

The stable isotope composition of waters of the eastern Mediterranean Sea

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Abstract Waters of the eastern Mediterranean portray an unusual pattern of stable isotope composition compared with other evaporitic systems: an increase in ¹⁸O concentration up to value of $\delta^{18}\text{O} = +2.2\%$ is not matched by a commensurate increase of deuterium. It is shown that this unusual pattern is an expression of the "medi-terranean" location of the sea, where the air-sea interaction with relatively dry and isotopically depleted continental air masses dominates the evaporation process in winter and where the diluting meteoric waters are extremely depleted in the heavy isotopes. As a result, the slope of the evaporation line in $\delta(^2\text{H})-\delta(^{18}\text{O})$ space is lower than in other marine systems, whereas the mixing line between the meteoric waters and the seawater is very steep. This pattern provides an independent method for the estimation of the evaporation E and freshwater influx terms M of the water balance of the Mediterranean Sea. In winter the ratio of evaporation to freshwater input is found to be $E/M = 1.20$, whereas in summer this ratio $E/M = 1.83$.

1. Introduction

The stable isotope composition of ocean waters complements temperature-salinity data in providing information on the origin and mixing pattern of water masses [Craig and Gordon, 1965; Ferronsky and Brezgunov, 1989; Anati and Gat, 1989]. The isotopic composition of the oceanic water masses changes as a result of water loss by evaporation that enriches the heavy isotopic species (H_2^{18}O and $^1\text{H}^2\text{HO}$) in the surface waters, the "E" process on the one hand, and on the other hand by the "P" process, namely, the addition of meteoric waters from precipitation over the sea or from continental runoff. As a rule, such meteoric waters are depleted in the heavy isotopes compared with the mean ocean waters [Craig, 1961a]. Unlike the salinity, which is directly proportional to the excess of evaporation over precipitation inputs and remains unchanged when $E = P$, the isotopic signature of these two processes is not simply additive, as will be discussed.

An extreme example of an evaporative marine basin with $E \gg P$ is the Red Sea, where evaporation is practically the sole process that changes the isotope composition of seawater; there is no riverine input, and precipitation is scarce. The waters of the Red Sea were indeed found to be enriched in the heavy isotopes compared with the Indian Ocean waters which enter through the straits at Bab-el-Mandeb. The most enriched waters reported were $\delta(^{18}\text{O}) = +2.0\%$. The following relationships were established by Craig [1966] between the isotopic and salinity parameters of the Red Sea (both S and the δ values are given in

per mil, where S is the gram amount of solids in a kilogram of seawater or equivalent formulations [Lewis and Perkin, 1981]; the isotopic δ value represents the difference of the isotopic ratio of oxygen and hydrogen, respectively, from that of the mean ratio of the ocean (SMOW) [Craig, 1961b], relative to the latter, with positive values indicating the enrichment of the heavy isotopic species ¹⁸O and ²H and negative values their depletion):

$$\begin{aligned} \Delta\delta(^{18}\text{O})/\Delta S &= 0.29; \quad \Delta\delta(^2\text{H})/\Delta S = 1.72; \\ \Delta\delta(^2\text{H})/\Delta\delta(^{18}\text{O}) &= 6.0 \end{aligned}$$

Examples for the other extremes of marine systems, where $E \ll P$, are brackish water basins, such as the Baltic Sea [Ehhalt, 1969; Forstel, 1983], the Black Sea [Swart, 1991], and estuaries, as well as the high-latitude oceans. In these systems, waters are depleted in the heavy isotopic species and the isotopic values fall along a mixing line between the isotopic composition of seawater and that of the freshwater input. The slope of such a mixing line $\Delta\delta/\Delta S$ increases when the δ value of the freshwater decreases [Friedman et al., 1964].

In the major ocean basins the precipitation returns most of the evaporated moisture, so that the changes in the isotopic value of the seawater are moderate and usually correlated with the salinity. For example, Craig and Gordon [1965] reported a value of $\Delta\delta(^{18}\text{O})/\Delta S = 0.11$ for the equatorial ocean where $P > E$, whereas higher values are encountered in the trade wind belt ($P < E$) and the northern Atlantic [Eremeev, 1972]. In these regions, ¹⁸O and deuterium variations are also linearly correlated [Ferronsky and Brezgunov, 1989].

In the Mediterranean Sea both evaporation and addition of freshwaters play a significant role in its water budget. $E > P$ in the basin as a whole, and the net inflow through the Straits of Gibraltar is estimated to be $1.2 - 2.5 \times 10^{15} \text{ m}^3 \text{ yr}^{-1}$ [Carter, 1956]. There are major freshwater inputs both from river inflow and direct precipitation, all of these with varied isotopic compositions. The Mediterranean Sea, as its name implies, differs from the open oceans in that evaporation is affected by the moisture of continental air masses, whose isotopic composition differs considerably from typical marine air, and most of the

