

OXYGEN-18, DEUTERIUM AND TRITIUM IN THE BLACK SEA AND THE SEA OF MARMARA

ÖZSOY, E., I, SALİHOĞLU,
Institute of Marine Sciences, Middle East Technical
University, P. O. Box 28, Erdemli, İçel 33731
Turkey

D. RANK,
Bundesforschungs und Pruefzentrum Arsenal,
Geotechnisches Institut, Postfach 8, A-1031 Vienna,
Austria

Abstract

The stable isotopes oxygen-18 ^{18}O and deuterium ^2H , as well as tritium ^3H transient tracer were used to study pycnocline and deep mixing, to identify water masses in the Marmara and Black Seas, and to characterise exchange through the Turkish Straits System.

1. INTRODUCTION

The stabilising effects of excess fresh water and two-layer stratified exchange through the Turkish Straits System have led to anoxic conditions below the pycnocline in the Black Sea with partial renewal through the Bosphorus. While the ventilation of the upper pycnocline is driven by turbulent convection, it occurs through cascading of the shelf-mixed Mediterranean water at the continental slope [1-3], and double diffusive convection [4-7] mechanisms in the lower pycnocline. The post-Chernobyl radioisotopes [8], ^{14}C [9, 10] and tritium [11] measurements were consistent with the above results, showing very little penetration below a depth of about 500 m, and increasing age of waters near the bottom. On the other hand, the Marmara Sea has a mean residence time of a few months for surface waters, and about 6 years for the deep waters [13, 14]. Radioisotopes have been used widely for mixing and transport studies in the Black Sea [15-18].

We report on recent measurements of ^{18}O , ^2H and ^3H from samples collected in March-April, 1995, along the continental shelf and deep waters of the western and southern Black Sea (Fig. 1) and in the middle of the Marmara Sea, aboard the R/V BİLİM of the IMS-METU. Of the 11 stations in the Black Sea, 6 were sampled down to a depth of 150m, 4 stations extended to 250m, and deep samples down to 1500m could only be obtained at a single station. The three stations in the Marmara Sea extended to 1200m. Other details of the sampling and analyses were given in [19,20].

2. STABLE ISOTOPES ^{18}O AND ^2H

Mixing between the *i.e.* the Mediterranean and the Black Sea waters is well reflected in the stable isotope data, with sharp contrasts across the pycnocline and constant levels in deep waters of both seas (Fig. 2). Freshwater influence from major rivers (Danube, Dniepr and Dniestr) in the northwestern shelf region of the Black Sea results in decreased $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values near river mouths and along the shelf [20]. There are large horizontal and vertical variations within the thin (20m) upper layer of the

Marmara Sea, as a result of entrainment and mixing between Black Sea and the Mediterranean waters. In general, our results are similar to those of [16, 17], and [21], but contain much less noise. The sub-halocline (Mediterranean water) $\delta^2\text{H}$ variance in the Marmara Sea is slightly larger than the $\delta^{18}\text{O}$ variance, in contrast to [21].

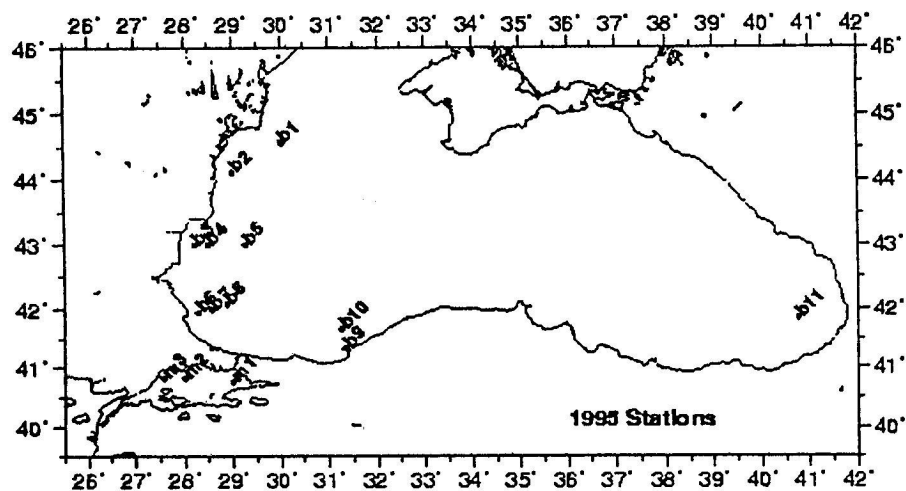


Fig. 1. Black Sea and Marmara Sea stations in 1995.

