Deuterium and oxygen-18 in precipitation and other natural waters Some theoretical considerations[1]

By ERIK ERIKSSON, *International Meteorological Institute, Stockholm*

ABSTRACT

In the paper an attempt is made to express the isotope concentration in precipitation as a function of the atmospheric process which transport water vapor. It is found that the fractionation which takes place is considerably less when the atmospheric transport is due to eddy motion than when transport is simply advective. In the latter case fractionation follows the Rayleigh condensation formula. In the case of eddy transport fractionation may under special circumstances follow the same formula although with a factor $(\sqrt{\alpha}-1)$ instead of $(\alpha-1)$. More complicated transport patterns in the atmosphere are rather difficult to express mathematically.

As to the vertically integrated transport it is at present difficult to derive explicit relations over ocean areas because of the exchange which takes place between air and water. Over continents, however, the relation can be formulated more explicit under certain conditions.

Available data show a general relation between oxygen-18 and precipitable water which indicates that eddy transport is of major importance for distributing water vapor in the atmosphere.

As to isotope concentrations in surface waters, exchange of water between air and liquid water is rather important and cannot be neglected in cases where data are applied to specific hydrologic problems.

1. Background

The presence of deuterium and oxygen-18 in natural waters has been known for a considerable time, though systematic collection of reliable data was not possible until masspectrometric analysis techniques had been refined to the present extent. During the last 10-year period a few scientists have analysed various natural waters collected at different localities. Among notable contributors should be mentioned FRIEDMAN and coworkers, EPSTEIN, DANSGAARD, CRAIG, and GONFIANTINI *et al.* (see references). The analyses include a considerable number of precipitation samples as well as glacier ice samples and a considerable amount of data have been published by DANSGAARD (1964), LORIUS (1963), FRIEDMAN *et al.* (1964) and others (cf. references). Since 1961 there is in operation a global network for collection of monthly precipitation samples organized jointly by the International Atomic Energy Agency and the World Meteorological Organisation for the study of isotopes, hydrogen and oxygen in precipitation. These data are released at regular intervals and one will thus have better opportunities to evaluate the meteorological significance of deuterium and oxygen-18 in the near future.

As is well known, water molecules containing deuterium or oxygen-18 differ slightly in their physical properties from ordinary water, i.e. H_2O. They show a somewhat lower vapor pressure which causes a certain fractionation of the isotopes when water evaporates or condenses. Water vapor in equilibrium with liquid water shows a slight deficit of these isotopes when compared to the liquid phase.

Fractionation during evaporation can under special circumstances be expressed mathematically by the so-called Rayleigh distillation formula and a similar formula, often called Rayleigh condensation formula, accounts for fractionation which takes place during condensation. In connection with the composition of precipitation the latter formula is of the greatest interest.

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Condensation of water vapor takes place when it is cooled below a temperature which corresponds to its saturation vapor pressure. The cooling can be achieved in various ways in the atmosphere and so far two possibilities have been considered. One is cooling due to expansion of air during ascent. In this process also the total pressure changes which affects the saturation pressure of the water vapor. The temperature dependence on the percentage removal of water vapor in this process differs somewhat from the case when condensation takes place at constant air pressure, for instance due to loss of heat by radiation. These two cases, cooling by wet-adiabatic ascent and cooling by radiation at constant pressure, are discussed thoroughly by DANSGAARD (1953, 1961, 1964). Both processes give theoretically reasonably linear relations between the isotopic composition of the condensed water (i.e. precipitation in nature) and the temperature. However, there is a considerable scatter in the isotope data on precipitation when related to the average temperature of the place of collection and one can suspect that other circumstances should be considered as well. The relations referred to are also rather sensitive to the original composition of the water vapor and the temperature at which condensation starts. Further complications are added because the fractionation is in itself temperature dependent. For certain purposes the experimental temperature relation found is extremely useful as has been demonstrated by Dansgaard in his work on Greenland glacier ice. For meteorological purposes these relations may also be useful but can hardly be used to describe more complicated cases for reasons that will be apparent later.

Water vapor is not only advected in the atmosphere; a considerable eddy transport also takes place both vertically and horizontally and it is not evident that cooling of water vapor transported by eddy diffusion lead to a fractionation which can be expressed by the Rayleigh condensation formula. DANSGAARD (1953) is aware that vertical mixing complicates the fractionation but is unable to derive any relationship between fractionation and cooling under these circumstances. He is, however, concerned with very short time intervals of the order of the time it takes for convective precipitation to develop. When mixing is considered in connection with fractionation, the time scale has to be enlarged to such an extent that the random elements involved are averaged satisfactorily.

When trying to derive theoretically the meteorological implications of deuterium and oxygen-18 in precipitation, it seems reasonable to use the transport of water vapor in the atmosphere as a basis and from this derive, if possible, the transport pattern of deuterium and oxygen-18 in the atmosphere with the help of the fractionation coefficients which are simply the ratios of the vapor pressure of ordinary water to that of water containing either of the isotopes deuterium or oxygen-18. Deviations of the transport pattern of ordinary water in the atmosphere from that of the isotopes will give isotope concentrations in precipitation that depend on these deviations. Because of this expected relation, observations of these isotopes in precipitation may give information on features in the atmospheric water vapor transport. As to isotope data on other natural waters, interpretation of data has so far been made mostly in a qualitative way. FRIEDMAN *et al.* (1964) have discussed the water balance of lakes from deuterium data but have neglected exchange with air moisture, which may be important.

II. Significant features of the water circulation in nature in relation to isotopic fractionation

The main source for atmospheric water is the sea which also receives most of the precipitation. Estimates of the earth's water balance have been made, among others by WÜST (1954), from which most of the present information is taken. Of the yearly evaporation from ocean areas about 90 % is precipitated over the sea while only 10 % is brought back to the sea in rivers from continents. The actual precipitation over land is, of course, greater, in fact somewhat more than twice the run-off, but is still small compared to oceanic precipitation. It is obvious that the ocean areas have a great influence on the part of the water circulation of interest here.

The greatest sources of water vapor in ocean areas are the so-called trade wind belts centered around 20° latitude, south and north. In the whole area between 40° S and 40° N evaporation exceeds precipitation except for

a narrow strip close to the equator. North of 40° N and south of 40° S evaporation is less than precipitation. Thus a net transport takes place from the source areas polewards. This transport amounts to 13 % of the total evaporation over the sea.

The source regions of water vapor, i.e. the trade wind belts, shift south and north with the season together with the whole picture of the atmospheric transport of water vapor. This is, of course, the reason for the seasonal variation in deuterium and oxygen-18 observed in precipitation.

The precipitated water is, of course, transported back, to the source regions by ocean currents and the whole circulation of water can be looked upon as a stationary state. Such a steady circulation will, of course, set up specific patterns in the surface distribution of elements in sea water for which evaporation implies fractionation. The strongest fractionation will take place for dissolved salts and it has been shown by Wüst (l.c.) that their surface water concentrations are practically linearly related to the net evaporation, i.e. evaporation minus precipitation. The highest surface salinity is thus found in trade wind regions decreasing regularly polewards and equatorwards. As far as is known deuterium in surface ocean water shows a meridional distribution strikingly similar to that of salinity (FRIEDMAN *et al.*, 1964). For oxygen-18 surface ocean water data seem to agree with those of deuterium but are not very abundant. It is obvious that a better inventory of deuterium and oxygen-18 in surface ocean water is needed, especially to establish the detailed pattern of the surface water fractionation enrichment of these isotopes. It has been suggested that rapid evaporation from sea water should increase the fractionation and that this increase is on a relative basis much greater for oxygen-18 than for deuterium. Consequently, water vapor is believed to be enriched in deuterium relative to oxygen-18. If this really takes place it would show up in ocean surface water which should be enriched in oxygen-18. On the other hand, such an enrichment in oxygen-18 would tend to reduce the effect of fractionation because we are dealing with a stationary state circulation. Further, the pattern of the ocean circulation would also influence the enrichment.