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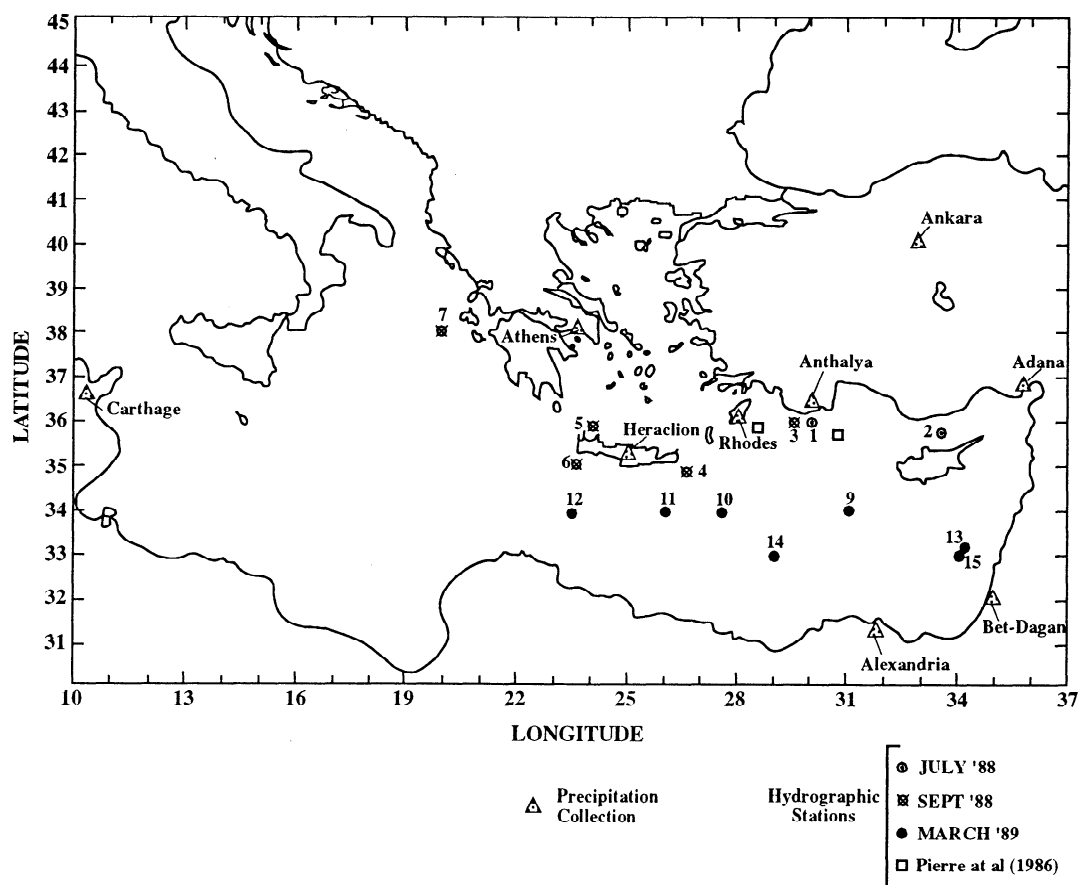


Figure 1. Location map of the hydrographic stations in the eastern Mediterranean, from which water samples were taken for isotopic analysis. Precipitation collection stations belong to the International Atomic Energy Agency - World Meteorological Organization network.

precipitation/runoff originates from outside the region proper. As a result, one can expect rather unusual isotopic signatures of these processes, yielding unique and distinguishable isotopic values in the Mediterranean water masses.

Isotopic measurements reported by *Pierre et al.* [1986], *Anati and Gat* [1989] and by Dansgaard [private communication, 1963], show enrichments of ^{18}O up to a value of $\delta(^{18}\text{O}) = +1.68\text{‰}$ in surface waters of the eastern Mediterranean. *Fontes et al.* [1965] reported a value of $\delta(^{18}\text{O}) = +2.3\text{‰}$ in coastal waters in the western Mediterranean for a salinity of 38.5‰. Only few deuterium values have been reported for the Mediterranean Sea [*Anati and Gat*, 1989].

We report a detailed set of oxygen and hydrogen isotope data from samples obtained during 1988/1989. The samples were collected with a view toward establishing the stable isotopes as a tracer to unravel the water balance and to characterize the water masses of the eastern Mediterranean.

2. Sampling Program and Results

Figure 1 shows the hydrographic stations where water was sampled for isotopic analysis (^2H , ^3H , ^{18}O) between July 1988 and March 1989 during cruises related to the Physical Oceanography of the Eastern Mediterranean (POEM) program [*POEM*, 1985]. Locations of the stations in the eastern Mediterranean for which *Pierre et al.* [1986] reported ^{18}O data are also shown.

Temperature (T) and salinity (S) were measured in situ at the sampling stations using standard oceanographic techniques. The isotopic analyses were performed at the Rehovot Isotope Laboratory (RIL). Stable isotope analyses were performed on a Finnigan-MAT 250 mass spectrometer using standard techniques (i.e., CO_2 -water equilibration for ^{18}O measurements and reduction on uranium metal for the hydrogen isotopes). All samples were run in duplicates, and the results are reported in $\delta(\text{‰})$ units with reference to SMOW [*Craig*, 1961b]. Overall reproducibility (1σ error) of the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ measurements are $\pm 0.035\text{‰}$ and 0.53‰ , respectively. Such a high analytical performance is required in marine systems where the variability of isotopic composition is very small.

The results of the analysis for the water samples at the different stations are given in Table 1. The isotope data from the eastern Mediterranean are shown in Figure 2 in $\delta(^2\text{H})$ versus $\delta(^{18}\text{O})$ space. The remarkable and surprising feature of these results is the almost constant $\delta(^2\text{H})$ value throughout the basin, irrespective of the changes in salinity and $\delta(^{18}\text{O})$. In greater detail, as shown in Figure 3, this property is especially notable in the surface waters during the winter months, whereas in summer the observed $\Delta\delta(^2\text{H})/\Delta S$ slope of 1.64 is close to that found in the Red Sea by *Craig* [1966].

The explanation of this pattern and its utilization for deriving information on the water budget of the eastern Mediterranean is the focal point of the following discussion, after a brief review of the isotopic characterization of different water masses.

Table 1. Station Location and Hydrographic and Isotopic Parameters of All Samples

