

On the isotopic composition of precipitation

Sur la composition isotopique des précipitations

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ABSTRACT – The paper discusses some aspects of the isotopic composition (tritium and stable isotopes) of global precipitation which is being monitored since the late fifties through the network established by the International Atomic Energy Agency.

Three quarters of the tritium formed during the atmospheric thermonuclear tests were released in the biennium 1961-1962. The successive five years of test moratorium provide a unique information on the tritium transfer rate from the stratosphere to the troposphere. The tritium concentration decreased steadily, and the decrease rate appears to be greater at high latitude. This fact can possibly be explained by precipitation recycling by evapotranspiration, which is more important at low latitudes, and tritium injections by jet streams. In the northern hemisphere, the mean tritium concentration ratio between two successive years, is close to 0.68 ± 0.02 , with the exception of the year 1965, when the tritium content dropped to 0.50 ± 0.02 with respect to the previous year.

At latitudes between 30 and 60°, the correlations between $\delta^2\text{H}$ and $\delta^{18}\text{O}$ show almost identical slopes in winter and summer precipitation, but different intercepts. The correlations are: $\delta^2\text{H} = (8.36 \pm 0.13)\delta^{18}\text{O} + (14.2 \pm 4.2)$ for January and $\delta^2\text{H} = (8.33 \pm 0.13)\delta^{18}\text{O} + (8.2 \pm 3.9)$ for July. This reflects a different seasonal deuterium excess (defined as $d = \delta^2\text{H} - 8\delta^{18}\text{O}$), which has a mean value of $10.7 \pm 0.6\text{‰}$ in January and $5.8 \pm 0.5\text{‰}$ in July, and a higher average value in stations with prevailing winter rains. Also, the slope becomes about 8 when summer and winter precipitation are considered all together.

The altitude effect on the isotopic composition of precipitation on Mount Cameroun is re-examined. The model which best fits the data is based on the adiabatic condensation of the atmospheric vapour with a liquid/vapour ratio increasing from 0.15 at sea level to 0.45 at 4,000 m asl.

Keywords: tritium, deuterium, 18-oxygen, deuterium-excess.

RÉSUMÉ – On discute certains aspects de la composition isotopique (tritium et isotopes stables) des précipitations mondiales, échantillonnées depuis la fin des années cinquante par le réseau établi par l'Agence internationale de l'énergie atomique de Vienne.

Les trois quarts du tritium formé lors des essais thermonucléaires effectués dans l'atmosphère ont été relâchés en 1961 et 1962. Les cinq années qui ont suivi correspondent à une période de suspension des essais nucléaires. On assiste alors à une diminution progressive et continue de la teneur en tritium des précipitations, qui permet d'étudier la vélocité de transfert du tritium de la stratosphère à la troposphère. La concentration en tritium diminue plus rapidement aux hautes latitudes. Le recyclage des pluies par évapotranspiration, plus intense aux basses latitudes, ainsi que l'injection de tritium stratosphérique par les courants-jet, peuvent expliquer cette différence latitudinale. Dans l'hémisphère nord, le rapport moyen de la concentration en tritium des précipitations entre deux années successives est proche de $0,68 \pm 0,02$, à l'exception de l'année 1965, pour laquelle la teneur en tritium a chuté de 50 % par rapport à celle de l'année précédente.

Entre 30 et 60 °N et 30 et 60 °S de latitude, les droites de corrélation entre $\delta^2\text{H}$ et $\delta^{18}\text{O}$ des précipitations d'hiver et des précipitations d'été ont des pentes très voisines, mais des interceptions à zéro différentes. La corrélation est : $\delta^2\text{H} = (8,36 \pm 0,13)\delta^{18}\text{O} + (14,2 \pm 4,2)$ en janvier, et $\delta^2\text{H} = (8,33 \pm 0,13)\delta^{18}\text{O} + (8,2 \pm 3,9)$ en juillet. L'excès en deutérium (défini comme $d = \delta^2\text{H} - 8\delta^{18}\text{O}$) diffère donc selon les saisons, avec une valeur moyenne de $10,7 \pm 0,6\%$ en janvier et de $5,8 \pm 0,5\%$ en juillet. Par conséquent, sa valeur moyenne annuelle est plus élevée dans les stations où les pluies hivernales sont dominantes. La pente approche la valeur de 8 lorsque la corrélation est établie pour l'ensemble des précipitations d'hiver et d'été.