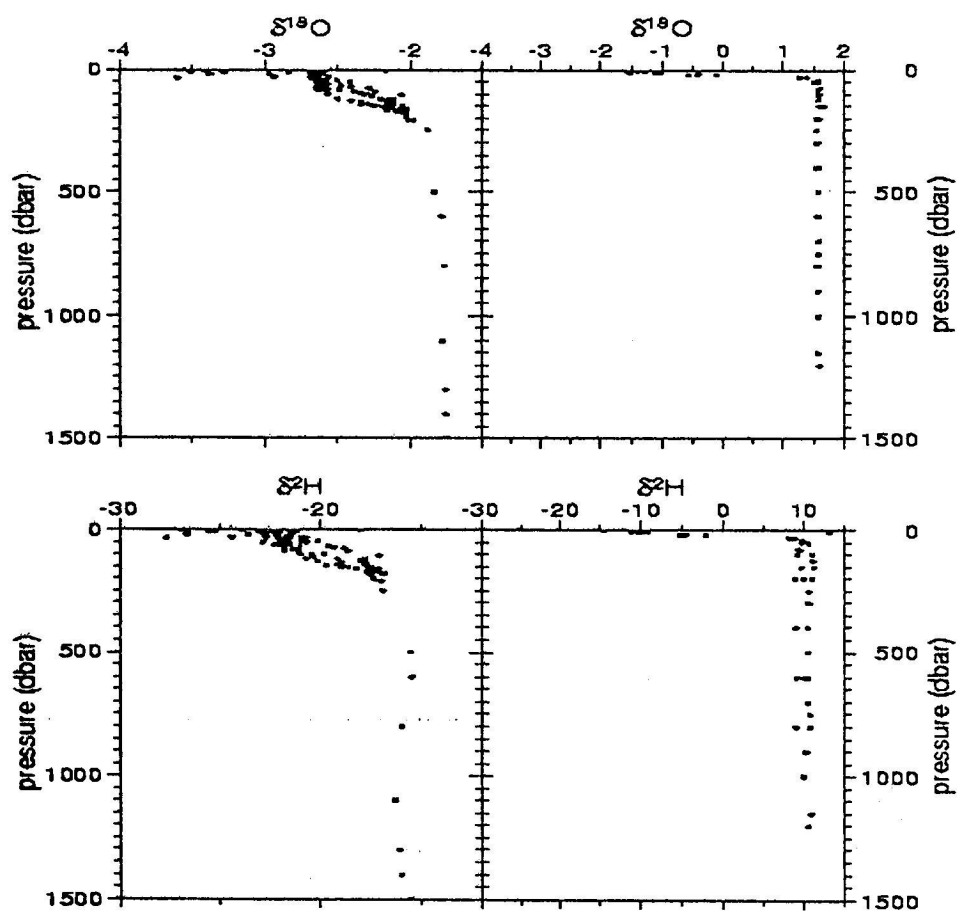


Fig. 2. Vertical distribution of stable isotopes in 1995; left: Black Sea; right: Marmara Sea; top: $\delta^{18}\text{O}$ measurements; bottom: $\delta^2\text{H}$ measurements.

3. TRITIUM

In the Black Sea, below the pycnocline, where the tritium decreases rapidly below 500m to very low values near the bottom. Although we only have data from one deep station in 1995, it is evident that the concentrations decrease to almost zero in deep water, within the precision of the measurements. In the Marmara Sea, only very small variations, typical of the efficiently ventilated Mediterranean region, occur below a depth of 25m.

The tritium distribution in the lower layer of the Marmara Sea has a maximum at mid-depths and possibly a slight increase near the bottom. These slight variations in the small basin indicate local changes in relative age, depending on seasonal, transient renewals by intrusions of Mediterranean water [13, 14] which are also evident in the salinity and temperature fine structures. We observe that $\delta^2\text{H}$ and ^3H have slightly larger variability compared to $\delta^{18}\text{O}$ in the subhalocline waters. Our ^3H measurements appear to have less scatter than the earlier measurements, and clearly demonstrate physical variations.

4. DENSITY DEPENDENCE

Because mixing between the surface and deep waters is limited by stratification, the dependence between chemistry and physical mixing of scalar properties produces self-similar profiles [22, 7], especially in the lower part of the pycnocline where turbulence rapidly declines. The linear dependence of stable isotopes versus σ_θ density (Fig. 4) eliminates the effects of dynamical displacements, and implies that the water mass evolution has followed the history of contact with the atmosphere. This is an independent verification of a hypothesis of deep water mass formation by a mixture of Mediterranean and near-surface, relatively fresh water masses, based on temperature -salinity analyses alone [3, 5], and the late quaternary history of Black Sea [23, 24].

