

An 8-year record of the seasonal variation of ^2H and ^{18}O in atmospheric water vapour and precipitation at Heidelberg, Germany

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ABSTRACT

Continuous time series of δD and $\delta^{18}\text{O}$ in atmospheric water vapour and precipitation at Heidelberg are presented for the years 1981 to 1988. It is often not possible to derive the isotopic composition of the water vapour from the isotopic composition of precipitation for individual months. However, a close relationship does exist between the isotopic composition of the vapour and the precipitation on a timescale of a few years. The correlation of isotopic composition with temperature is much better for the vapour data than for the precipitation data. The $\Delta\delta/\Delta T$ relationship of the seasonal variations is itself a function of temperature, being much lower during warmer periods than during cold periods. Especially during summer months, the admixture of water vapour originating from plant transpiration plays an important role in biasing the $\Delta\delta/\Delta T$ relationship towards lower values. This effect complicates the calculation of paleotemperatures using isotopic data.

1. Introduction

The content of the stable isotopes ^2H (deuterium = D) and ^{18}O in a water sample is usually expressed as the deviation from Standard Mean Ocean Water (SMOW)

$$\delta_{\text{sample}} = \frac{R_{\text{sample}} - R_{\text{SMOW}}}{R_{\text{SMOW}}} \cdot 1000 \text{ (in } \text{‰}), \quad (1)$$

where R is the isotopic ratio of the sample (e.g., $R = ^2\text{H}/^1\text{H}$). Spatial and temporal variations of δD or $\delta^{18}\text{O}$ in atmospheric water vapour and in precipitation are caused by isotopic fractionation associated with evaporation and condensation processes during the global water vapour circulation. In these phase transitions, the isotopically labelled water molecule species HDO and H_2^{18}O preferentially remain in the liquid phase or are transferred into the liquid phase. Thus, precipitating air masses are progressively being depleted in ^2H and ^{18}O during the process of moist adiabatic cooling. This explains why the observed variations of δD and $\delta^{18}\text{O}$ in precipitation are

correlated with local temperature variations (“temperature effect”).

Variations of δD or $\delta^{18}\text{O}$ measured in ice cores, groundwater or plant material (tree rings) are interpreted as indicators for changing climatic conditions in the past. But up to now, the problem of how to *quantify* differences in isotopic composition, for example, as temperature differences, has not been satisfactorily solved. In most cases, it is difficult to establish the proper relationship between the apparent isotopic variations and the underlying variations in temperature.

The isotopic composition of groundwater, glaciers and polar ice sheets is directly derived from precipitation in the past. To understand the processes underlying the isotopic variations in precipitation, it is necessary to first determine how the isotopic composition of *modern* precipitation is linked to the climatic conditions *of today*. Due to the worldwide precipitation sampling network established by the IAEA and the WMO, an extensive isotopic data set does exist for recent precipitation, which was already statistically analysed (see, e.g., Yurtsever and Gat, 1981). To

obtain a physical understanding of the changing isotopic composition in precipitation, a model of the global water vapour transport including stable isotopes is necessary (Eriksson, 1965; Sonntag et al., 1983). Model simulations of spatial and temporal variations of δD or $\delta^{18}O$ in the local water vapour and precipitation should be based on continuous time series of the isotopic composition of atmospheric water vapour (which is continuously available) rather than on isotopic data of precipitation (which is derived from the water vapour in a more or less sporadic manner).

Continuous measurements of stable isotopes in atmospheric water vapour at ground level (sampling periods: 1 or 2 days) and in the local precipitation (sampling intervals: 1 to 7 days, depending on the amount of precipitation) at Heidelberg (49.8° N, 8.7° E, 110 m a.s.l.) started in June 1980. The data from June 1980 until April 1983 and the sampling procedure are published elsewhere (Schoch-Fischer et al., 1984). During the years 1981, 1982 and 1983, a sampling network was in operation which included Paris (France), Hannover (Germany) and Cracow (Poland). This study showed that temporal changes in isotopic composition of local water vapour on a time scale of a few days are dominated by the large-scale synoptic weather patterns, variations in the degree of rainout of the moisture in the air masses concerned being the most important parameter

(Schoch-Fischer et al., 1984). A precipitation sampling program in Israel yielded similar results (Rindsberger et al., 1990). Now, continuous time series of isotopic data for atmospheric water vapour and precipitation at Heidelberg are available which range over more than 8 years. This long record makes it possible to better investigate the seasonal variations of the isotopic composition in water vapour and precipitation. To obtain a better comparison with the data from the IAEA/WMO precipitation network, monthly mean values of δD and $\delta^{18}O$ in atmospheric water vapour and precipitation at Heidelberg were calculated. The statistical treatment of these data was guided by two questions.

