On the deuterium-salinity relationship in the Baltic Sea

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ABSTRACT

Two vertical deuterium profiles at the Bornholm Basin in the Baltic Sea are described. Both profiles show a uniform deuterium content from the surface down to about 40 m. At greater depths the deuterium content increases. Supplemented by measurements of Friedman (1964) the usual linear relationship between deuterium content and salinity is established. This linear relationship is also derived theoretically from the consideration of a box model and the resulting balance equations for water, salinity and isotopes in the upper layer. Comparison of the experimental and theoretical deuterium-salinity relationship yields ratios of hydrographic parameters such as the ratio of annual evaporation to fresh water inflow, which in the case of the Baltic Sea can be checked with the known value.

Introduction

The heavy hydrogen isotope, deuterium, is present in natural water with a concentration of about 150 parts per million. Already the first investigations demonstrated large variations of the natural deuterium content, but precise and reliable data have only been obtained since the use of masspectrometric analysis techniques (Friedman, 1953).

The variation of the deuterium content in natural waters is caused by the slightly different vapor pressures, P_{H_2O}, P_{HDO}, of the isotopic water molecules H_2O and HDO. HDO, being less volatile than H_2O, is enriched in the condensed phase. This isotopic fractionation is usually expressed by the equilibrium fractionation factor $\alpha = P_{H_2O}/P_{HDO}$, which increases with decreasing temperature ($\alpha = 1.079$ at 20°C). The isotopic ratio R_L of the liquid ($R = D/H$) is then related to the isotope ratio R_v of the vapor by

$$R_L = \alpha \cdot R_v.$$

The same is true for the heavy oxygen isotope, oxygen-18. It is customary to express the D-content and oxygen-18-content as relative deviation from the isotopic content of standard mean ocean water, SMOW, (Craig, 1961*a*):

$$\delta = 1000 \cdot \left(\frac{R_{sa}}{R_{smow}} - 1 \right) \text{ in } ‰$$

R is the Isotope ratio of sample and standard respectively. A deuterium δ-value of—10‰ indicates that the water sample contains 10‰ less deuterium than ocean water. Due to the fractionation oceanic water vapor is depleted in the heavy isotopes relative to ocean water. Furthermore, as the heavy isotopes are also condensed more readily, continuing condensation and precipitation leads to a depletion of the heavy isotopes in the water vapor of an air mass. Accordingly rain falling at the later stages of the condensation process contains less deuterium than at the beginning. Thus rain and fresh water in central Europe have a deuterium content of about $\delta = -70‰$, whereas ocean surface water is very close to $\delta = 0‰$.

It has been shown that condensation indeed takes place under equilibrium conditions (cf. Dansgaard, 1964). In this case the variations of oxygen-18 content and deuterium content are parallel:

$$\delta_D = 8 \cdot \delta_0 + 10 \text{ (Craig, 1961}b\text{)}.$$

Evaporation usually takes place under non-equilibrium conditions. Then a kinetic fractionation is superimposed on the equilibrium fractionation which is much greater for oxygen-18 than for deuterium (Ehhalt & Knott, 1965). The δ-values of deuterium and oxygen-18 are still proportional, however the slope changes from 8 to about 5 (cf. Craig, 1961*b*).

There have been several attempts to study the evaporation of lakes using the fact that the isotopic fractionation enriches the heavy isotopes in the remaining water (cf. Friedman, 1964). If the δ-values of deuterium and oxygen-18 of the inflowing and outflowing water, of the water vapor and of the lake are known, balance equations of the isotopes can be set up.

Assuming steady conditions these equations have been solved for the hydrologic parameters like annual evaporation, precipitation and inflow. In a recent, extensive study, Craig & Gordon, 1965, applied the same considerations to the mixed layer of the ocean. They attempted to characterize sea water by its isotopic composition to add another tool to the conventional means of temperature and salinity measurements. Using some model assumptions for the open ocean, they point out that oceanographic parameters such as annual precipitation, evaporation, and mixing of the surface layer with the water below the thermocline can be calculated if a complete set of isotopic data is available in addition to salinity measurements. Actually only the ratios of these parameters can be obtained.

