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TELLUS

Isotope composition of air moisture over the Mediterranean Sea: an index of the air–sea interaction pattern

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ABSTRACT

The isotope composition of atmospheric moisture over the Mediterranean Sea, collected during the cruise of the research vessel *meteor* in January 1995, confirmed that the intensive air–sea interaction near the coast under conditions of a large humidity deficit labels the resultant atmospheric waters with a large deuterium-excess parameter. The present data set shows this effect to result both when cold air from the European continent moves over the sea as well as when warm and dry air from North Africa is involved. The situation in the eastern and western Mediterranean differ in the vertical structure of the isotope composition further away from the coast, as expressed by the gradients of the d_{excess} values with altitude over the sea surface, i.e. increasing with altitude in the eastern Mediterranean, whereas the opposite effect is noted in the western section and near the coast. A comparison of the isotopic composition of the samples with the expected buildup of moisture over the sea, based on the Craig–Gordon model, suggests that up to one half of the added moisture may have resulted at times from the evaporation of sea-spray droplets, without any significant isotope fractionation, in addition to the vapour-mediated transport from the sea surface, which favors the lighter isotopic species.

1. Introduction

The Mediterranean Sea is a land-locked marine water body where, especially in winter, continental air masses impinge on seawater under conditions of a large humidity deficit, a strong temperature contrast between air and water and isotopic disequilibrium between the atmospheric moisture and the water body. It is amply documented that the resultant instability in the air and water column, which accounts for the Mediterranean rain pattern, is accompanied by a notable isotope signal in the atmospheric as well as the marine waters. This effect was first recognized by virtue of the high value of the d_{excess} of the stable isotopes in the winter precipitation in the eastern Mediterranean Sea region (Gat and Dansgaard, 1972). Later similar patterns were recognized on the leeside of continents, in the China Sea (Liu, 1984), in Japan (Matsuo et al., 1979) and along the Atlantic coast of the North American continent (Gat et al., 1994).

The d_{excess}, defined as $d = \delta^2\text{H} - 8\delta^{18}\text{O}$ (Dansgaard, 1964), places the isotope composition of a precipitation sample relative to that of the Global Meteoric Water Line (GMWL, for which $d = 10‰$); $\delta^2\text{H}$ and $\delta^{18}\text{O}$ are the measure of the isotope abundances in δ-nomenclature (Craig, 1961).

A conceptual model based on both stable isotope and tritium data in precipitation in the eastern Mediterranean region (Gat and Carmi, 1970) postulated a large effect close to the European shores due to the intensive air–sea interaction process. Further

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seawards, as humidity builds up over the sea, the isotopic signature of this strong interaction is somewhat relaxed by moisture exchange with the sea surface.

The evidence for this process to date was circumstantial, in that it was based only on measurements of precipitation from coastal and island stations. A one-year survey of the isotope composition of air moisture in the coastal plain of Israel (Tzur, 1971) confirmed the elevated d_{excess} values in air moisture, peaking at the time of the winter precipitation. However, a reliable check of the model concept would require a direct measurement of the isotopic composition of air moisture over the sea. Hence a vapour sampling program was initiated during cruise M31/1 of the research vessel *Meteor* in the Mediterranean Sea in 1995.

2. The *Meteor* vapour-sampling program

During the cruise of the *Meteor* into the Mediterranean in January–February 1995, sampling of air moisture was performed at two heights above the sea, namely at deck and mast height, 20.35 and 27.9 m above the waterline, respectively. Air was drawn at a rate of about 5 L min^{-1} for about 10 h from the intake points through a trap immersed in a dry ice/acetone mixture, yielding up to 15 mL of water. The water in the trap was subsequently allowed to thaw for several hours and then poured into glass bottles. The trap, shown in Fig. 1, was designed to insure complete removal of all the vapour, in order to avoid isotope fractionation during sampling. The sampling protocol is obviously not ideal due to operational constraints, in particular the necessity to sample while the ship was in motion. In order to avoid the interception of spray droplets, sampling was conducted high above the water line.

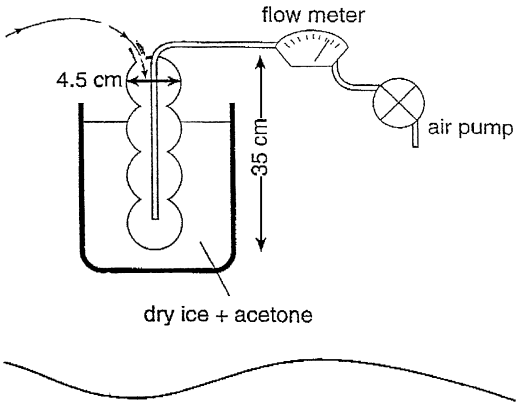

Fig. 1. Sampling device for air moisture (schematic representation).

Isotope analysis on the water samples was performed at the Rehovot Isotope Laboratory using a MAT-250 MS and standard measurement techniques (Gonfiantini, 1981); values are reported as per mil deviations from the standard VSMOW. Measurement reproducibility of duplicates was better than ±0.1‰ for δ^{18}O and ±1‰ for δ^{2}H.

Figure 2 shows the location of the ship and the track length at the time of sampling, starting from the western Mediterranean, continuing into the Adriatic and hence across the Aegean Sea into the eastern basin, finishing at Alexandria, Egypt. The positions are numbered consecutively. The sampling coordinates are recorded in Table 1.

At the time of sampling, wind speed and direction and the humidity were recorded at mast height; unfortunately, the humidity at deck height is not available. The wind direction and speed at the sampling site are also shown in Fig. 2, relative to the cruise direction. As will be seen, this is, however, not necessarily an indicator of the origin of the long-range trajectory. The temperature of the surface waters (SST) is given in Table 1. The isotope composition of surface waters in the Mediterranean during this cruise, shown on Fig. 3, averaged $\delta^{18}\text{O} = 1.18 \pm 0.09$‰ in the central Mediterranean (between Sicily and Crete) and $\delta^{18}\text{O} = 1.33 \pm 0.13$‰ in the eastern Mediterranean. The highest values were encountered in the more northern segments close to the European coast, especially at the mouth of the Adriatic and the Aegean Seas. The value of $\delta^{18}\text{O} = +1.64$‰ was measured near the Bay of Anthalya.

