

INTRODUCTION

The discovery of hydrogen and oxygen stable isotope natural variations during the thirties, and of tritium, the radioactive hydrogen isotope, in the late forties, together with the establishment of adequate techniques for the routine measurements of these isotopes, led to the birth of a new field of scientific investigation of natural water systems, which later was called isotope hydrology. Environmental hydrogen and oxygen isotopes appeared almost ideal tracers of water, because they are incorporated in the water molecules and therefore their behaviour and variations reflect the origin of, and the hydrological and geochemical processes underwent by, natural water bodies.

However, it was clear from the beginning that the use of isotopic tools in hydrology and hydrogeology required the detailed knowledge of the spacial and temporal variations of stable isotope and tritium concentration in precipitation, which is the main source of recharge of hydrological systems. In addition, monitoring the tritium content of precipitation was important for environmental reasons, because large amounts of tritium were produced and injected in the natural water cycle by the atmospheric thermonuclear tests carried out in the decade 1952-1962 by USA, USSR and UK, and later from 1967 to 1980 by China and France.

The global monitoring of the isotopic composition of precipitation was initiated by the International Atomic Energy Agency in Vienna in co-operation with the World Meteorological Organization in Geneva, through the establishment in the late fifties of a network of more than 100 stations for the collection of monthly precipitation samples for stable isotope and tritium measurement. This network, partly re-organized and extended with the inclusion of several national networks, is still in operation. The results are published at regular intervals. IAEA is also publishing the statistical evaluation of these data, the updated version of which appeared in 1992.

The isotopic composition of global precipitation has been discussed in several papers, among which one must mention Dansgaard (1964), Craig and Gordon (1965), Schell *et al.* (1974), Merlivat and Jouzel (1979), Jouzel (1986), Rozanski *et al.* (1991, 1993). Thus, the objective of this paper will be limited to summarize some of the scientific achievements reached through the data generated by the IAEA-WMO network on isotopes in precipitation, and to discuss some aspects which appear of particular interest to the author.

TRITIUM IN PRECIPITATION

Natural and thermonuclear tritium in the atmosphere

In 1953, when the tritium concentration of precipitation sharply increased as a consequence of the first atmospheric thermonuclear tests performed in

balance of lakes (Gat, 1970; Gonfiantini *et al.*, 1979; Lipps *et al.*, 1992). The exchange with ice is less efficient because of the lack of mixing in the solid phase and re-evaporation of tritiated vapour condensed on surface (Moser and Stichler, 1980).

The rate of tritium removal from the stratosphere can be derived from the tritium concentration in precipitation in the period 1963-67. In these years the thermonuclear tritium stored in the stratosphere is by far the largest but finite tritium source, and the natural tritium is negligible. Therefore, according to the simple model for the tritium removal from the stratosphere

$$\frac{dT_s}{dt} = -kT_s,$$

where T_s is the stratospheric tritium (normalized for decay) and k the removal rate constant, the tritium concentration in precipitation must decrease exponentially vs. time. This is in fact observed, as shown in Fig. 1 and 2 for selected continental and marine stations. In marine stations, the tritium concen-

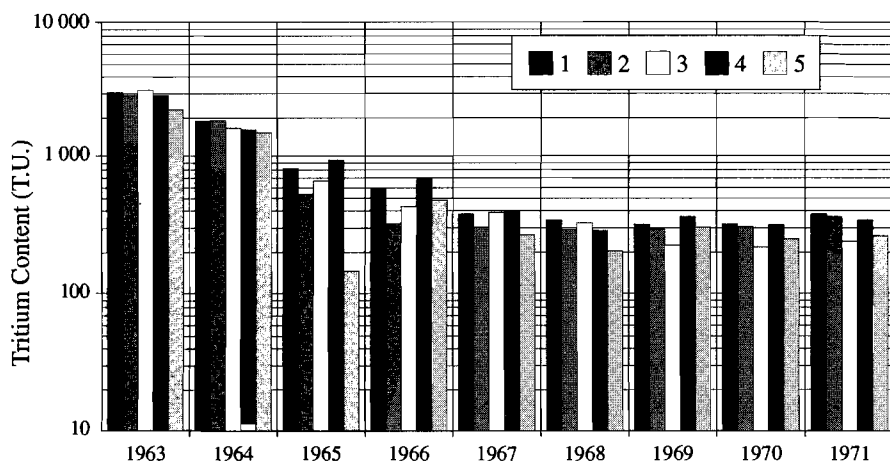


FIGURE 2.