(1) Is it possible to calculate the isotopic composition of local water vapour if the isotopic composition of precipitation is known?

(2) What is the relationship between seasonal variations in isotopic composition and changes in temperature?

2. Results and discussion

In Table 1, monthly means of δD and $\delta^{18}O$ in atmospheric water vapour and precipitation at Heidelberg are presented for the years 1981 to 1988 together with the amount of precipitation

Table 1. *Monthly mean values and yearly mean values of $\delta^{18}O$ and δD in atmospheric water vapour and precipitation, the ground-air temperature and the amount of precipitation at Heidelberg, FRG, for the years 1981 to 1988*

		$\delta^{18}O_v$ (‰)	δD_v (‰)	$\delta^{18}O_p$ (‰)	δD_p (‰)	T (°C)	P (mm)
Jan	81	-20.41	-151.3	-9.23	-63.4	-0.5	78.75
Feb	81	-21.72	-163.7	-9.90	-76.2	1.3	34.93
Mar	81	-18.10	-132.7	-6.16	-43.7	9.1	78.51
Apr	81	-18.23	-133.2	-13.10	-92.3	10.7	59.00
May	81	-17.74	-131.4	-7.55	-53.8	14.7	94.25
Jun	81	-16.31	-119.4	-5.70	-39.6	17.4	69.69
Jul	81	-15.39	-112.4	-4.79	-31.5	18.5	79.60
Aug	81	-15.80	-113.9	-3.32	-20.7	18.7	54.39
Sep	81	-16.65	-120.3	-4.76	-32.3	16.2	45.06
Oct	81	-19.09	-138.1	-9.49	-65.6	9.7	117.07
Nov	81	-19.06	-135.3	-9.32	-61.8	6.3	52.45
Dec	81	-24.90	-180.1	-11.99	-88.7	0.3	107.10
		-18.62	-136.0	-8.15	-57.3	10.2	870.8

Table continued

Table 1. *Continued.*

	$\delta^{18}\text{O}_V$ (‰)	δD_V (‰)	$\delta^{18}\text{O}_P$ (‰)	δD_P (‰)	T (°C)	P (mm)
Jan 82	-25.25	-186.8	-10.77	-83.0	-1.4	44.60
Feb 82	-23.67	-174.8	-8.79	-69.2	1.6	24.45
Mar 82	-19.64	-142.9	-7.65	-56.7	6.1	35.50
Apr 82	-20.06	-146.7	-4.84	-28.8	9.1	35.65
May 82	-17.46	-128.1	-7.36	-50.9	14.4	68.20
Jun 82	-15.59	-116.3	-5.51	-37.9	18.8	65.25
Jul 82	-14.89	-107.3	-5.49	-37.9	21.5	58.75
Aug 82	-15.00	-108.0	-6.52	-45.0	19.2	34.20
Sep 82	-14.96	-107.5	-5.76	-39.1	17.9	38.05
Oct 82	-20.13	-148.1	-11.68	-83.9	10.4	111.90
Nov 82	-19.03	-146.1	-12.64	-94.1	7.2	36.40
Dec 82	-21.11	-157.2	-11.32	-91.5	4.0	84.50
	-18.90	-139.2	-8.61	-63.0	10.7	637.45
Jan 83	-17.66	-129.6	-6.21	-45.0	5.0	51.15
Feb 83	-24.99	-184.2	-10.72	-89.7	0.8	38.30
Mar 83	-18.98	-141.8	-7.85	-59.1	6.3	58.40
Apr 83	-19.24	-142.9	-9.16	-70.1	10.8	82.94
May 83	-17.55	-131.1	-7.73	-52.5	12.5	155.40
Jun 83	-15.84	-116.6	-5.29	-37.4	18.7	24.36
Jul 83	-15.59	-116.0	-6.01	-44.3	23.4	20.00
Aug 83	-16.24	-118.0	-3.87	-29.5	21.2	13.30
Sep 83	-15.30	-111.2	-4.52	-29.0	15.7	61.80
Oct 83	-15.61	-112.6	-4.73	-27.9	10.5	37.16
Nov 83	-19.32	-139.8	-8.28	-60.2	3.9	28.38
Dec 83	-21.58	-157.6	-8.55	-67.1	1.3	32.90
	-18.16	-133.5	-7.32	-53.1	10.8	604.09
Jan 84	-20.14	-146.3	-9.14	-67.8	3.2	48.27
Feb 84	-23.14	-173.5	-10.31	-73.3	2.2	41.05
Mar 84	-22.70	-169.5	-11.13	-87.5	4.4	27.10
Apr 84	-22.89	-171.0	-11.09	-85.6	8.9	21.40
May 84	-20.69	-154.0	-9.60	-67.8	12.0	146.19
Jun 84	-17.33	-128.5	-6.11	-46.8	16.1	73.69
Jul 84	-16.14	-120.8	-7.35	-53.6	18.6	59.26
Aug 84	-16.70	-121.8	-5.42	-36.8	18.9	41.00
Sep 84	-17.33	-125.4	-7.01	-46.8	14.2	99.10
Oct 84	-17.85	-131.9	-10.13	-74.5	11.4	40.50
Nov 84	-20.03	-146.0	-8.13	-55.9	5.6	38.10
Dec 84	-20.87	-156.2	-11.23	-85.6	2.5	29.80
	-19.65	-145.4	-8.36	-61.4	9.8	665.46
Jan 85	-26.57	-197.6	-10.47	-78.5	-3.4	34.28
Feb 85	-23.62	-178.1	-12.08	-92.6	-1.3	25.30
Mar 85	-22.48	-168.5	-10.66	-81.1	5.2	26.94
Apr 85	-17.42	-129.1	-6.30	-44.7	10.2	36.80
May 85	-17.37	-128.2	-6.25	-42.9	15.3	85.30
Jun 85	-16.74	-122.7	-7.68	-55.6	15.9	52.80
Jul 85	-15.15	-109.4	-4.64	-24.7	20.4	57.70
Aug 85	-15.01	-109.1	-4.05	-33.3	18.3	48.40
Sep 85	-14.55	-105.5	-3.48	-18.1	16.0	21.90
Oct 85	-16.93	-123.6	-3.75	-21.0	9.7	6.00
Nov 85	-25.82	-187.4	-11.75	-85.7	1.9	58.70
Dec 85	-19.64	-145.8	-12.14	-94.9	4.6	46.50
	-19.28	-142.1	-7.87	-56.9	9.4	500.62

