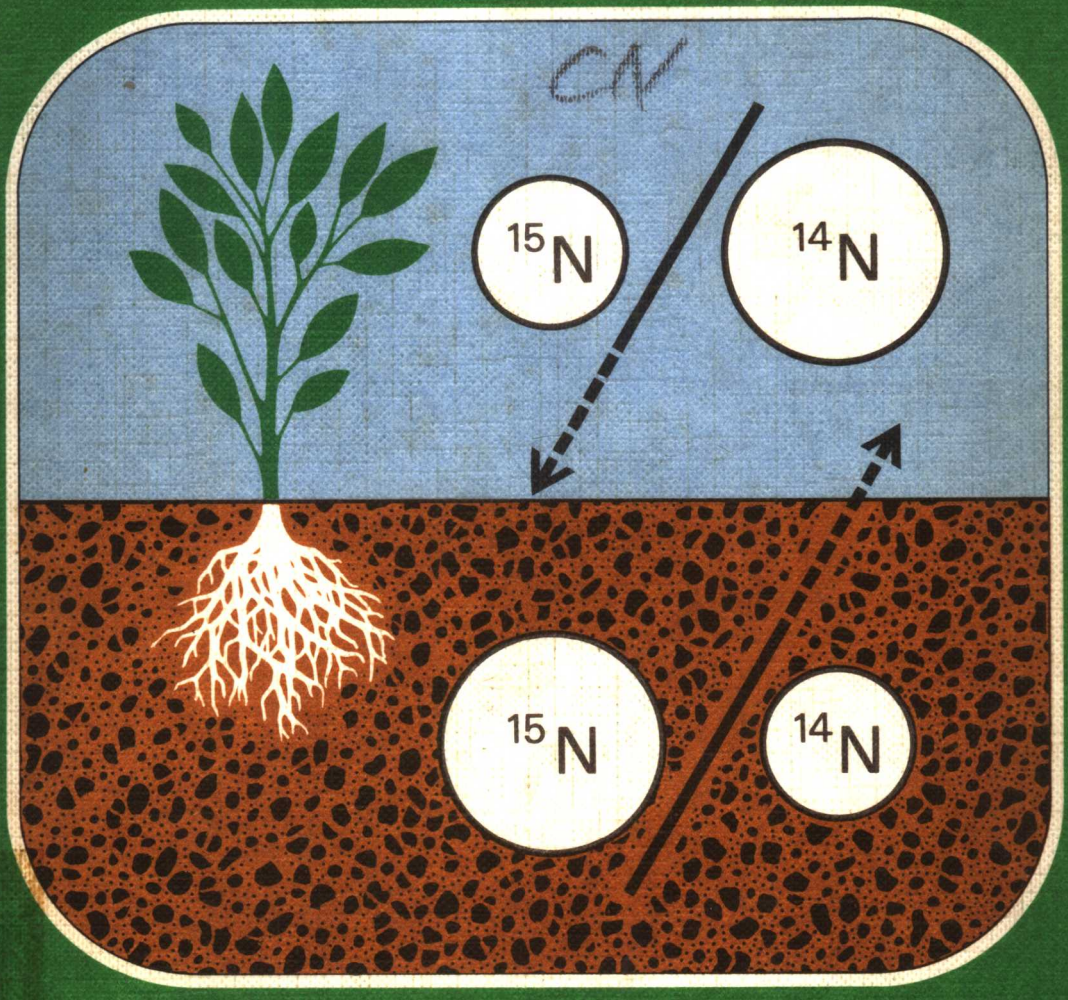
ISOTOPE RATIOS AS POLLUTANT SOURCE AND BEHAVIOUR INDICATORS

PROCEEDINGS OF A SYMPOSIUM
VIENNA, 18-22 NOVEMBER 1974
JOINTLY ORGANIZED BY THE IAEA AND FAO



INTERNATIONAL ATOMIC ENERGY AGENCY, VIENNA, 1975

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PROCEEDINGS SERIES

ISOTOPE RATIOS AS POLLUTANT SOURCE AND BEHAVIOUR INDICATORS

PROCEEDINGS OF A SYMPOSIUM ON
ISOTOPE RATIOS AS POLLUTANT SOURCE
AND BEHAVIOUR INDICATORS
JOINTLY ORGANIZED BY
THE INTERNATIONAL ATOMIC ENERGY AGENCY
AND THE FOOD AND AGRICULTURE ORGANIZATION
OF THE UNITED NATIONS
AND HELD IN VIENNA, 18-22 NOVEMBER 1974

INTERNATIONAL ATOMIC ENERGY AGENCY
VIENNA, 1975

ISOTOPE RATIOS AS POLLUTANT SOURCE
AND BEHAVIOUR INDICATORS
IAEA, VIENNA, 1975
STI/PUB/382
ISBN 92-0-010375-8

Printed by the IAEA in Austria
April 1975

FOREWORD

Releases or usage of chemical or radioactive substances may lead to the appearance of potentially undesirable residues as trace contaminants of food, the environment or living tissues. When they do, two important questions arise:

Given a specific release or usage, how does the substance behave and what is its ultimate fate?