Mean tritium concentration of precipitation in European, Asian and North American continental stations in the years 1963-1971. The values are normalized to 1963. The stations are: 1, Vienna, Austria, 48°15'N 16°22'E; 2, Thonon-les-Bains, France, 46°13'N 6°17'E; 3, Teheran, Iran, 35°41'N 51°19'E; 4, Ottawa, Ontario, Canada, 45°19'N 75°40'W; 5, Chicago, Illinois, USA, 41°47'N 87°45'W.

Concentration moyenne en tritium des précipitations sur des stations continentales d'Europe, d'Asie et d'Amérique pour la période 1963-1971. Les valeurs sont normalisées à 1963. Les stations sont : 1, Vienne, Autriche, 48°15'N 16°22'E; 2, Thonon-les-Bains, France, 46°13'N 6°17'E; 3, Teheran, Iran, 35°41'N 51°19'E; 4, Ottawa, Ontario, Canada, 45°19'N 75°40'O; 5, Chicago, Illinois, USA, 41°47'N 87°45'O.

- (i) the relative humidity and the temperature during the evaporation from the ocean, which is the main source of atmospheric vapour;
- (ii) the temperature and the degree of condensation of atmospheric vapour;
- (iii) the fraction and the nature of condensed phases (liquid water, ice) in clouds;
- (iv) the contribution of re-evaporated fresh water;
- (v) the evaporation during raindrop fall.

Broadly speaking, the main driving parameter is temperature, with which the isotopic composition of precipitation is almost always correlated. Even the modern increase of world mean temperature is reflected by the isotopic composition of precipitation (Rozanski *et al.*, 1992).

Correlation between deuterium and oxygen-18

The condensation of atmospheric vapour to form clouds and precipitation produces parallel and proportional variations of the $^2\text{H}/^1\text{H}$ and $^{18}\text{O}/^{16}\text{O}$ ratios in both the condensed phase and the residual vapour. As a consequence, $\delta^2\text{H}$ and $\delta^{18}\text{O}$ of precipitation are linearly correlated. In particular it has been found that, on a global scale, the equation which best fits the correlation between $\delta^2\text{H}$ and $\delta^{18}\text{O}$, expressed as difference in parts per mille versus the mean isotopic composition of the ocean water, i.e. the primary vapour source, is (Craig, 1961):

$$\delta^2\text{H} = 8 \delta^{18}\text{O} + 10 \quad (1)$$

Equation (1) represents the so-called World Meteoric Water Line (WMWL). Deviations from the behaviour predicted by equation (1), observed in certain regions and circumstances, can be expressed in terms of deuterium excess d , a parameter defined as:

$$d = \delta^2\text{H} - 8 \delta^{18}\text{O} \quad (2)$$

The deuterium excess can be significantly different from the value of 10 ‰ of equation (1).

The slope 8 of equation (1) is the overall result of the complex condensation process of atmospheric vapour to form liquid and ice. The Rayleigh condensation model, which is commonly adopted to describe the isotopic composition of precipitation, although it does not foresee the co-existence of vapour and condensed water phases as in clouds, gives on the whole a sound explanation of the relationship between isotopic composition and temperature. With this simple model it can be shown that the liquid water formed by atmospheric vapour condensation exhibits a correlation between $\delta^2\text{H}$ and $\delta^{18}\text{O}$ with a slope close to 8 if the condensation process takes place at the isotopic

equilibrium between phases. The same relationship, however, does not hold when the model is applied to ice condensation, for which the computed slope is lower than 8.