2.1. *The meteorological condition at the time of sampling*

In winter the warm waters of the Mediterranean Sea act to produce a trough which causes the Mediterranean to be a strong convergence and frontal zone and the route of many eastwards-moving cyclones. The disturbances then carry winter rainfall over an extensive area (Trewartha, 1961). The month in question (January 1995) was a cold one in parts of Europe, possibly even amplifying this process.

Based on the surface synoptic maps and the ship's logbook, one notes that rain occurred locally in the vicinity of the sampling sites in the case of samples

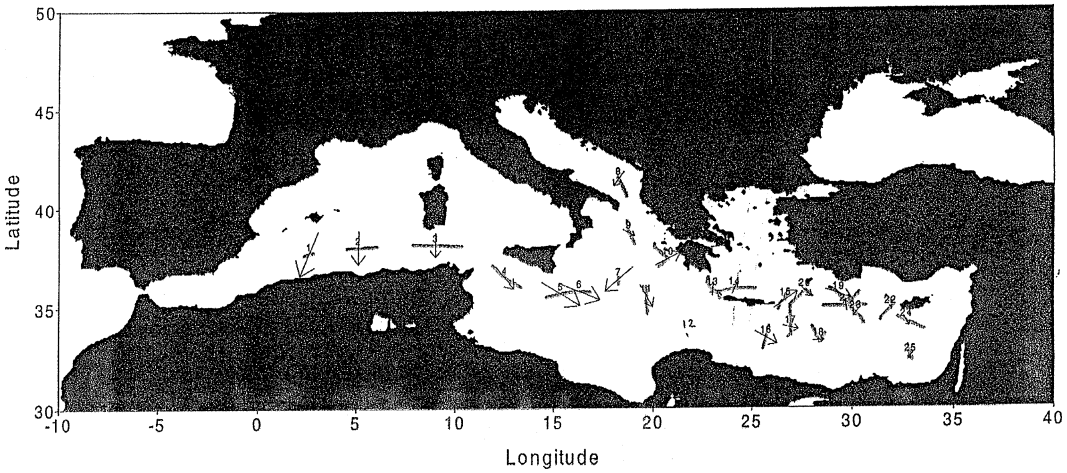

Fig. 2. Ship location and track length at time of vapour sampling. The vectors indicate the relative mean wind direction and speed. Numbers signify the consecutive sample number.

nos. 1, 2, 6, 7, 8, 10 and 19. Widespread rain over large parts of the region, as recorded in the weather charts, could also have affected samples nos. 3 and 5.

A backward three-dimensional trajectory calculation for the air masses concerned was performed at the ETH, Zurich, using the wind field from the ECMWF T213/L31 analysis data set (Wernli and Davies, 1997). These data are available every 6 h on 31 vertical levels and interpolated with a grid increment of 1°. At every full hour, backward trajectories were released (over a 3 d time period) starting at three vertical levels in the boundary layer above each sampling site, namely at 992, 972 and 945 hPa (in case of surface pressure value of 1000 hPa). Another analysis was performed for trajectories starting at the 700 hPa level. These trajectory calculations enable one to define the properties of the air masses that invade the Mediterranean air space in each case (the boundary conditions for the model calculations).

In addition, the vertical stability in the lower atmosphere was determined for every trajectory at the closest position to the measurement site where ECMWF temperature data were available, subject to the limitation that these are available only every 6 h. At this position the vertical difference of the equivalent potential temperature (THE) between (lat, lon, $p+50$ hPa) and (lat, lon, $p-50$ hPa) was calculated, thus giving an average stability value for the 100 hPa thick layer which sandwiches the trajectory position. The unit of

Table 1. *Position of the vapour sampling stations, SST and normalized air humidity*

Sample no.	Date (1995)	Longitude	Latitude	SST °C	Normalized humidity[a]
01	07.01	2.606	37.730	16.68	0.30
02	08.01	5.128	38.030	16.73	0.31
03	09.01	9.010	38.143	15.95	0.24
04	10.01	12.549	36.497	16.99	0.47
05	11.01	15.385	35.685	17.36	0.57
06	12.01	16.337	35.797	17.95	0.50
07	13.01	18.297	36.405	17.25	0.41
08	16.01	18.316	41.460	14.28	0.33
09	18.01	18.802	38.739	16.72	0.39
10	19.01	20.751	37.417	16.23	0.50
11	20.01	19.651	35.566	16.82	0.46
12	21.01	22.183	34.133		
13	22.01	23.017	35.876	16.55	0.51
14	23.01	24.120	35.883	16.60	0.57
15	24.01	26.709	35.324	16.75	0.60
16	25.01	25.717	33.466	17.48	0.66
17	26.01	26.971	33.951	18.55	0.52
18	27.01	28.349	33.311	17.32	0.65
19	28.01	29.335	35.599	16.02	0.54
20	29.01	27.674	35.766	17.23	0.40
21	30.01	29.694	34.998	16.24	0.57
22	31.01	31.868	34.868	16.82	0.52
23	01.02	30.168	34.631	16.74	0.57
24	02.02	32.639	34.218	17.81	0.46
25	03.02	32.843	32.498	18.22	0.55

[a]Based on shipboard humidity and temperature sensors, normalized to saturated vapour pressure at the sea surface.

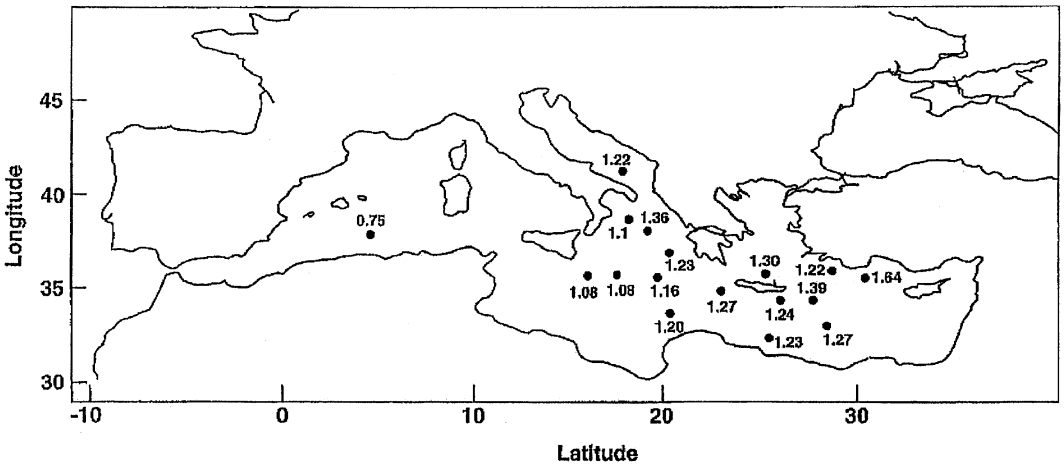

Fig. 3. Oxygen isotope composition, $\delta(^{18}O)_{VSMOW}$, of surface waters in the Mediterranean, as measured during the cruise of the *Meteor* in January–February 1995.

this stability parameter is 1 K per 100 hPa, where positive values signify stability and, in contrast, negative values signify unstable conditions. In the absence of observed temperature profiles, this parameter provides a simple and rough estimate of the vertical stability of the sampled air mass based upon meteorological analysis data.

