotopes, the distribution of which in natural compounds is governed by environmental conditions, are one of the most powerful tools to investigate the climatic variations and the response of the environment to changing climate. This article briefly shows how these isotopes have contributed to the progress of

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Table 1. Trends in concentrations of major atmospheric trace gases

Gas	Concentrations Pre-1850	Concentrations 1985	Observed trends for 1975–85 (%)	Mid-21st century
CO_2	275 ppmv	345 ppmv	4.6	400–600 ppmv
CH_4	0.7 ppmv	1.7 ppmv	11.0	2.1–4 ppmv
N_2O	0.285 ppmv	0.304 ppmv	3.5	0.35–0.45 ppmv
CFC-11	0	0.22 ppbv	103	0.7–3 ppbv
CFC-12	0	0.38 ppbv	101	2.0–4.8 ppbv

Source: Adapted from V. Ramanathan, *Science,* **240,** (1989) pp. 293–299.
ppmv = part per million (in volume).
ppbv = part per billion (in volume).

modern views in climatology and palaeoclimatology. The role played by the IAEA in the collection and elaboration of isotopic data of relevance for investigations related to climate and its history will also be shown.

How do isotopes work?

Perhaps the most characteristic application of environmental isotopes in geochemistry is their use as a dating tool. A great variety of methods based on decay of radioactive isotopes and/or buildup of daughter isotopes has been developed, which allows age determination of groundwater, ice, rock, sediment, etc.

In recent years a renaissance of these methods has been observed, owing to the development of accelerator mass spectrometry—a novel analytical technique allowing the detection of low concentrations of environmental radioisotopes in very small samples.

In climatology, many isotope dating methods in principle can be applied for establishing the proper time scale of past climatic events; the choice depends upon the age range and nature of the system being investigated. Both naturally produced (cosmogenic and *in situ*) and anthropogenic radioisotopes are used. By far, the most popular dating method was — and probably still is — the one based on carbon-14, the radioactive isotope of carbon, which, with a half-life of 5730 years, allows the determination of ages ranging from a few hundred to approximately 40 000 years. Many other radioisotopes currently are used in palaeoclimatology that have half-lives ranging from much shorter to much longer values than that of carbon-14. *(See Table 2.)*

Table 2. Isotopes used in climatological research

Isotope	Type of material studied	Type of climatic information derived
Stable isotopes: Deuterium (Hydrogen-2) Oxygen-18 Carbon-13	— marine sediments — lacustrine sediments — ice cores — cave deposits — groundwater — precipitation	temperature of the ocean, ocean circulation, volume of ice sheets, air temperature, relative humidity, dynamics of water cycle on regional and global scale
Anthropogenic radioisotopes: Tritium (Hydrogen-3) Krypton-85 Caesium-137 Carbon-14	— ocean water — oceanic carbonates — lacustrine sediments — groundwater — precipitation — atmosphere	dynamics of the ocean, dynamics of the atmosphere, sedimentation rates
Natural radioisotopes: Radon-222, Lead-210, Argon-39 Carbon-14, Thorium-230, Protactinium-231 Uranium-234, Uranium-238, Potassium-40	— marine sediments — lacustrine sediments — cave deposits — ocean water — groundwater — atmosphere	dating of deep-sea sediments, dating of lacustrine sediments, dating of cave deposits, dating of ocean water, dating of groundwater, dynamics of the atmosphere

The concentration of stable isotopes in natural compounds varies due to the slightly different, mass-dependent behaviour of isotopes in natural physico-chemical processes. As the magnitude of these isotopic effects, or fractionations, is a function of the parameters characterizing any given process, among which temperature is the most important, information on the environmental conditions at the time of formation can be derived from the stable isotope composition of water, ice, and minerals.

The stable isotope variations most frequently applied in climatological investigations are those of the heavy isotopes of hydrogen and oxygen, i.e. hydrogen-2 (or deuterium) and oxygen-18, which allow the effective tracing of climate-induced changes in the hydrological cycle. Also carbon-13, the heavy isotope of carbon, appears to be a powerful climatic indicator.

