Tellus (1982), *34*, 142–150

Factors controlling stable isotope composition of European precipitation

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(Manuscript received September 2, 1980; in final form May 12, 1981)

ABSTRACT

The seasonal and spatial variations of stable isotope ratios in present day European precipitation are simulated with a simple multibox model of the mean west–east horizontal transport of the atmospheric water vapour across the European continent. Isotope fractionation during the formation of precipitation leads to an increasing depletion of heavy isotopes in the residual air moisture as it moves towards the centre of the continent. This isotopic depletion is partly compensated, particularly in summer, by evapotranspiration, which is assumed to transfer soil water into the atmosphere without isotope fractionation. The model estimates are based on horizontal water vapour flux data, varying seasonally between 88 and 130 kg m^{-1} s^{-1} for the Atlantic coast region, and on the monthly precipitation, evapotranspiration and surface air temperature data available for various locations in Europe. Both continental and seasonal temperature effects observed in the stable isotope composition of European precipitation are fairly well reproduced by the model. The calculations show that the isotopic composition of local precipitation is primarily controlled by regional scale processes, i.e. by the water vapour transport patterns into the continent, and by the average precipitation-evapotranspiration history of the air masses precipitating at a given place. Local parameters such as the surface and/or cloud base temperature or the amount of precipitation modify the isotope ratios only slightly. Implications of the model predictions for the interpretation of stable isotope ratios in earlier periods as they are preserved in ice cores and in groundwater are also discussed.

1. Introduction

The IAEA/WMO precipitation network stations have provided information on the global scale variations of stable isotope composition of monthly precipitations for the last twenty years (IAEA, 1969, 1970, 1971, 1973, 1975, 1979). Moreover, many regional monitoring programs studying various aspects of these variations in more detail have been undertaken (e.g. Gat and Carmi, 1970; Schwabe, 1972; Lorius and Merlivat, 1975; Schriber et al., 1975; Kato, 1978; Smith et al., 1979; Salati et al., 1979; Siegenthaler and Oeschger, 1980). Usually the stable isotope composition of precipitation is correlated with various environmental parameters characterizing the given sampling point, like the altitude above sea level, distance to the coast, local surface air temperature and so forth (Dansgaard, 1964; Siegenthaler and Oeschger, 1980; Yurtsever and Gat, 1980). These purely empirical relations, so-called "effects", proved to provide a useful tool in stable isotope application to hydrology and glaciology. Dansgaard (1964) in his classical review paper proposed a qualitative explanation for the observed isotopic variations based on the Rayleigh distillation concept describing the isotopic evolution of a selected air mass treated as a closed system except for the removal of water by precipitation. A quantitative approach, however, has not been attempted so far, because of the complex nature of the meteorological processes controlling precipitation. Thus, the interpretation of isotope ratios in ancient precipitation as observed

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0040-2826/82/020142-09$02.50/0

in polar ice cores and in groundwater is subject to ambiguities (e.g. Dansgaard et al., 1973; Hanshaw et al., 1979).

In order to contribute to this problem, we have tried to model the observed variations of deuterium content in monthly precipitations collected by the European stations of the IAEA/WMO network. Our approach has been guided by two distinct regularities becoming obvious from the meteorological and isotopic data:

(a) the correlation between deuterium content in monthly precipitations and local surface air temperature (seasonal temperature effect) that becomes increasingly stronger towards the centre of the continent;
(b) the continuous depletion of deuterium in the monthly precipitation averages with increasing distance from the Atlantic coast (continental effect).

Fig. 1 shows, for three selected stations (Valentia Observatory 51.93° N, 10.25° W; Stuttgart 48.83° N, 9.20° E; Vienna 48.25° N, 16.37° E), the long-term average value of δD in monthly precipitations, i.e. of the ‰ deviation (from SMOW = Standard Mean Ocean Water isotopic standard) of the isotope ratio $[D]/[H]$ in an aliquot sample of total precipitation fallen during the month. All available data (the period over which isotope data are available is about 10 years) for the individual months are averaged to obtain the best estimate for the long-term mean value of δD for that month. The second diagram from the top shows the surface air temperature for the same stations. The apparent correlation between deuterium and local temperature increases as one moves inland. A linear regression fit yields the following relations.