In contrast, the transient tracer tritium versus σ_θ density in Fig. 4, indicates a significant change in tritium gradient with respect to density is evident below the pycnocline. Especially the fact that the break appears in the transient tracer and not in the stable isotopes shows that bomb tritium from the atmosphere has not yet been able to penetrate into the deeper Black Sea, and that the efficiency of penetration sharply decreases below the pycnocline, $\sigma_\theta \approx 16.3$. This result must reflect different mechanisms of renewal for intermediate and deep waters explored in a number of earlier interpretations [3, 5], *i.e.* turbulent mixing above the pycnocline, and rapidly diminishing turbulent mixing replaced with lateral intrusions of Mediterranean water below the pycnocline, extending down to a depth of about 500m or $\sigma_\theta \approx 17$. Indeed, below 500m, there is very little tritium.

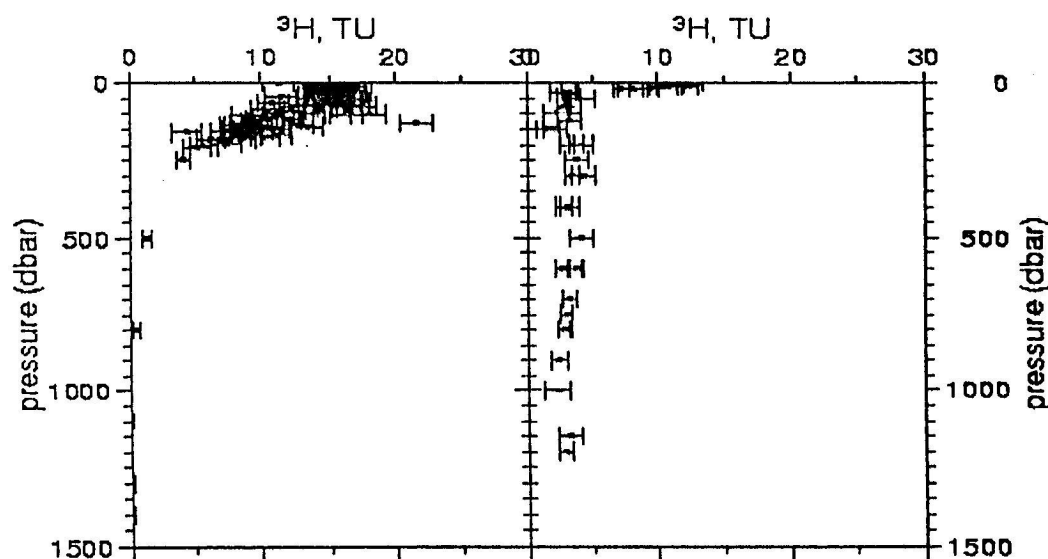


Fig. 3. Depth profiles of ^3H measurements, 1995. left: Black Sea; right: Marmara Sea; error bars show σ resulting from measurement uncertainty.

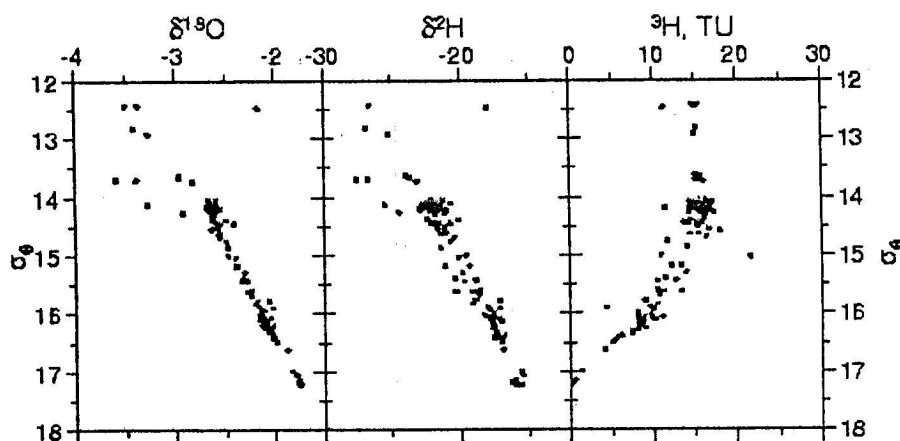


Fig. 4. Profiles of stable isotopes and tritium as a function of σ_{θ} density in the Black Sea. left: $\delta^{18}\text{O}$; center: $\delta^2\text{H}$; right: ^3H .

