

# The isotopic composition of atmospheric waters in the Mediterranean Sea area and their interpretation in terms of air-sea interactions

by

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Over oceanic areas the isotopic composition ( $^2\text{H}$ ,  $^3\text{H}$  and  $^{18}\text{O}$ )\* of atmospheric waters assume typical maritime levels. These are characterised by low tritium concentrations (HTO) which result from the loss of tritium supplied from aloft (from cosmic ray or man-made sources) to the oceanic sink by rainout or exchange [1, 2, 3]. The tritium content in the maritime atmosphere, which is proportional to the average residence time of the moisture in the air [4], undergoes seasonal and secular variations which reflect changes in the supply of tritium as well as variations in the intensity of air sea interactions.

The abundances of the stable water molecules HDO and  $\text{H}_2\text{O}^{18}$  in the marine atmosphere have been discussed by many authors [5, 6, 7]. Generally, water vapour over the sea is close to, but not quite at isotopic equilibrium with the surface waters.

As marine air masses move overland the tritium concentration increases with distance from the coast [7, 8]. At the same time the atmospheric moisture is depleted of the heavier isotopic species, because of their preferred removal in precipitation. The relative change of the isotopic abundances of the two isotopic species, D and  $\text{O}^{18}$ , during that process is then correlated by the relationship :  $\Delta\hat{\epsilon}(\text{D})/\Delta\hat{\epsilon}(\text{O}^{18}) \simeq 8$ .

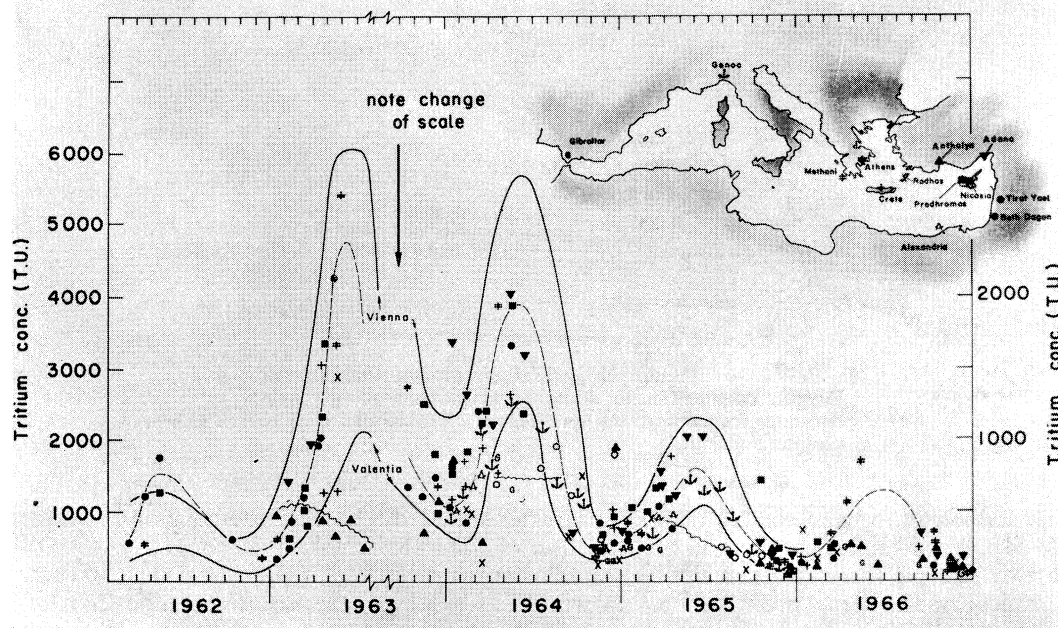


FIG. 1. — Tritium levels in precipitation of the Mediterranean Sea area. Symbols refer to sampling places, as shown on inset map. Data from Genoa, Alexandria, Vienna and Valentia are taken from IAEA tritium list. Open circles : tritium concentration in surface air at Rehovoth.

\*  $^2\text{H} = \text{D}$ ,  $^3\text{H} = \text{T}$

In coastal areas transition conditions apply : continental and maritime air masses mix and become modified, finally assuming the characteristics appropriate to their new environment. The build-up of tritium levels over the continental margins typically extends over a region of a few hundreds of kilometres [9]. Less is known about the relaxation length over the sea of the process of air mass modification by air-sea interactions, but the distances involved may be up to 1 000 km [10]. Since these are distances of typical trajectories of air masses over the Mediterranean Sea, it can be anticipated that the dimensions of that sea are too small for obtaining « maritime » steady state conditions.

The isotopic composition of atmospheric waters in this area may then be a measure of the degree and pattern of interaction between the Mediterranean Sea and its atmosphere.

Results from eight stations of the rain-collection network which had been established in the Eastern Mediterranean Sea area [11] as well as some additional data from other Mediterranean stations of the IAEA/WMO network [12] are shown in Fig. 1. It is immediately apparent that tritium levels in the area fall in between those of continental Europe and the Atlantic coast stations (Valentia, Ireland and Gibraltar). They are rather high considering their coastal location. Generally the seasonal and secular variations of tritium levels in the European stations are paralleled in this area. However, remarkably low tritium values appear at some stations during summer months, in particular at Yraklion (Crete), Rhodes and Anthalya. (Fig. 2). In the absence of summer rain in Israel one observes a similar effect in atmospheric moisture samples (open circles in Fig. 1). The tritium levels of near surface atmospheric waters in the spring to autumn season represent conditions of closer equilibrium with the sea surface, than those which give rise to the winter precipitations.