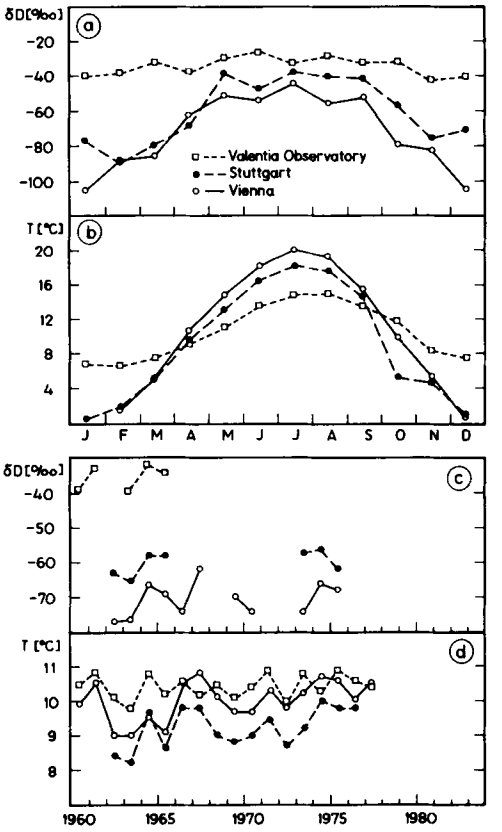

Fig. 1. (a). Long-term monthly arithmetic means of deuterium content of precipitation. (b). Surface air temperature for three European stations with increasing distance to the Atlantic coast: Valentia Observatory, Stuttgart and Vienna. (c). Annual arithmetic means of δD. (d). Surface air temperature values for the same stations. Data source: IAEA (1969, 1970, 1971, 1973, 1975, 1979).

Valentia Obs.

$\delta D = (1.3 \pm 0.6) \cdot t - (47.6 \pm 6.2)$,
correlation coeff. $r = 0.78$.

Stuttgart

$\delta D = (2.4 \pm 0.3) \cdot t - (80.5 \pm 4.2)$,
correlation coeff. $r = 0.89$.

Vienna

$\delta D = (2.7 \pm 0.3) \cdot t - (98.6 \pm 4.7)$,
correlation coeff. $r = 0.96$.

The lower part of Fig. 1 summarizes the annual arithmetic means of the δD and air temperature, evaluated for the same stations. The small number of data points does not allow any quantitative conclusion in this case; the correlation is poor, if any. At four stations in Switzerland, Siegenthaler and Oeschger (1980) did not find any significant correlation, either between the annual means of $\delta^{18}O$ or of the surface air temperature.

The continental effect, as observed in summer and winter precipitation in Europe, is shown in Figs. 2a and 3a. The points are long-term δD mean values for ten selected stations with the longest deuterium record: Valentia Obs.; Liège 50.70° N, 5.47° E; Groningen 53.21° N, 6.57° E; Sindorf 50.90° N, 6.68° E; Stuttgart; Hof 50.20° N,

11.88° E; Petzenkirchen 48.15° N, 15.15° E; Vienna; Podersdorf 47.85° N, 16.85° E; Kraków 50.05° N, 19.48° E. The resulting inland gradient of deuterium content amounts to −3.3 ‰/100 km in winter and −1.3 ‰/100 km in summer (linear fit). A significantly lower inland gradient for the winter season −2.4 ‰/100 km, if compared with summer data, was suggested by a previous estimate (Sonntag et al., 1976; Sonntag et al., 1978) based on a smaller set of data. An extremely small inland gradient of deuterium content, equal −0.6 ‰/100 km, has been observed by Salati et al. (1979) for the Amazon Basin.