Given a specific contaminant, where has it come from?

The answer to the first question may provide that to the second. But usually not. Both questions are fundamental to the development of any necessary monitoring or control programmes.

These questions and their significance are illustrated by an example from agriculture. An increasing amount of nitrogen (currently more than 30 million tonnes per year) is applied to the world's soil to meet growing world food needs. Rarely is more than half the applied nitrogen recovered in the harvested crop. The obvious first question arises: What happens to the missing half or residue? Half, incidentally, of a vital and increasingly costly agricultural input, especially for developing countries. How much gets returned to the atmosphere by soil "denitrification" processes? How much gets leached from the soil into local ground, surface, or even drinking waters? It has also been established that the levels of inorganic nitrate have shown a significant rise in certain ground and surface waters and in some cases already exceed WHO recommended limits for potable water. Thus, secondly, to what extent – if any – are these increases due to fertilizer nitrogen applications? To what extent from animal or municipal waste? These questions are urgent and important, not only from the point of view of fertilizer conservation and pollutant potential, but because wrongly directed controls would be a danger that vital agricultural practices might be impaired with little or no benefit to environmental quality.

Radioactive tracer techniques are well-established tools for studying the first main question under controlled or limited experimental conditions. Unfortunately, they have serious limitations for field studies involving existing environmental conditions: first, because of real or imaginary radiation hazards; second, because of radioactive decay and loss of detectability; and, sometimes, because of lack of a suitable radioactive isotope in any event (e.g. for nitrogen).

Recent years have witnessed significant advances in isotope techniques applicable to actual field or existing environmental conditions. Firstly, accurate measurement of stable and/or radioisotopic ratios of existing environmental contaminants can provide useful and sometimes unique information, not only on the levels of contamination but on the location or nature of the source. Secondly, the dramatic improvement in the supply and use of stable isotopes promises a "breakthrough" in tracer experiments on the field scale and under field conditions.

These questions and techniques were the subject of the Symposium on Isotope Ratios as Pollutant Source and Behaviour Indicators, jointly organized by the IAEA and the FAO and held in Vienna from 18 to 22 November 1974. The contributed papers and their discussions illustrate clearly the potential value of accurate measurement of existing or environmental stable and radioactive isotopic ratios as pollutant source indicators and confirm the advances made during the last decade in the preparation and use of stable isotopes as tracers under field conditions without the limitations of possible radiation hazard or loss of detectability through radioactive decay. Moreover, double-labelling with stable isotopes in certain cases can provide for specific detection of the labelled molecule after isotopic dilution which indeed compares favourably with that acceptable in experiments with a single radioactive label.

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STABLE ISOTOPE RATIOS AS POLLUTANT SOURCE AND BEHAVIOUR INDICATORS

(Sessions I and II)

Chairmen:

E. KAHL, Austria (Session I)
M. LACROIX, Belgium (Session II)

THE WORLD PATTERN OF OXYGEN-18 IN RAINWATER AND ITS IMPORTANCE IN UNDERSTANDING THE BIOGEOCHEMICAL OXYGEN CYCLE

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Abstract

THE WORLD PATTERN OF OXYGEN-18 IN RAINWATER AND ITS IMPORTANCE IN UNDERSTANDING THE BIOGEOCHEMICAL OXYGEN CYCLE.

The oxygen-18 content of precipitation is the basic value for studies on photosynthetic oxygen and the water economy of plant communities using naturally occurring isotopic fractionations. Thus a world-wide pattern of the $H_2{}^{18}O$ content of rainwater is necessary. This pattern can be deduced with the help of the two-dimensional interpolation program SYMAP. To produce world-wide maps the available number of stations is normally not sufficient. The authors have attempted to obtain a more detailed pattern by a simple correlation study. The map was interpreted with the help of an auxiliary program which computes latitude zonal averages (MAPCOUNT). The latitude histogram can be correlated with other information such as the productivity. The importance of a global program like SYMAP was demonstrated with the help of the $H_2{}^{18}O$ variation in precipitation.