Figure 4 shows the trajectories in the near-surface boundary layer for every sample. In addition, the stability value in each case is given.

The classical situation of a direct invasion of cold and dry air from the European continent into the Mediterranean air space (Gat and Carmi, 1970) applies to samples nos. 3, 8, 9, 12, 13, 20 and 21 and possibly also to no. 4. As is evident from Fig. 2, samples nos. 8, 9 and 20 were sampled in rather close proximity to the coast, whereas the other samples of this group are from sites further away from the coast.

In contrast, samples nos. 1, 2, 5, 6 and 7 (all from the western Mediterranean area) represent Atlantic marine air with a more or less lengthy path along the axis of the Mediterranean. A trajectory originating directly from North Africa characterizes sample no.10.

In the case of samples nos. 11, 15, 16, 18 and 19, the air motion changed during the sampling period, with air masses originating from the European continent part of the time and changing to air masses of marine or North African character for the rest of the day. A special case is that of samples 13 and 14, where the boundary layer trajectories differed significantly from those released at the 700 hPa level.

3. The isotopic composition of the air moisture

The isotopic composition of the air moisture collected during the METEOR cruise is given in Table 2. $\delta^{18}O$ and $\delta^{2}H$ values are given as deviations from the standard VSMOW in permil notation. The d_{excess} parameter is then calculated from these δ-values. The average data span a range of $-11‰$ to $-18.6‰$ in $\delta^{18}O$; the range of values of the d_{excess} parameter is from $d = 4‰$ to $d = 35‰$. This is to be compared to typical marine moisture values of between $\delta^{18}O = -11‰$ to $-14‰$ (Craig and Gordon, 1965) and to the normal range of d_{excess} values from both marine and European air moisture, which is from $d = 7‰$ to $d = 11‰$ (Gat, 2000).

The average values of the d_{excess} parameters of the measurements at deck and mast height, at each sampling point, are shown on the map of the Mediterranean Sea in Fig. 5. The highest values of the d_{excess} parameter are encountered south of Sardinia, at the mouth of the Adriatic Sea and off the Turkish mainland and the Bay of Anthalya. In those cases the air masses originated from the European continent. Extreme values of $d > 28‰$ are typically found close to the shoreline and more moderate ones, of $d \sim 15$–$22‰$, further into the Mediterranean basin.

The average difference in the δ-value between the samples collected at mast and deck height is $\Delta\delta^{18}O = (-0.08 \pm 0.49)‰$ (this 1σ value is about three times as large as the expected analytical one). The most

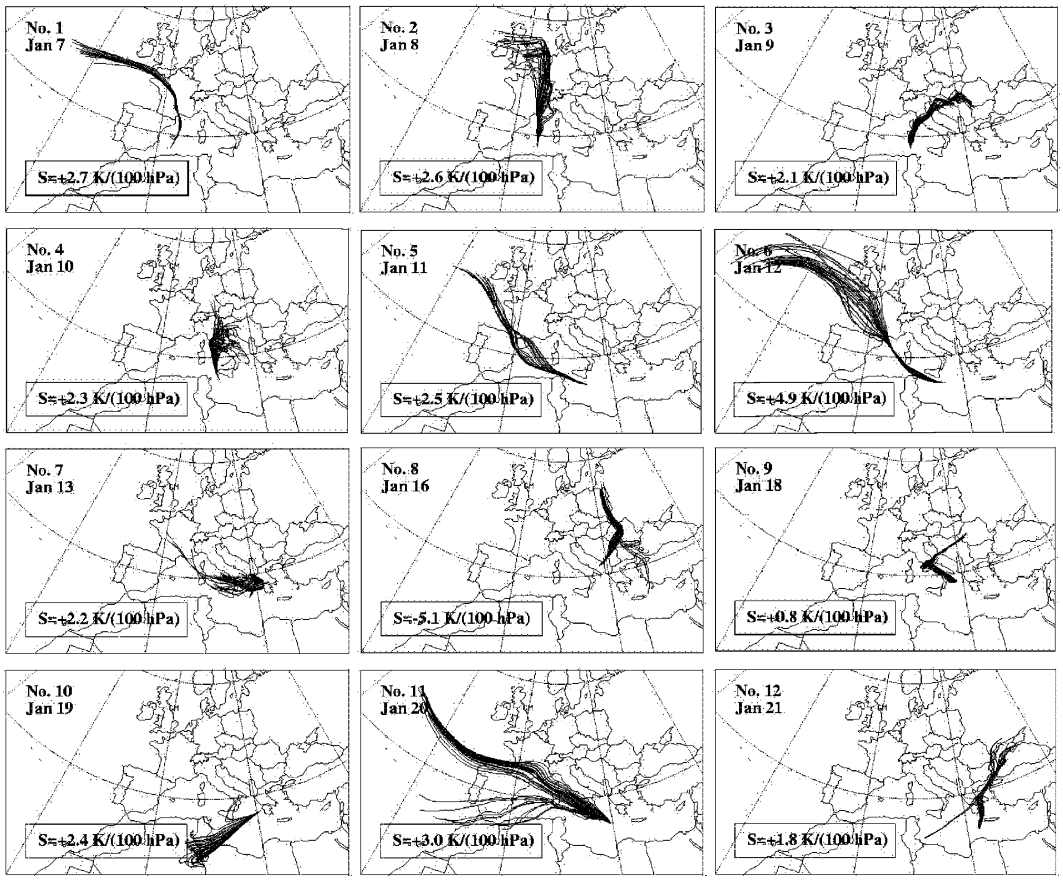

Fig. 4. Back-tracking of the sampled air masses in the boundary layer. Inserted is the stability value (S) in units of K per 100 hPa.

notable result, however, pertains to the d_{excess} parameter. One notes a remarkable pattern of higher d_{excess} values at deck height relative to the mast in the western and central Mediterranean, and the opposite trend at stations to the east of the Greek mainland, values being respectively:

$$\Delta d = (d^{\text{mast}} - d^{\text{deck}}) = -1.23 \pm 2.6‰ \quad \text{and}$$

$$\Delta d = 4.5 \pm 2.4‰.$$

Since the d_{excess} is a calculated parameter according to the definition given above, the combined error for Δd is $\sim\pm 2‰$, based on the analytical reproducibility of $\pm 0.1‰$ for $\delta^{18}O$ and $\pm 1‰$ for $\delta^{2}H$. Evidently the observed differences are significantly larger. As could be expected, the larger Δd values are observed during periods of high stability of the air column.