Deuterium data can be transformed to ^{18}O values via the proper $\delta D - \delta^{18}O$ relations. These relations evaluated from the data from all European IAEA/WMO network stations are the following:

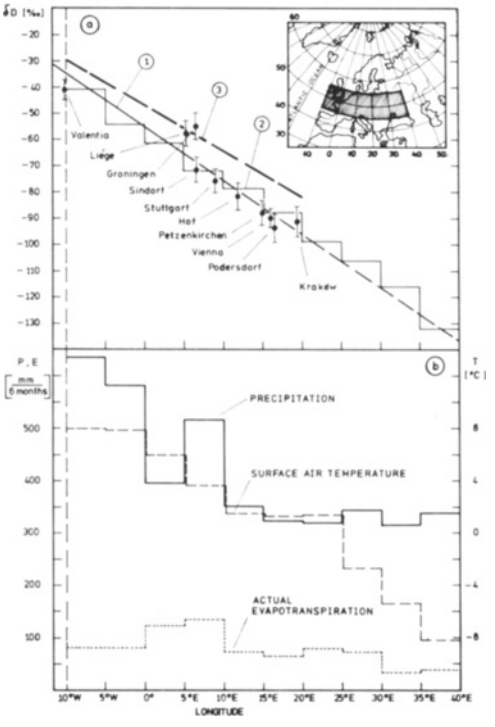

Fig. 2. (a). Continental effect observed in the deuterium isotopic composition of European winter precipitation (October–March). (1)—best linear fit of the data points, (2)—model prediction obtained for a winter mean value of the water vapour flux entering the continent of 88 kg m^{-1} s^{-1}, (3)—continental effect observed in shallow European groundwaters (Sonntag et al., 1979). (b). Precipitation, actual evapotranspiration and surface air temperature data for the winter half year, for the part of Europe in question.

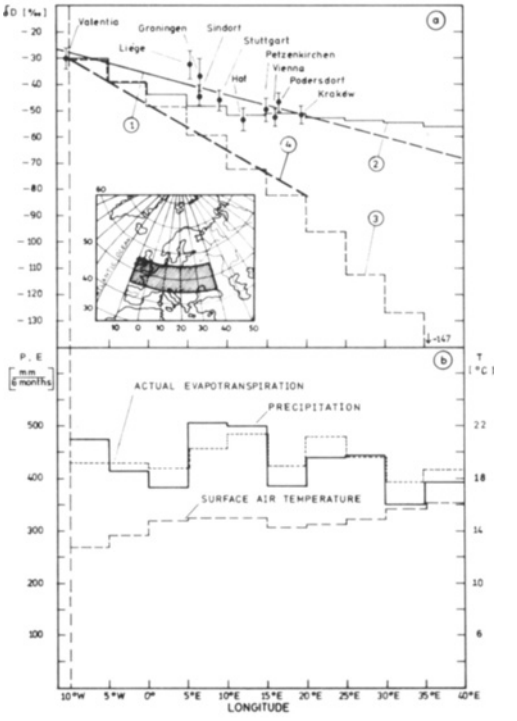

Fig. 3. (a). Continental effect observed in the deuterium isotopic composition of European summer precipitation (April–September). (1)—best fit of the data points, (2)—model prediction obtained with 35 % contribution of winter precipitation to summer evapotranspiration (see text for details), (3)—model prediction without evapotranspiration, (4)—continental effect observed in shallow European groundwaters (Sonntag et al., 1979). (b). Precipitation, actual evapotranspiration and surface air temperature data for the summer half year for the part of Europe in question.

winter (October–March)

$$\delta D = (7.6 \pm 0.2) \cdot \delta^{18}O + (6.5 \pm 2.1),$$
correlation coeff. $r = 0.98$;

summer (April–September)

$$\delta D = (6.0 \pm 0.4) \cdot \delta^{18}O + (-6.3 \pm 2.8),$$
correlation coeff. $r = 0.85$.

It is worth mentioning that the summer relation differs considerably from the commonly accepted global relation: $\delta D = 8 \times \delta^{18}O + 10$. The low value of the deuterium excess $d = \delta D - 8 \times \delta^{18}O = -6.3 \pm 2.8$ ‰ suggests that the isotopic

composition of summer precipitation is modified by the evaporation of raindrops below the cloud layer. This conclusion is somewhat surprising since the evaporation of raindrops has so far been thought to be an important process under warm and arid climatic conditions only.