L'effet d'altitude sur la composition isotopique des précipitations sur le mont Cameroun est réexaminé. Le modèle montrant le meilleur accord avec les données est celui d'une condensation adiabatique des masses de vapeur atmosphérique, avec un rapport liquide/vapeur qui augmente d'une valeur de 0,15 à 0,45 entre le niveau de la mer et 4 000 m d'altitude.

Mots clés : tritium, deutérium, oxygène-18, excès en deutérium.

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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

1952 by the USA in the atolls of Eniwetok and Bikini, only very few laboratories were ready to carry out tritium determinations in natural waters with the required accuracy. Thus, the only existing complete record of tritium in precipitation for the years 1953-57 is that of Ottawa, Canada (Brown, 1961). Other stations which started early to operate on a continuous basis, were Valentia, Ireland, from 1957, and Pretoria, South Africa, from 1958. Vienna, Austria, started in 1961.

The last large atmospheric thermonuclear tests were carried out in December 1962. From January 1st, 1963, the Limited Test Ban Treaty among the thermonuclear countries (UK, USSR and USA) came into force, by which it was agreed to ban explosions of nuclear devices of any type in the atmosphere, hydrosphere and all the sites from where released radioactive debris could migrate outside of the territorial limits of the country performing the test.

The tests carried out in the 1961-62 only, produced all together about 240 Mt of fusion energy (Carter and Moghissi, 1977), and an estimated release of 1.8×10^8 TBq of tritium (readily oxidized to water) with a yield of about 7.4×10^5 TBq·Mt⁻¹ (Miskel, 1973 ; UNSCEAR, 1982 and 1993). Three quarters of tritium were released in the northern polar atmosphere, and one quarter in the tropics; three quarters were injected and stored in the stratosphere, and one quarter remained in the troposphere from where it was readily washed out by precipitation and exchange with the ocean. The thermonuclear tritium released was two orders of magnitude higher than that naturally produced in the same biennium by the cosmic radiation, estimated to about 1.4×10^6 TBq (production rate 0.25 atoms·cm⁻²·s⁻¹; Peters, 1961, and Lal and Suess, 1968). In comparison the tritium produced by fission bombs, with a yield per Mt four orders of magnitude lower than that of fusion devices, is negligible. Also the thermonuclear ¹⁴C released in the 1961-62 biennium was high, about 1.6×10^5 Bq, versus a natural production of 3.1×10^3 TBq and a tropospheric inventory in air CO₂ of 1.7×10^5 TBq.

In spring 1963 the tritium concentration in precipitation reached a maximum value in the northern hemisphere - up to three orders of magnitude higher than the natural level in the most northern stations - and then it started to decrease with an approximately constant rate till 1967. Thus, the years 1963-67 were crucial for the understanding of the atmospheric tritium cycle. In 1967 the atmospheric thermonuclear explosions were resumed by China and, one year later, by France. China continued the experiments till 1980. Nevertheless, the fusion energy yield of Chinese and French explosions was limited, and the tritium produced was less than 5 % of that released in the biennium 1961-62. It was therefore capable to determine fluctuations of the tritium content of precipitation, but not to reverse the general decreasing trend. An estimate of tritium released in the atmosphere by thermonuclear tests is given in Table 1.

TABLE 1.

Tritium released in the atmosphere by thermonuclear tests

Test sites: USA: Eniwetok and Bikini, Marschall Islands, Pacific Ocean (11°30' N, 162-165 E); USSR: Novaya Zemlia, Barents Sea (75°N, 55°E); UK: Christmas Island, Pacific Ocean (2°N, 157°W); China: Lop Nor, Xin Jiang Desert (40°N, 90°E); France: Fangataufa and Mururoa, Tuamotu Archipelago, Pacific Ocean (16-22° S, 140°W).

Tritium relâché dans l'atmosphère par les essais thermonucléaires

Sites des essais : Eniwetok et Bikini, îles Marschall, océan Pacifique (11°30' N, 162-165 E); USSR: Novaya Zemlia, mer de Barents (75° N, 55° E); UK: île Christmas, océan Pacifique (2° N, 157° O); Chine : Lop Nor, désert de Xin Jiang (40°N, 90°E); France : Fangataufa et Mururoa, archipel de Tuamotu, océan Pacifique (16-22° S, 140° W).