In this paper the concept of the isotopic balance equations is applied to the Baltic Sea. The water balance of the Baltic Sea has been studied fairly extensively and annual precipitation, evaporation and fresh water inflow are known. Thus we can use it as a test case. The validity of the model used can be checked directly by comparing the ratios of these parameters with those calculated from the isotopic balance.

The D-content has been measured by the usual mass spectrometric analysis (cf. Friedman, 1953), using an Atlas MS 86 mass spectrometer. The technique used for the quantitative conversion of water to H_2, which serves as sample gas, is also described by Friedman, 1953.

The standard deviation of the δ-value is $\pm 2‰$.

Results

On August 28, 1960, a vertical profile of water samples was taken in the Bornholm Basin near Christiansø. The results of the D-measurements are shown in Fig. 1. The D-profile exhibits a marked increase in the D-content between 38 and 48 m with a nearly

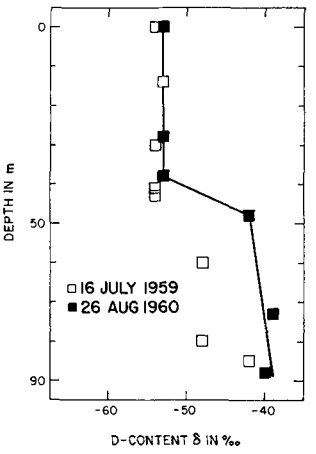

Fig. 1. Vertical deuterium profiles of samples taken on July 16, 1959 and August 28, 1960 in the Bornholm Basin at Christiansø, Baltic Sea (δ relative to SMOW). The 1960 profile is indicated by the line. For the 1959 profile the actual increase of the D-content with depth is not quite clear. It could have occurred in two shallow steps, one around 50 m depth and one close to the bottom. The salinity, however, increases more or less linearly from around 40 m to the bottom.

constant D-content above 38 m and below 48 m, indicating two different internally well mixed water layers overlying one another. In an earlier profile, taken July 16, 1959, the variation was somewhat different. The upper layer down to around 40 m again shows a constant D-content of $-53‰$, essentially identical with that for the 1960 profile; the deeper levels however show a gradual increase in the D-content with depth (Fig. 1). For the 1959 samples the salinity has been measured (S. Wellershaus, private communication). The salinity profile approximately parallels the Deuterium profile. The linear correlation between Deuterium content and salinity is shown in Fig. 2. The circles represent the measurements by Friedman *et al.*, 1964 (Fig. 18). The most saline sample had a salinity of 33.5‰. Since the water masses entering the Kattegat have a salinity of 33‰ (cf. Defant, p. 527), the D-content of this sample, $\delta_D = 0$, should closely represent the D-content of the inflowing saline North Sea water. Fitting a straight line by least squares and extrapolating to zero salinity gives $\delta_{ex} = -72.4 \pm 1.5‰$. In a similar diagram Friedman *et al.* (1964) obtained $-67‰$ for the extrapolated value. The extrapolated value represents the

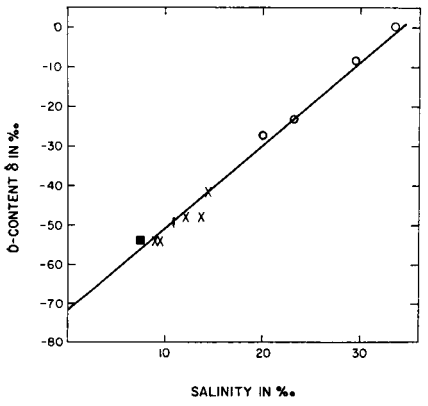

Fig. 2. Deuterium-salinity relation for the 1959 profile (δ relative to SMOW). Open circles represent samples taken from Friedman *et al.*, 1964. The square represents the three surface layer samples. Extrapolation to zero salinity gives -72.4 ± 1.5‰.

average D-content of the precipitation and fresh water inflow modified by isotopic exchange with water vapor and isotopic fractionation during evaporation from the surface.