Table continued

Table 1. *Continued.*

		$\delta^{18}\text{O}_V$ (‰)	δD_V (‰)	$\delta^{18}\text{O}_P$ (‰)	δD_P (‰)	T (°C)	P (mm)
Jan 86		-20.82	-153.0	-9.38	-68.9	2.7	45.00
Feb 86		-28.44	-222.8	-22.64	-176.5	-3.1	4.30
Mar 86		-20.81	-156.9	-9.14	-76.1	5.4	58.40
Apr 86		-20.32	-151.4	-9.93	-75.7	8.5	71.70
May 86		-16.71	-124.9	-6.01	-39.7	16.3	49.67
Jun 86		-19.44	-147.2	-9.73	-73.0	18.8	61.60
Jul 86		-15.92	-117.3	-5.64	-40.7	19.2	35.20
Aug 86		-15.67	-113.8	-5.39	-35.0	18.9	95.10
Sep 86		-16.64	-123.3	-8.12	-57.3	13.2	72.30
Oct 86		-15.86	-117.2	-7.71	-51.9	10.8	82.90
Nov 86		-18.00	-134.0	-7.16	-47.3	6.5	18.20
Dec 86		-19.67	-144.2	-7.92	-57.3	3.9	40.60
		-19.03	-142.2	-7.96	-57.6	10.1	634.97
Jan 87		-24.61	-181.4	-8.71	-60.4	-3.5	32.30
Feb 87		-22.24	-168.9	-8.31	-74.3	1.5	65.60
Mar 87		-22.71	-168.5	-9.78	-74.0	2.9	57.60
Apr 87		-17.62	-131.9	-2.84	-28.5	11.7	27.10
May 87		-17.47	-130.5	-7.60	-55.7	11.9	79.90
Jun 87		-16.96	-126.3	-7.84	-56.6	15.9	126.50
Jul 87		-15.76	-116.9	-6.70	-47.4	19.4	121.75
Aug 87		-15.28	-114.4	-4.80	-33.0	18.0	48.00
Sep 87		-14.62	-106.9	-5.36	-36.4	17.3	63.90
Oct 87		-17.93	-132.8	-8.54	-62.4	11.1	63.13
Nov 87		-20.62	-156.0	-10.04	-72.5	6.0	75.00
Dec 87		-20.58	-157.3	-6.72	-53.1	3.1	28.20
		-18.87	-141.0	-7.52	-55.8	9.6	788.98
Jan 88		-19.38	-150.5	-7.39	-59.9	4.9	66.70
Feb 88		-20.26	-149.6	-9.79	-75.9	3.7	45.90
Mar 88		-19.51	-143.9	-8.26	-62.5	5.4	109.30
Apr 88		-18.53	-136.5	-9.32	-70.3	10.5	50.00
May 88		-15.90	-116.3	-4.99	-33.6	16.3	56.40
Jun 88		-16.03	-119.0	-6.00	-44.3	17.2	40.50
Jul 88						18.8	
Aug 88						19.6	
Sep 88		-15.63	-112.8			15.1	
Oct 88		-16.94	-122.8			11.5	
Nov 88		-19.18	-139.2			4.1	
Dec 88		-18.16	-133.6			5.1	

and the monthly mean temperature. The precipitation data are weighted means, while the vapour data and the temperatures are presented as arithmetic means. As there are no precipitation data available from July 1988 to December 1988, the following statistical treatment includes only the months from January 1981 to June 1988 (totalling 90 months).