Sample	Depth, m	$\delta^2\text{H}$, ‰	$\delta^{18}\text{O}$, ‰	Temperature, °C	Salinity, ‰
<i>Station 1 (36°00'N, 36°00'E; Bottom, 1000 m; Sampled July 24, 1988; Turkey)</i>					
2498	5	8.44	2.188	27.915	38.894
2499	50	7.38	1.763	18.003	38.984
2500	100	8.04	1.726	16.404	39.007
2501	200	8.29	1.741	16.165	38.995
2502	300	7.49	1.949	15.704	38.991
2503	500	8.13	2.200	14.144	38.820
2504	1000	8.20	2.376	13.558	38.703
<i>Station 2 (35°40'N, 33°33'E; Bottom, 1000 m; Sampled July 7, 1988; Turkey)</i>					
2505	5	7.83	1.842	28.087	38.877
2506	50	10.36	2.044	16.819	38.996
2507	100	9.12	1.843	15.976	38.990
2508	200	10.29		14.796	38.911
2509	300	8.59	2.002	14.056	38.799
2510	500	9.74	2.132	13.631	38.717
2511	750	8.56	2.416	13.456	38.679
2512	1000	8.23	2.162	13.379	38.661
<i>Station 3 (36°00'N, 29°30'E; Bottom, 1930 m; Sampled Sept. 11, 1988; Greece)</i>					
2568	10			26.510	39.310
2569	75			17.800	38.940
2570	150	8.71	1.534	15.920	38.980
2571	200	8.71	1.477	15.400	38.980
2572	500	8.06	1.499	13.920	38.770
2573	650	8.71	1.507	13.870	38.760
2574	1000	8.04	1.482	13.650	38.690
2575	1600	7.38	1.535	13.610	38.660
2576	1930	6.38	1.388	13.650	38.660
<i>Station 4 (34°55'N, 26°30'E; Bottom, 2100 m; Sampled Sept. 14, 1988; Greece)</i>					
2577	10	9.14	1.549	24.980	39.250
2578	70	7.83	1.410	18.630	38.580
2579	100	6.57	1.519	15.330	38.970
2580	500	8.38	1.460	14.250	38.860
2581	800	8.14	1.460	13.990	38.800
2582	1200	7.61	1.898	14.050	38.810
2583	1600	7.83	1.429	13.740	38.700
2584	2100	8.39	1.629	13.670	38.660
<i>Station 5 (36°00'N, 24°12'E; Bottom, 1000 m; Sampled Sept. 15, 1988; Greece)</i>					
2585	10	8.15	2.108	24.200	39.140
2586	50	8.05	1.738	16.020	38.860
2587	125	7.79	1.640	15.100	38.960
2588	150	6.96	1.614	14.960	38.950
2589	400	7.76	1.547	14.620	38.930
2590	800	7.53	1.678	14.350	38.920
2591	1000	7.93	1.628	14.330	38.920

Table 1. (continued)

Sample	Depth, m	$\delta^2\text{H}$, ‰	$\delta^{18}\text{O}$, ‰	Temperature, °C	Salinity, ‰
<i>Station 6 (35°00'N, 23°30'E; Bottom, 3300 m; Sampled Sept. 16, 1988; Greece)</i>					
2592	10	8.87	1.505	24.020	39.090
2593	50	7.55	1.705	16.310	38.790
2594	75	8.92	1.510	15.750	38.930
2595	300	8.03	1.535	14.640	38.930
2596	400	7.47	1.190	14.320	38.880
2597	500	7.89	1.210	14.240	38.860
2598	850	8.16	1.195	13.820	38.750
2599	1500	7.45	1.330	13.680	38.680
2600	2100	7.78	1.130	13.640	38.650
2601	3300	7.54	0.985		
<i>Station 7 (38°00'N, 20°00'E; Bottom, 3650 m; Sampled Sept. 19, 1988; Greece)</i>					
2602	10	7.81	1.383	24.170	38.540
2603	25	7.71	1.386	22.020	38.380
2604	250	7.64	1.622	14.440	38.830
2605	300	8.48	1.551	14.390	38.830
2606	500	7.70	1.496	14.080	38.790
2607	900	8.43	1.427	13.750	38.720
2608	1500	8.41	1.815	13.640	38.670
2609	2100	8.26	1.538	13.650	38.650
2613	3650	6.90	1.407		
<i>Station 9 (34°00'N, 31°00'E; Bottom, 2250 m; Sampled March 2, 1989; Israel)</i>					
2660	10	7.51	1.802	15.677	39.075
2661	200	7.47	1.631	15.134	39.043
2662	300	8.59	1.610	14.439	38.913
2663	400	7.46	1.545	14.122	38.849
2664	500	7.07	1.573	13.975	38.821
2665	600	7.83	1.298	13.881	38.797
2666	700	7.92	1.448	13.785	38.771
2667	800	6.51	1.487	13.728	38.754
2668	1000	7.78	1.508	13.655	38.727
2669	2550	7.38	1.382	13.752	38.690
<i>Station 10 (34°00'N, 27°30'E; Bottom, 2400 m; Sampled March 12, 1989; Israel)</i>					
D2618	10	8.03	1.840	14.889	38.994
D2619	200	7.27	1.830	14.411	38.955
D2620	300	7.54	1.985	14.125	38.882
D2621	400	8.31	1.990	14.134	38.890
D2622	600	7.21	1.680	14.122	38.880
D2623	1000	7.12	1.606	13.749	38.760
D2624	2400	8.04	1.604	13.717	38.695

Table 1. (continued)

Sample	Depth, m	$\delta^2\text{H}$, ‰	$\delta^{18}\text{O}$, ‰	Temperature, °C	Salinity, ‰
<i>Station 11 (34°00'N, 26°00'E; Bottom, 2700 m; Sampled March 7, 1989; Israel)</i>					
2713	10	8.13	1.526	16.514	39.186
2714	100	8.23	1.936	16.547	39.227
2715	200	7.25	1.772	16.346	39.178
2716	400	8.44	1.761	15.446	39.060
2717	500	7.72	1.804	15.133	39.034
2718	600	7.03	2.027	14.880	39.001
2719	700	7.97	2.008	14.643	38.964
2720	800	7.54	2.167	14.730	39.010
2721	1000	6.97	2.076	14.465	38.943
2722	2700	7.62	1.575	13.774	38.692
<i>Station 12 (34°00'N, 23°30'E; Bottom, 2115 m; Sampled March 12, 1989; Israel)</i>					
2625	0	8.00	1.493	15.674	38.488
2626	50	7.05	1.724	15.528	38.533
2627	100	7.90	1.473	15.828	38.967
2628	150	8.40	1.945	15.181	38.950
2629	200	7.92	1.689	14.792	38.950
2630	400	7.80	2.174	14.083	38.850
2631	600	7.02	1.625	13.907	38.808
2632	800	7.09	1.954	13.805	38.780
2633	1000	7.30	1.742	13.680	38.739
2634	2115	7.19	1.371	13.648	38.690
<i>Station 13 (33°00'N, 34°00'E; Bottom, 1700 m; Sampled March 23, 1989; Israel)</i>					
2702	10	8.06	1.821	17.286	39.050
2703	50	8.40	1.685	16.658	39.083
2704	100	8.21	1.969	16.450	39.073
2705	150	7.38	2.050	16.430	39.094
2706	200	8.31	1.688	16.112	39.051
2707	300	7.92	1.606	14.877	38.923
2708	400	7.35	2.366	14.153	38.826
2709	500	7.81	1.831	13.946	38.784
2710	1000	7.47	1.555	16.641	38.702
2711	1500	7.33	1.796	13.610	38.675
2712	1700	7.75	1.744	13.629	38.673
<i>Station 14 (33°00'N, 29°00'E; Bottom, 2800 m; Sampled March 13, 1989; Israel)</i>					
2652	10	8.44	1.485	16.069	38.998
2653	100	8.28	1.635	15.878	39.000
2654	200	8.66	1.535	15.349	38.976
2655	300	8.05	1.485	14.805	38.957
2656	400	8.54	1.475	14.427	38.883
2657	600	7.93	1.495	14.007	38.797
2658	1000	7.91	1.270	13.703	38.710
2659	2800	8.09	1.305	13.788	38.660