The isotopic composition (at mast height) is plotted on the $\delta^{2}H$ vs. $\delta^{18}O$ diagram on Fig. 6. Samples nos.1, 2 and 4–6 from the western Mediterranean are situated rather close to the GMWL. All the rest of the samples are characterized by higher d_{excess} values. As expected, in most cases the data points related to the occurrence of precipitation show the more depleted δ-values. These obviously cannot be simply taken as a test for the buildup mechanism of the atmospheric moisture, since the values of both the humidity and its isotopic composition are shifted by the rainout. Only the d_{excess} value is expected to be conservative under rainout conditions, and indeed the values between

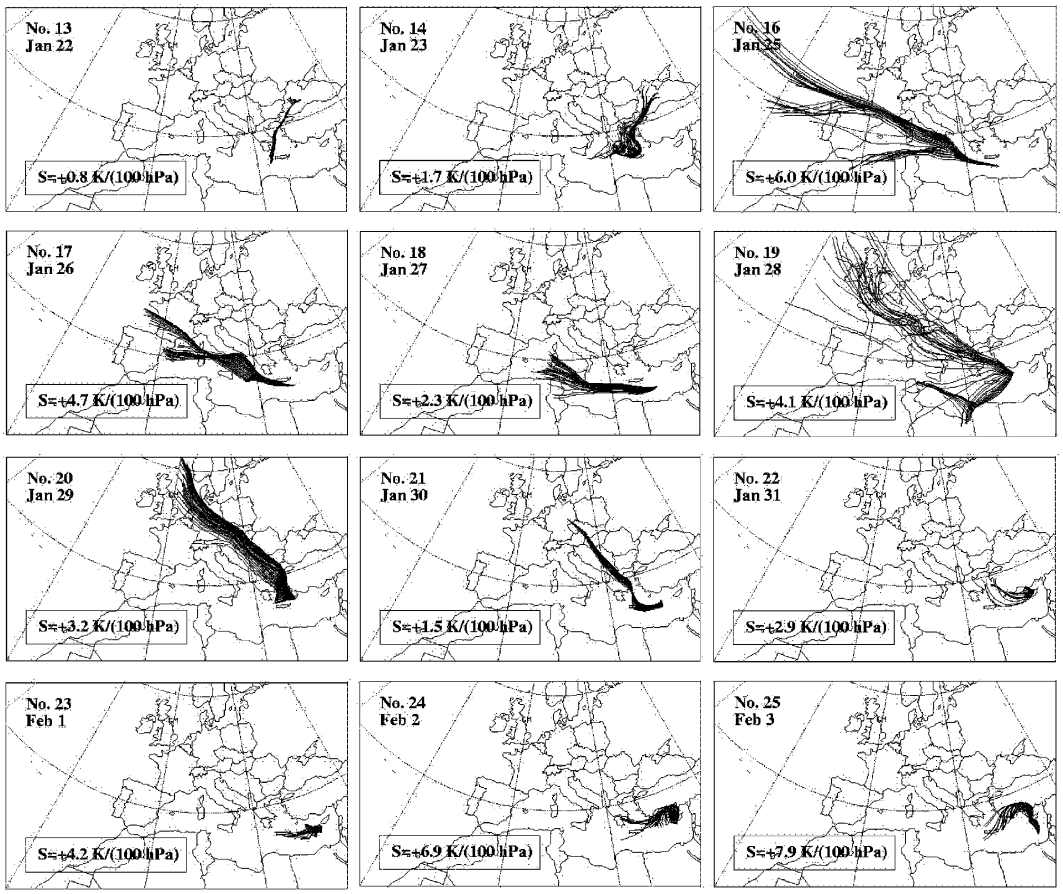

Fig. 4. (cont'd).

$d = 15‰$ and $d = 32‰$ of these samples are not out of line with the rest of the sample points.

4. Modeling the evolution of the isotopic composition of the atmospheric moisture over the Mediterranean Sea

As a reference frame for discussing the results obtained we consider three idealized models that describe the air–sea interaction and humidity buildup in (dry) continental air as it moves over the sea. A schematic representation of these three models is shown in Fig. 7. The first, the "box model," assumes a vertically well mixed parcel of air which changes its humidity and isotopic composition continuously as it moves over the sea by intermixing of the evaporative flux (whose isotope composition is δ_E) into the air parcel. Based on the Craig–Gordon evaporation model (1965), a simplified value of the evaporation flux's isotopic composition is:

$$\delta_E = (\delta_L - h\delta_a - \epsilon)/(1 - h). \quad (1)$$

The admixture of the evaporation flux into the airmass as humidity changes from h_0 to h' is given by the mixing equation:

$$\delta_{a,0}h_0 + \delta_E(h' - h_0) = \delta'_a h'. \quad (2)$$

h is the air humidity in the parcel relative to the saturated vapour pressure at sea surface temperature (SST) and sea surface salinity (SSS); δ_E, δ_a and δ_L are the stable isotope compositions of the evaporation flux, the air moisture and the seawater, respectively. The primed parameters h' and δ'_a refer to the modified conditions