2.1. Comparison between water vapour and precipitation

Schoch-Fischer et al. (1984) presented $\delta\text{D}/\delta^{18}\text{O}$ -correlations (including all data until April 1983) for Heidelberg, Cracow, and Paris. The slope of the correlation is close to 8 for the precipitation samples (values: 7.8, 7.9 and 7.9,

respectively), while the water vapour data had smaller slopes of 7.4 (Heidelberg), 6.8 (Cracow) and 7.0 (Paris).

The much bigger data set now available for Heidelberg produces slightly different correlations

$$\delta\text{D}_{\text{prec}} = (8.06 \pm 0.14) \cdot \delta^{18}\text{O}_{\text{prec}} + (5.9 \pm 3.7), \quad (r = 0.988); \quad (2)$$

$$\delta\text{D}_{\text{vap}} = (7.71 \pm 0.08) \cdot \delta^{18}\text{O}_{\text{vap}} + (6.0 \pm 2.4), \quad (r = 0.995), \quad (3)$$

which come closer to the Meteoric Water Line $\delta\text{D} = 8 \cdot \delta^{18}\text{O} + 10$ (Craig, 1961). Calculation of mean values of the deuterium excess $d = \delta\text{D} - 8 \cdot \delta^{18}\text{O}$ yielded $d_{\text{prec}} = 5.89\text{‰}$ and $d_{\text{vap}} = 11.44\text{‰}$. The fact that the d -value of the precipitation samples is significantly lower than that of the vapour samples may be caused by partial evaporation of raindrops beneath the cloud-base level. This process decreases the d of the liquid phase and increases the d of the vapour phase (Yurtsever and Gat, 1981). A higher d of the vapour might also be caused by an admixture of water vapour evaporated from bare soil, which is more depleted in ^{18}O due to kinetic fractionation and hence has a higher d . Plant transpiration, however, does not produce a fractionation between the two isotopes in the released vapour.

In general, the isotopic composition of the precipitation was fairly close to the isotopic composition of water, being in equilibrium with the water vapour at ground level. Some precipitation samples, however, showed rather large deviations from this equilibrium value. During periods of rainfall, these deviations occurred in both directions. During periods of snowfall, a systematic shift was observed: the precipitation was always isotopically "too light" compared with the vapour. This could be due to an incomplete isotopic exchange between falling snow-flakes and water vapour near ground level.

The correlation between the isotopic composition of precipitation and water vapour (monthly means) yields the relationships

$$\delta\text{D}_{\text{vap}} = (0.84 \pm 0.062) \cdot \delta\text{D}_{\text{prec}} - (91 \pm 13.8), \quad (r = 0.82); \quad (4)$$

$$\delta^{18}\text{O}_{\text{vap}} = (0.84 \pm 0.072) \cdot \delta^{18}\text{O}_{\text{prec}} - (12.2 \pm 1.97), \quad (r = 0.78). \quad (5)$$

As can be seen from the rather low correlation coefficients, these relationships are often not applicable for individual months. Using the monthly means of δD and $\delta^{18}\text{O}$ in precipitation we calculated a theoretical vapour that would be in equilibrium with the precipitation (δ_{eqvap}). The equilibrium fractionation factors used were calculated by inserting the monthly means of the air temperature into the formulas given by Majoube (1971). If there was a complete equilibrium between the vapour and the precipitation and if the monthly precipitation was indeed representative for the whole month, then the calculated values should be rather close to the measured monthly means (δ_{vap}). The relationships for the whole data set are:

$$\delta\text{D}_{\text{eqvap}} = (1.00 \pm 0.054) \cdot \delta\text{D}_{\text{vap}} - (2 \pm 12), \quad (r = 0.89); \quad (6)$$

$$\delta^{18}\text{O}_{\text{eqvap}} = (0.90 \pm 0.062) \cdot \delta^{18}\text{O}_{\text{vap}} - (1.4 \pm 1.82), \quad (r = 0.84). \quad (7)$$

The correlation of the deuterium data coincides with the expected linear relationship, and the ^{18}O -correlation comes close to it. However, a closer inspection of the data shows that there are rather large deviations of the calculated δ_{eqvap} from the measured δ_{vap} for individual months (Fig. 1). Because they occur in both directions they almost equalize each other on the given time scale of some years. For individual months, the isotopic composition of the water vapour cannot be derived from the isotopic composition of the precipitation while a good correlation does exist between the vapour and precipitation on the time scale of some years. On such a long time scale, it seems possible to derive the isotopic composition of atmospheric water vapour from the isotopic composition of precipitation (at least under humid climatic conditions). For the investigation of short-term variations it is always preferable to measure the isotopic composition of the water vapour directly.