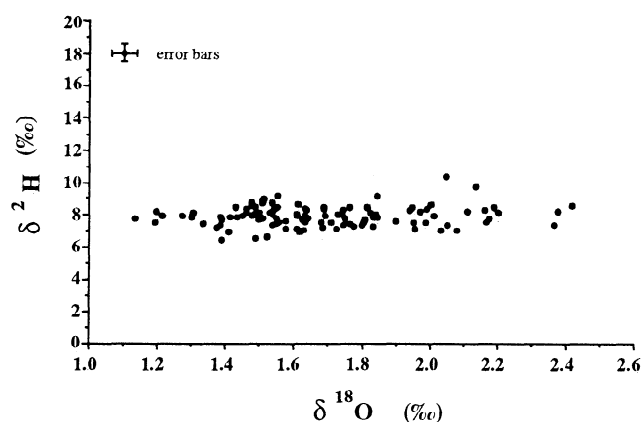


Figure 2. The isotopic data of all eastern Mediterranean seawater samples, on a $\delta(^2\text{H})$ versus $\delta(^{18}\text{O})$ plot. Per mil values are given relative to the SMOW standard.

3. Isotopic Characteristics of the Water Masses of the Eastern Mediterranean Sea

The water mass modification by air-sea fluxes of heat and fresh water (evaporation, precipitation, and river runoff) results in the formation of the deep waters of the Mediterranean Sea. The Levantine Intermediate Water (LIW) is believed to form south of

Asia Minor, with a temperature of about 15°C and salinity of 39.1‰. It flows from its formation site toward the Gibraltar Straits at a depth of about 200-400 m in the eastern Mediterranean and down to 600-700 m in the western Mediterranean. The deep water of the eastern Mediterranean lies below the LIW and is apparently formed mostly in the Adriatic Sea, with a temperature of 13.3°C and salinity of 38.65‰, although a change in these properties has recently been observed [Roether, private communication, 1995]. The deep water of the western Mediterranean is formed in the Gulf of Lions, with typical properties being $T=12.6^\circ\text{C}$ and $S=38.4\text{‰}$. This saline Mediterranean water flows into the Atlantic Ocean through the Straits of Gibraltar and can be traced throughout large parts of the world ocean. The Gibraltar outflow is balanced by the inflow of relatively fresh Atlantic Water (AW) that can be found throughout the Mediterranean basin below the surface water and above the LIW at a typical depth range of 25 to 75 m. Many studies deal with water mass analysis of the Mediterranean [Wüst, 1961; Pickard and Emery, 1990] (see also Malanotte-Rizzoli and Hecht [1988] and Hopkins [1988] for reviews of the eastern and western Mediterranean, respectively), but we still lack reliable estimates of the rate of formation of each water mass [Tziperman and Speer, 1994].

Some of the individual depth profiles, given in Table 1, show the clear isotopic signature of the different water masses. As an example, we note at station 6 the transition below the 300-m

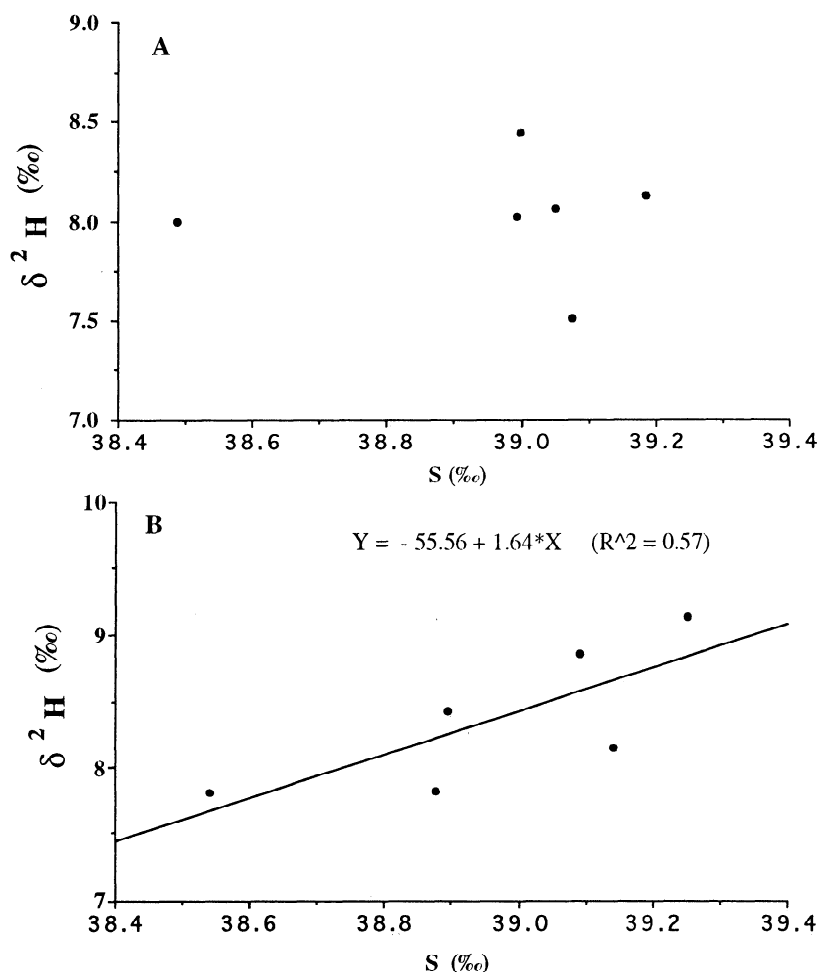


Figure 3. Plot of the $\delta(^2\text{H})$ values of the surface waters of eastern Mediterranean samples versus salinity for (a) winter and (b) summer. Station numbers (Table 1) are indicated.