A more complex model developed by Jouzel *et al.* (1980), takes into account that liquid water and/or ice co-exist together with water vapour in clouds. Deviations from equilibrium of the ice isotopic composition are observed during ice crystal accretion, which are due to vapour diffusion in supersaturated air, and determine a decrease of the apparent isotopic fractionation factors. With this model, the slope of the $\delta^2\text{H} - \delta^{18}\text{O}$ correlation in ice approaches the value of 8.

Seasonal variations of the deuterium excess

As already said, the deuterium excess is a way of expressing the deviations of the isotopic composition of water samples from the behaviour predicted by equation (1). The fact that the WMWL does not pass through the point (0,0) representing the mean isotopic composition of the ocean water, is mainly due to the additional diffusion fractionation during vapour transport in air, which sum up with the equilibrium isotopic fractionation at the liquid-vapour interface, according to the Craig and Gordon (1965) model.

The deuterium excess d increases with increasing moisture deficit $(1 - h)$ of the oceanic air masses, h being the air relative humidity normalized at the ocean surface temperature. The intercept value of 10‰ of the World Meteoric Water Line corresponds to an average relative humidity value of 81 % (Jouzel, 1986).

Let consider now the $\delta^2\text{H} - \delta^{18}\text{O}$ relationship in the temperate regions (latitude above 30°) in January, using the mean monthly values published by IAEA (1992) for each station of the IAEA-WMO network (Fig. 5). The equation of the reduced major axis line (Till, 1974) is:

$$\delta^2\text{H} = (8.05 \pm 0.09) \delta^{18}\text{O} + (11.6 \pm 4.5) \quad (3)$$

The same regression for July gives:

$$\delta^2\text{H} = (8.33 \pm 0.13) \delta^{18}\text{O} + (8.2 \pm 3.9) \quad (4)$$

The slightly lower slope in January is mainly due to the very negative δ -values of polar samples: this is in agreement with computations showing that, when the heavy isotope concentration becomes too low, i.e. in the final condensation stages of atmospheric vapour, the slope tends to decrease. Therefore, excluding five high latitude stations with $\delta^{18}\text{O}$ more negative than -25 ‰ in order to have similar $\delta^2\text{H}$ and $\delta^{18}\text{O}$ ranges for January and July, the correlation for January becomes:

$$\delta^2\text{H} = (8.36 \pm 0.13) \delta^{18}\text{O} + (14.2 \pm 4.2) \quad (5)$$

i.e. with a slope practically identical to that of July but a higher intercept.

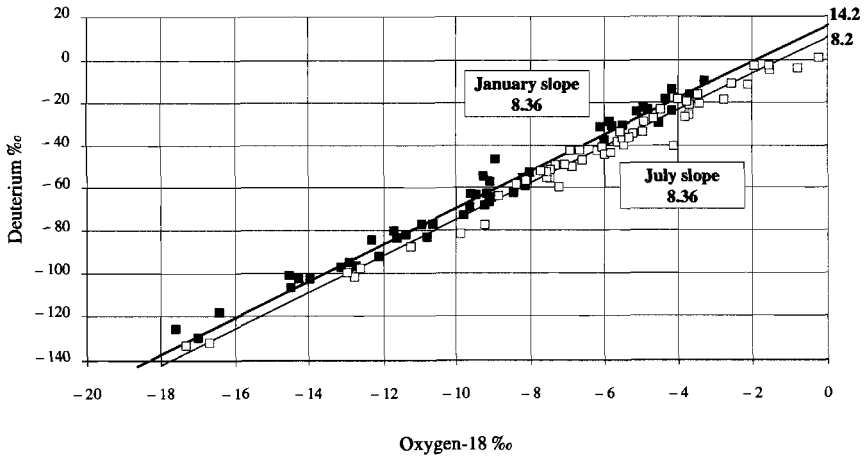


FIGURE 5.