2. Model calculations

The numerical approach presented here is based on the fact that the atmospheric circulation over the European continent has an essentially zonal character. Available data for the global water vapour transport in the atmosphere clearly show that the meridional component of this transport over Europe, is practically absent in winter and negligibly small in summer (UNESCO, 1978). We therefore need to consider only the water vapour flux entering Europe across its western boundary. In the model, the part of the European continent in question has been approximated by a rectangular field bounded by latitudes 45° N and 55° N and by longitudes 10° W and 40° E (see Fig. 2a). This field has been subdivided into 10 boxes, each 300 × 900 km in size (5° longitude, 10° latitude, respectively). The mean values of precipitation, of actual evapotranspiration rates as well as of the surface air temperature in each box have been evaluated on the basis of data published in UNESCO (1978) and CLINO (1962). Numerical values of the water vapour flux are available there only for two months: January and June (UNESCO, 1978). We assumed, therefore, that the water vapour flux entering Europe varied with the water vapour pressure above the Atlantic Ocean in the mid-latitude regions (30° N–40° N). Vapour pressure over the ocean is primarily controlled by the surface water temperature. This temperature for the region in question has been taken from the U.S. Naval Oceanographic Office Atlas (1967). The seasonal flux estimate has been fitted to the January flux value of about 80 kg m^{-1} s^{-1}. The resulting estimated water vapour flux variations are shown in Fig. 4b.

The basic concept in the modelling of isotope variations observed in precipitation attempted here, is that the marine water vapour entering the continent undergoes a Rayleigh process (Dansgaard, 1964; Sonntag et al., 1978) in which the increasing loss of vapour from the air mass by

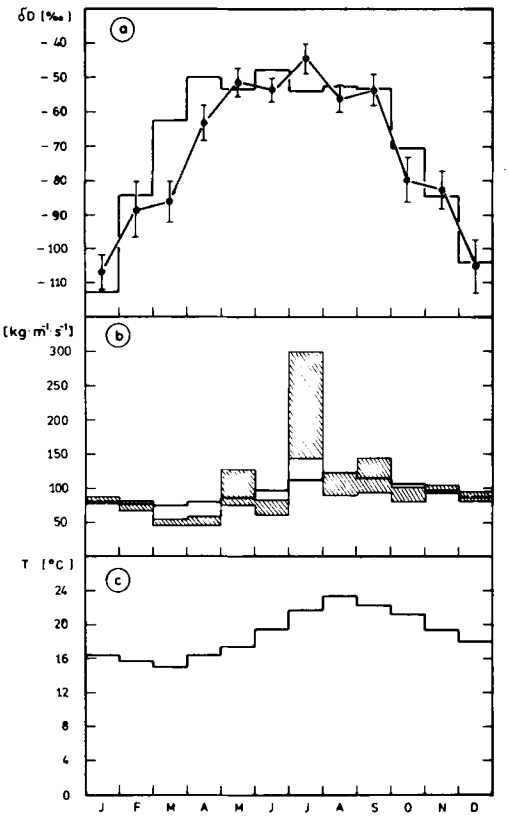

Fig. 4. (a). Observed and predicted seasonal temperature effect in the deuterium isotopic composition of Vienna precipitation. (b). Assumed variation of the water vapour flux entering the European continent at the western boundary (heavy line) as used for the prediction in Fig. 4a. The hatched error bars represent the r.m.s. uncertainty of the incoming vapour flux found by fitting the experimental points in Fig. 4a with the vapour flux as an open parameter (see text for details). (c). Seasonal temperature variation of the surface Atlantic Ocean between 30° N and 40° N latitude.

precipitation (minus evapotranspiration) makes the vapour increasingly depleted in the heavier isotropic species according to the Rayleigh eq. (1), derived by simple water removal from the air mass

$$R_p = \alpha \cdot R_0 \cdot F^{\alpha - 1}. \quad (1)$$

This equation describes the isotope ratio $R_p = \alpha \cdot R$ of precipitation at a certain distance from the coast, where the isotope ratio of the air mass vapour has developed from its initial value, R_0, to the value R due to the fact that the initial amount of vapour has been reduced to the fraction F by precipitation

removal during the passage. To use eq. (1), the fractionation factor has to be assumed to remain constant. Our model, in the one step better approximation to reality, assumes a stepwise development of R from box to box which means that now, for each consecutive box, i, we obtain

$$R_{p(i)} = \alpha_i \cdot R_{(i-1)} \cdot f_{(i)}^{\alpha i - 1} \tag{1a}$$

where $f_{(i)}$ represents the vapour reduction factor within a single box. This more detailed treatment allows a variable α as well as certain specific assumptions about the isotopic composition of the vapour being put back by evapotranspiration. $R_{p(i)}$, the isotope ratio of water leaving the box as precipitation, is calculated on the basis of eq. (1a) from $R_{(i-1)}$, the isotope ratio of the vapour coming from the preceding box. Then before going through the next calculation loop for the following box, the proper amount of vapour provided by evapotranspiration, based on the soil water isotopic composition, is added to the vapour still in the box. By mixing, one obtains the isotope ratio R_i entering the next box, etc.