Table 2. Water Mass Characterization in the Eastern Mediterranean

Depth, m	Salinity, ‰	Temperature, °C	δ ¹⁸ O, ‰	δ ² H, ‰
200 - 400, summer	38.92 ± 0.06	14.90 ± 0.11	1.62 ± 0.25	8.34 ± 0.80
200 - 400, winter	38.95 ± 0.09	14.80 ± 0.70	1.76 ± 0.25	7.92 ± 0.49
500 - 1000, all year	38.80 ± 0.10	14.00 ± 0.40	1.55 ± 0.19	7.83 ± 0.46
>1000, all year	38.68 ± 0.04	13.70 ± 0.10	1.51 ± 0.15	7.46 ± 0.41

depth to waters with the characteristics of the western Mediterranean. Similarly sharp transitions are noted at station 10 (below 400 m). In contrast, at stations 11 and 12 south of Crete, the more depleted isotopic values are encountered below 1000 m, whereas highly enriched (and somewhat cooler) intermediate waters are found at a depth of 400 to 1000 m. These evidently are relative young waters, as shown by their tritium content [Gat et al., 1995]. In order to delineate the movement and mixing of the waters, one would, however, require a more closely spaced (in time and space) sampling.

Average isotopic compositions of the water masses are given in Table 2. Owing to the significant seasonal and spatial variability of the parameters in the water column, the details are lost in these values, which are averaged over a water depth slice. However, the essential constancy of δ(²H) values for a range of 0.25‰ in δ(¹⁸O) is once more apparent.

4. Discussion of the Isotope Balance of the Mediterranean

4.1. The Balance Equations

Figure 4 shows the relationships of a body of surface water to its environment in a schematic fashion. In such a body of surface water of constant volume *V*, in which the inflow *F*_{in} and outflow *F*_{out} (for example, by advection and deep water formation) are balanced by evaporation *E* and freshwater inputs *M*, the isotope content δ and the salt concentration *C* are described by the following continuity equations:

$$V \frac{d\delta_{sw}}{dt} = F_{in}\delta_{in} - E\delta_E + M\delta_M - F_{out}\delta_{sw} + X \times (\Delta\delta) = F_{in}[\delta_{in} - \delta_{sw}] - E[\delta_E - \delta_{sw}] + M[\delta_M - \delta_{sw}] + X \times (\Delta\delta) \quad (1)$$

$$V \frac{dC_{sw}}{dt} = F_{in}C_{in} - F_{out}C_{sw} + X \times (\Delta C) = F_{in}(C_{in} - C_{sw}) + (E - M)C_{sw} + X \times (\Delta C) \quad (2)$$

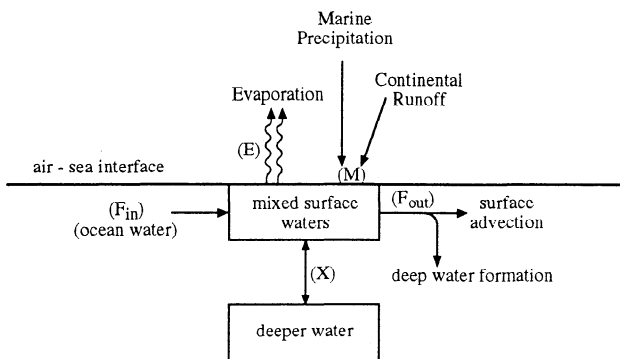


Figure 4. Scheme of the relationship of a (mixed) surface water parcel to freshwater influx, evaporation, and adjacent marine water bodies.

where the subscripts *E*, *M*, in, and *sw* refer to the evaporation flux, meteoric water inputs (by precipitation and runoff), the input waters, and the ocean surface waters, respectively. *X* represents a mixing (exchange) flux with other (e.g., deeper) oceanic water masses; Δδ and Δ*C* represent the isotope and salt concentration differences between the surface and the other ocean water layers with whom mixing occurs, respectively. In (2) the salt input by freshwater runoff has been neglected.

Assuming steady state conditions with regard to both isotopic values and salinity (and neglecting the exchange terms *X*), a rather simple relationship can be established between the isotopic buildup and the increase in salinity:

$$\delta_{sw} = \left\{ \delta_{in} - \frac{E}{F_{in}}\delta_E + \frac{M}{F_{in}}\delta_M \right\} \left(\frac{C_{sw}}{C_{in}} \right) \quad (3)$$

Having data for the two isotopes, ¹⁸O and ²H, respectively, one can then evaluate the value of *E*/*M* (section 4.4). As a first step, however, the terms δ_{*E*} and δ_{*M*}, as they apply to the system under consideration, have to be evaluated. The neglect of the mixing term *X*(Δδ) can be justified a posteriori and is due to the small value of Δδ when compared with the other terms in the balance equation.

4.2. The Isotopic Composition of the Evaporation Flux Over the Mediterranean Sea

The isotopic composition of the evaporation flux from an open water surface δ_{*E*} is not amenable to direct measurement. It differs from that of the liquid water which undergoes evaporation because of the following two superimposed fractionation effects: the depletion of the heavy isotopic species in the vapor film which is in equilibrium with the liquid (thermodynamic isotope effect) and an additional isotope separation effect (the so-called kinetic or transport effect) which results from the different rates of diffusion of the isotopic species of water molecules across the humidity gradient in the air boundary layer.