Some published data for precipitation and fresh water around the Baltic Sea are summarized in Table 1. The actual average D-content of the influx of fresh water could be somewhat lower than the -75‰ average of Table 1, due to inflow of melt water with low D-content during late spring and to water exchange with the Gulf of Bothnia, which may be fed by fresh water of lower *D*-content.

Discussion

The D-profiles, Fig. 1, are explained in the same way as the salinity profiles (cf. Dietrich & Kalle, 1957) since D-content and Salt-content of the North-Sea are high whereas fresh water has a low D-content and salinity. Baltic and North Sea are connected by narrow and shallow straits. The total inflow of river water, 467 km³, and precipitation, 206 km³, into the Baltic greatly exceeds the annual evaporation of 182 km³ (cf. Defant, 1961). The excess of fresh water results in a low salinity of 7‰ to 8‰ in the upper layer of the Baltic and in an outflow of water of low salinity to the North Sea. Only occasionally, due especially to water piled up by strong northwestern winds, water of high salinity and high D-content is pushed over the rises, which separate the Arcona Basin from the Kattegat. Due to its higher density, this water, only partly mixed, spreads along the bottom, forming a sublayer of higher salinity and D-content. Since their lower layers are separated by another rise, the transport of saline water from the Arcona to the Bornholm Basin is even more restricted. In the 1959 profile the two-layer system is less pronounced and vertical mixing is more complete than in 1960, apparently due to a longer period without inflow of saline water.

The linear correlation between D-content and salinity, shown in Fig. 2, is of more general interest. It is caused by the various degrees of mixing of fresh water with saline water and by

Table 1. *D-content of fresh water and precipitation in Northern Europe*

No.	Description	Date	‰	Author
1	Precipitation, Huddinge (Stockholm)	Averaged over 1958–1962	− 88.4	Östlund, Lundgren 1964[a]
2	Precipitation, Copenhagen	Annual average	− 66.8	Dansgaard, 1964[b]
3	Precipitation, Hojer, Denmark	Annual average	− 58.7	Dansgaard, 1964[b]
4	Precipitation, Ultuna, Sweden	Annual average	− 73.1	Dansgaard, 1964[b]
5	Lake Päijanne, Finland 61°50′ N, 25°30′ E	10–3–57	− 90.	Friedman *et al.* 1964
6	Kymmene River, Finland	8–30–57	− 79.	Friedman *et al.* 1964
7	River Weichsel, Poland, 54°20′ N, 18°57′ E	7–11–57	− 69.	Friedman *et al.* 1964
		Average	− 75.	

[a] Östlund and Lundgren present their D-data in ppm. To convert their data to δ-values relative to SMOW the absolute value of 161,9 ppm has been used for SMOW. The standard deviation (1σ) for their D-measurement is ± 3 ppm which corresponds to an absolute error for δ of ± 20‰. Thus their D-data can only be used here, since the large number of measurements allows to form a reliable average.

[b] Dansgaard reports the annual average of the 0–18 content of precipitation (Fig. 3, Dansgaard, 1964). The relation $\delta_D = 8 \cdot \delta_0 + 10$ (Craig, 1961 b) has been used to obtain the corresponding D-content.

the isotope fractionation during the evaporation from the sea surface. Therefore the quantitative explanation of the D–S-correlation will also serve to establish a relation between the annual evaporation and fresh water inflow, and the isotopic composition of the water.