Year <i>Année</i>	Country <i>Pays</i>	Fusion energy <i>Energie de fusion</i> Mt	Tritium released <i>Tritium relâché</i> TBq × 106
1952	USA	6.0	4.4
1953	USSR	?	?
1954	USA	17.5	13
1955	USSR	1.5	1.1
1956	USA, USSR	15.3	11.3
1957	UK, USSR	10.0	7.4
1958	UK, USA, USSR	31.1	23
1961	USSR	96.9	72
1962	USA, USSR	140.8	104
Limited Test Ban Treaty (UK, USA, USSR)			
1967	China	1.3	1
1968	China, France	2.6	1.9
1969	China	1.0	0.7
1970	China, France	1.2	0.9
1973	China	0.9	0.7
1974	China	0.15	0.1
1976	China	1.75	1.3
1980	China	0.15	0.1
1995	Thermonuclear tritium still present in the hydrosphere		36

Conversion factor: $7.4 \times 105 \text{ Tbq} \cdot \text{Mt}^{-1}$.

Removal of tritium from the atmosphere

From the stratospheric reservoir, thermonuclear tritium is injected into the troposphere through jet streams and, in spring and early summer, by the rise of the tropopause in polar regions (Eriksson, 1967, 1984), which determines the incorporation of part of the stratosphere in the troposphere. The latter mechanism, together with the fact that the most powerful explosions were carried out by the USSR at 75°N latitude, explains why spring precipitations at high northern latitudes have the highest tritium concentration. This is in principle valid also for natural tritium, two thirds of which are formed in the stratosphere through the reaction $^{14}\text{N}(n, ^3\text{H})^{12}\text{C}$, mainly at high and mid geomagnetic latitudes, where the cosmic radiation is preferentially conveyed by the Earth magnetic field (Begemann, 1961).

As already said, tritium is rapidly removed from the troposphere by precipitation and by molecular exchange of atmospheric water vapour with water and ice surfaces. The exchange with water removes a tritium amount comparable with that deposited by precipitation, as it has been shown from tritium

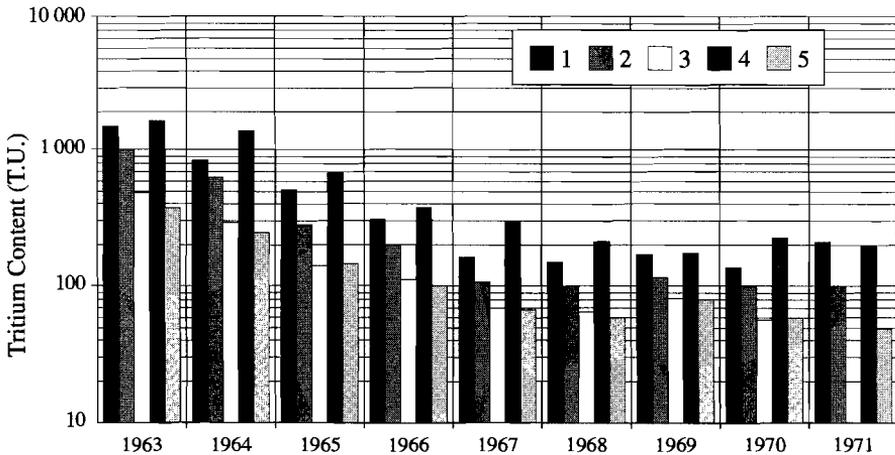


FIGURE 1.

Mean tritium concentration of precipitation in North Atlantic marine stations in the years 1963-1971. The values are normalized (corrected for decay) to 1963. The stations are: 1, Lista, Norway, 58°6'N 6°34'E; 2, Valentia, Ireland, 51°56'N 10°15'W; 3, Ponta Delgada, Portugal, 37°46'N 25°39'W; 4, Boston, Massachusetts, USA, 42°22'N 71°2'W; 5, Weathership E, USA, 35°0'N 48°0'W.

Concentration moyenne en tritium des précipitations sur des stations marines de l'Atlantique nord pour la période 1963-1971. Les valeurs sont normalisées à 1963. Les stations sont: 1, Lista, Norvège, 58°6'N 6°34'E; 2, Valentia, Irlande, 51°56'N 10°15'O; 3, Ponta Delgada, Portugal, 37°46'N 25°39'O; 4, Boston, Massachusetts, USA, 42°22'N 71°2'O; 5, Weathership E, USA, 35°0'N 48°0'O.

