# Recent Changes in Eastern Mediterranean Deep Waters

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Results from a recent hydrographic survey show that an influx of Aegean Sea water has replaced 20 percent of the deep and bottom waters of the eastern Mediterranean. Previously, the only source of such waters was the Adriatic Sea, and the waters of the eastern Mediterranean were in near-steady state. The flux changed the water characteristics and displaced older waters upward. Its cause was increasing Aegean Sea salinity, resulting from changes in either the circulation pattern or the large-scale freshwater balance. Current deepwater studies may be affected by the intrusion, but effects might be found also at shallower depths and over a larger region.

The eastern part of the Mediterranean Sea is subject to a vertical, or thermohaline (*1*), recirculation similar to that of the global ocean. Water densities in the eastern Mediterranean are comparably high and are governed by salt enrichment that is a result of a negative freshwater balance. New deep water is formed where and when surface waters preconditioned by high salinity become sufficiently dense by cooling.

Hydrographic surveys since early this century (*2*) consistently showed that for water below 1200 m over the entire eastern Mediterranean, the dominant source region was the Adriatic Sea. As observed last in 1987 (*3*), waters outflowing from the Adriatic were deposited near the bottom of the Ionian Sea, from where they spread south- and eastward (*4*, *5*). A recirculation in near–steady state prevailed, as indicated by temperature (*6*) and salinity decreasing slowly with depth but being homogeneous horizontally. The deepwater turnover time was approximately 100 years (average formation rate, $3 \times 10^5$ m$^3$ s$^{-1}$) (*7*), and stability of the water column below about 1500 m was low (*3*, *4*).

Another potential source area with outflow into the eastern Mediterranean is the Aegean Sea (*2*, *5*), but deposition from that source occurred at mid-depths only [<1000 m in 1987 (*3*)]. Although Aegean deep waters have been rather dense (that is, warm but saline) and fast turnover was indicated by high oxygen content (*8*, *9*), deep deposition was prevented by admixture of lower density water during the outflow. This basic pattern apparently remained unaffected by slow and steady increases in temperature and salinity in Mediterranean waters that have occurred in recent decades, ascribed primarily to river damming for agricultural purposes (*10*).

Observations obtained on a recent eastern Mediterranean cruise of F/S *Meteor* (cruise M31/1, January to February 1995) (Fig. 1) (*11*), however, document a new situation: whereas in 1987 deepwater salinities were rather homogeneous (Fig. 2A), the new survey (Fig. 2B) finds increased deepwater salinities in the vicinity of the island of Crete (Fig. 1), most strongly near the bottom and relaxing both upward and toward the ends of the section; salinities above 1000 m are partly lower than previous measurements. Additional information was obtained from sections for the chlorofluorocarbon CFC-12 . Ocean surface layer CFC concentrations have increased monotonically in time, so that water carried to depth more recently (that is, "younger" water) has higher concentrations. In 1987 (Fig. 3A), there was a concentration maximum at the base of the western slope and a minimum at mid-depths intensifying toward the east, in accordance with the Adriatic source for the deep circulation (*12*). In 1995 (Fig. 3B), the deep western maximum is still present, but near Crete one finds elevated CFC-12 amounts quite like those for salinity (Fig. 2B), and the CFC minimum is weaker and located at shallower depth.

A comparison of temperature-salinity (*T-S*) diagrams for 1987 and 1995 at different locations (Fig. 4) allows us to conclude that the changes are due to a recent, deep intrusion of Aegean waters: The western Ionian Sea (Fig. 4A) below 500 m (near $T$ = 14°C) has hardly changed, whereas a large and scattered shift toward higher salinity and temperature is present in the eastern Ionian Sea near the western passage of the Cretan Arc (Fig. 4B), with an inversion toward the bottom. Similar changes, but with less scatter and a distinct inversion, are present in the Levantine Basin (Fig. 4C; the inflection point is near 1200 m). Aegean deep waters (Fig. 4D), specifically, have become saltier and hence denser; properties corresponding to the depths of the sills of the connecting passages of the Cretan Arc (approximately 600 to 1000 m) are marked in the diagrams by an asterisk. Properties in 1995 below the inversion are an apparent linear combination of 1995 Cretan Arc sill properties and of deep *T-S* values as found in 1987 (Fig. 4, B and C). Noting that a *T-S* diagram is linear with respect to mixing, this result demonstrates that the waters below the inversion are a mixture of Cretan Arc sill waters and older deep waters; at the bottom, where the Aegean outflow contribution is largest, it amounts to 65% of the total.