In summary, we can say that in geochemical climatology, as in other fields of geochemistry, environmental radioisotopes are used as time indicators, and stable isotopes as temperature indicators. The brief overview which follows presents the major contribution of environmental isotope techniques to the investigation of the earth's climatic history.

The ocean

Because of its relative homogeneity, the ocean is an ideal environment to record major, long-term climatic variations. In fact, due to its large mass and the resulting thermal, chemical, and isotopic inertia, short-term climatic fluctuations would have a limited, often negligible impact on it.

Marine sediments were the first important source of isotope data used in palaeoclimatology. The oxygen-18/oxygen-16 ratio of the carbonate shells of marine protozoans called foraminifera, which are present in marine sediment cores, is a function of the oxygen-18/oxygen-16 ratio of sea water and of its temperature. These two factors act in the same direction during the glacial/interglacial climatic fluctuations, enhancing the isotopic variations in the calcium carbonate formed. It has been found that the oxygen-18/oxygen-16 variations of foraminifera shells are in reasonable agreement with the expected variations of insolation induced by the cyclic changes of earth's orbital parameters, and the resulting climatic fluctuations predicted by the Milankovitch theory. By the parallel dating of sediment core sections using radiocarbon, the uranium series disequilibrium or the potassium-argon method, it has been possible to establish a detailed chronology and to evaluate ocean temperature variations during most of the Quaternary. *(See Figure 1B.)*

Also, the application of environmental isotope techniques to modern physical oceanography can be regarded as an indirect contribution to climatology. In fact, in spite of the considerable homogeneity of the present ocean, small differences in isotopic and chemical composition do occur. These differences, together with the tritium and carbon-14 variations, can be used to trace different water masses, establish their circulation patterns at depth, and investigate the mixing between the shallow and deep ocean. The assessment of modern ocean circulation is essential to understand the impact of the ocean on the global climate and meteorology.

The high-latitude continental environment: The ice caps

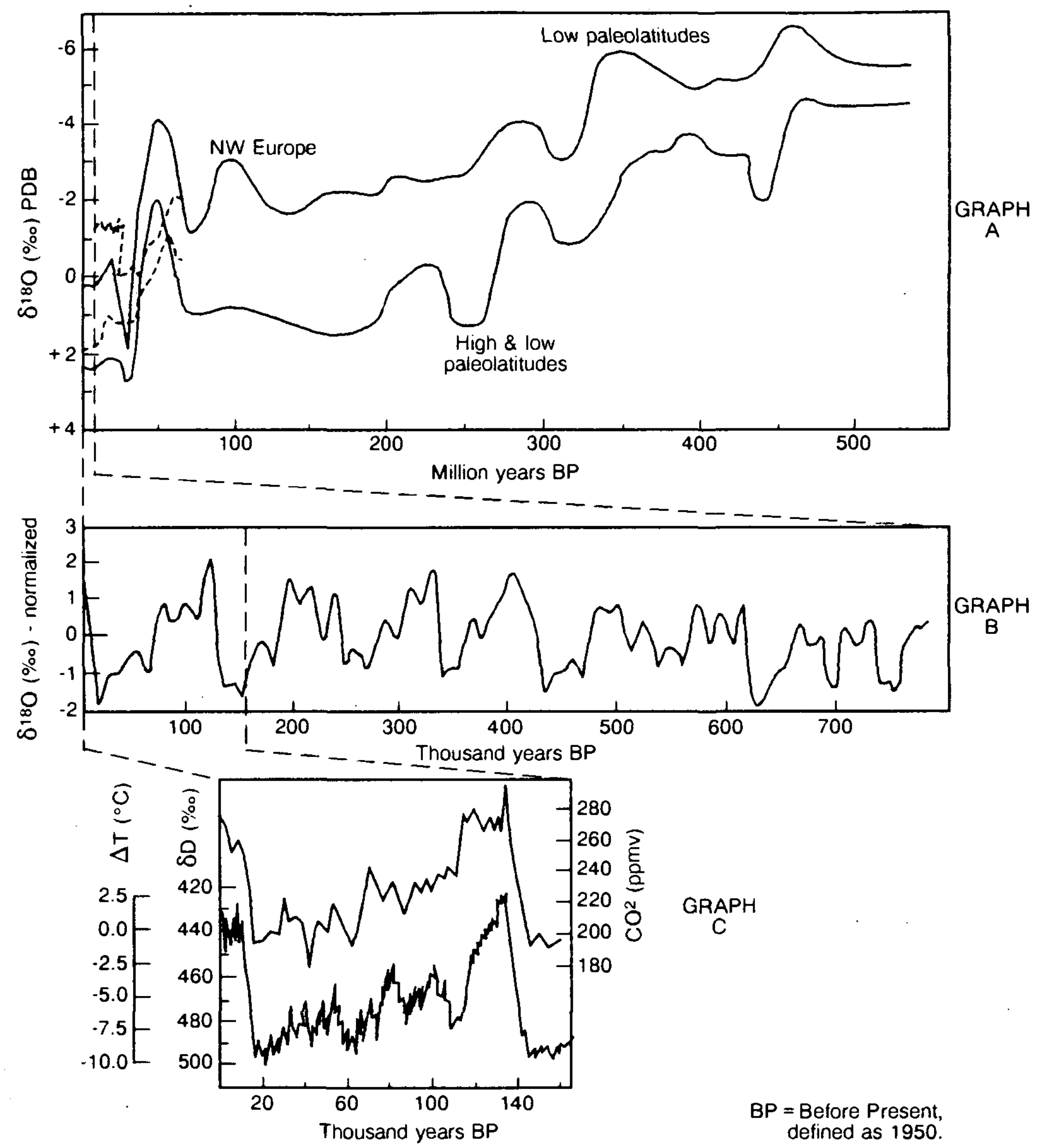
Large ice caps existing at high latitudes (Greenland, Antarctica) proved to be excellent archives of Pleistocene climate. Actually, a large part of our knowledge on Quaternary climatic variations is derived from the isotopic composition of the polar ice cover.