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-

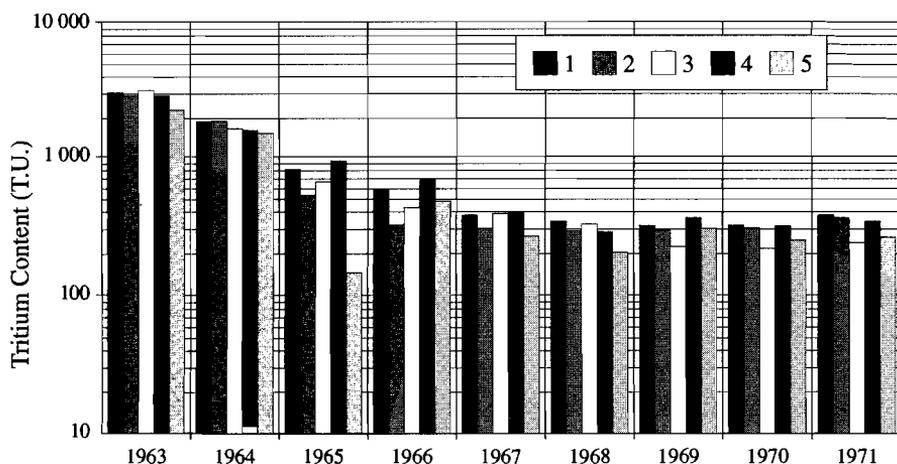


FIGURE 2.

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.

tration of precipitation is lower due to molecular exchange of the atmospheric vapour with the ocean surface and dilution by oceanic vapour, whose tritium concentration is low. This effect can be seen also in Fig. 3, which shows the tritium content of precipitation in the northern hemisphere as a function of latitude, confirming that most of the tritium is injected in the troposphere at high latitudes.

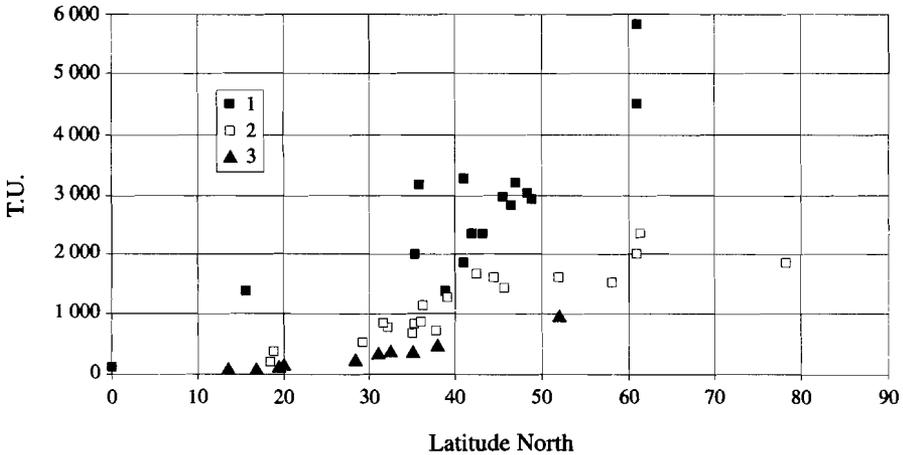


FIGURE 3.

Mean tritium concentration of precipitation in 1964 in the northern hemisphere as a function of latitude. 1, continental stations; 2, coastal stations; 3, island stations.

Concentration moyenne en tritium des précipitations de 1964 sur l'hémisphère nord en fonction de la latitude. 1, stations continentales; 2, stations côtières; 3, stations insulaires.

From 1967 till 1971, the tritium concentration remained almost constant, probably as a consequence of Chinese and French tests.

In the years 1963-67 the tritium concentration in precipitation decreased exponentially versus time with a slope $-k$, where k (dimensions t^{-1}) is the kinetic constant of tritium transfer from the stratosphere to troposphere. It appears that k decreases with latitude, as it is shown in Fig. 4: in other words, the tritium decrease rate is slowing down at lower latitude.

Considering only the five stations at latitude above 60°N , we obtain a mean value of k equal to $0.57 \pm 0.02 \text{ a}^{-1}$. The half time for the tritium transfer from stratosphere by the spring rise of troposphere in polar regions is therefore $1.22 \pm 0.05 \text{ a}$, and the mean residence time of tritium in the polar stratosphere is $1.75 \pm 0.07 \text{ a}$. All these values are depurated for tritium decay, and therefore apply also to water vapour in the stratosphere.