By integrating the so-determined contribution over the volume of the deep waters below the *T-S* inversion, we determined that the total amount of Aegean outflow water added between 1987 and 1995 is approximately $2.3 \times 10^{14}$ m$^3$ (*13*). An independent approach is to consider the volume required to bring about the observed lifting of the tracer minimum layer between 1987 and 1995 (from 1600 to 1100 m) (Fig. 3), which yields $3.8 \times 10^{14}$ m$^3$. Because the former value ignores contributions from above the inversion, and the latter additionally includes waters from above the

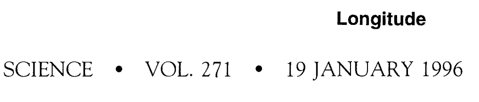

**Fig. 1.** Station positions of *Meteor* cruise M31/1 (January to February 1995) in the eastern Mediterranean; depth contour, 1000 m. The Adriatic Sea is located north of Station 15, and the Aegean Sea is located north of the islands and passages of the Cretan Arc.

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tracer minimum layer admixed to the outflow, the two estimates support one another, such that the first value should be a lower limit.

Much additional information is contained in the observations of the 1995 cruise. These observations allow us to assess the mixing that accompanied the Aegean water intrusion and to conclude that deep water formation from the Adriatic was continuing. Of special interest is the beginning of the intrusion caused by increased salinity of Aegean Sea waters. An abrupt salinity increase in the Aegean is in fact apparent after 1987 (Fig. 5). Because the eastern Mediterranean deep waters in 1987 were only marginally stable, 1988 is a plausible starting year of the intrusion. Accordingly, there should have been 7 years of intrusion by early 1995 (that is, 1988 through 1994), so that the calculated outflow volume ($2.3 \times 10^{14}$ m$^3$) converts to an average outflow rate of about $10^6$ m$^3$ s$^{-1}$. This is a minimum value, as the period is an upper limit and the volume a lower one, and it is at least threefold the rate deduced for the Adriatic source in the previous situation (7).

The salinity increase shown in Fig. 5 might be due to a jump in the freshwater balance of the eastern Mediterranean in about 1988. However, the salt addition to the deep waters effected by the Aegean water intrusion requires an increased net evaporation of at least 0.2 m per year for seven consecutive years over the entire eastern Mediterranean. Such change appears to be rather large, and the extended region implied contrasts with the rather localized salinity increase. A preferable alternative is suggested by the salinity decrease from 1987 to 1995 in part of the upper waters below the seasonal thermocline (Fig. 2). This salinity decrease points to a redistribution of salinity within the eastern Mediterranean waters. Such a vertical redistribution might be caused by a changed upper circulation, bringing into the Aegean increased amounts of water from the east, which have high salinity (5). If true, this might indicate an instability of the thermohaline circulation of the eastern Mediterranean, possibly triggered in some way by the general salinity increase of Mediterranean waters.

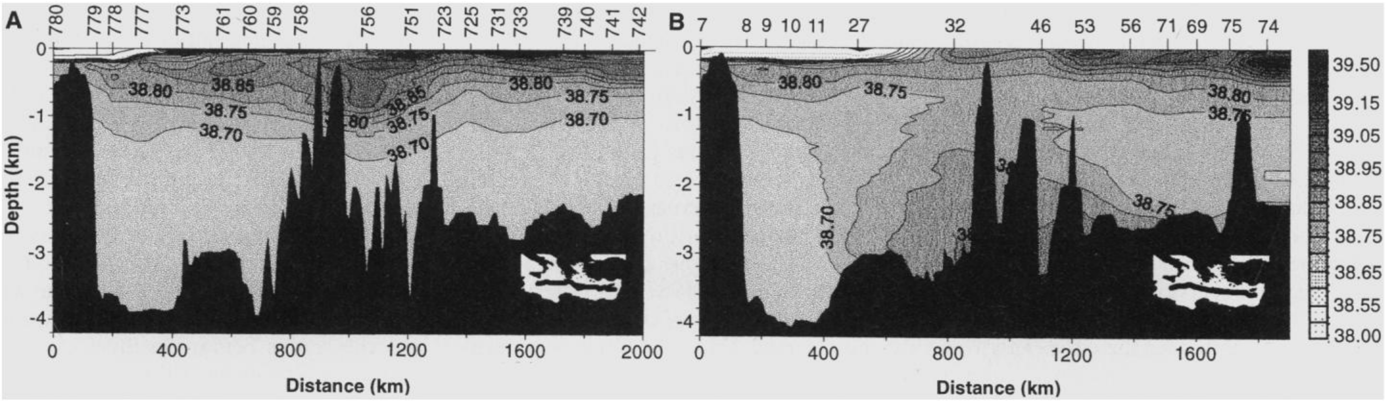
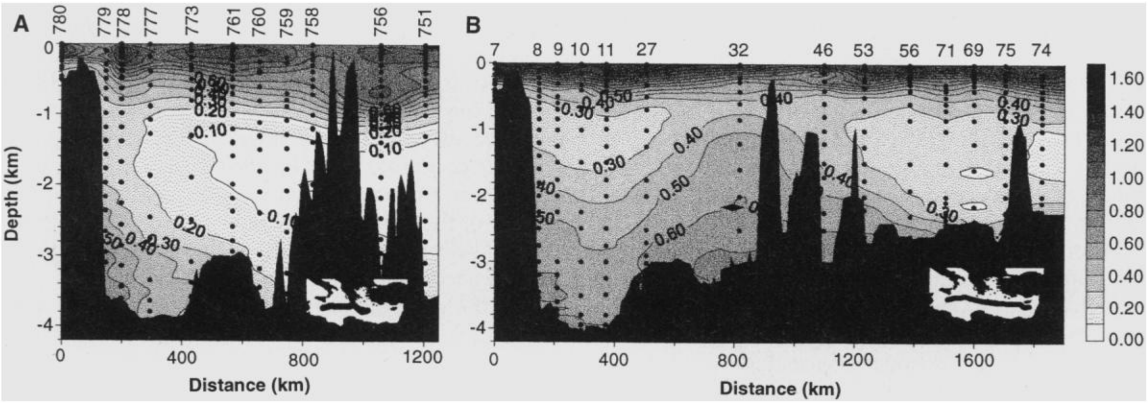