The transport of water (or flux of water) in the atmosphere takes place in advection, i.e. it is carried along with the air in its main direction, and in eddy transfer. The vertical transport can be regarded as entirely an eddy diffusion process. Horizontally one can distinguish between two types of large scale eddies, transient eddies and stationary eddies. The latter are due to stationary high pressure cells found over ocean areas and the associated transport is thus advective. The transient large scale eddies are connected with moving disturbances, e.g. cyclones, and are mainly responsible for the poleward transport of water. The transport due to these eddies is of a random nature in so far that it takes place along average vapor density gradients in the same way as molecular diffusion. It is often treated as such a process and the diffusion coefficient which characterizes this process is of the order 10^{10} cm^2/sec for horizontal transports. In the vertical direction it is of the order 10^5 cm^2/sec.

The net influx of maritime moisture to continental areas is, as mentioned earlier, about 10 % at the total evaporation from the sea. The total influx is, of course, greater. Precipitation over land is about 2.5 times greater than runoff, hence nearly 60 per cent of the precipitation evaporates. This evaporation, which is also called evapo-transpiration, is largely due to the water consumption by vegetation, the water being led up from soil through the plants and evaporated on the surface of leaves. Most of the rest of evaporation takes place from soil, the water being brought to the surface by capillary action. Thus, most of the evapotranspiration from land takes place by evaporation from capillary systems. The implication of this fact is that very little effective fractionation can take place through evaporation from continental areas. Evaporation from a capillary system will initially cause fractionation of the isotope but this rises the concentration of the isotope in the evaporating parts which, of course, increases the rate of evaporation of the isotope to such an extent that the rate of flow of the isotopes through capillaries to the evaporating surface equals the rate of which it is evaporated. Only a thin film of water is thus being enriched, a film which has no means of mixing with the large reservoir of ground and soil water. The groundwater will acquire the average composition of precipitation with respect to the isotopes. This is prin-

cipally extremely important and, as far as observations go, also the actual case. It simplifies considerably the theoretical treatment of isotope transports in the atmosphere above continents.

III. The atmospheric transport of water, deuterium and oxygen-18

We will use the following symbols:

- q specific humidity of air,
- $\mathbf{v}$ rate and direction of movement of air (a vector),
- R the concentration of deuterium or oxygen-18 in water or water vapor,
- α the fractionation coefficient, i.e. the ratio of the saturation water vapor pressure of H_2O to that of HDO (water with deuterium) or H_2O 18 (water with oxygen-18),
- $\mathbf{f}$ the flux of water (H_2O) in water vapor (a vector) at a point,
- $\mathbf{f}^*$ the flux of HDO or H_2O^{18} in water vapor at a point,
- $\mathbf{F}$ the total horizontal (vertically integrated) flux of water vapor (H_2O),
- $\mathbf{F}^*$ the total horizontal (vertically integrated) flux of HDO or H_2O^{18},
- W the vertically integrated amount of water (H_2O) per unit area, (precipitable water).

The flux of water vapor is then given by

$$\mathbf{f} = q\mathbf{v} \tag{1}$$

and that of an isotope (always referring to either H_2DO or H_2O^{18}) by

$$\mathbf{f}^* = Rq\mathbf{v} = R\mathbf{f}. \tag{2}$$

Averaging over time is done in the usual manner denoting average values by a bar and deviations from the average by a prime. Thus we get

$$\bar{\mathbf{f}} = \overline{q\mathbf{v}} = \bar{q}\bar{\mathbf{v}} + \overline{q'\mathbf{v}'}. \tag{3}$$

The term $\overline{q'\mathbf{v}'}$ depends on the correlation between q and $\mathbf{v}$ and is recognized as the eddy flux of water vapor. For the isotope we get

$$\bar{\mathbf{f}}^* = \overline{Rq\mathbf{v}} = \overline{Rq}\,\mathbf{v} + \overline{(Rq)'\mathbf{v}'} \tag{4}$$

where Rq, in analogy to q, can be called the "specific humidity" of the isotope.

Evaluation of the eddy transports has to be done in the usual manner by assuming them to be proportional to the gradients, thus

$$\overline{q'\mathbf{v}'} = -K\nabla\bar{q} \tag{5}$$

$$\overline{(Rq)'\mathbf{v}'} = -K\nabla\overline{Rq} \tag{6}$$

where K is an eddy diffusion coefficient. The actual nature of K need not be discussed here. In the following we regard the whole term as a vector returning to the interpretation of K later.

As to eq. (6), the eddy flux can also be written as two terms

$$-K\nabla\overline{Rq} = -K\nabla(\bar{R}\bar{q}) - K\nabla\overline{R'q'}$$

and the total flux of the isotope

$$\bar{\mathbf{f}}^* = \bar{R}\bar{q}\bar{\mathbf{v}} + \overline{R'q'}\bar{\mathbf{v}} - K\nabla(\bar{R}\bar{q}) - K\nabla\overline{R'q'}. \tag{7}$$

We have thus to evaluate $\overline{R'q'}$, i.e. the correlation between R and q. Such a correlation can be expected but the question is how important it is. As R' and q' refer to fluctuations in R and q these may under extreme conditions be due to changes incurred during condensation and removal of the condensate. Under such conditions we can assume R and q to follow the Rayleigh condensation formula in the form

$$\frac{dR}{R} = (\alpha - 1)\frac{dq}{q}.$$

In another circumstance, like mixing of air of different R's and q's, the correlation between R and q may be smaller, hence the Rayleigh condensation formula can be expected to give the greatest possible correlation between the two. Now we can put $R' \cong dR$ and $q' = dq$ and get

$$\frac{R'}{\bar{R}} = (\alpha - 1)\frac{q'}{\bar{q}}$$

so that

$$\overline{R'q'} = (\alpha - 1)\frac{\bar{R}}{\bar{q}}(q')^2 = (\alpha - 1)\bar{R}\mathring{q} \tag{8}$$

where

$$\mathring{q} = \frac{\overline{(q')^2}}{\bar{q}}.$$

Thus, if $\overline{(q')^2}$ is known as well as its variation in space, the importance of the two terms containing $\overline{R'q'}$ can be assessed.

TABLE 1. *Half-yearly zonal averages of* $\overline{(q')^2}/\bar{q} = \mathring{q}$ *and of* $\bar{q}$ *in the Northern Hemispherein 1950.*

($\mathring{q}$ computed from PEIXOTO, 1958, pp. 22 and 23, and $\bar{q}$ from PEIXOTO, 1958, p. 22).