Ice caps, formed by snow precipitation over large, almost flat regions with negative mean annual temperatures, preserve the vertical stratification, although the thickness of annual layers decreases with depth primarily due to the compaction process in which the snow is transformed firstly into firn or granular ice and then into compact ice.

The oxygen-18/oxygen-16 and hydrogen-2/hydrogen-1 ratios of precipitation are strongly correlated with the temperature of formation: lower formation temperature leads to isotopically depleted precipitation. At middle and high latitudes, where the seasonal variations of temperature are large, this implies parallel seasonal variations of the isotopic composition of precipitation, with the heavy isotope concentration being higher in summer than in winter. These seasonal isotopic variations are preserved in the ice cap down to a considerable depth (about 1 to 1.5 km), despite the diffusion which tends to smooth off the differences. The counting of the annual isotopic cycles along a vertical profile constitutes a method of ice dating and evaluating the accumulation rate.

The correlation between temperature and isotopic composition allows also the identification of ice deposited during the glacial periods, which is expected to be considerably depleted in heavy isotopes with respect to modern precipitation. In fact, this has been observed in all deep ice cap drillings carried out to date. Variations of oxygen-18 and deuterium content preserved in ice made possible detailed reconstruction of the high-latitude palaeotemperatures during the last glacial/interglacial cycle. *(See Figure 1C.)* Furthermore, the chemical analyses of air bubbles trapped in ice, coupled with the isotopic composition of ice, led to the reconstruction of the history of the carbon dioxide and methane concentration in air during the last 160 000 years. The profile of carbon dioxide concentration derived from the Vostok ice core (Antarctica) *(Figure 1C)* mimics the temperature curve derived from the deuterium profile, pointing to a strong linkage between carbon dioxide and climate. It is believed that the observed carbon dioxide variations are linked with climate-induced oceanic circulation changes rather than

Figure 1. Environmental isotopes as palaeoclimatic indicators.



BP = Before Present, defined as 1950.

These graphs show selected examples of climate-induced variations of oxygen-18 and deuterium concentration, preserved in environmental archives, namely oceanic sediments and polar ice sheets. The solid lines in graph A show ranges of the oxygen isotopic composition of well-preserved marine macrofossils. This isotope record can be converted, under certain assumptions, to the temperature record. It is believed that beyond approximately 50 million years ago, the observed isotope variations are mainly caused by dramatic changes in ocean circulation, leading to substantial isotope differences between the shallow and deep ocean.