A simplifying step can be made by assuming that evapotranspiration is isotopically identical with the precipitation—which in some cases may be a reasonable assumption (see Zimmermann et al., 1967; Münnich, 1978)—so that evapotranspiration acts like a partial ground "reflection" of the precipitation water flux. The remaining water vapour fraction $F(n)$ in box number n can be expressed by the following equation:

$$F(n) = \frac{M - \sum_{i=2}^{n} (P_i - E_{i-1})}{M} \tag{2}$$

where M is the water vapour flux across the western boundary of the system, P_i, E_{i-1} the precipitation and evapotranspiration fluxes in boxes number i and $i-1$, respectively (see the plots in Figs. 5b and c). It should be noted that calculations of $R_{p(i)}$ and $F(n)$ values actually start from box no. 2 (5° W – 0° longitude). Since the region 10° W – 5° W is covered mostly by the ocean, we therefore decided to leave the water vapour flux and its isotopic composition unchanged within this box (thus $F(1) \equiv 1$).

It has been postulated (Rozanski and Sonntag, 1982) that rain leaving the cloud system is in isotopic equilibrium with the water vapour close to the cloud base. Therefore, we adopted the temperature at the 850 mbar level (corresponding to the average cloud base level) as the condensation temperature in selecting the proper isotope fractionation factor. The initial isotopic composition of the water vapour entering the continent has been estimated from the mean monthly δD values of precipitation collected at the Valentia Station, again assuming isotopic equilibrium at the 850 mbar level.

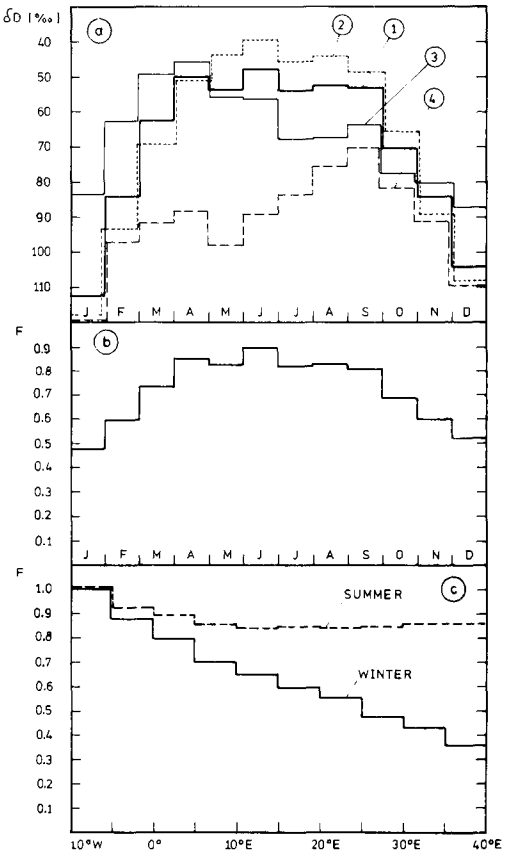

Fig. 5. (a). Model predictions of the seasonal temperature effect in the deuterium isotopic composition of Vienna precipitation. (1)—model prediction of Fig. 4a obtained for the solid histogram water vapour flux in Fig. 4b. (2) to (4)—model parameter modifications of the prediction (1) (see text for details). (b). Seasonal variation in the remaining water vapour fraction, F, characterizing the rainout history of the precipitating air masses (see text), evaluated for the Vienna station. (c). Decrease of water vapour fraction F as obtained in the model as one proceeds from west to east (average values for winter and summer, respectively).