Pressure level (mb)	Item	Latitude 70°	60°	50°	40°	30°	20°	10°	0°
Summer data									
1000		0.58	0.75	0.98	0.87	0.69	0.54	0.33	0.16
		3.4	4.8	6.4	9.0	12.1	14.5	16.2	16.3
850		0.73	0.88	0.94	0.88	0.68	0.62	0.50	0.36
		2.7	3.7	4.7	6.0	7.8	9.2	10.5	11.2
700		0.71	0.76	0.95	0.95	0.77	0.77	0.67	0.52
		1.4	1.9	2.7	3.4	4.2	5.2	6.0	6.2
500		0.22	0.36	0.45	0.49	0.46	0.59	0.48	0.60
		0.4	0.7	0.8	1.0	1.4	1.7	2.1	2.4
Winter data									
1000		0.45	0.80	0.90	0.82	0.92	0.82	0.43	0.14
		1.1	1.8	3.2	5.4	8.5	11.7	14.7	15.9
850		0.45	0.62	0.77	0.95	1.10	0.87	0.40	0.18
		0.8	1.3	2.2	3.4	4.7	7.2	9.9	11.0
700		0.15	0.40	0.67	0.80	1.02	1.00	0.90	0.84
		0.6	0.9	1.2	1.8	2.5	3.6	4.9	6.3
500		0.05	0.13	0.22	0.27	0.45	0.49	0.51	0.53
		0.2	0.3	0.4	0.6	0.8	1.0	1.6	2.3

Rewriting eq. (7) expressing $\overline{R'q'}$ according to eq. (8) gives

$$\overline{\mathbf{f}^*} = \bar{R}\bar{\mathbf{v}}[\bar{q} + (\alpha - 1)\mathring{q}] - \bar{R}K[\nabla\bar{q} + (\alpha - 1)\nabla\mathring{q}] - \bar{q}K\nabla\bar{R}.$$

PEIXOTO (1958) made a study of the humidity conditions in the northern hemisphere during 1950 and computed also half-yearly averages of $\overline{(q')^2}$ at four different levels in the atmosphere as well as of $\bar{q}$ itself. The geographical variation can be seen in the zonal averages he computed. (l.c. p. 23). On the basis of these and the $\bar{q}$ values, $\mathring{q}$ has been computed and is given in Table 1 for various latitudes, altitudes and seasons. Looking at these data we find that on all occasions $\bar{q}$ is greater than $\hat{q}$. At certain levels and altitudes $\mathring{q}$ may reach about 0.5 $\bar{q}$, but it may also be as low as 0.01 $\bar{q}$. Considering that $\alpha - 1$ is around 0.1 for deuterium and 0.01 for oxygen-18, we see that at high altitudes (500–700 mb) in mid-latitudes and at high latitudes also close to the ground $(\alpha - 1)\hat{q}$ may amount to as much as 5 % of $\bar{q}$ in the case of deuterium and 0.5 % in the case of oxygen-18. Advection of deuterium can thus be enhanced by 5 % at most but on the whole the effect is much less and may well be neglected. As to $(\alpha - 1)\nabla\hat{q}$ compared to $\nabla\bar{q}$ we find that meridionally, where eddy diffusion is of greatest importance, the effect is pronounced only at high altitudes and high latitudes. As an example between 60° N and 70° N at the 500 mb level $\nabla\bar{q} = 0.1$ and $\nabla\mathring{q} = 0.08$, thus $(\alpha - 1)\nabla\mathring{q}$ may amount to 10 % of $\nabla\bar{q}$. This is, however, an extreme case and the transport of water vapor is furthermore very small because $\bar{q}$ is small. At the 850 mb level which is so to speak the centre of gravity for atmospheric water vapor we find the following set of $\nabla\bar{q}$ and $\nabla\mathring{q}$ for successive 10° intervals in summer, going from 0°

$\nabla\bar{q}$	−0.7	−1.3	−1.4	−1.8	−1.3	−1.0	−1.0
$\nabla\mathring{q}$	0.14	0.12	0.04	0.20	0.06	−0.06	−0.15

For deuterium $(\alpha - 1)\nabla\hat{q}$ is at most 2 % of $\nabla\bar{q}$.

For individual stations on a half-year basis one finds that $\hat{q}/\bar{q}$ is rather regularly distributed amounting to about 0.10 in ocean areas although sometimes it is as low as 0.01. Continental areas in temperate regions show values of around 0.15 while polar areas have values around 0.40. This means that for deuterium the contribution over ocean areas ranges from zero up to 1 % and for temperate continental regions between 1 and 2 %, while for polar areas the contribution is up to 4 %, all taken at the 850 mb level.

As a conclusion it can be stated that neglecting the term $\overline{R'q'}$ may introduce an error of 1 to 2 % in the expression for the isotope flux in most areas and up to 5 % in high latitudes in the case of deuterium but for oxygen-18 it is of no importance. For the divergence of the flux the effect of neglecting $\overline{R'q'}$ is somewhat less on a percentage basis.

We can thus continue with the equation

$$\overline{\mathbf{f}^*} = \bar{R}\bar{q}\bar{\mathbf{v}} - K\nabla(\bar{R}\bar{q}) \tag{9}$$

for the isotope and

$$\bar{\mathbf{f}} = \bar{q}\bar{\mathbf{v}} - K\nabla\bar{q} \tag{10}$$

for water vapor.

When considering the divergence of flux we must also consider the air density, therefore

we multiply the fluxes by ϱ and investigate the expressions derived from the divergence of these fluxes. Thus we get

$$\nabla \cdot (\varrho \bar{\mathbf{f}}) = -\bar{p} \tag{11}$$

and

$$\nabla \cdot (\varrho \bar{\mathbf{f}}^*) = -\overline{\alpha_e R p} \tag{12}$$

where ϱ is the rate of removal of precipitation and α_e is the apparent fractionation coefficient.

In a cloud R may be lower than where condensation just starts. This can be seen as follows. If q_l is the specific humidity of liquid water and q_v that of water vapor in a cloud we have

$$q_l + q_v = q$$

where q is the specific humidity of the air in which the cloud was formed. Similarly, for the isotope ratios we have

$$R_l q_l + R_v q_v = Rq$$

where R_l refers to liquid water and R_v to the vapor in the cloud. As we also have

$$R_v = \alpha R_l$$

we can derive that

$$R_l = \frac{\alpha R}{1 + (\alpha - 1)\dfrac{q_l}{q}}.$$

Thus, the apparent fractionation coefficient α_e is given by

$$\alpha_e = \frac{\alpha}{1 + (\alpha - 1)\dfrac{q_l}{q}}$$

and depends on the ratio of liquid water to total water. The relation is, further, valid only as long as full equilibrium is maintained between the cloud droplets and the water vapor in the air. Thus, raindrops or large cloud droplets falling should not be considered for the moment.

Determinations of liquid water in clouds have been done to some extent in the past. Two methods have been employed. By one method, cloud droplet size distribution is determined by suitable sampling devices and from these distributions the liquid water content is computed. This method has been used for instance by SQUIRES (1958). An instrument for direct determination has been developed by WARNER (cf. WARNER, 1955) and has been used widely also by others (cf. ACKERMAN, 1959 and 1963). The results obtained from clouds of various types indicate an average content varying 0.2 and 0.6 gm^{-3} of air, on occasions up to 1.6, and in general much below the values expected from condensation due to wet-adiabatic ascent of moist air, indicating rather strong mixing with environmental air within the clouds. Sometimes higher liquid water contents than that accounted for by wet-adiabatic ascent are found, but this is generally explained as due to accumulation of falling drops, which may not be in equilibrium with the environmental air. Looking at some cases in hurricanes, investigated by ACKERMAN (1963) and estimating the saturation specific humidity from a normal temperature profile gives the following set of q_l and q.

Hurricane	Altitude	q_l	q	q_l/q
Helene	9,000	1.0	9	0.11
	13,000	1.0	8	0.13
Daisy	13,000	2.6	8	0.33
	15,600	1.0	6	0.17
Becky	15,600	1.2	6	0.20
Carrie	18,000	1.0	5	0.20

It is seen that q_l/q mostly is below 0.2 in these rather violent storms, hence this may be a maximum value under most circumstances and would make α_e about 20 % lower than α. It seems likely that the effect in general is of this order of magnitude or even less and thus the effective α is about 80 % or greater of the real α. Still we have neglected and will neglect any effect of exchange between raindrops passing through the cloud because there are hardly any simple and feasible ways to take this into account. Further, we have to average over time and consider possible correlations between R and p and α_e. Also, these effects, which are presumably small, are nearly impossible to evaluate, hence we may include them all into the effective α and write

$$\nabla \cdot (\varrho \bar{\mathbf{f}}^*) = -\alpha_e \bar{R} \bar{p}. \tag{13}$$

Combining eq. (11) and (13) gives

$$\alpha_e \bar{R} \nabla \cdot (\varrho \bar{\mathbf{f}}) = \nabla \cdot (\varrho \bar{\mathbf{f}}^*). \tag{14}$$

Equation (14) together with eqs. (9) and (10) are now the basic equations to be used in the

following. They can be regarded as reasonably accurate expressions for the average transport and conservation of water and stable isotopes of water in the atmosphere although some assumptions which have been made are not entirely satisfactory. Exchange between water vapor and falling precipitation may be important if vertical gradients are steep. If not, it may be possible to neglect. Only actual data can tell whether the neglect of exchange is justified or not.