The balance equations

In order to derive an expression for the linear D–S-correlation a box model approximation shall be considered. The salinity of the upper layer of the Baltic proper shows variation of a few percent with depth and season, and a decrease of about 10% of the average value from southwest to northeast. Similar variations can be expected in the D-content. To assume the upper layer to be well mixed should, therefore, hold as a first approximation. With the further assumption of steady state, the following balance equations for the upper layer are obtained:

$$\text{water: } P - E + F_0 - F = 0, \tag{1}$$

$$\text{salinity: } -S \cdot F + S_0 \cdot F_0 = 0, \tag{2}$$

$$\text{isotopes (D, O-18): } \delta_p \cdot P - \delta_e \cdot E + \delta_0 \cdot F_0 - \delta \cdot F = 0, \tag{3}$$

where

P = total annual fresh water inflow from precipitation and river runoff (675 km³, Defant, 1961),
E = annual evaporation (182 km³, Defant, 1961),
F = annual outflow from the Baltic,
F_0 = annual inflow of North Sea water into the Baltic,
S = average salinity of the upper layer,
S_0 = salinity of the inflowing water (33‰, Defant, 1961, p. 527),
δ_p, δ, δ_0 = isotopic δ-values of the fresh water inflow (−75‰), of the upper layer (−53‰) and of North Sea water (0‰),
δ_e = the isotopic δ-value of the net flux of water vapor. It is determined by the isotopic exchange across the water surface and by the eddy transport of water vapor into the atmosphere (see below).

Assuming the upper layer to be well mixed, the isotope content and salinity of the outflowing water have been taken to be equal to their values in the upper layer. Eqs. (1), (2), and (3) which applies independently for D and O-18 are homogeneous in P, E, F_0, F. There is therefore no unique solution for those parameters. The different sets of solutions differ by a common factor. Only ratios, like P/F, E/F, and F_0/F, can be determinded. For that purpose it suffices to know the δ-values of one isotope in addition to the salinity data. From eqs. (1), (2), (3) we can derive a linear relation between the D-content of the upper layer and the salinity:

$$\delta - \delta_0 = \frac{(S/S_0 - 1)}{E - P} \cdot (P \cdot (\delta_p - \delta_0) - E \cdot (\delta_e - \delta_0)). \tag{4}$$

This relation is equivalent to eq. (3) of Craig & Gordon, which had been derived for the open ocean. Extrapolation of (4) to zero salinity yields:

$$\delta_{ex} = \frac{P \cdot \delta_p - E \cdot \delta_e}{P - E}. \tag{5}$$

This incidentally is equivalent to the steady state solution for a reservoir with only fresh water influx and outflow. Solving (5) for E/P, one obtains

$$E/P = \frac{\delta_p - \delta_{ex}}{\delta_e - \delta_{ex}}. \tag{5a}$$

In the present case, in which $\delta_0 = 0$, it also follows that

$$\delta = (1 - S/S_0) \cdot \delta_{ex} \tag{6}$$

or

$$F_0/F = 1 - (\delta/\delta_{ex}) \tag{6a}$$

since

$$S/S_0 = F_0/F.$$

If the experimental values for δ and δ_{ex} from above are inserted in (6a), $F_0/F = 0.25$, i.e. the flow of Baltic Sea water into the North Sea is four times greater than the flow of North Sea water into the upper layer of the Baltic. The same result is, of course, obtained from the salinity data.

Comparison of the experimental and theoretical D-S-Relationship

The validity of the presented box model can be tested by comparing the experimental slope and δ_{ex} of the deuterium-salinity relationship (Fig. 2) with the values calculated from eqs. (5) and (6). However, δ_e, which is needed for this calculation, is not known for the Baltic Sea. Fortunately it can be extrapolated from Craig & Gordon's data for the open ocean. Before this is done, a comment on δ_e is in order. δ_e which we have called the δ-value of the net vapor flux is the δ-value of the amount of water removed from the liquid by evaporation. It is not identical with the δ-value of the water vapor and cannot be measured directly. Craig and Gordon determined δ_e from the isotopic mass balance over the ocean. In principle δ_e can also be calculated:

$$1 + \delta_e = \alpha_t^{-1} \cdot (1 + \delta), \tag{7}$$

where

$$\alpha_t = \frac{\sqrt{D/D'} \cdot (1-h)/h}{1/(\alpha_p \cdot h) - (1+\delta_v)/(1+\delta)}, \tag{8}$$

and h = relative humidity (air and water temperature are assumed to be equal).