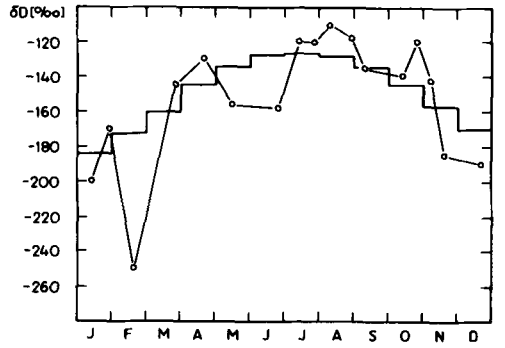

Fig. 6. Observed and predicted seasonal variations of the deuterium content in atmospheric moisture at 850 mbar level. The experimental points are derived from the vertical deuterium profiles measured by Taylor (1972).

Model predictions of the average continental effect for the winter and summer season, respectively, are presented in Figs. 2a and 3a. The same calculation, performed for each individual month separately, further yields a prediction of the seasonal temperature effect at a given place. The comparison between the observed and calculated temperature effect for the Vienna Station is shown in Fig. 4a. The good predictive quality of this model encouraged us to experiment with it to find out which parameters are primarily responsible for the observed stable isotope composition of precipitation at a given place. A few examples of these calculations are summarized in Fig. 5a. As a by-product, the model provides the isotopic composition of the atmospheric water vapour in each box. In Fig. 6 the deuterium content in atmospheric water vapour measured at the 850 mbar level in the Heidelberg region (Taylor, 1972) is compared with the prediction of the model.

3. Discussion

The model proposed provides here, despite its rough character, an acceptable first approximation to the observed variations in isotopic composition of precipitation over the main part of the European continent. The histograms of the continental effect produced by the model generally resemble the experimental data. Model predictions for the summer months (Fig. 3a) reveal the important role of evapotranspiration for the observed inland gradient of deuterium content, especially for the more continental areas. The fact that winter precipitation contributes to summer evapotranspiration has also been considered in the calculations. A rough estimate based on the water mass balance in each box provides a figure of 35% for the mean contribution of the winter precipitation to the summer evapotranspiration in the area in question. Therefore, we adopted this value as an input parameter in a model calculation of the inland gradient of deuterium for the summer months (histogram 2, Fig. 3a). Further calculations showed, however, that the inland δD gradient depends only slightly on the exact size of this fraction. The data points for the Groningen and Sindorf Stations illustrate the variability of the δD values within this specific box. Groningen is a typical coastal station and the influence of the North Sea becomes obvious, particularly in winter. A good insight into the regional distribution of deuterium in precipitation over this part of Europe can be obtained from the isotopic composition map for shallow European groundwaters by Sonntag et al. (1979).

The modifications of the model shown in Fig. 5a are particularly interesting. Keeping the other parameters fixed and assuming a constant condensation temperature (i.e. constant isotope fractionation in the precipitation process) throughout the year, the model yields (histogram 2) an even stronger seasonal temperature effect in the δD values than for the case with the observed temperature variations. This reflects the role of local temperature; lower temperature causes larger isotope fractionation in the local condensation process, and thus leads to isotopically heavier precipitation, counteracting the main effect of low temperature (lower than the ocean evaporation temperature) namely, that it controls the size of F in eq. (1). Further, if the water vapour flux entering the continent is assumed (histogram 3) to remain constant at 93 kg m^{-1} s^{-1} (yearly average value, see Fig. 4b), the seasonal variations of δD are considerably damped. Finally, neglecting evapotranspiration (histogram 4) leads to seasonal δD variations quite different from the observed ones. All these cases are artificial to some extent, since parameters like the water vapour flux or precipitation and evaporation rates depend on temperature. The complete temperature function of the variations observed in stable isotope composition of local precipitation is, however, in no way as