IV. The general equations for atmospheric transports

In the way the equations were derived eddy transport is expressed as a flux vector of the type $-K\nabla\bar{q}$ and $-K\nabla\bar{R}$. Considering the density which appears in the eq. (14) this may be combined with K by writing $\varrho K = A$ where A is the austausch coefficient. Basically, however, A must be a second order tensor A_{ij}, hence the eq. (14) is most suitably written in tensor notation. Using eqs. (9) and (10) the general form of eq. (14) becomes.

$$(\alpha_e-1)\bar{R}\varrho v_i\frac{\partial\bar{q}}{\partial x_i}-(\alpha_e-1)\bar{R}\frac{\partial}{\partial x_i}\left(A_{ij}\frac{\partial\bar{q}}{\partial x_j}\right)$$
$$=\bar{q}\varrho v_i\frac{\partial\bar{R}}{\partial x_i}-\frac{\partial\bar{R}}{\partial x_i}A_{ij}\frac{\partial\bar{q}}{\partial x_j}-\frac{\partial\bar{q}}{\partial x_i}A_{ij}\frac{\partial\bar{R}}{\partial x_j}$$
$$-\bar{q}\frac{\partial}{\partial x_i}\left(A_{ij}\frac{\partial\bar{R}}{\partial x_j}\right). \qquad (15)$$

For the present purposes it can be assumed that A_{ij} is rather uncomplicated, being independent of wind speed and direction. With the type of anisotropy encountered in the atmosphere A_{ij} has then only three components, A_{11}, A_{22}, and A_{33} or say A_x, A_y and A_z.

V. The vertical variation of $\bar{R}$

In the absence of horizontal gradients of $\bar{q}$ and $\bar{R}$ equation (15) takes the form

$$(\alpha_e-1)\bar{R}\frac{d}{dz}\left(A_z\frac{d\bar{q}}{dz}\right)=2A_z\frac{d\bar{q}}{dz}\frac{d\bar{R}}{dz}$$
$$+\bar{q}\frac{d}{dz}\left(A_z\frac{d\bar{R}}{dz}\right). \qquad (16)$$

The same is also true provided that

$$(\alpha_e-1)\bar{R}\varrho\left[\bar{u}\frac{\partial\bar{q}}{\partial x}+\bar{v}\frac{\partial\bar{q}}{\partial y}\right]-(\alpha_e-1)\bar{R}\left[\frac{\partial}{\partial x}\left(A_x\frac{\partial\bar{q}}{\partial x}\right)\right.$$
$$\left.+\frac{\partial}{\partial y}\left(A_y\frac{\partial\bar{q}}{\partial y}\right)\right]=\bar{q}\varrho\left[\bar{u}\frac{\partial\bar{R}}{\partial x}+\bar{v}\frac{\partial\bar{R}}{\partial y}\right]-2A_x\frac{\partial\bar{R}}{\partial x}\frac{\partial\bar{q}}{\partial x}$$
$$-2A_y\frac{\partial\bar{R}}{\partial y}\frac{\partial\bar{q}}{\partial y}-\bar{q}\left[\frac{\partial}{\partial x}\left(A_x\frac{\partial\bar{R}}{\partial x}\right)+\frac{\partial}{\partial y}\left(A_y\frac{\partial\bar{R}}{\partial y}\right)\right]. \qquad (17)$$

It is seen that if $\bar{q}$ is an exponential function of x, y and z, $\bar{R}$ will also be an exponential function of x, y and z. We can regard eqs. (16) and (17) as representing steady conditions over continental areas or ocean areas where $\bar{q}$ may change regularly and well defined. There are of course cases where they do not apply, e.g. when dry air is passing over a limited source of water. In such cases eqs. (16) and (17) are certainly not valid.

As to eq. (16) we may assume A_z to be independent of z which eliminates A_z from the equation and we are left with

$$(\alpha_e-1)\bar{R}\frac{d^2\bar{q}}{dz^2}=2\frac{d\bar{q}}{dz}\frac{d\bar{R}}{dz}+\bar{q}\frac{d^2\bar{R}}{dz^2}. \qquad (18)$$

If, now, $\bar{q}$ can be written $\bar{q}=q_0e^{\lambda z}$, we get

$$\frac{d^2\bar{R}}{dz^2}+2\lambda\frac{d\bar{R}}{dz}-(\alpha_e-1)\lambda^2\bar{R}=0$$

and
$$\bar{R}=R_0e^{\lambda(\sqrt{\alpha_e}-1)z} \qquad (19)$$

for the vertical variation of $\bar{R}$.

From eq. (19) one can further deduce

$$\frac{d\bar{R}}{\bar{R}}=(\sqrt{\alpha_e}-1)\frac{d\bar{q}}{\bar{q}} \qquad (20)$$

which is similar to the Rayleigh condensation formula except that the square root of α_e enters instead of α_e. It is difficult to give any physical interpretation to this difference, apart from the fact that vertical mixing takes place which would certainly tend to even out vertical differences in $\bar{R}$.

VI. Horizontal variation of $\bar{R}$

If there is no horizontal mixing to consider, eq. (17) will take the form

$$(\alpha_e-1)\bar{R}\varrho\left(\bar{u}\frac{\partial\bar{q}}{\partial x}+\bar{v}\frac{\partial\bar{q}}{\partial y}\right)=\bar{q}\varrho\left[\bar{u}\frac{\partial\bar{R}}{\partial x}+\bar{v}\frac{\partial\bar{R}}{\partial y}\right]$$

from which is seen that when considering conditions the direction of flow

$$(\alpha_e - 1)\,\bar{R}\bar{V}\frac{d\bar{q}}{ds} = \bar{q}\bar{V}\frac{d\bar{R}}{ds}$$

where $\bar{V}$ is wind speed in the wind direction measured along s. This gives immediately

$$\frac{d\bar{R}}{\bar{R}} = (\alpha_e - 1)\frac{d\bar{q}}{\bar{q}} \tag{21}$$

i.e. the Rayleigh condensation formula irrespective of how $\bar{q}$ varies along the path of travel. Thus, this equation has a more general applicability than eq. (20) but requires on the other hand absence of eddy transports.

If eddy transport takes place along with advection the fractionation which occurs can be shown to be intermediate between those given by eqs. (20) and (21). In temperate regions the meridional transport of water vapor is to a large extent by large scale eddy diffusion whereas advection is the main mechanism for transport in the longitudinal direction. Thus, fractionation may be of different nature in the meridional and in the longitudinal directions and a general application of Rayleigh condensation formula according to eq. (21) seems to be less justified.

VII. Vertically integrated transports

If eqs. (9) and (10) are multiplied by the air density and integrated vertically we get the total flux within the moist layer. As before it is necessary to make some reasonable simplifications to achieve any explicit results. First we require $\bar{q}$ and $\bar{R}$ to be expressable as simple exponential functions of altitude, i.e.

$$\bar{q} = q_0(x, y)\,e^{\lambda z}$$
$$\bar{R} = R_0(x, y)\,e^{\lambda(\sqrt{\alpha_e} - 1)z}.$$

Further we consider two cases with respect to $\bar{v}$ and K. In the first case we require $\varrho\bar{v}$ and ϱK to be constant with altitude writing $\overline{\mathbf{m}} = \varrho\bar{v}$ and $A = \varrho K$. For the second case we require $\bar{v}$ and K to be constant with altitude expressing ϱ by

$$\varrho = \varrho_0 e^{\lambda_1 z}$$

The first case represents a horizontal momentum which is independent of altitude.