At the Equator, k reaches the value of $0.68 \pm 0.02 \text{ a}^{-1}$, as computed from the regression equation of Fig. 4. Recycling of precipitation by evapo-transpiration and tritium injection by jet streams may contribute to this effect.

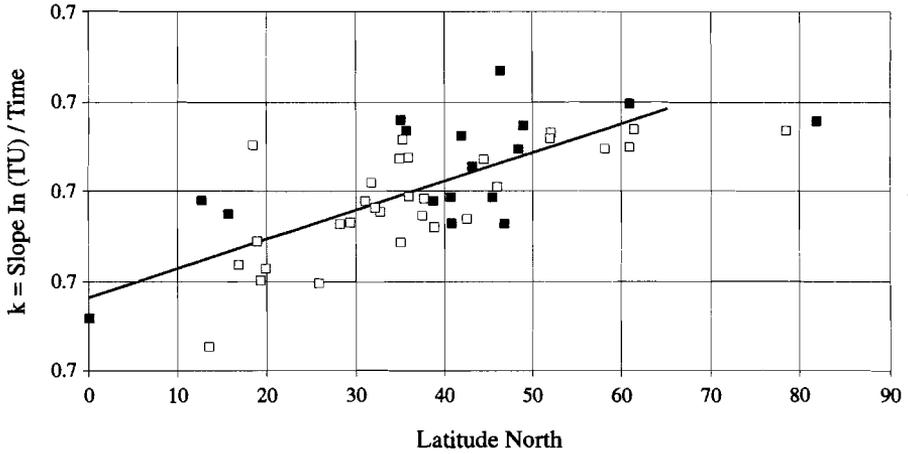


FIGURE 4.

Plot of k (1963-1967) vs. latitude.

The regression is: $k = (0.0032 \pm 0.0005) \text{ Lat. N} + (0.38 \pm 0.02)$ with a correlation coefficient of 0.696 and $n = 45$. The two stations at latitude above 70°N , have been excluded. There is no evidence of systematic difference between continental (filled squares) and marine stations (open squares).

Distribution de k (1963-1967) en fonction de la latitude.

La régression est : $k = (0,0032 \pm 0,0005) \text{ Lat. N} + (0,38 \pm 0,02)$ avec un coefficient de corrélation de 0,696 et $n = 45$. Les deux stations de latitude supérieure à 70° sont exclues. On n'observe pas de différence systématique entre les stations continentales (carrés noirs) et les stations marines (carrés blancs).

If the tritium transfer mechanisms operate at a constant rate, the ratio of tritium concentration between two successive years, in the period 1963-67, must be constant at the same place, if all other conditions are on the average constant. For the stations in the northern hemisphere, the mean values of such ratio are:

Tritium Concentration ratios	Mean Values	n
Tritium concentration in 1964/Tritium concentration in 1963	0.679 ± 0.022	45
Tritium concentration in 1965/Tritium concentration in 1964	0.499 ± 0.017	47
Tritium concentration in 1966/Tritium concentration in 1965	0.692 ± 0.024	47
Tritium concentration in 1967/Tritium concentration in 1966	0.672 ± 0.023	47

It is worth noticing that the 1965/1964 ratio is significantly lower than in other year pairs, and that this decrease occurred almost everywhere in the northern hemisphere. No adequate explanation has been found: if for some reasons the tritium transfer from the stratosphere was in 1964 greater than normal, or in 1965 smaller, this should be reflected also on the ratios 1964/1963 or 1966/1965, which should be higher than normal: this does not seem to happen.

Tritium from nuclear and industrial plants

Tritium is also released in the environment by nuclear plants in airborne and liquid effluents. The latter have no or little impact on tritium concentration of precipitation.

For airborne effluents, UNSCEAR (1993) reports that heavy water reactors, where tritium is formed by deuterium activation, discharged about 10,000 TBq of tritium in 1989, i.e. 970 TBq for GW(e) produced per year. Therefore, heavy water reactors, which produce only 5 % of the world nuclear power and are mainly located in Eastern Canada, are responsible for about 98 % of tritium released by nuclear power reactors in the atmosphere. For comparison, the ^{14}C released in airborne effluents by nuclear reactors in 1989 has been 10 TBq, the half of which by heavy water reactors, and the rest almost equally shared among pressured water reactors, boiling water reactors and gas cooled reactors.

Tritium discharges in the atmosphere by fuel reprocessing plants is estimated from data published by UNSCEAR to a value of $450 \pm 100 \text{ TBq}\cdot\text{a}^{-1}$, most of which by the Sellafield plant in the United Kingdom.