1. INTRODUCTION

The present composition of the oxygen-rich atmosphere is unique in our planetary system. The detailed history of this atmosphere, as we understand it at present, is still open to many questions. Knowledge of it, however, is necessary in order to describe thoroughly the biogeochemical oxygen cycle which we are interested in. Before life developed, oxygen may have been produced by the dissociation of atmospheric water vapour as a result of solar ultra-violet radiation. In this process hydrogen partly escaped into space, leaving behind a net source of atmospheric oxygen [1]. Under present conditions the only important sources and sinks are due to the liberation and the uptake of oxygen by living organisms. This can be seen if one compares the oxygen rates of various geochemically important processes, such as industrial burning and weathering. The turnover of the atmospheric oxygen pool can be calculated from productivity data, but up to the present it has not been possible to fully understand the mechanism.

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Junge [2] postulates that atmospheric oxygen is liberated by the deposition of unoxidized biological material. Its deposition has been proven by stable carbon isotope measurements and model calculations. Oxygen liberation and organic material production are related stoichiometrically.

One possible method of investigating the present oxygen cycle is to study the fractionation of the three stable oxygen isotopes ^{16}O, ^{17}O and ^{18}O during every turnover. We limit ourselves to the $^{16}O/^{18}O$ ratios, for the ^{17}O isotope is too rare and hence its effects are very small.

Interest in the oxygen isotope fractionation started with the observation that an ^{18}O enrichment exists in atmospheric oxygen compared to ocean water, the so-called Dole effect. We assume steady-state conditions within the whole cycle because no noticeable depositions of organic material have been observed in recent times. Thus, the sum of the fractionation factors produces the observed enrichment known as the Dole effect. Our experiments are designed to measure these fractionation factors. Since organic material is not transported over large distances the global pattern of productivity and oxygen turnover must be very similar. The different environmental conditions in the sea and on land have led us to divide the oxygen cycle into a marine one and a continental one.

The supply of oxygen is due to photosynthetic activity and its consumption is by respiration. The isotope fractionation during photosynthesis has been investigated by various authors. The latest measurements have been made by Nasarow and Kutjurin [3]. They found the same ^{18}O content within the photosynthetic oxygen as in the surrounding water. The limitation of the result for our purpose stems from the use of water plants instead of those from land. Gonfiantini et al. [4], Dongmann et al. [5, 6], Lesaint et al. [7], and Förstel et al. [8] reported an enrichment of $H_2{}^{18}O$ in the leaf water of land plants. This enrichment is doubtless due to the transpiration processes. The oxygen evolved from these $H_2{}^{18}O$-enriched leaves of land plants must have, according to present-day knowledge, an enriched ^{18}O content.

2. THE $H_2{}^{18}O$ ENRICHMENT IN LEAF WATER

The most surprising result of the $H_2{}^{18}O$ measurements of leaf water was the observation of a marked regular diurnal cycle. One of our latest measurements is given in Fig. 1. The $H_2{}^{18}O$ content in leaf water increases rapidly during the morning and decreases during the afternoon. At night a small linear decrease is observed. Any enrichment in the ^{18}O content of leaf water has to be considered as an enrichment relative to the soil water. The uptake of soil water by the roots and its transport to the branches shows no fractionation. Up to the branches the water flow can be considered as a pure mass transport. Our soil water samples in Jülich had an ^{18}O content of normal rainwater. We therefore consider the rain and soil water samples as identical for our purposes. For technical reasons we prefer to take the $H_2{}^{18}O$ content of branches as the inflowing water reference.

According to the literature on $H_2{}^{18}O$ fractionation during evaporation the fractionation can be explained by a purely physical model. But it should be mentioned that other processes, especially physiological regulation mechanisms, could affect the result, as we are dealing with biological material.