As before K or A is assumed to have only three components indexed by x, y and z. Finally, we use ∇_h to denote the operator in the two-dimensional $x-y$ plane after integration.

In the first case we get

$$\bar{\mathbf{F}} = -\frac{q_0}{\lambda}\overline{\mathbf{m}} + \frac{A}{\lambda}\nabla_h q_0 \tag{22}$$

$$\overline{\mathbf{F}^*} = -\frac{R_0 q_0 \overline{\mathbf{m}}}{\lambda\sqrt{\alpha_e}} + \frac{A}{\lambda\sqrt{\alpha_e}}\nabla_h(R_0 q_0) \tag{23}$$

where $q_0 \equiv q_0(x, y)$ and $R_0 \equiv R_0(x, y)$ as defined before.

In the second case we get

$$\bar{\mathbf{F}} = -\frac{q_0}{\lambda + \lambda_1}\varrho_0\bar{v} + \frac{\varrho_0 K}{\lambda + \lambda_1}\nabla_h q_0. \tag{24}$$

$$\overline{\mathbf{F}^*} = -\frac{R_0 q_0}{\lambda\sqrt{\alpha_e} + \lambda_1}\varrho_0\bar{v} + \frac{\varrho_0 K}{\lambda\sqrt{\alpha_e} + \lambda_1}\nabla_h(R_0 q_0). \tag{25}$$

An average $\bar{R}_m$ can be defined by

$$\bar{R}_m = \frac{\int_0^\infty R_0 q_0 \varrho_0 e^{(\lambda\sqrt{\alpha_e} + \lambda_1)z}\,dz}{\int_0^\infty q_0 \varrho_0 e^{(\lambda + \lambda_1)z}\,dz} = \frac{\lambda + \lambda_1}{\lambda\sqrt{\alpha_e} + \lambda_1} R_0 \tag{26}$$

and precipitable water $\overline{W}$ is defined by

$$\overline{W} = \int_0^\infty q_0 \varrho_0 e^{(\lambda + \lambda_1)z}\,dz = -\frac{\varrho_0 q_0}{\lambda + \lambda_1}. \tag{27}$$

Thus, we have

$$R_0 = \frac{\lambda\sqrt{\alpha_e} + \lambda_1}{\lambda + \lambda_1}\bar{R}_m \tag{28}$$

$$q_0 = -\frac{\lambda + \lambda_1}{\varrho_0}\overline{W}. \tag{29}$$

Then we get, using (28) and (29),

Case I

$$\bar{\mathbf{F}} = \frac{\lambda + \lambda_1}{\lambda}\frac{\overline{\mathbf{m}}\,\overline{W}}{\varrho_0} - \frac{\lambda + \lambda_1}{\lambda}\frac{A}{\varrho_0}\nabla_h\overline{W} \tag{30}$$

$$\overline{\mathbf{F}^*} = \frac{\lambda\sqrt{\alpha_e} + \lambda_1}{\lambda\sqrt{\alpha_e}}\frac{\overline{\mathbf{m}}}{\varrho_0}\bar{R}_m\overline{W} - \frac{\lambda\sqrt{\alpha_e} + \lambda_1}{\lambda\sqrt{\alpha_e}}\frac{A}{\varrho_0}\nabla_h(\bar{R}_m\overline{W}). \tag{31}$$

Case II

$$\bar{\mathbf{F}} = \overline{W}\bar{v} - K\nabla_h\overline{W} \tag{32}$$

$$\overline{\mathbf{F}^*} = \bar{R}\overline{W}\bar{v} - K\nabla_h(\bar{R}_m\overline{W}) \tag{33}$$

the only difference between the two cases being constants. The similarity of these equations to eqs. (9) and (10) are seen immediately.

For the divergence of the total fluxes we have

$$\nabla \cdot \bar{\mathbf{F}} = -\bar{P} + \overline{\varrho_w w_e} - \overline{\varrho_a w_e} = -\bar{P} + \bar{E} \tag{34}$$

$$\nabla \cdot \overline{\mathbf{F}^*} = -R_p \bar{P} + \overline{\frac{R_w}{\alpha_w} \varrho_w w_e} - \overline{R_0 \varrho_a w_e} \tag{35}$$

taking R_p as a weighted average of the concentration in precipitation. In these expressions ϱ_w is the saturation vapor density of the water at the earth's surface, ϱ_a the water vapor density at ground level, w_e is the rate of exchange of air between the earth's surface and the air (w_e is the transport velocity defined by ERIKSSON, 1961), R_w the isotope ratio in the water at the surface, and E the rate of evaporation.

As to eq. (35), conditions over land and over water differ appreciably. The last terms give the turbulent net transport of the isotope due to a water vapor exchange between air and the surface. It was pointed out before that no effective exchange can take place between the atmosphere and water in soils. Hence, over continents we can put

$$\overline{\frac{R_w}{\alpha_e} \varrho_w w_e} - \overline{R_0 \varrho_a w_e} = R_E \bar{E}$$

and also $R_p = R_E$. Here R_w has to be interpreted as the isotope ratio in the water film in plants and soils in contact with the atmosphere. Then we get

$$\nabla \cdot \overline{\mathbf{F}^*} = -R_p (\bar{P} - \bar{E})$$

over continents.

Hence, the equations derived can be combined by

$$R_p \nabla \cdot \bar{\mathbf{F}} = \nabla \cdot \overline{\mathbf{F}^*} \tag{36a}$$

over continents. Over oceans, this simple combination is hardly possible and a more elaborate one reads (including some further simplifications)

$$\nabla \cdot \overline{\mathbf{F}^*} = -R_p \bar{P} + \frac{\frac{R_w}{\alpha_e} - R_0 r}{1 - r} (\nabla \cdot \bar{\mathbf{F}} + \bar{P}) \tag{36b}$$

or

$$\nabla \cdot \overline{\mathbf{F}^*} = -R_p \bar{P} + \frac{\frac{R_w}{\alpha_e} - R_0 r}{1 + r} \bar{E} \tag{36c}$$

where $r = \varrho_a / \varrho_w$, i.e. the relative humidity of the air above the surface. As there are inadequate data for guidance a discussion of this will not be attempted here.

Comparing eqs. (30) and (31) with (32) and (33) we find that when their divergences are combined as in eq. (36a) there will not be much difference between the two cases. This can perhaps best be seen by writing

$$\frac{\lambda + \lambda_1}{\lambda} = 1 + \frac{\lambda_1}{\lambda} \quad \text{and} \quad \frac{\lambda \sqrt{\alpha_e} + \lambda_1}{\lambda \sqrt{\alpha_e}} = 1 + \frac{\lambda_1}{\lambda \sqrt{\alpha_e}}.$$

Hence, we can restrict the discussion to Case II.

From eq. (36a) comparing it to eq. (14) it is obvious that

$$\alpha_e \bar{R}_m = R_p \tag{37}$$

or using eq. (26)

$$R_p = \alpha_e \frac{\lambda + \lambda_1}{\lambda \sqrt{\alpha_e} + \lambda_1} R_0 \tag{38}$$

as the relation between the isotopic composition of precipitation and of water vapor at ground level.

If case I is considered we would arrive at

$$R_p = \alpha_e \sqrt{\alpha_e} \left(\frac{\lambda + \lambda_1}{\lambda \sqrt{\alpha_e} + \lambda_1} \right)^2. \tag{39}$$

For $\lambda = -4.10^{-6}$ cm^{-1} and $\lambda_1 = -1.3 \cdot 10^{-6}$ cm^{-1} we see that the difference between the two cases will not be very great.