Table 2. *The isotopic values of the vapour samples*

	Mast			Deck			(Δ = mast − deck)		
Sample no.	$\delta^{18}O$	$\delta^{2}H$	d_{excess}	$\delta^{18}O$	$\delta^{2}H$	d_{excess}	$\Delta\delta^{18}O$	$\Delta\delta^{2}H$	$\Delta(d_{excess})$
1	−11.69	−84.3	9.2	−12.52	−89.1	11.1	0.83	4.8	−1.9
2	−14.06	−97.5	15.0	−13.73	−95.3	14.5	−0.33	−2.2	0.5
3	−18.56	−123.7	24.9	−18.16	−116.8	28.5	−0.40	−6.9	−3.6
4	−13.88	−99.6	11.4	−14.46	−98.9	16.8	0.78	−0.7	−5.4
5	−12.57	−87.7	12.8	−12.36	−85.6	13.3	−0.21	−2.1	−0.5
6	−13.69	−95.2	14.3	−13.61	−92.0	16.9	−0.08	−3.2	−2.6
7	−15.22	−93.4	28.1	−14.78	−95.8	22.4	−0.44	2.4	5.9
8	−18.34	−116.6	30.1	−17.83	−108.5	34.1	−0.51	−8.1	−4.0
9	−14.44	−82.0	33.5	−15.88	−92.5	34.6	1.44	10.5	−1.1
10	−14.12	−91.0	22.0	−13.68	−91.1	18.3	−0.44	0.1	3.7
11	−13.75	−86.4	23.6	−13.35	−84.7	22.1	−0.40	−1.7	1.5
12	−14.82	−92.2	26.4	−14.67	−90.7	26.6	−0.15	−1.5	−0.2
13	−15.76	−101.3	24.8	−15.38	−101.2	21.8	−0.38	−0.1	3.0
14	−14.86	−98.0	20.9	−14.48	−95.3	20.5	−0.38	−2.7	0.4
15	−12.85	−83.6	19.2	−12.24	−83.2	14.7	−0.61	−0.4	4.5
16	−11.01	−69.1	19.0	−11.17	−80.8	8.6	0.16	11.7	10.4
17	−11.78	−77.9	16.3	−11.99	−81.7	14.2	0.21	3.8	2.1
18	−12.34	−80.4	18.3	−11.87	−83.2	11.8	−0.47	2.8	6.5
19	−12.18	−78.6	18.8	−12.37	−85.9	13.1	0.19	7.3	5.7
20	−14.63	−82.5	34.5	−14.52	−86.1	30.1	−0.11	3.6	4.4
21	−13.31	−82.4	24.1	−12.96	−83.0	20.7	−0.35	0.6	3.4
22	−13.59	−79.7	29.0	−13.77	−83.6	26.6	0.18	3.9	2.4
23	−12.23	−67.7	30.1	−12.51	−74.9	25.2	0.28	7.2	4.9
24	−13.24	−81.5	24.4	−12.98	−85.1	18.7	−0.26	3.6	5.7
25	−12.69	−81.9	19.6	−12.16	−82.7	14.6	−0.53	0.8	5.0

following the admixture of the evaporation flux; ε is the isotopic fractionation factor, including the thermodynamic (ϵ^*) and kinetic (diffusional, $\Delta\epsilon$) components, as prescribed by the Craig–Gordon model, namely $\epsilon = \epsilon^* + \Delta\epsilon$. $\Delta\epsilon$ can be expressed as

$$\Delta\epsilon = (1 - h)\theta n C_K \quad (3)$$

where θ is a weighting factor describing the ratio of the molecular diffusive transport resistance to the total sum of molecular and turbulent transport. When evaporation takes place from an open-water body under windy conditions, nC_K is assumed to be 13.1‰ for the deuterated and 15‰ for the ^{18}O labeled molecules, these values being based on the average value for C_K as given by Merlivat (1970) and Vogt (1976) and assuming $n = 0.5$. In the case of the simple box model, $\theta = 1$ and both δ_a and h in eq. (1) are changing parameters, as the humidity builds up in the air parcel.

A possibly more realistic model, termed the "lake model of air–sea interaction" (Gat, 1995), the "lake model" for short, which applies for non-convective conditions over the sea, accounts for the buildup of a deepening blanket of modified air over the air–sea interface as the air moves over the waters. In terms of the Craig–Gordon evaporation model, the deepening of the blanket of air corresponds to a continuing decrease of the parameter θ in the term $\Delta\epsilon = (1 - h)\theta n C_K$. The values of δ_a and h at the upper boundary of the air blanket are then assumed to be unchanged.

Both these models, however, neglect the strong vertical instability of the air column at the site of the first interaction between the continental air and the seawater on the leeward side of the continent, which is known to be a dominant feature of this system when the cold European air comes in contact with the relatively warmer Mediterranean Sea waters. A third model, the "leeside-convective model," then differs from the previous ones mainly in that the air aloft is a modified air mass having a relatively high d_{excess} value, which results from the convective transport of the coastal air with its high d_{excess} value to higher altitudes. In this case, unfortunately, the δ_a and humidity values can only be guessed at because of the absence of direct

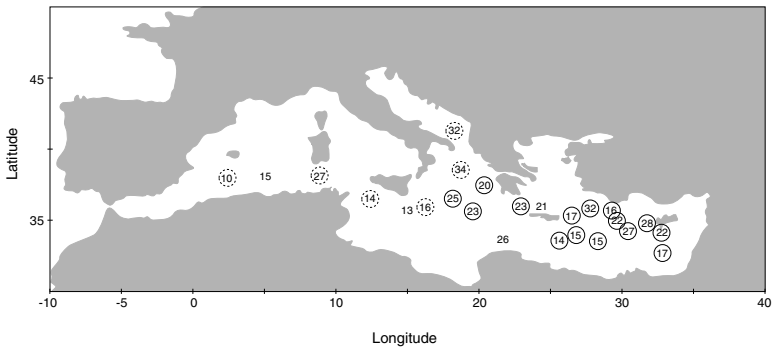

Fig. 5. The d_{excess} value as a function of the sampling position. Average values for the measurements at mast and deck, rounded up to full integer, are given. Samples with Δd ($d_{\text{mast}} - d_{\text{deck}}$) > 1 are marked by a full circle, those with Δd ($d_{\text{mast}} - d_{\text{deck}}$) < -1 by a broken circle. Uncircled numbers signify no significant vertical gradient of the d excess value.