To date, the best model to describe these processes is the linear resistance model of *Craig and Gordon* [1965], which gives the following expression for δ_{*E*}:

$$\delta_E (\%) = (\alpha^* \delta_{sw} - h\delta_a - \epsilon^* - \Delta\epsilon) / \left(1 - h + \frac{\Delta\epsilon}{10^3} \right) \quad (4)$$

where *h* is the relative humidity in the atmosphere with respect to the saturated vapor pressure at the ocean surface and δ_{*a*} is the isotopic composition of this humidity; δ_{*sw*}, as before, is the isotopic composition of the surface waters. The term α* is the unit isotope separation factor for the liquid to vapor phase transition at equilibrium and is given by α* = 1000(δ_v)/(1000+δ_l) < 1; ε* = (1-α*) × 10³ and Δε is an additional diffusive (kinetic) isotope fractionation. According to the *Craig and Gordon* [1965] linear resistance model, Δε has the form of Δε = (1-*h*) × θ × *C_k*, where *C_k* is a "kinetic" constant which

depends on the conditions at the air-water interface [Merlivat and Contiac, 1975]. For a water surface which is exposed to the free atmosphere we take a value of $C_k = 13\%$ and $C_k = 15\%$ for the $^1\text{H}^2\text{HO}$ and H_2^{18}O water species, respectively [Merlivat, 1970]. Here θ is a weighting factor, which for the linear resistance model is given by $\theta = \rho_{\text{mol}}/\rho_{\text{total}}$, where ρ_{mol} is the resistance to vapor transport in the sublayer above the surface in which the molecular diffusivities express themselves and ρ_{total} is the resistance to vertical water transport throughout the air boundary layer, as given by the expression $E=(1-h)/\rho_{\text{total}}$.

On applying these relationships to a large body of water, such as the eastern Mediterranean, where there is a buildup of an air layer in which the evaporated moisture mixes with the advected air and thus influences the E process, one is faced with a dilemma of fixing a reference height above the water surface for which the ambient parameters h and δ_a will be specified [Gat, 1995]. If one chooses a value close to the surface (i.e., at ship mast height), then the weighting term θ can be approximated to be $\theta \rightarrow 1$. On the other hand, owing to the humidity buildup over the sea, the δ_a value differs from that of the advecting continental air mass. The change in the isotopic composition of the atmospheric moisture as a result of the admixture of the evaporation flux is given by material balance considerations as

$$h \times \delta_a + (h-h) \cdot \bar{\delta}_E = h' \times \delta'_a$$

where $\bar{\delta}_E$ is the average value of the evaporative flux over the fetch of the air-sea interaction and the primed values refer to the downwind conditions, following the moisture buildup; all humidities are normalized relative to the saturated vapor pressure over the sea (a function of both temperature and salinity). A detailed set of measurements of both h' and δ'_a at ship mast height would then be required to evaluate $\bar{\delta}_E$; this is not yet readily available for the eastern Mediterranean.

The second alternative is to perform the balance estimate, based on the moisture in unperturbed higher-altitude air, where h and δ_a are the parameters of the advected air. However, in this case, one can no longer assume $\theta=1$. On the basis of the Craig and Gordon [1965] model, the value of θ can be calculated from a comparison of the near-surface air humidity and that of the advected air masses, which are h' and h , respectively. In this case, θ is given by $\theta = (1-h)/(1-h')$. In principle, this term can be evaluated from vertical humidity profiles over the sea.

In the case of the Mediterranean Sea, where the dominant air flow pattern of incoming air is from the Atlantic Ocean via the Iberian peninsula or France (for the western Mediterranean) or from the European continent (for the eastern Mediterranean), one can utilize the isotope data of the International Atomic Energy Agency - World Meteorological Organization (IAEA-WMO) precipitation network [IAEA, 1992] for the southern European stations in order to estimate a monthly averaged δ_a value of the advecting air masses, assuming isotopic equilibrium between precipitation and the air moisture over the continent. This appears to be a reasonable assumption over Europe [Craig and Horibe, 1967; Jacob and Sonntag, 1991]. The reported air humidity of these advecting air masses can then be normalized to the saturated vapor pressure over the sea to obtain a value of " h ". The humidity in the advected air masses compared with shipboard data of humidity [Markgraf, 1961; Oberhuber, 1988] provides us with the necessary information to assess the weighting factor θ .

Table 3 gives the database for calculating the seasonal $\bar{\delta}_E$ value for both hydrogen and oxygen isotopes over the western

and eastern portions of the Mediterranean according to the Craig and Gordon [1965] model. The slope of the evaporation line

$$S = (\delta_E - \delta_{SW})_{2\text{H}} / (\delta_E - \delta_{SW})_{18\text{O}}$$

can then be evaluated. As shown in Table 3, the value of this slope for the Mediterranean is close to a value of 4, lower than the value of 6 derived over other seas. The low slope of the evaporation line is attributed to the depleted δ value of the advecting continental air masses and to their relatively low humidities. Both parameters are an expression of the Mediterranean location of the evaporative system.

4.3. The Isotopic Composition of the Meteoric Water Input Into the Mediterranean

According to the water balance of the Mediterranean, as compiled by Carter [1956], most of the freshwater input into the Mediterranean Sea occurs as direct precipitation, especially in the northeastern part of the sea (estimated at about $1.0 \times 10^{12} \text{ m}^3 \text{ yr}^{-1}$), and as local runoff from the European and Turkish coast ($0.1 \times 10^{12} \text{ m}^3 \text{ yr}^{-1}$). The Nile river flow, which amounted to an estimated $48.4 \times 10^9 \text{ m}^3 \text{ yr}^{-1}$, has dwindled considerably since the building of the Aswan High Dam and so will be ignored by us. The Black Sea drainage basin, which includes the Danube and the large Russian rivers (Dniester and Dnieper) amounts to about $350 \times 10^9 \text{ m}^3 \text{ yr}^{-1}$. Another $230 \times 10^9 \text{ m}^3 \text{ yr}^{-1}$ are contributed by the direct precipitation over the Black Sea. Of these an estimated $200 \times 10^9 \text{ m}^3 \text{ yr}^{-1}$ to $300 \times 10^9 \text{ m}^3 \text{ yr}^{-1}$ are added to the Mediterranean by the net outflow through the Bosphorus and Dardanelles.