Graph B shows the composite curve of oxygen-18 variations in foraminifera shells extracted from five deep-sea cores. Isotope effects accompanying evaporation and condensation of ocean water lead to preferential storage of oxygen-16 in advancing ice sheets during the onset of the glacial period, and to corresponding enrichment of the remaining ocean. The retreat of ice sheets returns this isotopically depleted water back to the ocean. On the other hand, the oxygen-18 isotope fractionation between carbonate of foraminifera shells and sea water is temperature-dependent — shells formed at higher ocean temperatures tend to be enriched in oxygen-18. Calculations show that approximately 70% of the total amplitude of the oxygen-18 variations in this graph can be explained by changes in the volume of ice sheets. The remaining part is due to temperature variations.

Graph C shows the changes of carbon dioxide concentration in the atmosphere preserved in air bubbles (upper curve), and the surface air temperature derived from the deuterium isotope profile (lower curve), plotted against age in the Vostok ice core. The carbon dioxide profile mimics the temperature curve, pointing to a strong linkage between variations of carbon dioxide content in the atmosphere and the climate.

Notes: Concentrations of deuterium and oxygen-18 are expressed in δ values, defined as per mille deviations from the standard (which is PDB for oxygen-18 in carbonates and V-SMOW for oxygen-18 and deuterium in water).

Sources: *Graph A* — adapted from L.B. Railsback, *Geochimica et Cosmochim Acta*, **54** (1990) pp. 1601–1609. *Graph B* — Imbrie et al., *Milankovitch and Climate*, Part I, Eds A.L. Berger et al., D. Riedel Publishers (1984) pp. 269–305. *Graph C* — Barnola et al., *Nature*, 329, (1987) pp. 408–414.

directly with the greenhouse effect. A more precise interpretation would in particular require the determination of the variation of carbon-13 content in the carbon dioxide extracted from the air bubbles. The carbon dioxide and isotope profiles retrieved from ice cores drilled in Greenland ice sheets reveal striking similarities to the Antarctic profiles, suggesting general synchroneity of major climatic transitions in the Northern and Southern Hemispheres.

The middle- and low-latitude continental environment

The studies briefly discussed above are restricted to marine and polar environments. These are almost ideal for isotope investigations, the first one because of its homogeneity, allowing the effects of relatively small amplitude to be detected, and the second because the climatic variations are more dramatic.

There is, however, a considerable interest in detecting climatic changes also in middle- and low-latitude continental areas. This interest is stimulated by the fact that relatively large differences both in magnitude and timing of the climatic response to internal and external forcing are expected for different geographical regions. It is clear that learning what happened in the past to the climate in different regions of the world would be extremely instructive for predicting the consequences of future climatic changes.

Lacustrine sediments are one of the most valuable continental materials for palaeoclimatic reconstructions. This material often contains carbonate whose oxygen isotope composition is controlled by that of the lake water. For open lakes with fast water turnover, the water isotopic composition corresponds to that of precipitation over the lake basin, which in turn is temperature-dependent. Thus, periods of cold and mild climate are reflected by minima and maxima in the oxygen-18 content of the deposited carbonate.

More complex is the case of nearly closed lakes, where the isotopic composition of water is largely determined by evaporation and exchange with atmospheric moisture. Here the changes in water balance are responsible for the oxygen isotope variations recorded by the carbonate deposited, with dry periods marked by high oxygen-18 content due to increased evaporation, which preferentially removes isotopically light water from the lake.

Isotope studies carried out to date resulted in a detailed reconstruction of climatic and hydrologic conditions prevailing during the last glacial-interglacial transition and the early Holocene in Central Europe, North Africa, and North America. Substantial differences were found among these regions with respect to both timing and structure of this transition. For instance, several humid-arid oscillations have been recorded in lacustrine deposits in the Sahara and the Sahel. In the Sahara, the last important humid episodes occurred between 14 500 and 11 000 and between 9300 and 7500 years ago. Isotopic evidence exists that probably most of the groundwater stored in the Saharan aquifers was recharged at this time.