2.2. Correlation between isotopic composition and temperature

From a physical point of view no *direct* correlation exists between the isotopic composition of water vapour or precipitation with temperature. Variations in the isotopic composition are caused

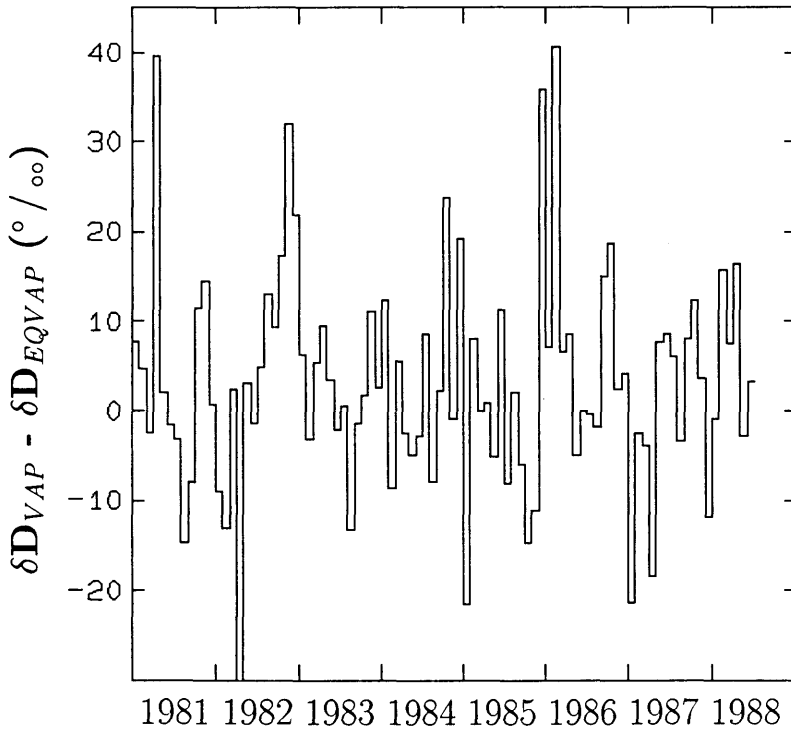


Fig. 1. The differences between the measured monthly means of δD in atmospheric water vapour at Heidelberg (δD_{vap}) and the δD of water vapour calculated from the monthly means of local precipitation under the assumption that it is in isotopic equilibrium with the precipitation at ground air temperature (δD_{eqvap}).

by isotopic fractionation resulting from condensation and evaporation processes during the circulation of atmospheric water vapour. Water loss caused by moist adiabatic cooling of air masses leads to a progressive depletion of the heavy isotopes in the remaining water vapour, which can be described by a Rayleigh condensation formula (Dansgaard, 1964). This formula links the isotopic ratio R of the water vapour to the moisture content of the local atmosphere, i.e., to the local precipitable water W :

$$\frac{R}{R_0} = \left(\frac{W}{W_0} \right)^{\alpha_e - 1} \quad (8)$$

$R_0 = R_{\text{SMOW}}/\alpha_0$ denotes the initial isotopic composition of the water vapour in the source region. The precipitable water $W = \int_0^\infty q(z) dz$ is given as the vertically integrated tropospheric water vapour content q . $W/W_0 < 1$ represents the degree of rainout of the precipitating air mass. $\alpha_e = \alpha_e(T)$

is the isotopic fractionation factor between the local water vapour and the condensate derived from it. T represents the air temperature at ground level (see Sonntag et al., 1983).

Variations in the mean monthly values of the isotopic composition of the local water vapour at Heidelberg can be explained by a water vapour advection model, assuming a Rayleigh condensation process along the course of the water vapour transport (Schoch-Fischer et al., 1984).

As can be seen from eq. (8), the isotopic composition of the local water vapour is mainly determined by the degree of rainout of the moist air mass and not by the local temperature. Nevertheless, it is often useful to establish a relationship between the variation of the isotopic composition ($\Delta\delta$) and the temperature variation (ΔT). Especially when paleotemperatures are calculated, for example from differences in isotopic composition between recent and ancient groundwaters, $\Delta\delta/\Delta T$ relationships are often used (e.g., Rozanski, 1985).