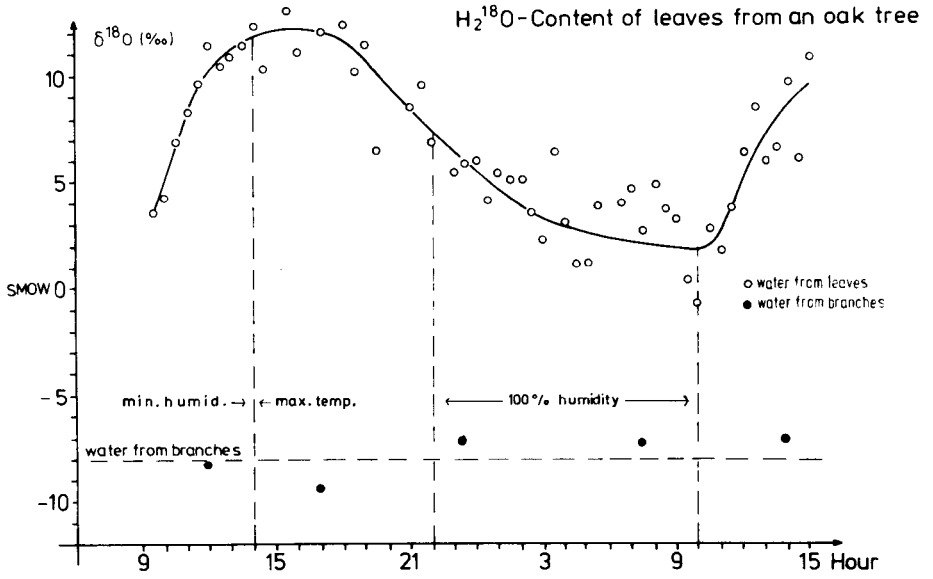


FIG.1. Diurnal cycle of $H_2{}^{18}O$ enrichment in the leaf water of an oak. Reference is the inflowing water from branches.

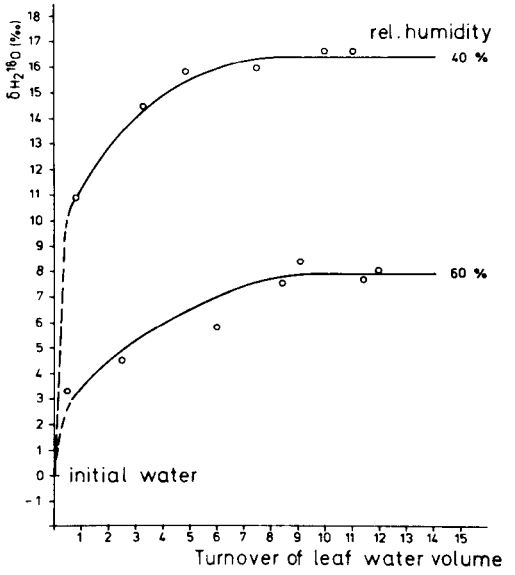


FIG.2. $H_2{}^{18}O$ enrichment in the leaf water of an oak (Quercus robur L.) due to the transpiration of leaves as a function of water turnover. Reference point is the 'culture water' of the plants.

In this simple model we take the leaf as a thin, well-mixed water film. In model experiments this situation could be realized by a thin wet filter disk of constant water volume. Though the morphology and physiology of a leaf are not so simple, the leaf behaves in a similar way to the filter disk. Figure 2 shows the enrichment of $H_2{}^{18}O$ in the leaves of Quercus robur L. The climatic and isotopic conditions have been kept constant within a wind track (Hotopp and Förstel [9]). The time dependence of enrichment has been measured at two different relative humidities. In both cases the total water content of the leaves had to be exchanged several times before a steady state was reached. As the water flow through the leaves is rather high under normal conditions the leaves of the trees always seem to be close to steady-state equilibrium.

The steady-state $H_2{}^{18}O$ enrichment of leaf water depends on the equilibrium and kinetic fractionation factors as well as on the relative humidity. The enrichment is based on the local $H_2{}^{18}O$ content in rainwater. Its total value amounts to:

$$\delta_1 = \epsilon_{eq.} + \epsilon_k + (\delta_a - \epsilon_k)\,h + \delta_s \qquad (1)$$

where δ_1 is the $H_2{}^{18}O$ enrichment in the leaf water, $\epsilon_{eq.}$ is the equilibrium enrichment ($\epsilon = 1 - \alpha$), ϵ_k is the kinetic enrichment, δ_a is the $H_2{}^{18}O$ content of water vapour in the air, δ_s is the $H_2{}^{18}O$ shift of soil water relative to SMOW, and h is the relative humidity.

Figure 3 shows laboratory experiments in the above-mentioned wind track with constant δ_s and δ_a values. Young oaks (Quercus robur L.) were kept at various relative humidities and the leaves harvested after they had reached steady-state conditions. The data reveal a straight line and are close to theory if we assume:

$\epsilon_{eq.} = -9‰$ (Baertschi and Thürkauf [10])
$\epsilon_k = -16‰$ (Dongmann et al. [6]).