4. SURFACE TRANSIENTS

The $\delta^{18}\text{O}$ for the Danube in Vienna [25, 26, 27] has a mean value of -11.5 ‰, and a range of -10.3 ‰ to -13.3 ‰. The average value near the mouth of the Danube is about -10.5 ‰. Stable isotopes within the upper 20m waters of the two seas, appear to have rather small seasonal and interannual variations, based on measurements in 1988 and 1993 [16].

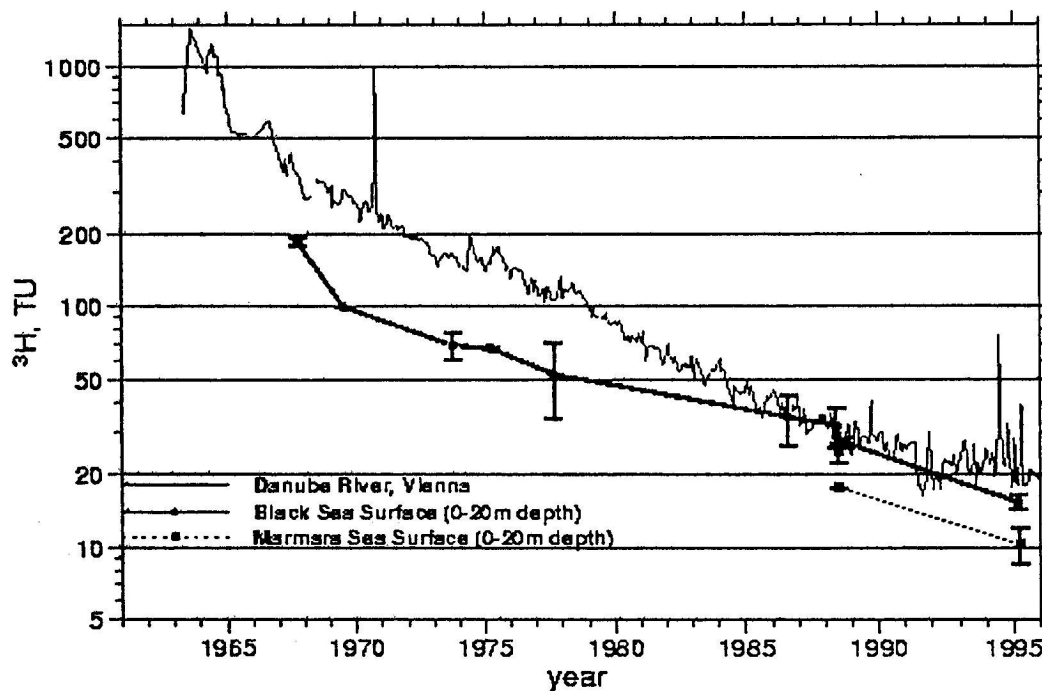


Fig. 5. Surface ^3H concentrations measured in the Black Sea and Marmara Sea surface layers (0-20m depth), superposed on a plot of ^3H measurements in the Danube River. Danube samples were obtained at Reichsbrücke (before Dec 1991), and Nussdorf-Schleuse (after Dec 1991) in Vienna.

The transient tracer tritium in precipitated water, the Danube waters [25, 26, 27] and the surface waters of the two seas has been decreasing since the 1963/64 maximum in fallout (Fig. 5), in agreement with other observations (e.g. [28]). The present input to the Black Sea is about 10-15 TU from precipitation (1995) and 20-25 TU from Danube water. This is at present on the same order of magnitude as the ^3H of Black Sea surface waters (15-17 TU). The comparison of riverine sources and surface marine observations indicate this difference to be larger in the 1960's and 1970's (Fig. 5), when the inputs were considerably larger but the underlying waters were less contaminated.

In the case of Marmara Sea waters, there is a larger difference in surface tritium concentrations with respect to the input functions. Despite the smaller size of the Marmara Sea, mixing with the underlying Mediterranean waters yields a further dilution in the surface waters. The main part of this mixing is believed to occur at the Bosphorus Strait and its exit region in the Marmara Sea (e.g. [12, 14]).