But the $\Delta\delta/\Delta T$ relationship itself is a function of temperature. Its temperature dependence was calculated by Dansgaard (1964, see especially p. 441–443). In this fundamental paper he showed that $\Delta\delta/\Delta T$ increases with increasing difference between the initial and the final temperature of the Rayleigh condensation process which the water vapour undergoes. $\Delta\delta/\Delta T$ also was shown to increase with decreasing initial temperature. The formula given by Dansgaard is very complicated, however.

Assuming that the temperature in the water vapour source region (e.g., the (sub)tropical North Atlantic) is almost constant during the year, Sonntag et al. (1983) calculated that the temperature variation of the isotopic composition in local water vapour and precipitation can be written as

$$\Delta\delta/\Delta T \approx (\alpha_e - 1) \left(\frac{dW}{dT} \frac{1}{W} \right) = (\alpha_e - 1)/T_0, \quad (9)$$

with an exponential temperature dependence of the local precipitable water $W(T) \sim e^{T/T_0}$ ($T_0 = 15^\circ\text{C}$).

The empirical relationship

$$\delta^{18}\text{O}_{\text{prec}} = 0.69T - 13.6, \quad (10)$$

which Dansgaard obtained for yearly mean values mainly from Greenland stations, is valid only for such regions with low temperatures. Rozanski et al. (1982) showed that the $\Delta\delta/\Delta T$ value of precipitation in western and central Europe increases with increasing distance from the Atlantic Ocean. By evaluating the data from the IAEA/WMO precipitation network Yurtsever and Gat (1981) found that

$$\delta^{18}\text{O}_{\text{prec}} = (0.34 \pm 0.03) T - 12.0 \quad (r = 0.785), \quad (11)$$

which is a worldwide median value for all network stations. However, their $\Delta\delta/\Delta T$ plot for all stations shows clearly that the $\Delta\delta/\Delta T$ relationship varies strongly, being low for the stations in high temperature regions and high in the low temperature areas.

Schoch-Fischer et al. (1984) reported for Cracow $\Delta\delta\text{D}/\Delta T = 3.3 \pm 0.3\text{‰}/^\circ\text{C}$ (vapour) and

$\Delta\delta\text{D}/\Delta T = 3.0 \pm 0.5\text{‰}/^\circ\text{C}$ (precipitation) and for Heidelberg (data until April 1983) $\Delta\delta\text{D}/\Delta T = 2.8 \pm 0.2\text{‰}/^\circ\text{C}$ (vapour) and $\Delta\delta\text{D}/\Delta T = 2.2 \pm 0.4\text{‰}/^\circ\text{C}$ (precipitation). The presently available data set for Heidelberg (until June 1988) yielded for the water vapour

$$\delta\text{D}_{\text{vap}} = (3.00 \pm 0.18) T - (169 \pm 12.0), \quad (r = 0.87), \quad (12)$$

$$\delta^{18}\text{O}_{\text{vap}} = (0.39 \pm 0.023) T - (22.8 \pm 1.50), \quad (r = 0.88), \quad (13)$$

and for the precipitation

$$\delta\text{D}_{\text{prec}} = (2.32 \pm 0.246) T - (82 \pm 17.4), \quad (r = 0.68), \quad (14)$$

$$\delta^{18}\text{O}_{\text{prec}} = (0.28 \pm 0.033) T - (10.8 \pm 2.2), \quad (r = 0.67). \quad (15)$$

The $\Delta\delta/\Delta T$ relationship is significantly smaller for the precipitation samples than for the vapour samples, whereas the equilibrium vapour ($\delta_{\text{eq,vap}}$), calculated from the precipitation data (see above), has almost the same slopes as the measured vapour ($\Delta\delta\text{D}/\Delta T = 3.17 \pm 0.24\text{‰}/^\circ\text{C}$, $\Delta\delta^{18}\text{O}/\Delta T = 0.37 \pm 0.033\text{‰}/^\circ\text{C}$). The difference between the $\Delta\delta/\Delta T$ relationships for water vapour and precipitation is at least partly caused by the non-linear temperature dependence of the fractionation factors.

The linear approximation was calculated to make comparison of our data with other results easier. In fact, a quadratic solution is in better agreement with our data:

$$\delta\text{D}_{\text{vap}} = -0.11T^2 + 5.17T - 175, \quad (16)$$

$$\delta^{18}\text{O}_{\text{vap}} = -0.014T^2 + 0.67T - 23.4. \quad (17)$$

In Fig. 2, this correlation, together with the linear fit, is shown for δD . From this plot it is obvious that the $\Delta\delta/\Delta T$ relationship varies with temperature. By separating our data in 3 groups of different temperature range we found:

- (1) $T \leq 5^\circ\text{C}$ (27 pairs of data)

$$\delta\text{D}_{\text{vap}} = (6.3 \pm 1.0) T - (177 \pm 12.8), \quad (r = 0.78); \quad (18)$$