The theoretical data are also plotted in Fig. 3. This clearly indicates that we can work with a model as expressed by Eq. (1).

Our aim is a global value for the $H_2{}^{18}O$ content in leaf water, which in turn requires the global $H_2{}^{18}O$ distribution of atmospheric water vapour, as seen from Eq. (1). The constants $\epsilon_{eq.}$ and ϵ_k can be measured in laboratory tests. The value of $\epsilon_{eq.}$ has often been determined (e.g. Baertschi and Thürkauf [10], Merlivat [11]) and is dependent on the conditions of the measurements, especially on the air flow conditions.

The kinetic values derived from experiments in a wind track and open air measurements are shown in Table I. The data are arrived at by extrapolating the results to relative humidities of h = 0 and h = 1. Measurements of δ_a and δ_s revealed constant values over the day.

The values of h, δ_a and δ_s show a global variation. The global pattern of h is easy to obtain as the humidity is a common value of weather reports. For a first approach we do not take into account the daily variations of the humidity.

The values for δ_a and δ_s which are needed for the evaluation of Eq. (1) present more problems. In this context it is very helpful to refer to the published data of the IAEA [12].

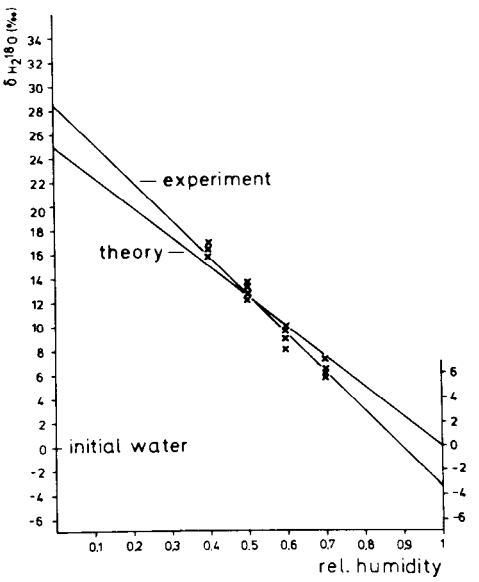


FIG.3. Steady-state $H_2{}^{18}O$ enrichment in the leaf water of an oak (Quercus robur L.) as a function of the relative humidity in a wind track.

TABLE I. KINETIC EFFECTS EXTRAPOLATED FROM LABORATORY AND OPEN AIR EXPERIMENTS

	Species	Wind velocity (m/s)	ϵ_k
Laboratory experiments	Oak	2	19
		0	23
Open-air conditions	Birch		13 - 18
	Oak		15
	Larch		28
	Fir		24

The $\delta\,{}^{18}O$ values of the relative humidity needed for Eq. (1) represent a great problem, as no world-wide data are available. We did some measurements at Jülich, which are at the moment the only data available to us. According to these measurements the ^{18}O content of water vapour on the ground is constant, showing no diurnal variations. Our measurements performed at various heights of a plant community at the Solling station of the International Biological Program (IBP) revealed the same results. In all cases the values seem to indicate that the $H_2{}^{18}O$ content of the water vapour – liquid phase, i.e. rainwater system – is in equilibrium. Whether this is true for all climatic conditions is open to discussion.