5. EXCHANGES BETWEEN BASINS

The average surface and deep properties and the inter-basin exchange characteristics are schematized in Fig. 6, based on average surface levels and those measured below a depth of 500m in the Black Sea and 50m in the Marmara Sea. The fresh water inflow, specifically from the Danube river, entering the sea with a low $\delta^{18}\text{O}$, has a significant influence in the northwestern shelf region, where it lowers the $\delta^{18}\text{O}$. The deep water of the Black Sea, with a historical Mediterranean contribution, is enriched in terms of $\delta^{18}\text{O}$. In contrast, the recent source of tritium at the surface has not been able to penetrate into the deep waters, the ^3H values decreasing rapidly below a depth of 500m. In the Marmara Sea, the ^{18}O and ^2H characteristics of surface waters evolve rapidly at the transitions across the Bosphorus and Dardanelles Straits, and from west to east by mixing with underlying Mediterranean waters. The subhalocline Marmara waters essentially bear the same signature as the Mediterranean waters.

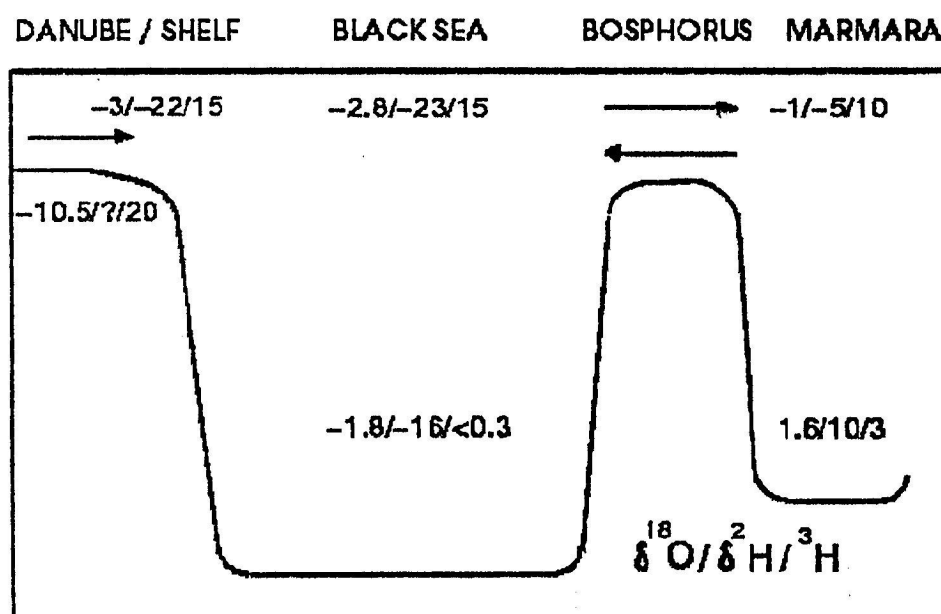


Fig. 6. Idealised surface (depth 0-20m) and bottom (depth >500m in the Black Sea, and depth >50m in the Marmara Sea) concentrations of isotopes, $\delta^{18}\text{O}/\delta^2\text{H}/^3\text{H}$, in the Danube river (Vienna), the northwestern shelf area, greater part of the Black Sea, and the Marmara Sea.

6. ISOTOPIC CORRELATIONS

Fig. 7 correlates all three isotopes studied. In the upper panel we observe that all the data in the two interconnected basins of Marmara and Black Sea to lie along the same straight line, slightly displaced from the meteoric water line, and with only a minor change in slope between basins, suggesting that these waters were formed by a continuous mixture of fresh water inputs and Mediterranean water. Mediterranean water in the Marmara Sea has slightly higher $\delta^2\text{H}$, compared to the Eastern Mediterranean [21].

In the oxygen-18 versus tritium plot (lower part of Fig. 7), Marmara and Black Sea data are located along different branches, as a result of differences in residence time of the deep waters in the two basins. The transient tracer tritium indicates age, while the oxygen isotope, is linearly related to stratification, and measures distance from the conditions determined by surface hydrology. The near-surface waters in the Black Sea form a cluster of rather uniform values; while a group of points displaced to the left from this cluster, and belonging to the northwestern shelf region is helpful in identifying