Mean isotopic composition of precipitation in January (July for southern hemisphere) and July (January for southern hemisphere) in stations at latitudes higher than 30° . Five high latitude stations with $\delta^{18}\text{O}$ more negative than -25‰ have been excluded from January correlation.

Composition isotopique moyenne des précipitation de janvier (juillet pour l'hémisphère sud) et de juillet (janvier pour l'hémisphère sud) aux stations de latitude supérieure à 30° . Cinq stations de haute latitude dont les valeurs de $\delta^{18}\text{O}$ sont inférieures à -25‰ ont été exclues pour la corrélation de janvier.

The difference between the intercepts is probably significant, and reflects a different mean deuterium excess, which in fact in January is $10.7 \pm 0.6\text{‰}$, while in July it is $5.8 \pm 0.5\text{‰}$ only. This indicates also that the mean relative humidity of air masses at the departure from the ocean contact, is on the average about 10 % lower in winter than in summer, as it can be deduced from Merlivat and Jouzel model (1979). A possible explanation is that in winter the air is cooler than the ocean surface, and the warming of air masses when they come into contact with the ocean promotes their uplift. This reduces the contact time between the ocean and the air masses, whose moisture content remains relatively low. The contrary occurs in summer.

The effect of the air-ocean temperature difference on the deuterium excess is illustrated in Fig. 6 for North Atlantic stations under the Gulf Stream influence.

The deuterium excess seasonal shift from higher values in winter to lower values in summer, explains why:

- (i) in correlating $\delta^2\text{H}-\delta^{18}\text{O}$ values at any given station, the slope is often significantly lower than 8. This effect has been attributed to evapora-

Amount effect in tropical oceanic stations

For 54 tropical stations (latitude less than 30°) the $\delta^2\text{H} - \delta^{18}\text{O}$ reduced major axis regression has been established using the data of the most rainy month when evaporation during raindrop fall is assumed to be minimal. Four stations, where the mean yearly precipitation is less than 300 mm, have not been included in the correlation because they were suspected of evaporation effects. The regression equation is:

$$\delta^2\text{H} = (7.84 \pm 0.22) \delta^{18}\text{O} + (10.0 \pm 3.6) \quad (7)$$

No correlation exists between isotopic composition of the most rainy month and precipitation amount at each station. If however only oceanic stations are considered, the correlation of Fig. 7 appears. A similar effect was already reported by Rozanski *et al.* (1993).

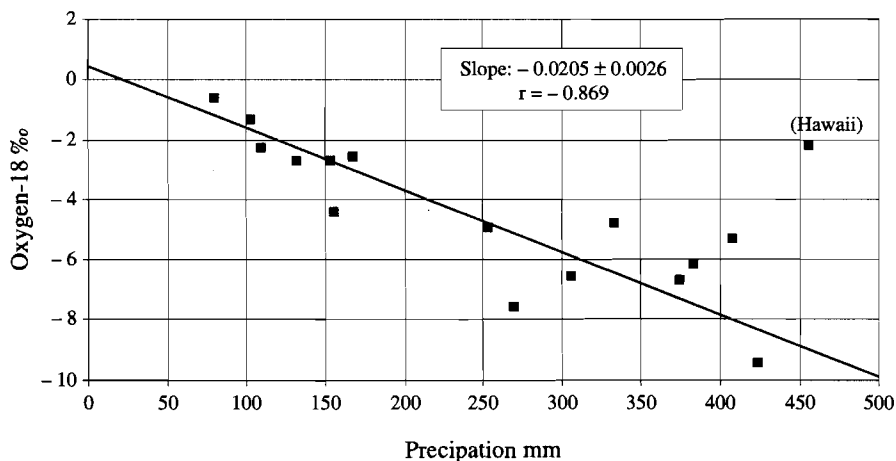


FIGURE 7.

Amount effect at oceanic tropical stations. Hawaii has been excluded from the regression.