δ_v = δ-value of the water vapor,

δ = δ-value of the water in the upper layer,

D, D' = diffusion coefficients of H_2O and HDO in air,

α_p = equilibrium isotopic fractionation factor.

Expression (8) for the total fractionation factor is based on the assumption that the water vapor directly above the interface is in isotopic equilibrium with the liquid water, and that the kinetic fractionation factor is caused by the different diffusion velocities of H_2O and HDO in the surrounding turbulent air. The total fractionation factor thus can be written as $\alpha_t = \alpha_p \cdot \alpha_k$. α_k, the kinetic fractionation factor, has been taken from eq. (10) of Ehhalt & Knott (1965), replacing the isotope ratios used there by δ-values. This expression for α_k also includes the isotopic exchange between vapor and liquid.

From eq. (8) α_t, and therefore δ_e seem to depend strongly on the relative humidity and the temperature of the sea surface, since α_p is temperature dependent. However, δ_v, the isotopic δ-value of the water vapor in the atmosphere itself depends on h and α_p, in addition to the vertical exchange. Any variation of h or α_p causes δ_v to vary in such a way that those variations nearly compensate each other and the change of α_t becomes very small. For example, if α_p is increased by 5 ‰, which corresponds to a temperature decrease of roughly 5°C, δ_v will decrease by 5 ‰ (assuming that the relative humidity of 75 ‰, the isotopic composition of the surface water and the vertical exchange remain the same), and the resulting increase of α_t is only 1.3 ‰. Therefore α_t should vary only moderately over large water bodies, where the influence of horizontal advection from adjacent land areas is relatively small. This is true for the Baltic Sea, where the isotopic compositions of the water vapor over land and sea do not differ greatly. In winter the Baltic Sea is covered with ice, or rather with snow, the evaporation of which does not cause isotopic fractionation. In winter, evaporation thus only decreases the amount of precipitation on the Baltic Sea. The average of δ_e is determined by the summer months. The average humidity over the Baltic Sea between April and October is close to 75% (calculated from the temperature and dew point maps of H. L. Crutcher & J. M. Meserve, 1966). This is the same value, which Craig & Gordon have used for their ocean-atmosphere model. Therefore $\alpha_t = 1.032$ found for the ocean (cf. their Fig. 15) should hold for the Baltic Sea as a good approximation. From eq. (7) and the δ-value of surface water, $\delta = -53$ ‰, we obtain $\delta_e = -83$ ‰. With that we have all the information necessary to calculate δ_{ex} and the slope of the deuterium-salinity relationship from eqs. (5) and (6). The comparison with the experimental values from Fig. 2 is shown in Table 2.

Table 2. *Comparison of the calculated and measured values of δ_{ex} and the slope of the deuterium-salinity relationship*

	Measured value	Calculated value
δ_{ex} in ‰	-72.4 ± 1.5	-72.0
Slope (δ in ‰ per salinity in ‰)	$2.16 \pm .08$	2.18

The agreement between experimental values of the slope and δ_{ex} from Fig. 2 and the ones calculated from the isotopic balance using the known annual amounts of precipitation and

evaporation is excellent. The presented model properly describes the measured deuterium-salinity relationship.