**Fig. 2.** Salinity isolines on sections across the Ionian Basin (see inset map); shown are data for *Meteor* cruises M5/6 (1987) (**A**) and M31/1 (1995) (**B**). Stations are at the top.

**Fig. 3.** Isolines of CFC-12 (pmol kg$^{-1}$) along the sections shown in Fig. 2. Shown here are data from cruises M5/6 (1987) (**A**) (no data beyond 1250 km) and M31/1 (1995) (**B**). Stations are at the top.



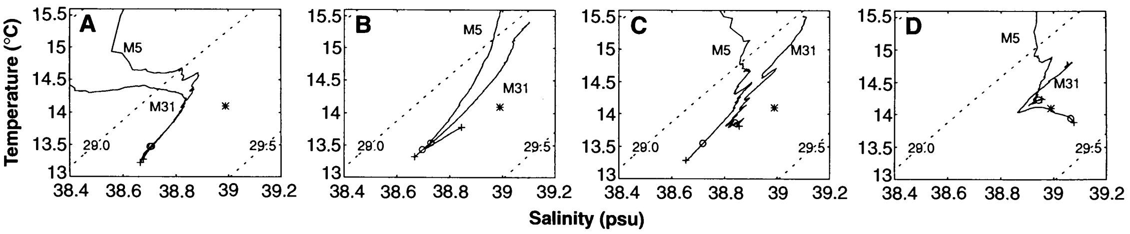


**Fig. 4.** Selected temperature-salinity diagrams for cruises M5/6 (1987) and M31/1 (1995), with density isolines (29 and 29.5 kg m$^{-3}$) superimposed; depth of 1200 m is indicated by open circles and the bottom by crosses; asterisks are 1995 *T-S* values at the sills of the Cretan Arc. (**A**) Stations 777 (M5/6) and 10 (M31/1), western Ionian Sea. (**B**) Stations 730 (M5/6) and 57 (M31/1), Levantine Basin. (**C**) Stations 759 (M5/6) and 37 (M31/1), eastern Ionian Sea. (**D**) Stations 753 (M5/6) and 41 (M31/1), Aegean Sea.

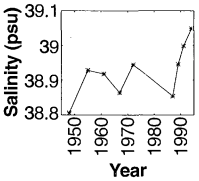


**Fig. 5.** Observed temporal trend in Aegean Sea salinities, 1948 to 1994. Data points are averages below 500 m in the years for which observations are available.

The intrusion of Aegean waters has changed appreciably the deep distributions of all properties in the eastern Mediterranean. There have been reports of inverted temperature gradients recently in sediments just below the water interface (*14*). The lifting of deep waters has brought nutrient-rich waters closer to the surface, so that in some areas seasonal mixing might bring extra nutrients into the euphotic layer, enhancing biological production. By the same mechanism, density in the so-called Levantine intermediate water layer—that is, the waters feeding the subsurface outflow through the Sicilian Passage into the western Mediterranean (*4*, *5*)—should have increased, enhancing water exchange through the passage. Salinity may also be affected, which could influence deep water production in the western Mediterranean and possibly beyond.