Effet de masse pour les stations océaniques tropicales. Hawaii n'est pas pris en compte dans la régression.

Altitude effect on Mount Cameroun

The change of isotopic composition of precipitation with altitude, although of quite general occurrence, is particularly evident in zones where the presence of a high, isolated mountain with a prevailing direction of the air mass advection, determines the air mass rise along the slope with consequent adiabatic cooling and vapour condensation. Among the known examples of isotopic altitude effect, that of Mount Cameroun is probably the cleanest and finest

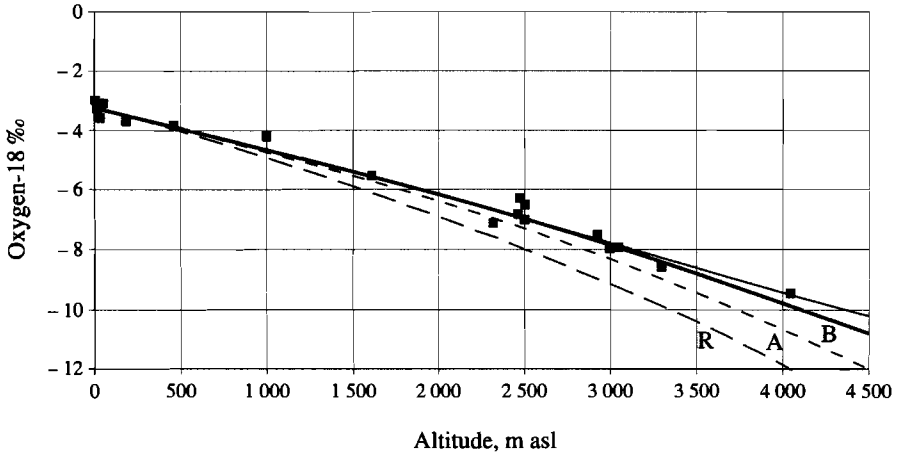


FIGURE 8.

Oxygen isotopic composition of precipitation on Mount Cameroun, Central Africa, as a function of altitude. The values are the average of measurements on yearly precipitation samples collected at 20 stations on the slope of Mount Cameroun in four different years (1972, 1973, 1974, and 1975). There is no apparent difference between windward and leeward stations. The regression line (LC) has the equation

$$\delta^{18}\text{O} = -(0.00155 \pm 0.00005) Z - (3.16 \pm 0.11)$$

Other lines represent: R, the Rayleigh condensation model with $L/V = 0$, where L/V is the cloud liquid/vapour ratio; A, model with $L/V = 0.15$, constant; B, model with L/V linearly increasing with elevation from 0.15 to 0.45. The model temperatures have been converted into altitude by using the gradient of $0.53^\circ\text{C}/100\text{ m}$ and taking $T = 16^\circ\text{C}$ for $Z = 0\text{ m}$ asl.

Composition isotopique en oxygène des précipitations sur le Mont Cameroun, Afrique centrale, en fonction de l'altitude. Les valeurs portées sont les moyennes des mesures d'échantillons de précipitations annuelles collectées en 20 stations sur les pentes du Mont Cameroun au cours de quatre années (1972, 1973, 1974 et 1975). On n'observe pas de différence apparente entre les stations au vent et les stations sous le vent. La droite de régression (LC) a l'équation suivante:

$$\delta^{18}\text{O} = -(0,00155 \pm 0,00005) Z - (3,16 \pm 0,11)$$

Les autres courbes représentent: R, modèle de condensation de Rayleigh avec $L/V = 0$, où L/V est le rapport liquide/vapeur dans les nuages; A, modèle avec $L/V = 0,15$, constant; B, modèle avec L/V croissant linéairement avec l'altitude de 0,15 à 0,45. Les températures utilisées dans le modèle ont été converties en altitude en considérant un gradient de $0.53^\circ\text{C}/100\text{ m}$, et $T = 16^\circ\text{C}$ pour $Z = 0\text{ m}$ (niveau de la mer).