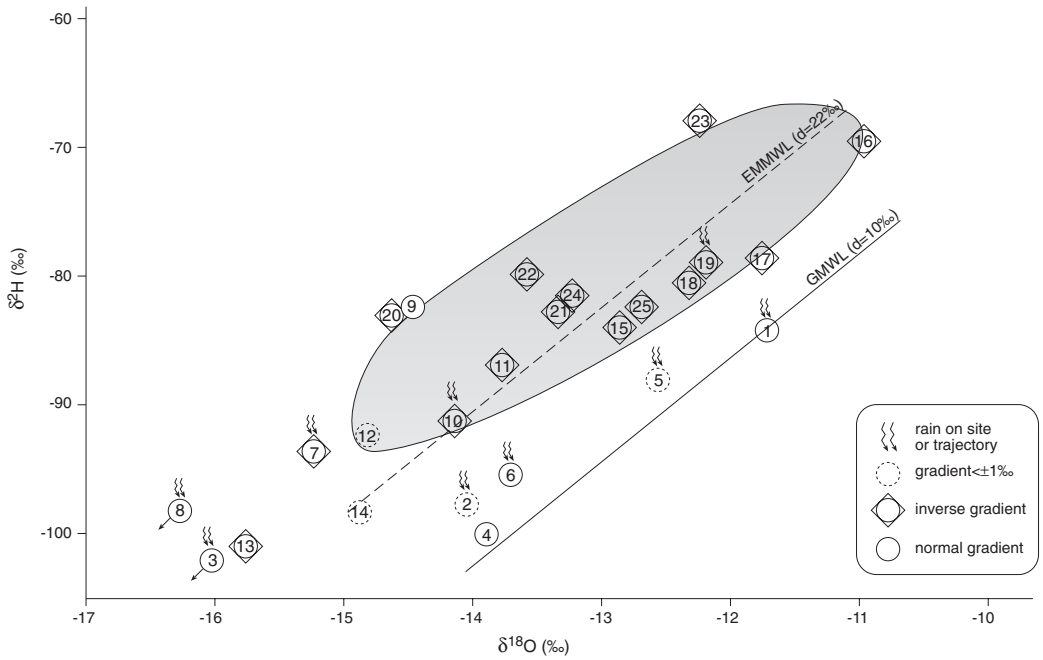

Fig. 6. The isotopic composition of air moisture collected at mast height, on a δ-diagram. The numbers refer to the sample number as given in Tables 1 and 2 and Fig. 2. The Global Meteoric Water Line (MWL) and the Eastern Mediterranean Line (EMMWL) are given for reference. The shaded area encompasses most of the no-rain data points.

measurements in the upper air layers. An estimate of the changing isotopic composition for these conditions can be approximated, however, by repeating the calculation performed for the "lake model," under substitution of the parameters of the modified coastal air (exemplified by sample no. 8) for those of the continental air.

The evaluation of the expected isotope composition for these different models requires an assessment of the isotopic composition of the air masses that invade the Mediterranean air space, from the west, the European continent or North Africa, as the case may be.

The Atlantic air, which advects from the west, can be considered to be typical oceanic air with δ^{18}O values of

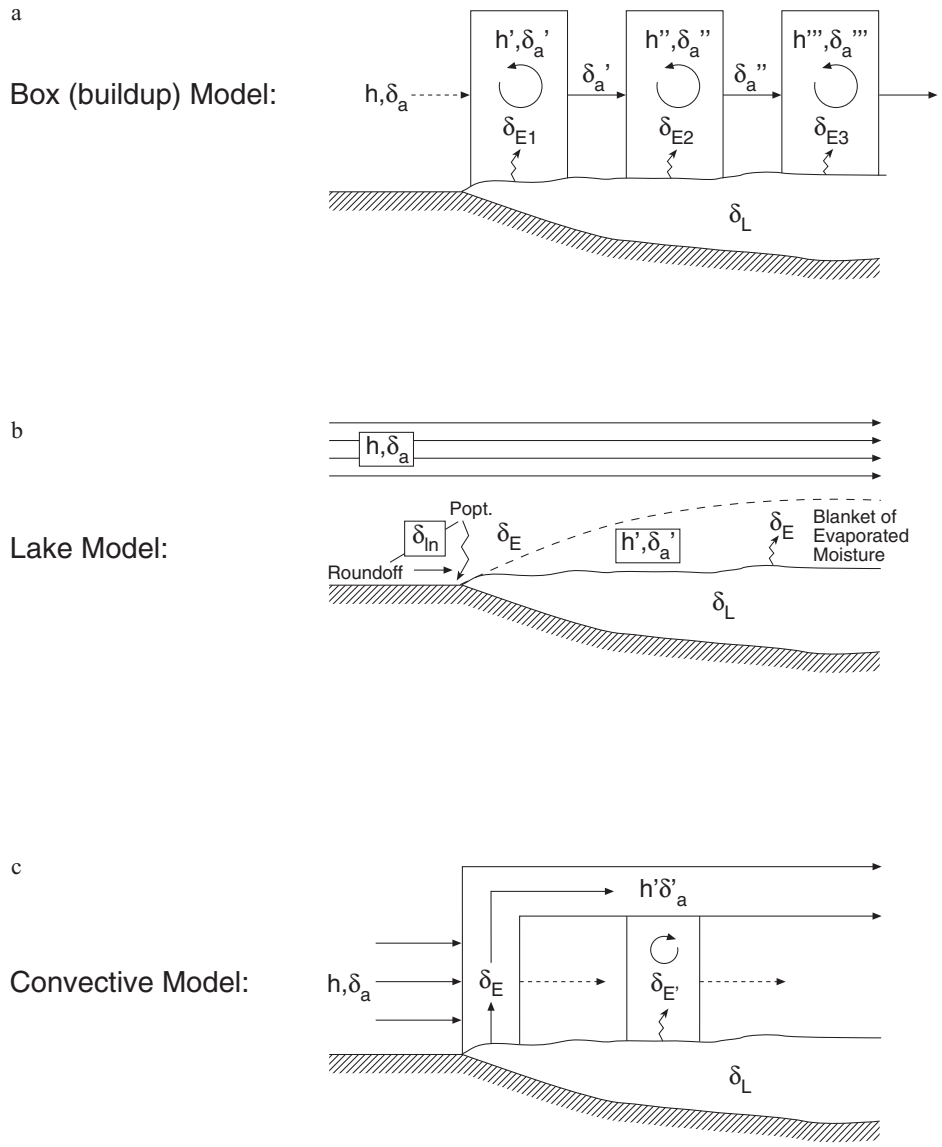

Fig. 7. Schematic representation of the three air-sea interaction models, namely: (a) the box (moisture buildup) model, (b) the lake model and (c) the leeside convective model.

between −11‰ to −12‰, situated close to the GMWL (Craig and Gordon, 1965). Sample no. 1 at mast height apparently resembles this western component.