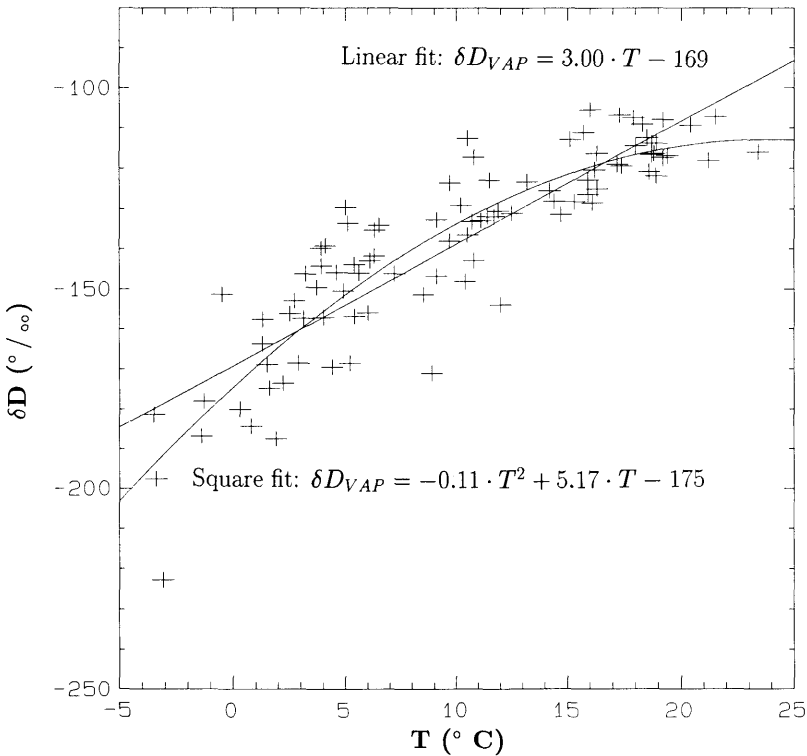


Fig. 2. δD in atmospheric water vapour versus air temperature (T) at ground level (monthly means from January 1981 to June 1988).

(2) $5^{\circ}\text{C} < T \leq 15^{\circ}\text{C}$ (33 pairs of data)

$$\delta D_{\text{vap}} = (2.6 \pm 0.7) T - (164 \pm 11.2)$$

$$(r = 0.56); \tag{19}$$

(3) $15^{\circ}\text{C} < T$ (30 pairs of data)

$$\delta D_{\text{vap}} = (1.0 \pm 0.82) T - (135 \pm 8.5)$$

$$(r = 0.22). \tag{20}$$

The same correlations for the precipitation data yielded comparable results, however, with much worse correlation coefficients ($r = 0.41, 0.25,$ and $0.04,$ respectively). For monthly mean temperatures above 15°C no correlation at all exists between δD_{prec} and T ($r = 0.04!$).

The slopes decrease much more strongly with increasing temperature than would be expected from the temperature dependence of the fractiona-

tion factor α_e in formula 9. Table 2 shows a comparison between the theoretical and experimental values. While during low temperature periods both values are rather close together, large differences occur for medium and especially for high temperatures. These differences can be explained by the influence of water vapour released by plant transpiration. The admixture of this vapour disturbs the isotopic composition of atmospheric water vapour, because the plants transpire soil moisture being a mixture of precipitation which infiltrated days, weeks or months before the actual data. Thus, plant transpiration smoothes out isotopic variations in atmospheric water vapour and by these means it destroys the correlation of the isotopic composition of water vapour with the local temperature. The release of water vapour by plant transpiration is, of course, not a local phenomenon, but occurs along the path of an air mass over the continental area. In Fig. 3, the mean

Table 2. Comparison between the experimentally determined $\Delta\delta/\Delta T$ relationships and theoretical values calculated with formula 9 for different temperatures; the last column (Transp) shows the calculated share of water vapour released by plant transpiration (for explanation see text)

T ($^{\circ}\text{C}$)	$\Delta\delta\text{D}/\Delta T_{\text{exp}}$ ($^{\circ}/_{\text{oo}}/^{\circ}\text{C}$)	$\Delta\delta\text{D}/\Delta T_{\text{theo}}$ ($^{\circ}/_{\text{oo}}/^{\circ}\text{C}$)	Transp (%)
<5	6.3 ± 1.0	7.5 (0°C)	15
5–15	2.6 ± 0.7	6.5 (10°C)	60
>15	1.0 ± 0.8	5.7 (20°C)	80

monthly values of the ground air temperature and of δD in atmospheric water vapour are presented for the period from January 1981 to December 1988. It can be clearly seen that there is a systematic deviation between the two curves. In spring and early summer (April to July), the δD of water vapour is "too low" and in late summer and fall (especially in September and October) the δD of the vapour is "too high" compared with the seasonal variation of the temperature. Due to the influence of plant transpiration the mean isotopic composition of the vapour remains virtually constant during the months of July to September, which explains why the $\Delta\delta\text{D}/\Delta T$ correlation for months with $T > 15^{\circ}\text{C}$ has a slope of only 1.0 and a very low correlation coefficient ($r = 0.22$).