A weighted δ value of the freshwater inflows δ_M can be estimated from the averaged precipitation data of the pertinent station in southern Europe and the Mediterranean Sea area [IAEA, 1992] and isotope data of the rivers and the Black Sea outflow to the Mediterranean. The Black Sea data are given as $\delta(^{18}\text{O}) = -2.4\%$, $\delta(^2\text{H}) = -18.95\%$ [Swart, 1991]. The mean precipitation values for the stations of Adana and Antalya (Turkey), Bet Dagan (Israel), and Athens (Greece) that characterize the eastern Mediterranean are $\delta(^{18}\text{O}) = -5.61\%$, $\delta(^2\text{H}) = -28.12\%$ [IAEA, 1992]. For the western Mediterranean precipitation, mean values of $\delta(^{18}\text{O}) = -5.95\%$, $\delta(^2\text{H}) = -36.65\%$ are based on the precipitation at Barcelona (Spain) and Genoa (Italy). The continental drainage is somewhat more depleted in the heavy isotopic species. For example, the mean annual value for the Danube is $\delta(^{18}\text{O}) = -10\%$ (D. Rank, personal communication, 1993) and the mean values of the southern European precipitation stations (Ljubljana, Odessa, Thonon les Bains, Zagreb) are $\delta(^{18}\text{O}) = -9.3\%$, $\delta(^2\text{H}) = -64.4\%$ [IAEA, 1992]. These values are used to characterize the runoff from the European continent into the eastern Mediterranean.

A weighted value of the annually averaged isotopic composition of the meteoric waters input to the Mediterranean is calculated to be

$$\delta_M(^{18}\text{O}) = -6.12\% \quad ; \quad \delta_M(^2\text{H}) = -37.96\%$$

This value of δ_M and the appropriate value of δ_{SW} define a mixing line between the seawater and the fresh waters in $\delta^{18}\text{O} - \delta^2\text{H}$ space with a slope of about $[\Delta\delta^2\text{H}]/[\Delta\delta^{18}\text{O}] = 5.9$. This slope is significantly steeper than that of the evaporation line calculated above for the Mediterranean (Table 3). It is this feature that causes the apparently anomalous $\delta(^{18}\text{O}) - \delta(^2\text{H})$ relationship.

Table 3. Calculation of the Slopes of the Evaporation Lines

	Surface Waters ^a			Advecting Air Masses ^b					Marine Air ^c		δ_E			
	$\delta_{sw}^{(18)}$, ‰	$\delta_{sw}^{(2)}$, ‰	T, °C	$\delta_p^{(18)}$, ‰	$\delta_p^{(2)}$, ‰	T, °C	$\delta_a^{(18)}$, ‰	$\delta_a^{(2)}$, ‰	h, %	h', %	θ	$\delta_E^{(18)}$	$\delta_E^{(2)}$	Slope of EL
<i>Western Mediterranean</i>														
Summer,	+1.405	+7.85	23.3	-3.93	-21.92	22.6	-13.53	-97.72	63.5	82	0.493	-6.31	-22.6	3.94
Winter,	+1.35	+7.50	13.7	-5.53	-33.0	10.8	-16.0	-118.4	62.0	–	0.500	-4.84	-17.5	4.03
<i>Eastern Mediterranean</i>														
Summer,	+1.70	+8.40	25.2	-6.42	-43.7	18.8	-16.17	-119.93	45.5	77.2	0.418	-6.71	-25.8	4.06
Winter	+1.66	+8.03	16.0	-12.19	-88.8	1.3	-23.51	-179.5	30.1	67.73	0.462	-8.88	-36.6	4.24

Here $\delta^{(18)}$ and $\delta^{(2)}$ denote isotopic compositions of oxygen and hydrogen, respectively. Subscripts *sw*, *P*, *a*, and *E* stand for surface waters, precipitation, air moisture and evaporation flux, respectively. The *h* and *h'* are relative humidity, with the prime denoting downwind conditions. EL is evaporation line. Summer is defined as July-September, Winter as January-March.

^a Isotopic surface water data based on present survey and Pierre et al. [1986]. Temperature data based on Tziperman & Manolotte-Rizzoli [1991].

^b Values are based on mean precipitation data from Faro, Barcelona, Marseille and Geneva for Western Mediterranean and from Locarno, Thonon, Regensburg, Konstanz, Vienna, Zagreb, Ankara, Ljubljana, Odessa and Rostov-on-Don for the Eastern Mediterranean; from IAEA (1992) and assuming isotopic equilibrium between the precipitation and air moisture.

^c Values are based on shipboard data of Markgraf [1961] for summer; estimated for winter based on Oberhuber's [1988] compilation.