For the case of the European air masses, one can use the data for the isotopic composition of precipitation from the GNIP (Global Network of Isotopes in Precipitation) (IAEA, 1992) for stations in central and southeastern Europe, namely from Locarno, Thonon, Constance, Regensburg, Zagreb, Vienna, Ankara, Oddessa and Rostov-on-Don, and then, on the assumption of isotopic equilibrium between vapour and precipitation, estimate the vapour's isotope composition. During the winter months, December–February, the isotope composition of precipitation is usually rather

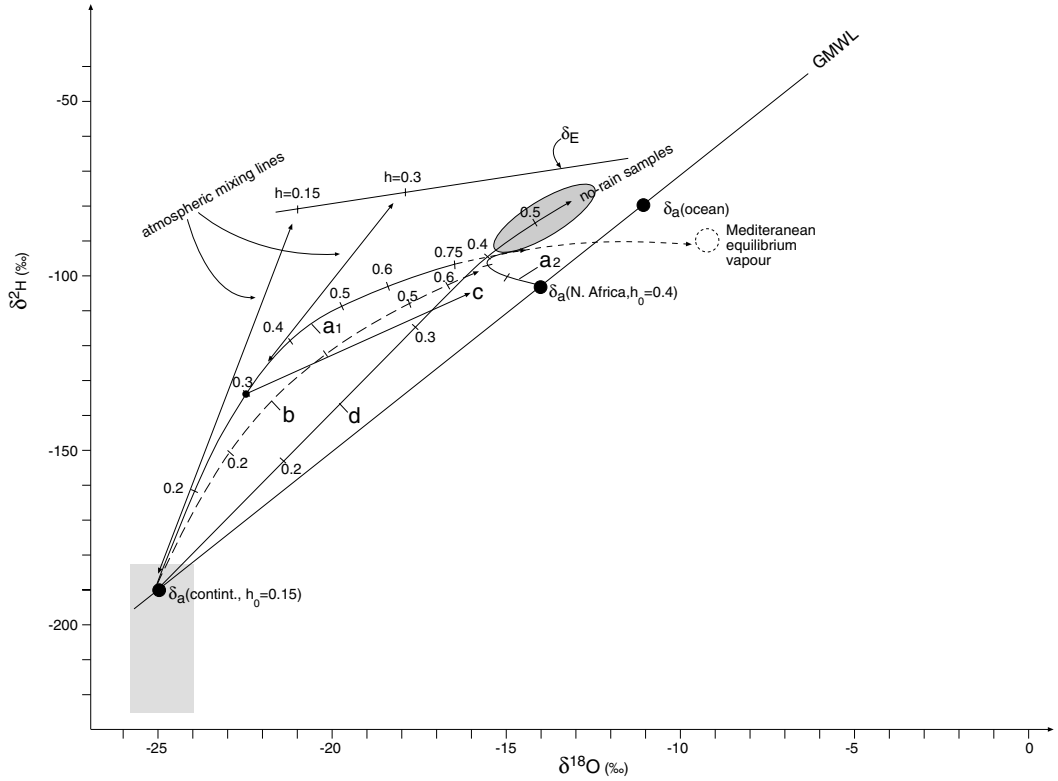

Fig. 8. The value of δ_E (according to the Craig–Gordon model) and the evolution of the isotopic composition of air moisture in an air mass of continental origin as humidity builds up over the sea according to the box model [for European and North African air masses, curves (a-1) and (a-2), respectively], the lake model [curve (b)] and the leeside-convective model [curve (c)]; in the latter case the assumed starting airmass is that produced by the box model with $h = 0.3$. Curve (d) applies to the case when 50% of the humidity results from evaporation of sea spray ($X = 1/2$); numbers shown are the relative humidity values of the air masses concerned as the humidity increases by incorporation of the evaporate. The shaded area around the point δ_a (contint. $h = 0.15$) represents the possible variations in the input, as discussed in the text.

uniform over this area, with a mean value of $\delta^{18}O = -12.5 \pm 1.5‰$ (IAEA, 1992). The particular month in question, January 1995, was no exception (IAEA–GNIP data set). At the prevailing temperature of around the freezing point, the equilibrium isotope separation factor of the oxygen isotopes between the vapour and the liquid precipitation is $\epsilon^*(^{18}O) = 11.7‰$ and that of the hydrogen isotopes $\epsilon^*(^2H) = 111‰$ (Majoube, 1971). One can then expect a range of $\delta^{18}O$ values between −23.7‰ and –25.7‰ in the atmospheric moisture which moves over the sea from the European continent. The corresponding δ^2H values could range between −185.5‰ and −216‰, based on the mean d_{excess} value of $d = 10.16 \pm 3.3‰$ for the precipitation at the abovementioned stations. Based on the vapour content in the continental air, one calculates the value of $h_0 = 0.15$ relative to the saturated vapour pressure over the warm sea (SST = 17 °C).

For the case where warmer air from the North African continent is involved, the estimated value is δ_a (^{18}O) ≅ −14‰ and δ_a (^2H) ≅ −102‰. In this case the initial humidity value is assumed to be close to $h_0 = 0.4$.

The evolution of isotopic composition of air moisture in the modified air over the sea is described in Fig. 8 for the box model as the air humidity increases to saturation, based on the boundary conditions as they apply in the Mediterranean during this cruise. The

upper line shows the δ_E values as calculated according to eq. (1) for the changing humidity deficit over the sea. Increments of these compositions, equivalent to additions of 0.05 in the humidity, added to the ambient moisture along the appropriate mixing lines then yield the modified isotopic composition of the air moisture as the humidity builds up. It can be seen that although the initial boundary conditions are quite different for the cases of European or North African air masses, the computed values converge on rather similar ones as humidity builds up to high values of relative humidity. The expected changes in the isotope content in air moisture for the case of the "lake model" as well for the "leeside convective model" are also shown in Fig. 8.

In the case of the first two models, namely the box and the lake model, one would expect a negative gradient of the d_{excess} parameter upwards from the sea surface, i.e. $(d^{mast} - d^{deck}) < 0$. Conversely, in the case of the "leeside convective model" one obviously expects $(d^{mast} - d^{deck}) > 0$, as indeed seems to be the case in the eastern Mediterranean area.