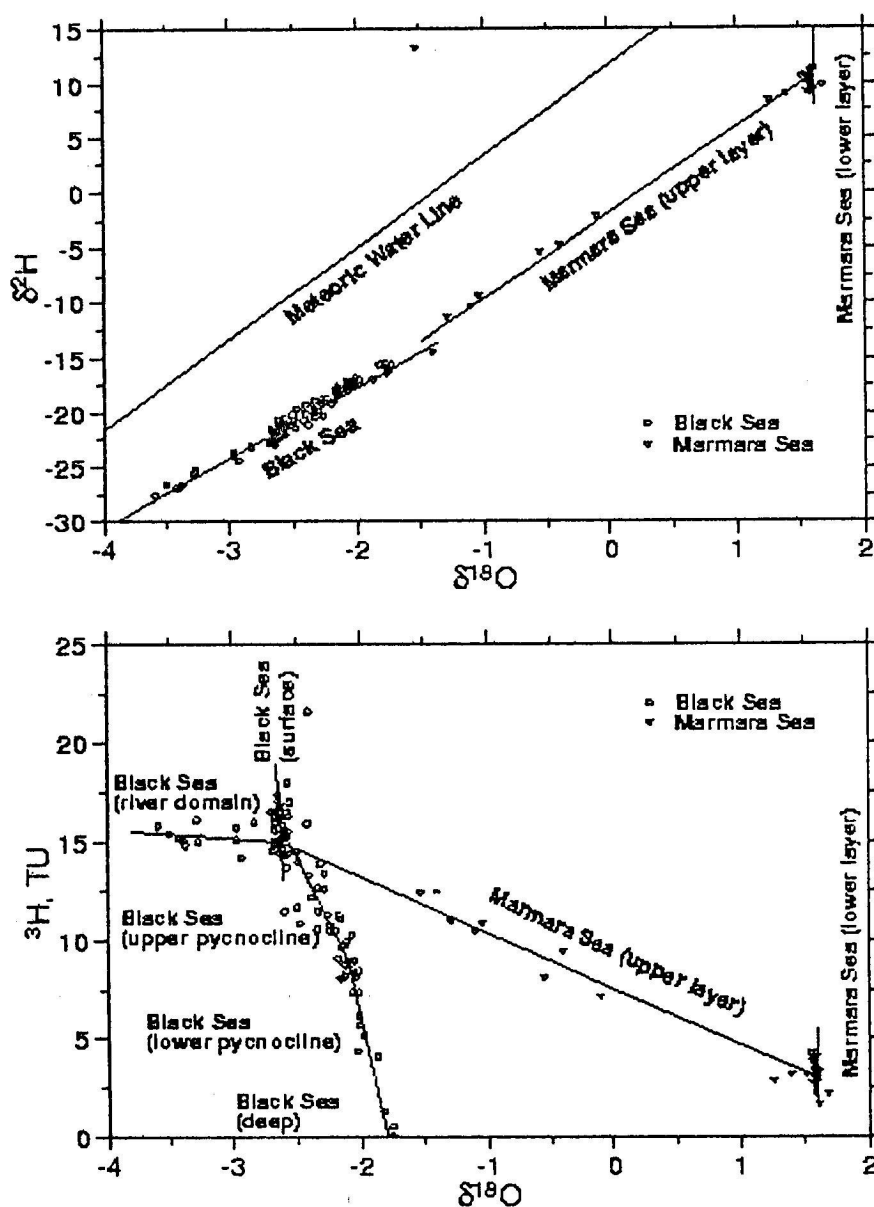


Fig. 7. top: $\delta^{18}\text{O}$ versus $\delta^2\text{H}$, bottom: $\delta^{18}\text{O}$ versus ^3H for the Black Sea and Marmara Sea, 1995.

riverine effects. Fresh water is tagged by the oxygen isotope, but not by tritium, which is similar in all surface samples. Below the surface, tritium decreases and oxygen increases with depth. In the Black Sea, we observe that there is a well defined change of slope occurring immediately below the pycnocline, clearly showing that two different mechanisms are responsible for the renewal of the water masses above and below it.

7. CONCLUSIONS

The use of stable isotopes together with transient tracers in the Black Sea and Marmara Sea has yielded new results which help to understand the mixing and renewal in these semi-enclosed basins of greatly differing characteristics.

Stable isotope measurements in precipitation and river runoff, characterising fresh waters and the atmosphere, are relatively constant in time, and their ratios help identify mixing between waters with different origins. In the region studied, there is nearly a linear correlation between oxygen and deuterium for all water samples, showing that the waters in both basins are continuously proportional mixtures of surface fresh water inputs to the Black Sea and salty waters of the Mediterranean.

In the Marmara Sea, stable isotopes at the surface evolve rapidly at the transitions across the Bosphorus and Dardanelles Straits, and in an east to west direction in the Marmara Sea interior by mixing with the lower layer Mediterranean waters. Both isotopes show very little change below 500m in the Black Sea, and below 25m in the Marmara Sea, consistent with hydrographic observations, showing common sources.

On the other hand, tritium is decreasing in precipitation, river runoff and the surficial waters of Black Sea and Marmara Sea, consistent with fallout and decay. Mixing with underlying waters determine the delayed response of the Black Sea and Marmara Sea surface waters, which differ in their settled characteristics. The surface and deep waters in both Seas are separated by a sharp pycnocline identified in all three tracers. Stable isotopes have a continuous linear dependence on density, while tritium shows a discontinuous dependence showing different renewal mechanisms for deep and intermediate waters.