We can also derive relations between R_p and $\bar{W}$ under various conditions. If the horizontal transport is due entirely to eddy diffusion and $\bar{W}$ changes exponentially with distance we get, as in the vertical case

$$\frac{dR_p}{R_p} = (\sqrt{\alpha_e} - 1) \frac{d\bar{W}}{\bar{W}}. \tag{40}$$

If advection is entirely responsible for the transport we get

$$\frac{dR_p}{R_p} = (\alpha_e - 1) \frac{d\bar{W}}{\bar{W}}. \tag{41}$$

For mixed transports we will have some intermediate relations.

The integrated transport equations are derived under rather stringent conditions with

respect to the wind vector, $\bar{\mathbf{v}}$. In temperate latitudes the variation in wind direction with altitude is normally so small that for the present purpose it can be neglected. In low latitudes, however, this is rarely the case in the neighbourhood of large continental blocks. In such cases a complete reversal in wind direction can be found at some level. From Peixoto's work this can be found in the central African region where moisture is transported from west to east at low levels and is transported from east to west at higher levels. It is obvious that under such conditions the integrated fluxes derived here are not applicable and consequently neither eq. (40) nor eq. (41).

VIII. Applications to available data

It is seen from eqs. (38) and (39) that the isotope concentration in precipitation—and in groundwater—is higher than the isotope concentration in water vapor close to the ground. The reason for this is, of course, the fact that the vertical exponential decrease of the isotope concentration is somewhat greater than that of water vapor. If the ratio of the evaporation rates for the isotope and water must be R_p, the ground level concentration of the isotope must be lower than R_p.

There are rather few data available for demonstrating this difference between R_p and R_0. DANSGAARD (1954) sampled and analysed water vapor at ground level in Copenhagen for oxygen-18 during a year. Taking the period April to September as representing the season when evapo-transpiration is taking place—the rest of the year evaporation can be disregarded —the average oxygen-18 concentration (expressed as the absolute difference from a reference with 1955 ppm) was $\Delta O^{18} = 8.1$ ppm. Danish groundwater contains, on the same scale 22 ppm in excess of the reference. The difference is thus $22 - 8.1 = 13.9$ ppm which should represent $R_p - R_0$. Taking $+10°$ as a likely average for this period the α for oxygen-18 is 1.01012 and $\sqrt{\bar{\alpha}} = 1.0051$. Further, λ can be taken to be $-4 \cdot 10^{-6}$ cm^{-1} and $\lambda_1 = -1.3 \cdot 10^{-6}$. With these values using eq. (38) we get

$$R_p - R_0 = \frac{1.01012 \cdot 5.3 - 4 \cdot 1.0051 - 1.3}{4 \cdot 1.0051 + 1.3} \cdot$$

$$(1955 + 8.1) = 12.3 \text{ ppm}$$

as a predicted value compared to 13.9 ppm as found. The agreement is thus satisfactory in view of the uncertainties involved. If we instead use the average isotopic composition of ground level water vapor for the whole year which was about 5 ppm (Dansgaard gives 4.7 but October is missing and is likely to be about 8 ppm) we should use a lower temperature for α_{18}. For $+5°$C we have $\alpha_{18} = 1.01062$ and $\sqrt{\bar{\alpha}_{18}} = 1.00532$ and compute 12.8 ppm for $R_p - R_0$ whereas it is 17 ppm experimentally.

In view of the difference in vertical variation of $\bar{q}$ and $\bar{R}$ we may inquire whether this difference is reflected in precipitation collected at different altitudes. An ideal place for this should be a high mountain peak close to the sea which does not cause any large scale lifting. In other words, the air at lower levels should rather pass around the mountain than above it. Precipitation thus formed should represent the moisture above the place of collection. Fanaråken in Norway may represent such a place and DANSGAARD (1961) compared the oxygen-18 concentration in precipitation collected at the summit of this mountain (2100 m above sea level) with that collected at Stend at sea level. The averages of 17 months collection from each station were:

Fanaråken 12.8 ppm
Stend 21.9 ppm

expressed as differences from the 1955 ppm reference. If the vertical distribution of the isotope concentration is

$$\bar{R} = R_0 e^{\lambda(1/\bar{\alpha}_e - 1)z}$$

and R_p is proportional to $\bar{R}$ (as can be shown) we find that the difference between the two places should be

$$\Delta R_p = R_{p_0}(1 - e^{\lambda(1/\bar{\alpha}_e - 1)z_1})$$

where z_1 is the altitude of the high station while R_{p_0} is the isotope concentration at sea level. With $\lambda = -4 \cdot 10^{-6}$, $z_1 = 2.1 \cdot 10^5$ cm and $\sqrt{\bar{\alpha}_e} = 1.0055$, corresponding to about 0°C we get with good approximation

$$\Delta R_p = 4 \cdot 10^{-6} \cdot 0.0055 \cdot 2.1 \cdot 10^5 \,(1955 + 21.9)$$
$$= 9.1 \text{ ppm}$$

while that measured is $21.9 - 12.9 = 9.1$ ppm thus is good agreement.

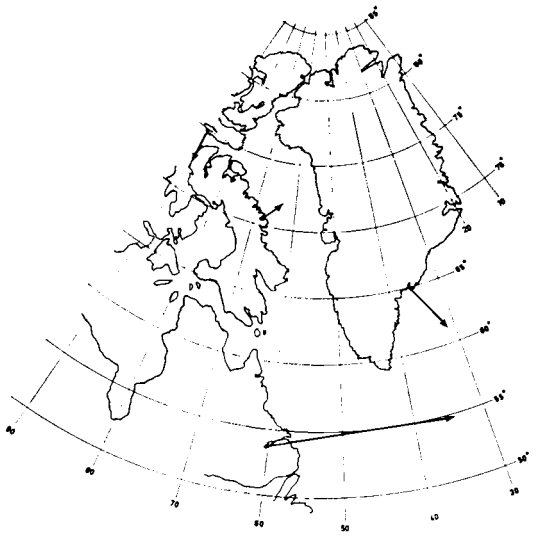

FIG. 1. Yearly averages of vertically integrated water vapor flux at stations in the Greenland area (Computed from data by PEIXOTO, 1958.)

There are, however, cases where this relation does not hold. As an example the oxygen-18 variation in Greenland ice with altitude can be mentioned, discussed also by Dansgaard. He found that the vertical variation in the oxygen-18 content to be about three times greater than that at the west coast of Norway, being even greater than expected from the Rayleigh condensation formula. The "ideal" altitude effect by wet-adiabatic ascent is about -0.9 ppm/100 m whereas the found effect is -1.26 ppm/100 m. The effect, expected from the formula used here is about -0.4 ppm/100 m. The explanation for this discrepancy must be sought in the geographical and meteorological feature of the Greenland area. Looking at Peixoto's data for the meridional and zonal components of total water vapor flux at the stations Resolute Bay, Clyde River on the Canadian side and on Angsmalik on the east side of Greenland one gets the impression (see Fig. 1) that water vapor must be picked up from the Labrador Sea during the passage of the cold and dry air from Canada. Hence it must pick up a rather high concentration of oxygen-18 from the Labrador Sea. As the distance across the Labrador Sea is only about 500 km it is doubtful if this oxygen-18 can reach the vertical distribution expressed by eq. (16); it probably has a great excess near sea level considering that the air originally comes off the Canadian continent and is poor in oxygen-18. On the whole, the presence of the comparatively narrow Labrador Sea is probably mainly responsible for the rather unique vertical distribution of oxygen-18 in the Greenland precipitation. A rough check on this possibility can be done by considering the function

$$1-\operatorname{erf}\frac{z}{2\sqrt{Kt}}$$

which will determine the degree of adjustment at different times and altitudes when an air mass, in equilibrium with respect to the vertical distribution of water vapor and an isotope is carried out over a surface which will change the distribution. In the present case t is represented by the time taken for the air to pass the Labrador Sea which, at a wind velocity of 5 m/sec can be estimated to 10^5 sec. As to K for the vertical transfer this is of the order 10^5 cm^2/sec so that the percentage adjustment when the air arrives at the Greenland coast, is given by

$$\left(1-\operatorname{erf}\frac{z}{2\cdot 10^5}\right)100.$$

For different altitudes the following adjustment percentages are found

z in m	0	500	1000	1500	2000
$\left(1-\operatorname{erf}\frac{z}{2\cdot 10^5}\right)100$	100	72	48	29	16

This shows that the Labrador Sea is too narrow for the isotope to reach a stationary state distribution in the vertical. The vertical isotope variation in the precipitation over the western part of Greenland will consequently be abnormally great.