Groundwater is also a source of palaeoclimatic information. The isotopic composition of groundwater generally corresponds to the mean isotopic composition of precipitation in the recharge region. Consequently, the isotopic variations of precipitation connected with climatic changes are reflected by the groundwater's isotopic composition. Also, atmospheric noble gases dissolved in groundwater (neon, argon, krypton, xenon) may, under favourable conditions, provide valuable palaeoclimatic information. In porous aquifers, concentrations of noble gases in groundwater are directly related to the mean annual temperature of the recharge area and, consequently, can be used for the reconstruction of temperature changes in the past.

There are, however, a number of difficulties in using groundwater as climate indicator. Groundwater can seldom be considered a closed system. Diffusion and dispersion in aquifers, mixing between groundwater stored in different aquifers through leakages or discontinuities in the separating formations, and interactions with the rock matrix, tend to mask or smooth off the climatic differences and make difficult the dating of groundwater by carbon-14. Nevertheless, a distinct climatic signal — a shift in the deuterium and oxygen-18 contents accompanying the Late Glacial-Holocene transition — has been identified in a number of confined aquifers of the Northern Hemisphere.

Also the calcium carbonate deposited in karstic caves in a variety of forms — stalactites, stalagmites, flowstones, all designated with the common name of speleothems — is of potential relevance in isotopic palaeoclimatology. The speleothems are slowly precipitated from percolating groundwater over long periods of time, in conditions close to thermodynamic equilibrium, in an environment where the seasonal variations of temperature, atmospheric humidity, and isotopic composition of water and dissolved carbon dioxide are smoothed off. Thus, only the long-term climatic variations should be recorded by the isotopic composition of calcium carbonate and of water inclusions trapped in speleothems, the dating of which is usually carried out by the uranium series disequilibrium method.

Another material suited for palaeoclimatic investigations is the plant organic matter, the oxygen and hydrogen isotopic composition of which is connected — through a rather complex chain of processes and chemical reactions — to that of soil water and precipitation. This material, however, should be used with caution because it may also reflect the variations of conditions in the restricted environment where the plant is growing.

The atmosphere and global circulation models

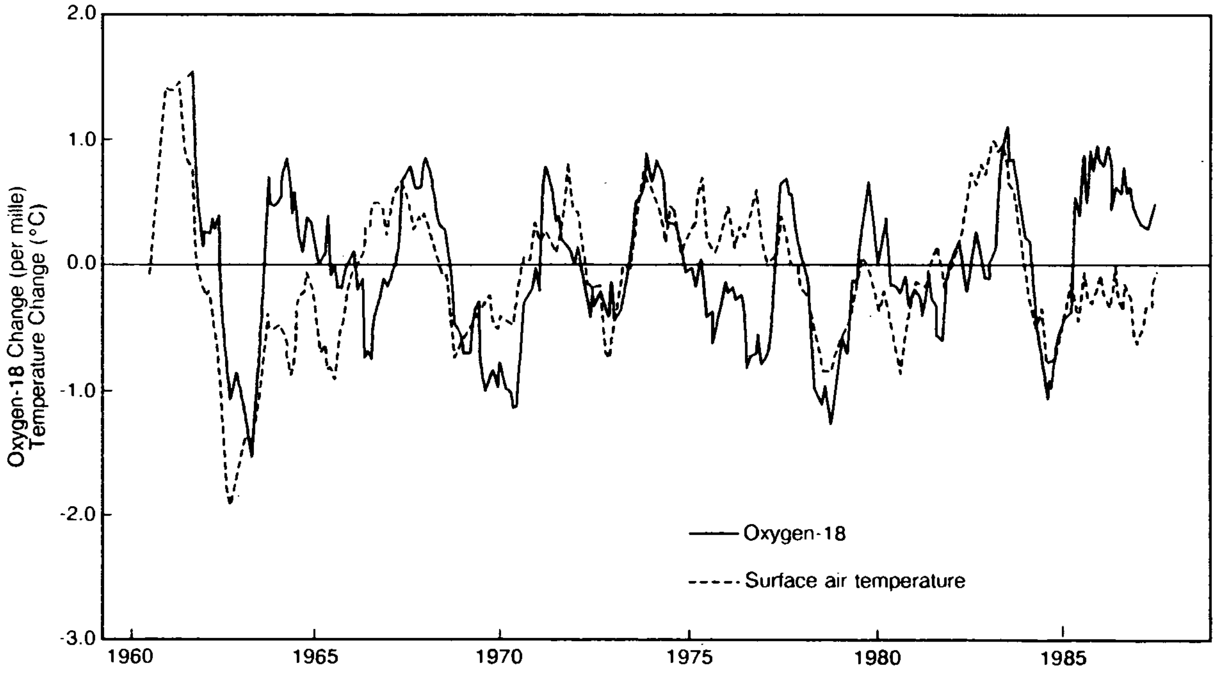
Systematic determinations of the isotopic composition of meteoric waters (precipitation, atmospheric vapour) help in understanding the links between precipitation and the main factors governing meteorological conditions and climate. In this field, a crucial role has been played by the global network of stations jointly operated by the IAEA and World Meteorological Organization (WMO) since the beginning of the 1960s, where monthly precipitation samples are collected for tritium, deuterium, and oxygen-18 content determinations. The majority of samples are analysed in the Isotope Hydrology Laboratory at IAEA headquarters in Vienna, and the remaining samples in several co-operating laboratories. Incidentally, in recent years the number of stations for which isotope composition analyses of precipitation are performed has increased, because national networks have been set up in several Member States.