Tritium is used in luminescent dies and other luminous industrial products, the disposal of which is also a source of tritium released in the environment.

Nuclear reactors and industrial releases may determine in certain regions an almost permanent tritium contamination of the atmospheric moisture, which is observed in precipitation. However, these contamination sources are generally located in restricted areas at ground level and their impact can be noticeable but limited in extent. Possibly, investigations carried out on atmospheric water vapour may offer the opportunity of studying the characteristics and effects of these contaminations in some details.

STABLE ISOTOPES IN PRECIPITATION

The stable isotope variations of precipitation depend upon meteorological and climatological factors, and therefore are commonly used in the validation of general circulation models of the atmosphere (see, for instance, Jouzel *et al.*, 1987 and 1991). The main processes and parameters which determine the stable isotope composition of precipitation are related with season, latitude, altitude, distance from the ocean (continentality effect), amount, etc., and are:

- (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.

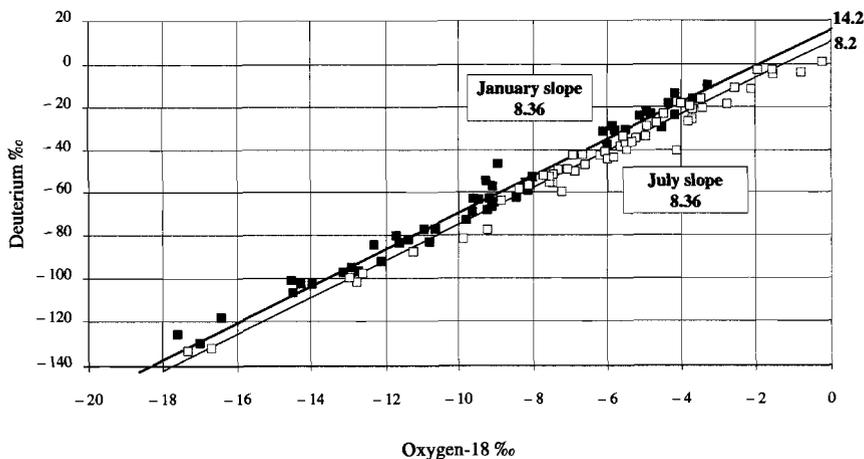


FIGURE 5.

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-

tion during raindrop fall in summer, but another reason may be the different conditions of the vapour formation over the ocean between summer and winter described above;

- (ii) the overall correlation for all $\delta^2\text{H} - \delta^{18}\text{O}$ values has slope close to 8. For example, the regression for January and July values together is:

$$\delta^2\text{H} = (8.36 \pm 0.13) \delta^{18}\text{O} + (14.2 \pm 4.2) \quad (6)$$

However, a slope value of 8.30-8.40 seems to fit better the isotopic data of precipitation when samples from any single season are considered, which have been formed under comparable climatic conditions;

- (iii) in stations with prevailing winter precipitations, the weighted mean deuterium excess is usually higher than in other climatic conditions. Examples are the eastern Mediterranean stations, Ponta Delgada, Azores Islands, ($d = 13.7\text{‰}$), Bahrain, Persian Gulf (14.1‰), Kabul, Afghanistan (17.2‰), Cape Town, South Africa (14.7‰), Perth, Australia (16.2‰).

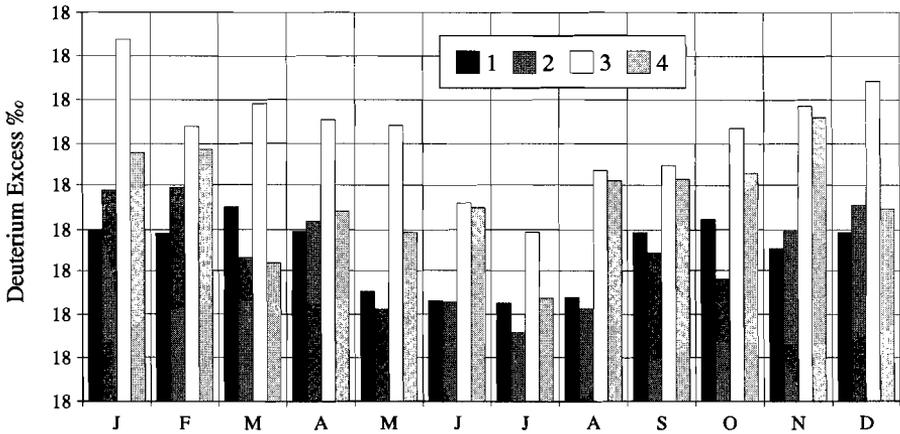


FIGURE 6.