The deviation from a steady state indicated in the Greenland case should be important on east coasts in the westerlies and on the west coast in the easterlies but not on the windward side of continents, where the air has been in contact with the sea for a considerable length of time. That this deviation is not foreseen in the equations developed is, of course, because the cases discussed so far have been developed with extremely simplifying assumptions.

As to the variations of R_p with $\overline{W}$ there are some oxygen-18 data available (DANSGAARD, 1964) which can be combined with average precipitable water data from Peixoto's paper. As to precipitable water most of the data are

interpolated from his chart with isolines and are probably not very accurate. From the discussion one would expect at least under certain circumstances to obtain a relation between R_p and $\overline{W}$ of the form

$$\frac{dR}{R} = (\beta - 1)\frac{d\overline{W}}{\overline{W}}$$

where β should vary between $\sqrt{\alpha_{18}}$ and α_{18} (α_{18} = fractionation coefficient for oxygen-18). Integrated this relation can be written

$$\ln\frac{R}{R_0} = (\beta - 1)\ln\frac{\overline{W}}{\overline{W}_0}$$

or, since δ is defined by $\delta = \dfrac{R - R_0}{R_0}$

$$\ln(1+\delta) = (\beta - 1)\ln\frac{\overline{W}}{\overline{W}_0}$$

or with good approximation

$$\delta = (\beta - 1)\ln\frac{\overline{W}}{\overline{W}_0}$$

and in terms of Brigg's logarithms

$$\delta = 2.3\,(\beta - 1)\log\overline{W} + \text{const.}$$

In Fig. 2 δ (in per mille) has been plotted against log $\overline{W}$ for stations in the global IAEA/WMO network. For comparison the relation above is shown by the two dashed lines corresponding to $\beta = 1.0045$ and $\beta = 1.009$ ($= \alpha_{18}$).

As seen from the figure there is a considerable scatter of points especially in the areas where $\overline{W}$ is high, i.e. in tropical regions. However, the stations in the North Atlantic and its surroundings seem to fall to a great extent in the region between the two dashed lines indicating that the transport processes are partly eddy partly advective in this region, and that the assumptions made during the derivation of the integrated flux are not too unrealistic in this region. Actually considering all the stations, the relation between R_p and $\overline{W}$ seems to be closer to a $\sqrt{\alpha}$ dependence. But there are, obviously, a number of factors which influence the isotope contents, among these many which had to be left out of consideration in this paper. Some of these have been discussed by DANSGAARD (1964) e.g. evaporation from falling raindrops. Others cannot in any simplified

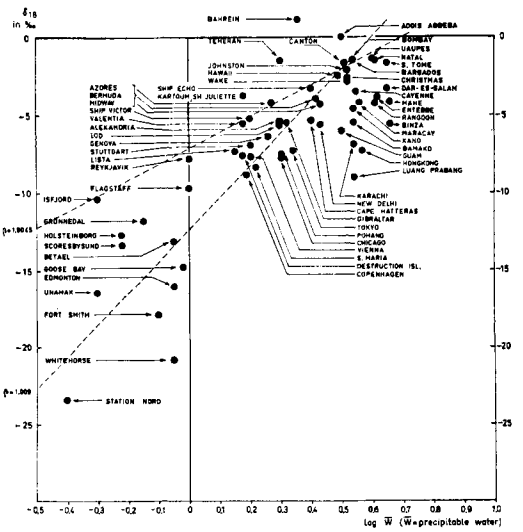

FIG. 2. Yearly averages of oxygen-18 abundance in precipitation samples collected on the Northern Hemisphere, plotted against the logarithm of average precipitable water, oxygen-18 data (as O_{18} in per mille) from DANSGAARD (1964), precipitable water from PEIXOTO (1958).

form be included in the expression for the divergence of the integrated transport like wind variations in the vertical, exchange between ocean and air, etc. More information is needed especially on the geographic distribution of isotopes in ocean surface water.

IX. Fractionation during evaporation of surface waters

There have been a number of suggestions as to the application of isotope data to hydrologic problems, especially to the question of the water budget of lakes. FRIEDMAN *et al.* (1964) have derived equations for this purpose but neglected the effect of isotope exchange between the air and the lake water. It may be of interest to consider the complete balance equation for the isotope under some specific circumstances.

We introduce the following symbols.

V the volume of a surface reservoir,
R_w the isotope ratio of the water in the reservoir,
R_a the isotope ratio in atmospheric moisture above the surface,
R_p the isotope ratio in precipitated water,

R_i the isotope ratio in water running into the reservoir,
ϱ_w saturation water vapor density,
ϱ_a water vapor density of air above the surface,
P liquid water added to the reservoir (precipitation and/or river water),
V_a a volume of air.

For the total amount of isotope in the reservoir VR_w we get the following condition

$$\delta(VR_w) = -\varrho_w \frac{R_w}{\alpha}\delta V_a + \varrho_a R_a \delta V_a + R_p \delta P \quad (42)$$

where δ is an operator indicating a small change (variation) in the quantities. In this expression the two first terms express the subtraction and addition of the isotope due to gaseous exchange.

For water alone we have in the same manner

$$\delta V = -\varrho_w \delta V_a + \varrho_a \delta V_a + \delta P. \quad (43)$$

Also here air exchange accounts for the quantity $-\varrho_w \delta V_a + \varrho_a \delta V_a$ which is the change due to evaporation or condensation.

A number of special cases can be considered. As the first case we choose one where $\varrho_a = 0$ and $\delta P = 0$. This represents evaporation from a water body into completely dry air. Then we get

$$\delta V = -\varrho_w \delta V_a \quad (44)$$

$$\delta(VR_w) = -\varrho_w \frac{R_w}{\alpha}\delta V_a. \quad (45)$$

As the latter can be written

$$V\delta R_w + R_w \delta V = -\varrho_w \frac{R_w}{\alpha}\delta V_a$$

we get by eliminating δV_a

$$\frac{\delta R_w}{R_w} = \left(\frac{1}{\alpha} - 1\right)\frac{\delta V}{V} \quad (46)$$

i.e. the Rayleigh distillation formula.