The use of Deuterium as tracer for oceanic evaporation

The next question is what kind of information on annual evaporation, precipitation, inflow and outflow can be extracted from the isotopic data and the experimental deuterium-salinity relationship. We have already seen that only the ratios of these parameters can be obtained. The ratio, which can most readily be checked with the values quoted by Defant (1961) is E/P. Using his figures ($E = 182$ km^3, $P = 673$ km^3) one obtains $E/P = 0.27$. The ratio of evaporation to fresh water inflow obtained from eq. (5a) by inserting $\delta_p = -75$‰, $\delta_e = -83$ ‰ and $\delta_{ex} = -72.4$ ‰ is $E/P = 0.25$. The agreement seems to be very good. However, at present it has to be considered as somewhat fortuitous. The right side of eq. (5a) is the quotient of small differences of large numbers, the differences being of the same order as the present errors of the δ-values. Thus the error of the ratio E/P is large. This is due to the fact that the δ-value of the water vapor flux δ_e differs so little from the δ-value of the fresh water inflow δ_p. Thus even considerable evaporation produces only a comparatively small effect on δ_{ex} (cf. eq. (5)).

It is difficult to estimate the mean standard deviation of the present value of E/P. Only the mean standard deviation of δ_{ex}, $\Delta\delta_{ex} = \pm 1.5$ ‰, is known. $\Delta\delta_e$ is unknown and so is $\Delta\delta_p$, since it does not seem appropriate to use the mean standard deviation (± 4.3 ‰) one could calculate from Table 1. The uncertainty of δ_p depends on the uncertainties in the D-contents and in the size of the contribution from the individual sources. Using a mean standard deviation based on the differences between the D-contents of the contributors has therefore little meaning and might overestimate $\Delta\delta_p$, because the δ-values of the sources which contribute to the inflow vary systematically, depending on the climate. If we could assume ± 1.5 ‰ to be valid for $\Delta\delta_p$ and $\Delta\delta_e$ also, a mean standard deviation of ± 0.18 would follow for E/P.

In order to yield a reliable ratio E/P, an investigation of this kind requires more accurate values, especially of δ_p and δ_{ex}, than have been obtained here. By extending the measurements to provide the longterm averages of the significant contributors, i.e. by measuring more precipitation and river samples as well as vapor and surface water samples, this accuracy can be obtained.

It might be mentioned in passing, that a reliable average over an area is more easily obtained for the D-content of rain than for the amount of rain itself, because generally the D-content varies much less with location.

Conclusion

Consideration of a box model and the resulting balance equations led to a simple explanation of the deuterium-salinity relationhip in the Baltic Sea. Although the box model satisfactorily describes the variation of the isotope content with salinity, it has been shown in the preceding discussion that a higher precision of the δ-values is needed before isotopic data can be used to derive reliable estimates of the water balance. As mentioned just above it will be possible to obtain the required accuracy by the proper choice of sampling locations and increasing the number of D-measurements. An uncertainty of ± 0.5 ‰ should be attainable. The present investigation shows that with this precision isotopic studies should indeed provide an additional source of information for oceanographic and hydrologic studies.

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О СООТНОШЕНИИ МЕЖДУ КОНЦЕНТРАЦИЕЙ ДЕЙТЕРИЯ И СОЛЕНОСТЬЮ В БАЛТИЙСКОМ МОРЕ

Описываются два вертикальных профиля концентрации дейтерия, полученные в Балтийском море в районе о. Борнхольм. Оба профиля показывают постоянство концентрации дейтерия от поверхности до глубины порядка 40 *м*. На больших глубинах концентрация дейтерия увеличивается. С привлечением измерений Фридмана (1964) устанавливается обычное линейное соотношение между концентрацией дейтерия и соленостью. Это линейное соотношение выводится также теоретически из рассмотрения модели резервуаров и получающихся из этой модели уравнений баланса для воды, солености и концентрации изотопов в верхнем слое. Сравнение теоретического и экспериментального соотношений концентрация дейтерия — соленость дает возможность установить соотношения между гидрографическими параметрами, например, соотношение между годичным испарением и притоком пресной воды, которое для Балтийского моря может быть сравнено с известной величиной.