Deuterium excess in North Atlantic stations: 1, Valentia, Ireland, $51^{\circ}56'N$ $10^{\circ}15'W$; 2, Reykjavik, Iceland, $64^{\circ}8'N$ $21^{\circ}56'W$; 3, Ponta Delgada, Portugal, $37^{\circ}46'N$ $25^{\circ}39'W$; 4, Weathership E, USA, $35^{\circ}0'N$ $48^{\circ}0'W$.

Excès en deutérium pour des stations de l'Atlantique nord: 1, Valentia, Irlande, $51^{\circ}56'N$ $10^{\circ}15'O$; 2, Reykjavik, Islande, $64^{\circ}8'N$ $21^{\circ}56'O$; 3, Ponta Delgada, Portugal, $37^{\circ}46'N$ $25^{\circ}39'O$; 4, Weathership E, USA, $35^{\circ}0'N$ $48^{\circ}0'O$.

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).

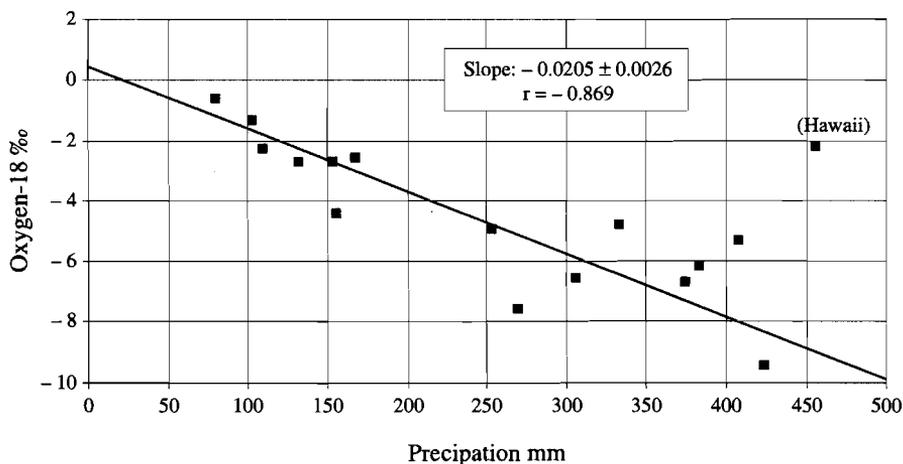


FIGURE 7.

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

ever reported (Fontes and Olivry, 1976; Fontes, 1976; Fontes and Olivry, 1977). Mount Cameroun, at $4^{\circ}13'N$ and $9^{\circ}10'E$, rises sharply up to 4095 m asl on the Atlantic coast of western equatorial Africa. The yearly precipitation $\delta^{18}O$ in four different years in 20 stations along the slope, ranges from about -3 at sea level to about -10‰ at 4050 m asl. The mean isotopic gradient with altitude is $-0.155 \pm 0.005 \delta^{18}O\text{‰}$ per 100 m (Fig. 8). This gradient may appear rather small if compared for instance with that of -0.27 ± 0.03 observed on samples of a single snowfall collected along the slope of Mount Kilimanjaro between 4600 and 5700 m asl (Tongiorgi, 1970). In the second case, however, the temperature was much lower.

Let us assume that the air masses have a temperature of $25^{\circ}C$ and a relative humidity of 80 % when they leave the contact with the ocean, and the $\delta^{18}O$ of the atmospheric moisture is -12‰ . Under adiabatic expansion conditions, the air masses reach saturation and start to condense at about $20^{\circ}C$, and when a temperature of $16^{\circ}C$ is reached, the liquid water formed has a $\delta^{18}O$ of about -3‰ as that of rain at sea level elevation on the foothill of Mount Cameroun. Using the mean temperature gradient of $-0.53 \pm 0.01^{\circ}C/100$ m obtained in vertical profiles by sounding balloons in Douala (Fontes and Olivry, 1977), $16^{\circ}C$ are reached at 1700 m asl, which is assumed to represent the mean altitude of formation of rains falling at 0 m asl. These values of condensation temperature ($16^{\circ}C$), $\delta^{18}O$ (-3‰) and altitude of formation (1700 m asl), are considered typical of the first rains formed from the oceanic air masses along the mountain slope. With the temperature gradient of $-0.53 \pm 0.01^{\circ}C/100$ m, the rains falling at 4000 m have a mean temperature of $-5^{\circ}C$ and a mean altitude of formation of 5700 m asl.