With the simplifying assumption that the isotopic composition of water vapour which was released by plant transpiration is not correlated

with temperature ($\Delta\delta/\Delta T = 0$) the share of water vapour released by plant transpiration was calculated for different temperatures (see Table 2).

The correlations of yearly mean values (1981 to 1987) of the isotopic composition of atmospheric water vapour with temperature yielded steeper slopes than the correlations of monthly means:

$$\delta\text{D}_{\text{vap}} = (5.3 \pm 2.4) T - (194 \pm 3.1),$$

$$(r = 0.70), \quad (21)$$

$$\delta^{18}\text{O}_{\text{vap}} = (0.60 \pm 0.29) T - (25.0 \pm 0.4),$$

$$(r = 0.68). \quad (22)$$

The uncertainty of the slopes of the correlation lines is high, presumably because of the small range in yearly mean temperatures during our eight year record (only between 9.4 and 10.8°C). Therefore, it is doubtful if one can conclude from equations 21 and 22 that the $\Delta\delta/\Delta T$ relationships are higher for yearly mean values than for monthly means.

Yearly weighted means of the isotopic composition of precipitation showed no correlation with temperature ($r < 0.1$), which is compatible with a similar result for 5 Swiss stations (Siegenthaler and Oeschger, 1980). The lack of correlation shows that within small temperature ranges (e.g., 1.4°C), the scatter in the precipitation data destroys the correlation between isotopic composition and the air temperature, while a correlation still exists for the water vapour data.

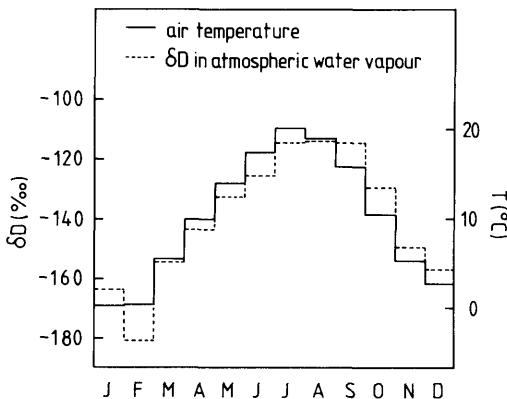


Fig. 3. Mean monthly values of the air temperature (T) and of δD in atmospheric water vapour over the period 1981 to 1987. The scaling factor between T and δD was derived from eq. (12) (see text).

3. Conclusions

Under the prevailing climatic conditions of central Europe, it is possible to derive the isotopic

composition of the precipitation from the isotopic composition of the local water vapour on a time scale of a few years. For individual months, however, there are often rather large differences between the measured value of the vapour and the calculated values of a vapour that would be in isotopic equilibrium with the precipitation at ground air temperature. Therefore, water vapour data are necessary to investigate the causes for short-term isotopic variations. On longer time scales (climatological periods), precipitation data might be sufficient. However, as far as δD and $\delta^{18}O$ in tree rings as paleoclimatic indicators are concerned, the investigation of short-term variations of the isotopic composition in atmospheric water vapour is necessary since the isotopic composition of plant cellulose is strongly affected by the local water vapour during the growing season.

The $\Delta\delta/\Delta T$ relationship ("temperature effect") for atmospheric water vapour at Heidelberg is much smaller in summer than in winter. This can only partly be explained by the temperature dependence of the fractionation factor α_e . The main reason for the observed effect is the admixture of water vapour originating from plant transpiration to the atmospheric water vapour. The latter process is most important during summer and reduces the $\Delta\delta/\Delta T$ relationship. It is likely that the $\Delta\delta/\Delta T$ relationship was higher in the past

during colder climatic conditions than at present. Therefore, temperature differences between the last ice age and the recent climate calculated from differences in isotopic composition between, e.g., recent and ice age formed groundwaters by using the modern $\Delta\delta/\Delta T$ relationship are probably too high. Or, in other words, the thus derived paleotemperatures are too low.

This adds another difficulty to the already existing problems for the calculation of paleotemperatures using isotopic data. Even if the basic assumption holds that there exists a good analogy between the *seasonal* variations of today and the *climatic changes* of the past, one has to make sure that (a) the water vapour circulation pattern did not change too much and (b) the proportion of summer and winter precipitation, which was deposited on glaciers or which infiltrated to form groundwater was about the same.

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