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11. Temperature was measured by conductivity, temperature, and depth probe (CTD) (±0.005 K), salinity by Autosal [±0.002 practical salinity units (psu) scale], and amounts of CFC-12 by electron-capture-detector capillary gas chromotography (±1%).
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13. Volume estimates for the *T-S* classes were obtained with the relative frequency of occurrence of a certain class from the CTD profiles (Fig. 1). A linear average of these was normalized by the total volume of the eastern Mediterranean (2.35 × $10^{15}$ $m^3$). The implicit assumption is that the set of CTD profiles forms an unbiased representation of the total volume, which naturally is only approximately true. The estimated volume of Aegean waters of 2.3 × $10^{14}$ $m^3$ corresponds to 20% of the water in the eastern Mediterranean below 1200 m.
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# Chromophores with Strong Heterocyclic Acceptors: A Poled Polymer with a Large Electro-Optic Coefficient

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Syntheses of a series of conjugated donor-acceptor chromophores, based on a strongly electron-withdrawing heterocyclic acceptor, have led to compounds with large second-order optical nonlinearities. Incorporation of one of these chromophores into polycarbonate at 20 percent weight loading yielded, after poling at 150 volts per micrometer, a polymer film with an electro-optic coefficient, $r_{33}$, of 55 picometers per volt at 1.313 micrometers. This value is roughly twice that of lithium niobate. A variant of one of these chromophores exhibited improved thermal stability as needed for use in polymers with higher glass transition temperatures. The chromophore was soluble in common organic solvents, had a scalar product of the dipole moment, $\mu$, and the molecular first hyperpolarizability, $\beta$ (corrected for dispersion), of roughly 5000 × $10^{-48}$ electrostatic units, and showed less than 10 percent decomposition after heating for 20 minutes in air and at 200°C in an inert organic solvent.

Materials that exhibit the electro-optic effect have refractive indices that can be modulated by application of an external electric field (*1*, *2*). Such materials can be used for a variety of telecommunications and signal processing applications that require light to be modulated or routed within a fiber optic network (*3*). The promise of organic poled polymers with electro-optic coefficients ($r_{33}$) that surpass those of inorganic crystals such as lithium niobate, whose $r_{33}$ is 30.8 pm/V (*4*) at telecommunication wavelengths of 1.3 and 1.5 $\mu$m, has provided the impetus for the development of highly nonlinear chromophores (*3*). In poled polymers, the electro-optic coefficient is proportional to $\mu\beta$, the scalar product of the dipole moment $\mu$ and the molecular first hyperpolarizability $\beta$.

Recent studies show that for conjugated organic donor-acceptor polyene dyes, there is a specific degree of polarization and concomitant bond length alternation, BLA (the difference between the average lengths of adjacent carbon–carbon bonds), in the ground state of the molecule that is required to optimize $\mu\beta$ (*5*). This point is reached when there is the correct combination of donor and acceptor strengths for a given conjugated $\pi$-electron bridge structure (*6*). Beyond this point, stronger donors or acceptors, which lead to increased polarization, can attenuate $\mu\beta$ (*6*, *7*). Most molecules examined to date, such as stilbene and diphenylpolyene donor-acceptor compounds, are not sufficiently polarized to optimize $\mu\beta$. Here, we report the synthesis of a series of chromophores, based on a strong heterocyclic acceptor, that have large molecular optical nonlinearities. One such chromophore has led to a polymer film with an electro-optic coefficient roughly twice that of lithium niobate (*4*).

In an attempt to develop molecules with large values of $\mu\beta$, we synthesized and characterized a series of chromophores based on a very strong acceptor, [3-(dicyanomethylidene)-2,3-dihydrobenzothiophen-2-ylidene-1,1-dioxide] (*8*), which contains two strong electron withdrawing groups, the dicyanomethylidene group and the sulfone group. A commercially available dye, Foron Blue (*8*), incorporating this acceptor has been examined for applications involving anomalous dispersion and phase-matched generation of second harmonics (*9*), but to our knowledge this acceptor has not been used in dyes for electro-optic applications. Accordingly, we reacted 3-(dicyanomethylidene)-2,3-dihydrobenzothiophene-1,1-dioxide (*8*) with (4-*N*,*N*-dimethylamino)phenyl-$(CH{=}CH)_n$ CHO or with (5-piperidyl)-thio-

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