simple as the commonly accepted empirical relation with local temperature (see e.g. Dansgaard, 1964) suggests. The predictions of the model rather indicate that the isotopic composition of local precipitation is related to the whole travel history of precipitating air masses. Such factors as evaporation conditions from the ocean, the mutual relation between precipitation and evapotranspiration over the whole distance to the precipitation place, and possible mixing with other air masses are to be taken into account. From Fig. 5 it becomes evident that the inland gradient as well as the seasonal variations of δD or $\delta^{18}O$ in precipitation are primarily controlled by the remaining fraction, F, of water vapour in the air masses travelling across the continent (cf. eq. (1)). This fraction F comprises the essential information on the previous history of the precipitating air mass. Therefore, the isotopic variations observed in precipitation should rather be discussed in terms of possible changes in F. As we have already mentioned, the crucial influence of the average (e.g. monthly) local temperature lies in the fact that via the vapour saturation pressure curve, it serves together with the ocean evaporation temperature as an overall control on F. It has recently been shown by Kato (1978) that the isotopic composition of snow collected at the Syowa Station in Antarctica is largely controlled by water vapour transport patterns connected with a cyclone activity, but no relation has been observed between measured $\delta^{18}O$ values in snow and the temperature of cloud layers during precipitation events.

Individual fitting for the observed monthly δD values of the Vienna Station with the incoming vapour flux at the western boundary of the whole system as the only open parameter, provides the r.m.s. uncertainty of this flux shown in Fig. 4b in the form of the hatched error bars. Note that the length of each hatched bar originates from the error in the corresponding δD only (observed values in Fig. 4a). Comparison of Figs. 4a and 4b shows that the isotopic composition of precipitation is much less sensitive to changes of the vapour flux in summer than it is in winter. This is mainly caused by the fact that in the Rayleigh equation, the isotopic composition of the water precipitated varies only little with F, when F values are close to unity. The winter δD values of the Vienna precipitation, however, very critically define the incoming vapour flux (Fig. 4b) which comes out close to the January vapour flux value, derived from UNESCO (1978). The solid histogram prediction of our model in Fig. 4a has therefore been based on this value.

Line 3 in Fig. 2 and line 4 in Fig. 3, represent the continental effect of deuterium content in European shallow groundwaters as measured by Sonntag et al. (1979). The position of these lines suggests that both summer and winter precipitations contribute to groundwater formation in Europe. A rough estimate based on Figs. 2a and 3a shows, for example, that for the region 0°–10° E, the contribution of summer precipitation to the total yearly infiltration reaches some 40%. Long-term isotopic lysimeter studies in this area (Blavoux, 1978) also yield a figure of about 40%. The role of summer precipitation in groundwater formation seems, however, to be smaller for more continental areas. This is probably due to the higher summer air temperatures and lower precipitation rates in these regions.

4. Concluding remarks

The most promising application of stable isotopes as a paleoclimatic indicator preserved in ice-cores and ancient groundwaters is still seriously limited by our poor knowledge of all factors controlling the isotopic composition of precipitation. Simple model calculations carried out for the western part of Europe show that the whole history of precipitating air masses must be known if one is to try to predict the isotopic composition of local precipitation. The stable isotope composition of local precipitation is controlled by regional scale processes like the water vapour flux variations in the atmosphere, the evaporation conditions from the ocean, and the precipitation-evapotranspiration rates over the whole distance to the sampling point. Local parameters such as surface and/or cloud base temperature or amount of precipitation modify the isotope ratios only slightly.

The travel history of precipitating air masses is controlled by the prevailing circulation patterns in the atmosphere. If major climatic fluctuations in the past were associated with dramatic changes of atmospheric circulation, it may be that isotopic variations preserved in ice-cores have a quite different relation to the local temperature than that extrapolated from the present situation. Therefore,

any attempts in the quantitative interpretation of stable isotope ratios in ancient precipitation should be preceded by careful examination of possible changes of atmospheric circulation in the past.

An additional difficulty arises when we try to interpret stable isotope ratios observed in ancient groundwaters. In this case one should also take into account the possible modification of the infiltration regime with fluctuating climate. Large seasonal variations observed in stable isotope composition of precipitation, especially for more continental areas, mean that even small changes in average infiltration conditions produce large effects in the isotopic composition of groundwater. This effect is independent of the long-term fluctuations of the stable isotope composition of precipitation. For example, warm and dry surface atmosphere conditions can reduce the contribution of summer precipitation to the yearly infiltration, whereas the stable isotope ratios of newly formed groundwater will rather suggest a generally cooler climate.

Further investigations into the influence of the climate on stable isotope ratios observed in precipitation and groundwaters are highly desirable. It is believed that combined isotopic studies of such materials as lake deposits, speleotherms, tree rings, and subglacially precipitated calcite can significantly improve our knowledge of the problem.

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