River (freshwater) influence is identified along the western Black Sea continental shelf, on the basis of isotope correlations. Tritium measurements show a rapid decrease across the Black Sea pycnocline, and constant levels below the pycnocline in the Marmara Sea. Comparison of tritium with stable isotopes can characterize all distinct water masses in the two basins.

Acknowledgements

This paper is a result of cooperation, under project no. 302-K4-TUR-7333, part of a Coordinated Research Programme (CRP) of the International Atomic Energy Agency, entitled 'The Application of Tracer Techniques in the Study of Processes and Pollution in the Black Sea'.

We were greatly encouraged by K. Fröhlich, and M. S. Baxter of the IAEA for our contribution to the Programme. We thank the Turkish Scientific and Technical Research Council and the NATO Science for Stability Program for funding research in the Black Sea, which enabled us to carry out the work. We are also grateful to Zafer Top of the University of Miami, for providing his 1988 data for comparative evaluations [29], and for his help with the manuscript. Many other individuals, including the scientists of the IMS-METU, and the captain and crew of the R/V BİLİM, have made valuable contributions during the course of the study.

References

- [1] BUESSELER, K. O., LIVINGSTON, H. D. and S. CASSO (1991). Mixing Between Oxic and Anoxic Waters of the Black Sea as Traced by Chernobyl Cesium Isotopes, *Deep-Sea Res.*, 38, Suppl. 2, S725-S745.