Three models have been adopted to fit the isotopic data, which are illustrated in Fig. 8:

- (i) the Rayleigh model, in which the condensed liquid is removed as soon as it is formed. This model shows large deviations from the measured values at altitudes above 1500 m;
- (ii) a model in which vapour and liquid co-exist in clouds with a constant liquid to vapour ratio equal to 0.15. This model fits better the isotopic values than the previous one, but significant deviations appears at altitudes above 2500 m;
- (iii) a model in which the liquid/vapour ratio increases linearly with altitude from a value of 0.15 at sea level to 0.45 at 4000 m. This model produces the best fitting of the isotopic data. Therefore, an increase of the liquid/vapour ratio with altitude is assumed to approach reality rather well.

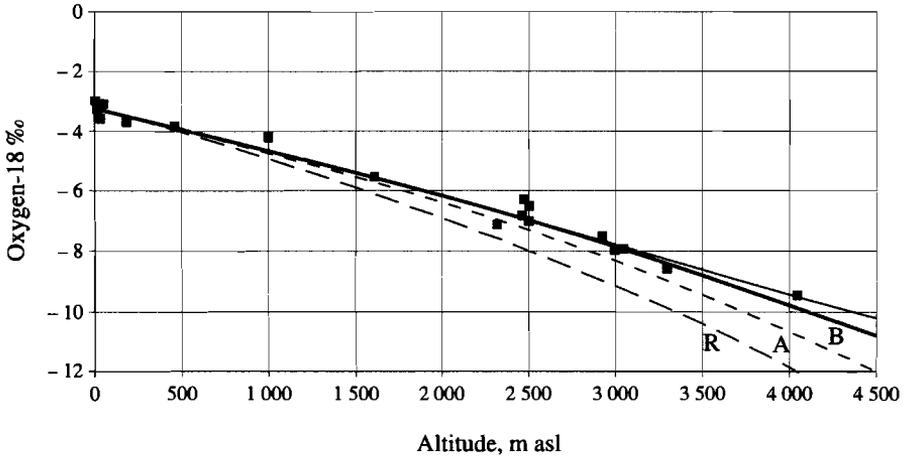


FIGURE 8.

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 $0.53\text{ }^\circ\text{C}/100\text{ m}$ and taking $T = 16\text{ }^\circ\text{C}$ 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 $0.53\text{ }^\circ\text{C}/100\text{ m}$, et $T = 16\text{ }^\circ\text{C}$ pour $Z = 0\text{ m}$ (niveau de la mer).

GENERAL CONCLUSIONS

The IAEA database on isotopes in precipitation is still far from being fully exploited. The tritium concentration in precipitation from 1963 to 1967, when the thermonuclear tritium was high and natural tritium negligible, is crucial for the understanding of atmospheric part of the hydrological cycle, and especially of the stratosphere-troposphere interrelations, the atmospheric vapour-liquid exchange, and re-evaporation and re-cycling of precipitation. For instance, the change of tritium decrease rate with latitude, although admittedly not yet fully understood, provides an indication of increasing re-cycling of rains at low latitudes.

Nowadays, tritium has reached in precipitation levels similar to those occurring before 1952, i.e. before the thermonuclear tests. These low concentrations strongly limit the use of tritium in investigations on atmosphere global dynamics. However, in contaminated areas, tritium can be used to investigate vapour migration under different meteorological conditions, by sampling atmospheric vapour.

Stable isotopes are a powerful tool in meteorological and climatological investigations, and have been widely applied in atmospheric general circulation models. The processes governing the isotopic composition of precipitation are known in their general lines, but detailed studies in selected regions and seasons may help in investigating them in depth and in identifying deviations from the average behaviour. For instance, in the temperate zone, the deuterium excess seems to be different in different seasons, but the slope of the $\delta^2\text{H}-\delta^{18}\text{O}$ relationship does not seem to be affected and remains constant at the value of 8.30-8.35, which is slightly higher than that of 8 computed by Craig for the overall global precipitation and generally adopted.

A better understanding of the relationships between isotopes and their response to external factors, will also enhance the usefulness of stable isotopes in palaeoclimatological investigations and in climatic change prediction.

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