As the second case[1] we put $\delta P = 0$ i.e. no water is added in liquid form. This represents a case where a water body loses water by evaporation to air with a moisture density equal to ϱ_a. Then we get

[1] This case has also been considered by E. Roth, Centre d'Etudes Nucléaires de Saclay, France, who arrived at a formula similar to that in eq. (50).

$$\delta V = -(\varrho_w - \varrho_a)\delta V_a \quad (47)$$

$$\delta(VR_w) = -\varrho_w \frac{R_w}{\alpha}\delta V_a + \varrho_a R_a \delta V_a. \quad (48)$$

These equations give after eliminating δV_a

$$V\delta R_w = R_w \frac{\frac{\varrho_w}{\alpha} - (\varrho_w - \varrho_a)}{\varrho_w - \varrho_a}\delta V - R_a \frac{\varrho_a}{\varrho_w - \varrho_a}\delta V. \quad (49)$$

It is thus seen that this case cannot be reduced to the Rayleigh distillation formula because of exchange of water vapor and the isotope. However, it is seen that δR_w can be zero for a certain value of R_w. This can be interpreted to mean that as evaporation proceeds a state is finally reached at which R_w remains constant independent of the volume of the liquid phase. Putting $\delta R_w = 0$ we get

$$R_w = R_a \frac{\varrho_a}{\frac{\varrho_w}{\alpha} - (\varrho_w - \varrho_a)}. \quad (50)$$

When α is given R_w depends only on R_a and $\varrho_a/\varrho_w = r$, the relative humidity, and can be expressed by

$$R_w = \frac{\alpha r}{1 - \alpha(1 - r)} R_a. \quad (51)$$

We can also express α in terms of R_w, R_a and r by

$$\alpha = \frac{1}{1 + r\left(\frac{R_a}{R_w} - 1\right)}. \quad (52)$$

Craig *et al.* (1963) published some experimental results on the change in isotope composition of water by free evaporation into air of reasonably well known humidity (experiment 1). They found that the isotope concentrations go asymptotically towards certain values and from their Fig. 1 (l.c.) one can estimate that δ_D (rel. to SMOW) at the end of the experiment is +29‰ and δ_{18} +6.6‰. As to the outside air during this experiment they estimate that the relative humidity was on an average 75 % and the deuterium and oxygen-18 −86‰ and −12‰ respectively. As R can be written $R_{SMOW}(1 + \delta)$

we find that $\frac{R_a}{R_w} = \frac{1-0.086}{1+0.029}$ for deuterium and $\frac{1-0.012}{1+0.0066}$ for oxygen-18.

Then we get ($r = 0.75$)

$$\alpha_D = 1.092 \qquad \alpha_{18} = 1.014$$

It is interesting to compare these figures with those obtained by CRAIG *et al.* (l.c.) when evaporating water using dry nitrogen. This corresponds to the first case when Rayleigh distillation formula is valid as Craig found. From their experimental data we obtain

$$\alpha_D = 1.090 \qquad \alpha_{18} = 1.015$$

It is seen that the agreement between these computed here from their first outdoor experiment and those found experimentally by Rayleigh distillation agree very well.

There is one remarkable thing in these α_D and α_{18} as they point out They deviate considerably from those obtained from equilibration experiments. CRAIG *et al.* give the corresponding equilibrium values during the same conditions as $\alpha_D = 1.074$ and $\alpha_{18} = 1.009$. The fractionation factors by evaporation are thus larger than those at equilibrium but the ratio of $\alpha_D - 1/\alpha_{18} - 1$ which is about 8 at equilibrium attains a value at about 6 during evaporation. There is thus a kinetic effect which increases fractionation. However, it increases more for oxygen-18 than for deuterium.

As a third case we can consider all the terms in eqs. (41) and (42) during a steady state, i.e. when $\delta(VR_w)$ is zero as well as δV. This means that we consider a volume of water in contact with the atmosphere which loses as much water by evaporation as it receives in precipitation and by net influx. There are, however, a couple of subcases to consider here. In one we assume no outlet, corresponding to a salt lake, in the second δP is divided into incoming and outgoing which of necessity must have different R's.

For a salt lake we would have

$$\delta P = (\varrho_w - \varrho_a)\,\delta V_a \tag{53}$$

Here δP is the total contribution of liquid water to the lake, i.e. precipitation plus contribution by streams and groundwater. As R is assumed to be the same for precipitation and for groundwater we get from eqs. (41) and (53)

$$-\varrho_w \frac{R_w}{\alpha} + \varrho_a R_a + R_p(\varrho_w - \varrho_a) = 0$$

i.e.
$$R_w = \alpha[R_a r + R_p(1-r)] \tag{54}$$

in which α is the fractionation coefficient for evaporation. FRIEDMAN *et al.* (1964) discusses a number of salt lakes and set balance equations for these. However, they do not consider isotopic exchange and have therefore no values available for R_a and r. Hence, it is not possible to test eq. (54) until more complete data are available. Eq. (54) shows, however, that the interpretation of isotope concentrations in salt lakes is not so simple

The second subcase is perhaps of greater interest as it concerns fresh water lakes, i.e. lakes with run-off. In this case the term $R_p\delta P$ as well as δP have to be rewritten because their interpretation has to be changed. As δP is equal to evaporation when δV is zero it can be divided into two portions, δP_i and δP_o so that

$$\delta P = \delta P_i - \delta P_o. \tag{55}$$

Similarly for $R_p\delta P$ we divide it into two fractions $R_i\delta P_i$ and $R_o\delta P_o$. But if the lake is reasonably mixed we can identify R_o with R_w. Hence we write

$$R_p\,\delta P = R_i\,\delta P_i - R_w\,\delta P_o \tag{56}$$

noting that R_p now in fact is the isotope concentration in the evaporated water. The condition $\delta V = 0$ now gives

$$-\varrho_w\,\delta V_a + \varrho_a\,\delta V_a + \delta P_i - \delta P_o = 0 \tag{57}$$

i.e.
$$\delta P_i - \delta P_o = (\varrho_w - \varrho_a)\,\delta V_a. \tag{58}$$

Then we get from $\delta(VR_w) = 0$

$$-\left(\varrho_w \frac{R_w}{\alpha} - \varrho_a R_a\right)\frac{\delta P}{\varrho_w - \varrho_a} + R_i\delta P_i - R_w\delta P_o = 0 \tag{59}$$

or
$$\delta P = \frac{(1-r)(R_i\delta P_i - R_w\delta P_o)}{\frac{R_w}{\alpha} - R_a r} \tag{60}$$

As this represents a stationary state we can write $\delta P = E$, evaporation, from the lake $\delta P_i = F_i$ and $\delta P_o = F_o$, incoming and outgoing water

$$(F_i - F_o)\left(\frac{R_w}{\alpha} - R_a r\right) = (1-r)(R_i F_i - R_w F_o) \quad (61)$$

As F_o is probably easier to measure in many cases than F_i we can solve for F_i and express it in the form

$$\frac{F_i}{F_o} = \frac{\frac{R_w}{\alpha} - R_a r - R_w(1-r)}{\frac{R_w}{\alpha} - R_a r - R_i(1-r)}. \quad (62)$$

In this case R_i will mostly be the same as in precipitation and can thus be measured. As also the other unknowns can be determined it is seen that F_i can be computed when F_o is known. This form of the equation is, of course, most useful for shallow lakes with well defined outlets but poorly defined tributaries. FRIEDMAN *et al.* (l.c.) have also considered the use of deuterium for such computations but neglected the effect of direct isotope exchange between air and water.

There are, thus, several possible applications of stable isotopes in water to hydrologic problems provided all the necessary information on the isotopes is collected.

X. Conclusions

The present discussion of stable isotopes of water and their possible applications in meteorology and hydrology is largely theoretical but shows nevertheless the complexity of the problems which are involved. For atmospheric moisture available data, although rather inadequate, show reasonable agreement with theory where such agreement can be expected. The theory, however, shows how complex the transport of these isotopes is in relation to that of water vapor. It seems that more information is needed on the vertical distribution of isotope ratios and also on the isotope ratios in sea surface water and near surface atmospheric moisture.

As to hydrological applications the effect of exchange of isotopes between the air and surface water has to be taken into account as it is by no means negligible. However, provided proper care is taken it this respect it seems highly probable that the stable isotopes of water can be of great help in studies of water budgets of lakes.

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