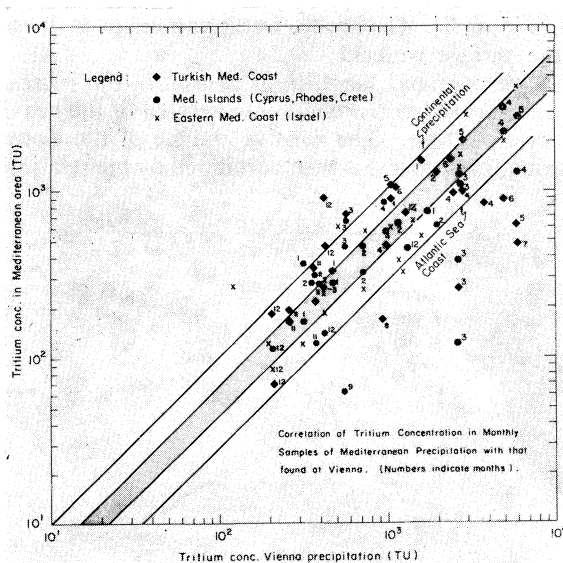


FIG. 2. — Tritium concentration of precipitation of Eastern Mediterranean stations, normalised to the synchronous concentrations at Vienna. Numerals refer to sampling month.

The stable isotope abundances define a characteristic Mediterranean composition of atmospheric waters [6, 13]. In precipitations we find a correlation of  $\delta D = 8 \times \delta^{18}O + 22$  (‰ rel to SMOW) between the two isotopic species, rather than the more common relation of  $\delta D = 8 \delta^{18}O + 10$  (per 1000), which is typical of European precipitation. In winter, as expected, the isotopic composition of water vapour does indeed fall on the local meteoric water line, as defined by the precipitation. However, once again the isotopic composition of the vapour collected during the summer months does not fit this typical Mediterranean relationship (Fig. 3).

According to a widely accepted view [5] the offset of these meteoric water lines from the origin (Dansgaard's parameter  $d$ , [6]) is fixed at the site of the evaporation and is characteristic of the vapour

source; large values signify a large kinetic effect. The large value of the 'd' parameter (+ 22 per 1 000) which characterizes the winter precipitation in the area suggests rather extreme non-equilibrium conditions during water transport at the interface, such as would occur during rapid evaporation into relatively dry air. It has no equal in the precipitation of adjacent continental areas (average European values are  $d = + 10$  per 1000, and in Central Africa  $d = + 14$  per 1000) nor in the air masses above the Atlantic Ocean [6].

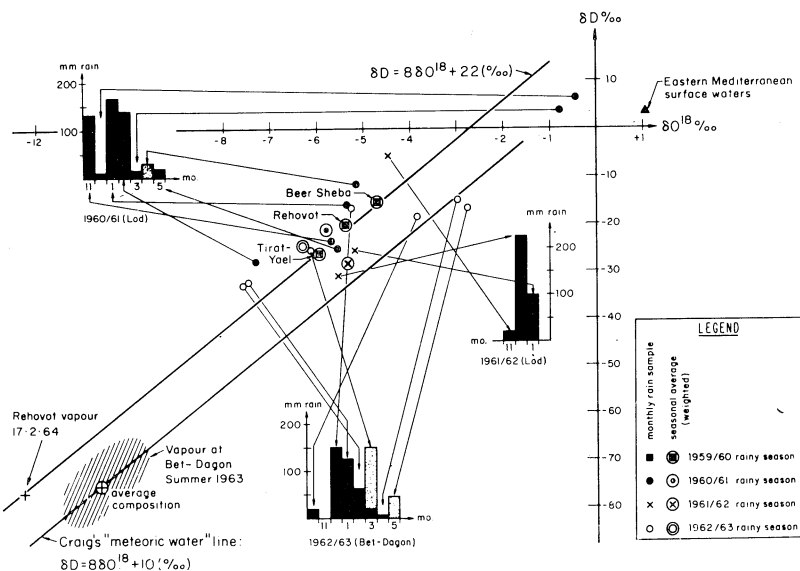


FIG. 3. — Stable Isotopic composition of precipitation in Israël. Rain amounts, corresponding to these samples, are shown as insets. Taken from ref. 13.

Summing up, the isotope data of atmospheric waters from the Eastern Mediterranean Sea area indicate conditions of a prolonged contact with the sea during summer months, and short but intensive interactions during winter.

The Mediterranean Sea has been shown to be an area of convergence in winter and a favoured path for atmospheric disturbances [14]. The meeting of cold dry continental air with the relatively warm water masses results in extensive vertical instability and cyclogenesis. In summer, on the other hand, a « general subsidence with divergent air flow characterizes much of the Mediterranean area, so that air is stable and the weather element weak » [14]. Rains are then few and mainly of the orographic type.

The pattern of isotope distribution is an immediate reflection of this meteorological pattern. During winter the intensive but short meeting of dry air and warm sea results in rapid evaporation, which results in the large value of the d-parameter in the local meteoric water line. At the same time the vertical disturbance and continuous convergence of air which is rapidly carried aloft, seems effective in tapping upper air levels with their higher tritium content. This addition of tritium compensates to some extent the loss of tritium into the sea and results in the relatively high tritium levels of the area. In summer, on the other hand, the air masses remain in long contact with the sea surface, under stable atmospheric conditions. Rains are then mainly local phenomena and not connected with large scale vertical atmospheric disturbances. Hence their extremely low tritium levels which are characteristic, probably, only for a thin layer of air above the sea. Low tritium levels in orographic rains have indeed been noted, even during winter, at the high altitude station of Prodhromos in Cyprus [11].

## References

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