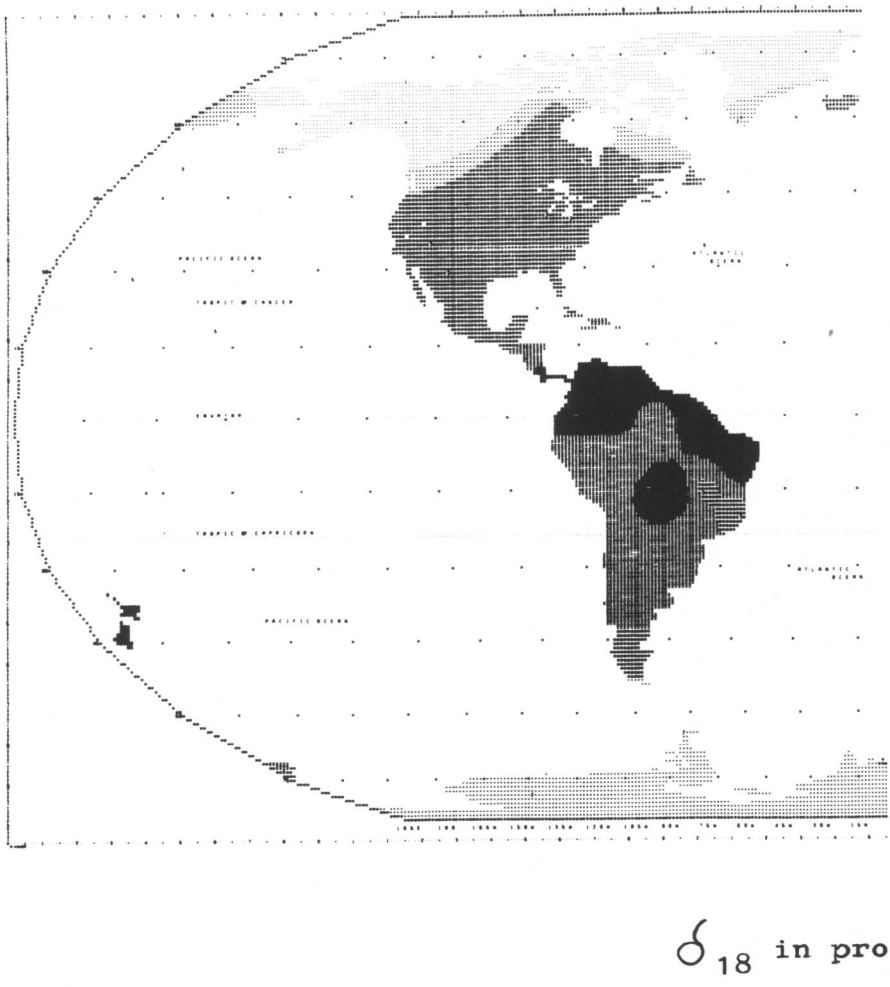
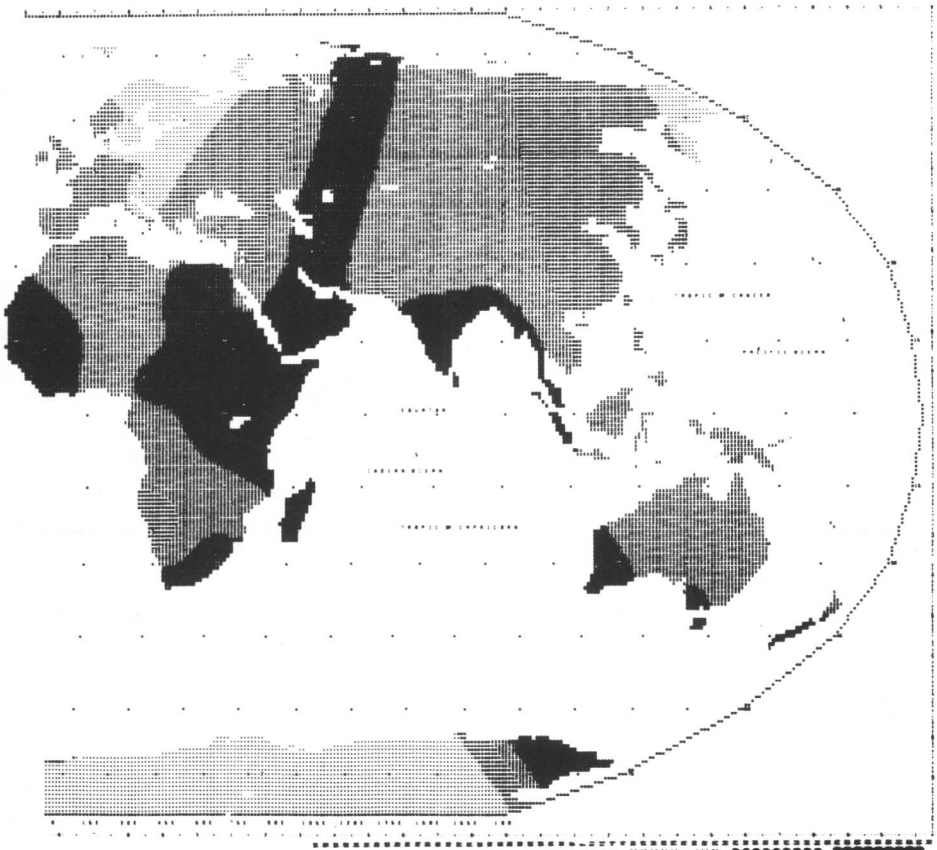


FIG. 4. Global ^{18}O distribution in precipitation. Data: IAEA 1966.



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