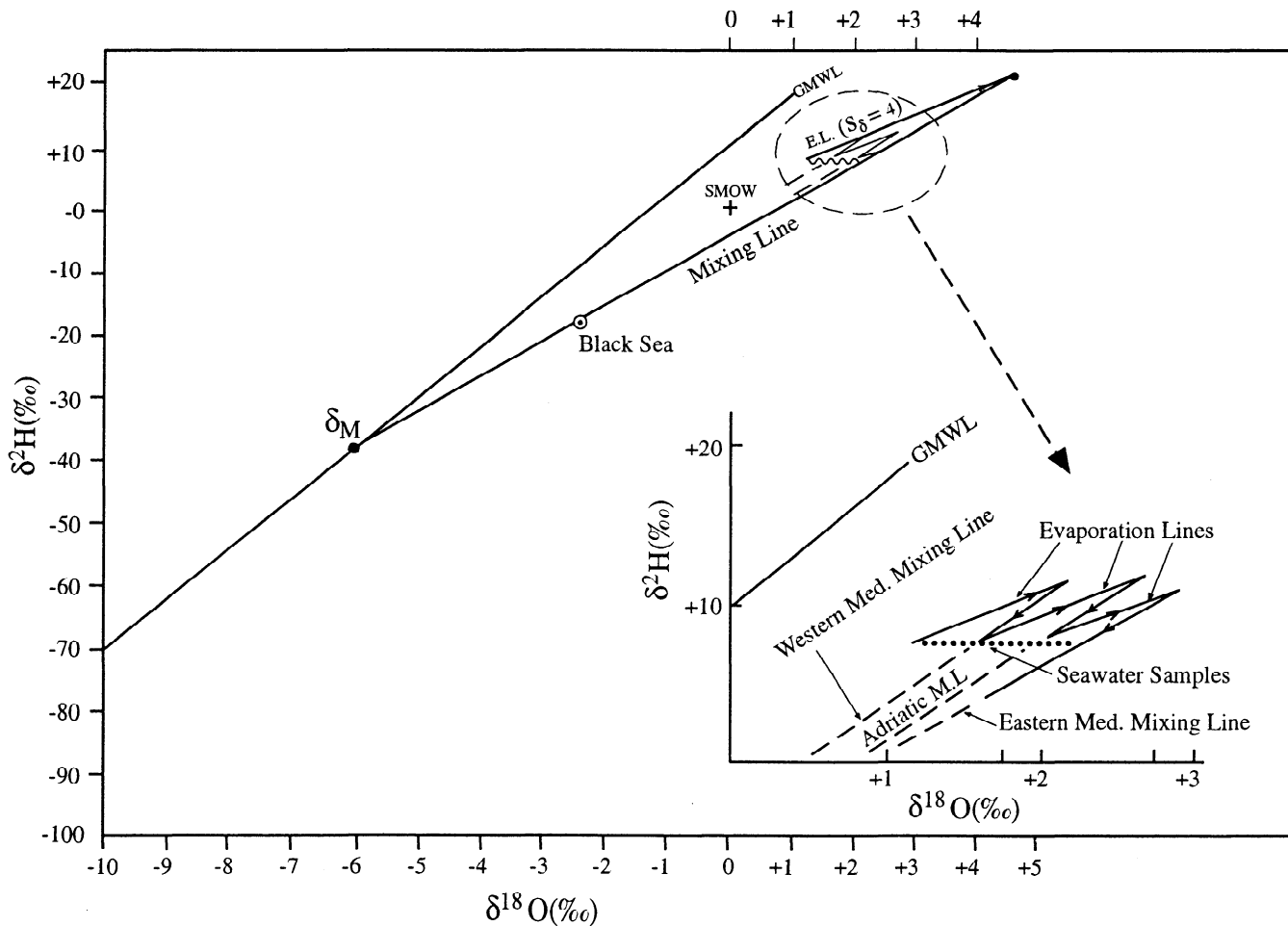


Figure 5. Isotopic relationship of the water masses of the eastern Mediterranean on a $\delta(^2\text{H})$ versus $\delta(^{18}\text{O})$ plot. EL stands for evaporation line, ML for mixing line between the seawater and the freshwater inflow. GMWL is the global meteoric water line, as defined by Craig [1961a]. Black Sea data are given by Swart [1991].

4.4. The Isotopic Balance

On the basis of the data and calculations presented above, an annually averaged isotope balance for the eastern Mediterranean is shown in $\delta(^{18}\text{O}) - \delta(^2\text{H})$ space (Figure 5). The evaporation process alone would be expected to move the isotope value of the surface waters along the E line with a slope close to 4.0. The mixing with the continental runoff and local precipitation results in the final position of the surface waters, which is shifted by about 1‰ in $\delta(^{18}\text{O})$ relative to the inflow waters, with only a minor change in $\delta(^2\text{H})$.

In reality, the E and P processes occur concurrently, producing a zigzag pattern, as shown in the inset of Figure 5. However, our limited data set does not permit us to follow the details of this development. Clearly, in summer, when $E > P$, the coherent increase of the two isotopic species dominates. During winter, with its excess of isotopically depleted freshwater inflows, the changes in these two isotopes are decoupled.

Solving (3) for the eastern Mediterranean with the data presented in Table 3 and taking into account salinity data for surface waters [Tziperman and Malanotte-Rizzoli, 1991], one obtains the following preliminary estimates for the ratio of evaporation and meteoric input fluxes to the inflows (E/F_{in} and M/F_{in} , respectively). In winter these ratios are calculated to be 0.073 and 0.061 with $E/M = 1.20$; for summer the values are

0.076 and 0.041, respectively, yielding a value of $E/M = 1.83$. These estimates can be compared with the numbers given for the year round averages for the total Mediterranean area by Carter [1956], namely, 0.0956 and 0.0476 for the ratios of E/F_{in} , and M/F_{in} , respectively, with uncertainties of more than a factor of 2 for these estimates. Evidently, the isotopic method, even with the limitation of a rather sparse data set, holds the promise of becoming a quantitative measure of the water balance.

5. Conclusions

The relative high enrichment of ^{18}O in waters of the eastern Mediterranean basin provides an oceanographic tracer with potential application to the process of deep water formation and the study of the dynamics of the water masses. However, a denser data network will be required to do full justice to this potential.

The location of the Mediterranean Sea, in between continental areas, expresses itself in an unusual pattern of the $\delta(^2\text{H}) - \delta(^{18}\text{O})$ and the isotope-salinity relationships. In particular, the relative constancy of the deuterium concentrations over a wide range of salinity and $\delta(^{18}\text{O})$ values is noteworthy. A number of factors combine to yield this unique pattern, especially during the winter months. The low humidity and depleted isotopic values of the moisture in the advecting continental air result in a low-slope

isotopic enrichment of surface waters during the air-sea interaction of the continental air with the relatively warm Mediterranean. For this reason, also, the atmospheric moisture over the Mediterranean is distinguishably characterized by a large deuterium excess, as was previously discussed [Gat and Carmi, 1970]. The mixing into the enriched surface waters of the isotopically depleted meteoric waters (direct precipitation and river runoff from the European continent) then results in the finally observed pattern.

By means of these isotopic relationships it is then possible to estimate the evaporation and freshwater input terms in the water balance of the Mediterranean basin. The more readily available salinity changes are a measure only of the surplus of evaporation over inflow.

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