This unique isotope database, accumulated during 30 years of observations and still growing, provides the basis for the understanding of isotope variations in precipitation, both in terms of local geographic and meteorological features, and global atmospheric circulation. The stable isotope variations are a consequence of the isotope effects accompanying each step of the water cycle. As already mentioned, temperature is the most influencing parameter. *(See Figure 2.)*

Stable isotope patterns in precipitation are particularly useful in the elaboration of global circulation models. These models simulate the behaviour of the whole atmospheric system, including its interaction with the ocean, and can be used to predict the response of the system to different types of internal and external forcing, such as the growing concentration of atmospheric greenhouse gases and changes in insolation.

The predictive power of the models depends on the proper calibration of the parameters, and isotopes are of help for this purpose. Transient tracers of anthropogenic origin such as the bomb-produced tritium in precipitation, radiocarbon in atmospheric carbon dioxide and methane, and krypton-85 released into the atmosphere by nuclear fuel reprocessing plants, are used to understand the dynamics of the ocean–atmosphere system, i.e. the general features of atmospheric and oceanic circulation and their interaction. Tritium and stable isotopes are applied to investigate the water vapour transport between hemispheres and on the continents, to evaluate the fraction recycled by evapotranspiration, and to study

Figure 2. Long-term fluctuations of isotopic composition of precipitation and surface air temperature.



The graph shows the changes in surface air temperature and oxygen-18 isotope composition of monthly precipitation for eight European stations of the IAEA/WMO monitoring network over the period 1960–87. The composite curves represent 12-month running means, eliminating seasonal fluctuations. The reference level was arbitrarily set as the 1960–87 mean value for the Vienna station.

the interaction between troposphere and stratosphere. Radiocarbon and carbon-13 help to evaluate the contribution of various sources (biogenic versus fossil) to the increase of carbon dioxide and methane in the atmosphere and to investigate their residence times, removal by sinks, and interchange with the ocean.

International research

The enormous quantity of isotopic data of various types accumulated so far, has shown that environmental isotopes are a powerful tool to investigate climate. In particular for the past climate, they may provide information which otherwise would not be accessible. Climatological investigations making use of isotope techniques are being conducted in many laboratories in the world, and in many cases the ultimate aim is the thorough understanding and the detailed prediction of the announced climatic changes, which should already become evident during the next century.