5. Discussion and summary

The isotopic vapour data agree in a general way with the concept that large d_{excess} values in atmospheric waters of the Mediterranean region result from the intensive evaporation near the coast, under conditions of a large humidity deficit. This is seen in the present data set both along the European coast, most prominently off the coast of Albania in the southern Adriatic and south of Turkey, and to a lesser extent in the case of air masses originating from northern Africa.

In confirmation of the classical pattern of air–sea interaction (Gat and Carmi, 1970), the high d_{excess} values are encountered whenever cold and dry air from the European continent impinges on the warmer waters of the Mediterranean. A somewhat unexpected feature of this data set are those cases in the Mediterranean with relatively high d_{excess} values (e.g. samples nos. 10 and 15), where the air masses originate from North Africa and are quite warm.

The lowered d_{excess} values further away from the coast, which were postulated in the classical air–sea interaction model, are also noteworthy.

In order to explore the details of the processes at play, the data points are compared to values expected for the different air–sea interaction models. It is seen that the measured values are in qualitative agreement in their position above the Global Meteoric Water Line (Fig. 8) but deviate considerable from the model values expected for the measured humidity, being further enriched by up to 5‰ in ^{18}O (Fig. 9).

In the models used, the isotope fractionation results from diffusive transport from the liquid surface layer according to the classical Craig–Gordon (1965) model. This model does not account for a possible additional flux resulting from the evaporation of sea-spray droplets that does not fractionate between the isotopic species in those cases when the droplets evaporate completely. As already recognized by Craig and Gordon (1965) such a bypass flux may have to be reckoned with in the open sea under strong wind conditions. In terms of the models presented one would then substitute the weighted value of $\delta'_E = X\delta_E + (1-X)\delta_{SS}$ for the value of δ_E as given by the diffusion model [eq. (1)], where X is the fraction of the evaporation flux which follows the Craig–Gordon model for diffusive transport and δ_{SS} is the isotope composition of the sea-surface layer, which is assumed to be also that of the sea-spray droplets.

In Fig. 9 the isotope values which accompany the buildup of atmospheric moisture for the assumed values of $X = 2/3$ and $X = 1/2$, respectively, are shown. The latter value appears to give good agreement to the measured data points. These relationships are also shown on the δ^2H vs. $\delta^{18}O$ diagram in Fig. 8, by line (d). The relative importance of the evaporation by means of the sea-spray mechanism is not too surprising, in view of the known large increase in the air–sea interaction under "whitecap" conditions.

One should, of course, also consider the possibility that deviations from the expected model values may have resulted from the trapping of droplets in the sampling device. Such a scenario is not too plausible in view of the high elevation of the sampling input point, more than 20 m above the sea surface. Measurements on sea spray and sea salt by Taylor and Wu (1992) have shown that already at a height of 10 m above the sea surface, even under high wind conditions, the number of droplets is very small. The admixture of spray droplets would have resulted in an even stronger deviation from the MWL than actually observed; only the sampling points nos. 9, 20 and 23 show an isotopic composition that could be consistent with such a scenario, most noticeably sample no. 23, the isotope value of which is indeed an outlier. However, the meteorological logs do not indicate any unusual wind conditions even in this case.

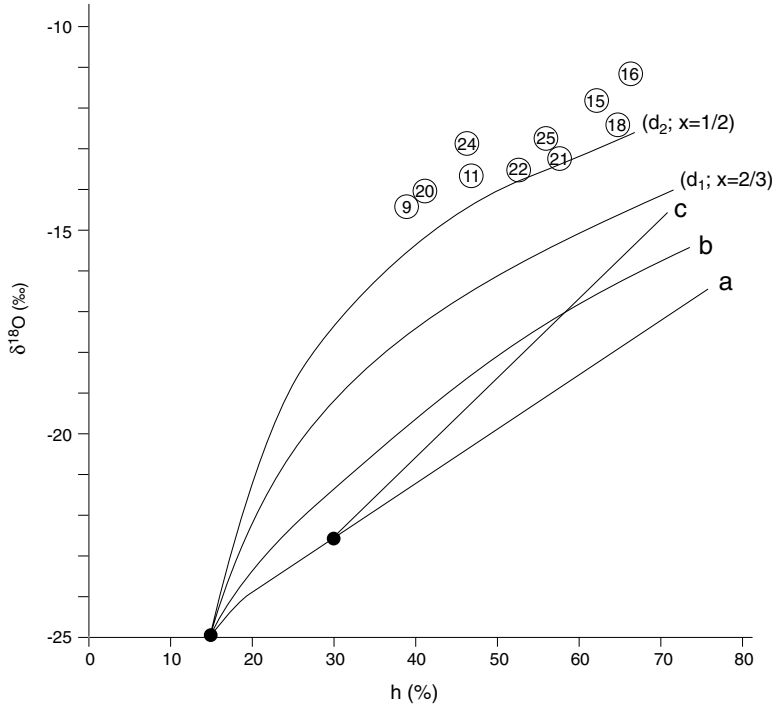

Fig. 9. Comparison of measured ^{18}O data (for no-rain conditions) during the buildup of the air moisture with the calculated values, as a function of the humidity. Lines (a), (b) and (c) correspond to the simple box model, the lake model and the leeside-convective model, respectively. Lines (d-1) and (d-2) correspond to the case where part of the humidity results from non-fractionating evaporation of sea spray; the two curves shown correspond to the situation where, respectively, $X = 2/3$ and $X = 1/2$ of the evaporation is by diffusive transport. [Obviously $X = 1$ in the case of lines (a)–(c).

It should be noted that as humidity builds up in an air mass by means of a vapour-mediated process the isotopic values in such an air mass trend towards that of the "equilibrium vapour," whereas the addition of sea-spray moisture obviously moves the data in the direction of the sea-water isotopic composition. It is this difference that enables one to use the isotopic data to distinguish between these effects. In confirmation, however, future sampling campaigns should also record the sea-spray spectrum and salt content at the air intake position, in order to eliminate samples suspect of this admixture.

The best indication of which of the three models considered best represents the air–sea interaction mode over the Mediterranean is given by the vertical gradient of the d_{excess} values. It is gratifying that these seem to confirm the basic working hypothesis of the Mediterranean moisture regime, namely the importance of the convective motions in the north-eastern margin of the Mediterranean, which give rise to the special attributes of the "Mediterranean climate".

In order to enable more reliable modeling, a more detailed and continuous data set along the air-mass paths would be most desirable, including a vertical vapour isotope profile to higher altitudes, a record of the vertical stability and the documentation of "white-cap" conditions.

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