- [2] MURRAY, J. W., Z. TOP and E. Özsoy, (1991). Hydrographic Properties and Ventilation of the Black Sea, *Deep Sea Res.*, 38, Suppl. 2, S663-S689.
- [3] ÖZSOY, E., Z. TOP, G. WHITE, J. W. MURRAY, (1991). Double Diffusive Intrusions, Mixing and Deep Sea Convection Processes in the Black Sea, in: *The Black Sea Oceanography*, E. İzdar and J. M. Murray (editors), NATO/ASI Series, Dordrecht, Kluwer Academic Publishers, 17-42.
- [4] ÖZSOY, E., ÜNLÜATA, Ü. and Z. TOP. (1993). The Mediterranean Water Evolution, Material Transport by Double Diffusive Intrusions, and Interior Mixing in the Black Sea, *Prog. Oceanogr.* 31, 275-320.
- [5] ÖZSOY, E. and Ş. BEŞİKTEPE, (1995). Sources of Double Diffusive Convection and Impacts on Mixing in the Black Sea, pp. 261-274, in: Brandt, A. and H. J. S. Fernando (editors), *Double-Diffusive Convection*, Geophysical Monograph 94, American Geophysical Union, 334 pp.
- [6] ÖZSOY, E. and Ü. ÜNLÜATA (1997). Oceanography of the Black Sea: A Review of Some Recent Results, *Earth Science Reviews*, 42, 231-272.
- [7] ÖZSOY, E. and Ü. ÜNLÜATA (1998). The Black Sea, in: A. R. Robinson and K. Brink (editors), *The Sea: The Global Coastal Ocean II, Regional Studies and Syntheses*, 11, Wiley Interscience (in press).
- [8] BUESSELER, K. O. and H. D. LIVINGSTON (1997). Time-Series Profiles of ¹³⁴Cs, ¹³⁷Cs and ⁹⁰Sr in the Black Sea, in: E. Özsoy and A. Mikaelyan (editors), *Sensitivity to Change: Black Sea, Baltic Sea and North Sea*, NATO ASI Series, Kluwer Academic Publishers.
- [9] ÖSTLUND, H. G. (1974) Expedition Odysseus 65: Radiocarbon Age of Black Sea Water, in: *The Black Sea - Geology, Chemistry and Biology*, E.T. Degens and D. Ross (editors), The American Association of Petroleum Geologists, Memoir No. 20.
- [10] ÖSTLUND, H. G. and D. DYRSSEN, (1986) Renewal Rates of the Black Sea Deep Water, in: *The Chemical and Physical Oceanography of the Black Sea*, Univ. of Göteborg, Rep. on the Chemistry of the Sea XXXIII. Presented in the Meeting on the Chemical and Physical Oceanography of the Black Sea, Göteborg, Sweden, June 1986.
- [11] TOP, Z., ÖSTLUND, H. G., POPE, L. and C. GRALL (1991). Helium and Tritium in the Black Sea: A Comparison with the 1975 Observations, *Deep Sea Res.*, 38, Suppl. 2, S747-S760.
- [12] ÜNLÜATA, Ü., T. OĞUZ, M. A. LATIF and E. ÖZSOY (1990). On the Physical Oceanography of the Turkish Straits, in: *The Physical Oceanography of Sea Straits*, L. J. Pratt (editor), NATO/ASI Series, Kluwer, Dordrecht, 25-60.
- [13] BEŞİKTEPE, Ş., ÖZSOY, E. and Ü. ÜNLÜATA (1993). Filling of the Sea of Marmara by the Dardanelles Lower Layer Inflow, *Deep-Sea Res.*, 40, 1815-1838.
- [14] BEŞİKTEPE, Ş., SUR, H. İ., ÖZSOY, E., LATIF, M. A., OĞUZ, T., and Ü. ÜNLÜATA (1994). The Circulation and Hydrography of the Marmara Sea, *Prog. Oceanogr.*, 34, 285-334.
- [15] MURRAY, J. W. (editor) (1991). The Black Sea, *Deep Sea Res.*, 38, Suppl. 2.
- [16] SWART, P. K. (1991a). Factors Affecting the Oxygen Isotopic Composition of the Black Sea, *The Black Sea Oceanography*, E. İzdar and J. M. Murray (editors), NATO/ASI Series, Dordrecht, Kluwer Academic Publishers, 75-88.
- [17] SWART, P. K. (1991b). The Oxygen and Hydrogen Isotopic Composition of the Black Sea, *Deep-Sea Res.*, 38, Suppl. 2, S761-S772.
- [18] FABRY and K. FRÖHLICH (1992). The Application of Tracer Techniques in the Study of Processes and Pollution in the Black Sea, Consultants' Meeting Report, International Atomic Energy Agency, 39 pp.
- [19] ÖZSOY, E., İ. SALİHOĞLU, D. RANK and D. CAN (1997). Measurement of Selected Isotope Tracers in the Black Sea and the Sea of Marmara, Report for the Coordinated Research Programme "The Application of Tracer Techniques in the Study of Processes and Pollution in the Black Sea", submitted to the IAEA, Institute of Marine Sciences, METU, Erdemli, İçel. [20] RANK, D., ÖZSOY, E. and İ. SALİHOĞLU (1997). Oxygen-18, Deuterium and Tritium in the Black Sea and the Sea of Marmara, *J. Env. Rad.*, (in press).
- [21] GAT, J. R., A. SHEMESH, E. TZIPERMANN, A. HECHT, D. GEORGOPOULOS and Ö. BAŞTÜRK (1996). The Stable Isotope Composition of Waters of the Eastern Mediterranean Sea, *J. Geophys. Res.*, 101, 6441-6451.
- [22] TUĞRUL, S., Ö. BAŞTÜRK, C. SAYDAM and A. YILMAZ (1992). Changes in the Hydrochemistry of the Black Sea Inferred from Water Density Profiles, *Nature*, 359, 137-139.

- [23] STANLEY, D. J., and C. BLANPIED (1980). Late Quaternary Water Exchange between the Eastern Mediterranean and the Black Sea', *Nature*, 285, 537-541.
- [24] BOUDREAU, B. P., and P. H. LEBLOND (1989). A Simple Evolutionary Model for Water and Salt in the Black Sea, *Paleoceanography*, 4, 157-166.
- [25] RANK, D. (1992). The Danube as a Main Input to the Black Sea: Isotope Ratios and Radioactivity, in: Fabry and Fröhlich, The Application of Tracer Techniques in the Study of Processes and Pollution in the Black Sea, Consultants' Meeting Report, International Atomic Energy Agency, p. 27.
- [26] RANK, D. (1995). Umwelttritium im Donauraum, *Limnologische Berichte Donau 1994* (Editor: Internationale Arbeitsgemeinschaft Donauforschung), Dubendorf/Wien, II, 243.
- [27] RANK, D. (1996). Die Isotopenverhältnisse im Donauwasser als Indikatoren für Klimaschwankungen im Einzugsgebiet, *Limnologische Berichte Donau 1996* (Editor: Internationale Arbeitsgemeinschaft Donauforschung), God/Vacratot, Hungary (in press).
- [28] IAEA (1992). Statistical Treatment of Data on Environmental Isotopes in Precipitation, *Technical Reports Series*, No. 3331, International Atomic Energy Agency, Vienna.
- [29] TOP, Z. and W. B. CLARKE (1983). Helium, Neon and Tritium in the Black Sea, *J. Mar. Res.*, 41, 1-17