To date, the Agency's major activity related to meteorology and climate has been constituted by the IAEA/WMO network for isotopes in precipitation, which was originally initiated for hydrological applications of environmental isotopes. In addition, the Agency, through its Isotope Hydrology Section, has been active in the field of palaeohydrology, because this is directly connected with the appraisal of water resources in arid countries, which often consist of palaeowaters, i.e. groundwater recharged under past, more favourable climatic conditions.*

Also an Advisory Group Meeting on the application of isotope techniques to palaeoclimatic investigations related to water resources was convened 10 years ago, and the proceedings were published by the IAEA under the title *Palaeoclimates and Palaeowaters: A Collection of Environmental Isotope Studies.* (STI/PUB/621)

In the near future, the IAEA's Division of Physical and Chemical Sciences is planning to organize two co-ordinated research programmes (CRPs) related to climate studies. The first, devoted to isotope variations of carbon dioxide and other trace gases in the atmosphere, has the objective of gaining deeper understanding on the role of greenhouse and other trace gases in the global ecosystem. It involves investigating their dynamics and improving the current knowledge on their rates of release and removal by natural and anthropogenic processes. This CRP is expected to start in 1991, after a preparatory consultants' meeting in December 1990.

The second CRP, scheduled to start in 1992, will focus on palaeoclimatic reconstructions for continental areas using isotope indicators. Also in this case, a preparatory consultants' meeting will be convened towards the end of 1991.

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* See "Investigating the water resources of the desert: how isotopes can help", *IAEA Bulletin*, Vol. 23, No.1 (1981).

Nuclear techniques for investigating migration of pollutants in groundwater

A report on some practical applications for preventing pollution of water resources

by V.T. Dubinchuk, A. Plata-Bedmar, and K. Froehlich

Protecting groundwater resources from pollution has been a high-priority topic in recent years.

Usually purer and cleaner than surface water, groundwater is naturally protected by an excellent filtering system. The system includes soil, clays, and rock particles that remove some soluble species, suspended particles, bacteria, and, to a large extent, viruses.

If such a filtering system is overloaded or bypassed, however, the aquifer itself may become polluted. The same type of pollutants that affect surface water — including domestic and industrial waste, seepage from septic tanks, mine drainage, sanitary landfills, and agricultural chemicals — may have a greater impact and more prolonged effect on groundwater. Pollution in aquifers is retained for hundreds to tens of thousands of years, thus jeopardizing water supplies for future generations.

Aquifers in some areas are less exposed to contamination than in others because geological and hydrochemical conditions limit the risk. The sensitivity of groundwater quality to anthropogenic activities causing pollution is termed "aquifer vulnerability to pollution." A variety of processes, and soil and aquifer properties, affect aquifer vulnerability. The determination of the parameters characterizing these processes is essential for modelling and predicting the migration of pollutants in groundwater systems. Major objectives are to prevent pollution and degradation of groundwater resources, or, if contamination has already occurred, to identify its origin so that remedies can be proposed.

At the IAEA, emphasis has been placed on practical applications of nuclear and isotope techniques that are directly or indirectly related to the solution of groundwater pollution problems. This article reports on how some of these techniques have been used in practice.

Migration of pollutants

An unsaturated (aeration) zone is a thin "skin" of geological bodies through which pollutants start their way from the earth's surface to shallow groundwater aquifers. Special instruments are required to study how fast the groundwater and pollutants move through the soil. A number of investigations have been, or are being, done using such instruments and isotope tracers within some national and international programmes, including those sponsored by the IAEA.

In the Crimean region, for example, investigations were performed in 1985–86 to study salinization of groundwater. In the Chernobyl area, investigations are directed at the migration of radionuclides released as a result of the nuclear power plant accident in 1986.*

In both cases, a number of sites for complex isotope tracer investigations were constructed. At these sites, water containing tritium was injected into the ground to study its redistribution over space and time in the soil. This was done in order to measure the velocity of the groundwater's movement in the unsaturated zone, and to evaluate the residence time (or age) of the groundwater and its recharge rate to shallow aquifers. Simultaneously at the same sites, pollutants labelled with isotopes were injected and their movements were observed.

In the Crimea, results obtained near Djankoy show that salt is transported upwards. This is due to high evapotranspiration and the low depth of the water

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* Both of these studies were performed at the All Union Scientific Research Institute of Hydrogeology and Engineering Geology in Moscow by the researchers V.T. Dubinchuk, Yu. A. Tsapenko, A.V. Borodin, and A.V. Gladkov.