years. Therefore, the differences in ultraviolet between the sites were larger than normal. In recent years the TOMS and Dobson records at each site show similar variations, although over Lauder the TOMS measurements are ~2-3% higher than the Dobson measurements. The Dobson data show a stronger trend in New Zealand, whereas the TOMS data show a stronger trend in Germany, particularly in the early 1980s. The reasons for the anomalously low ozone in Europe in 1983 have been discussed[17,18]. Tropospheric ozone levels have increased at Hohenpeissenberg in recent years, and ground based measurements show that the 1980s, the increases in tropospheric ozone have largely offset the decreases in stratospheric ozone[19]. Evidently, the increases in tropospheric ozone have not been fully recognized by the TOMS instrument, so that hemispheric differences in ultraviolet received at the surface are larger than would be expected from an analysis of TOMS data alone.

Hemispheric differences in ultraviolet irradiance therefore seem to have increased in recent years. In future, an increase in ultraviolet is expected in Germany, as tropospheric ozone levels stabilize[20]. There are considerable day-to-day variability as well as diurnal changes in ultraviolet, which may well be an important issue in future studies. ☐

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Changes in the hydrochemistry of the Black Sea inferred from water density profiles

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DURING the past two decades, catastrophic changes have occurred in the Black Sea ecosystem: the influx of pollution from the major rivers has caused intense eutrophication at the northwest coastal margin[1], and fish stocks have collapsed throughout the sea[2]. The hydrochemical details of these events are still poorly understood[3–7], and a way needs to be found to distinguish long-term variations from short-term natural fluctuations[3,4] if future management of the Black Sea ecosystem is to be successful. We show here that a coherent description may be achieved by analysing the hydrochemical data as a function of water density rather than depth. Our findings suggest that, contrary to the suggestion of Murray *et al.*[3], the upper boundary of the low-lying anoxic waters has remained stationary since 1969, whereas the intermediate suboxic zone has enlarged, reducing the overall depth of the oxygenated upper waters by ~20 m. Moreover, a long-term increase in the nitrate concentration and a concomitant decrease in the silicate and ammonia concentrations in this upper layer are indicative of the considerable changes taking place in the biochemical regime of the Black Sea.

Put simply, the Black Sea, an enclosed sea and the largest anoxic basin in the world, consists of a deep basin of sulphidic saline water overlain by ~100 m of oxygenated brackish water[8,9]. Between these two layers, an oxic–anoxic interface of a few tens of metres has developed across which the magnitude of the electrochemical oxidation-reduction (redox) potential changes markedly[8,9]. This suboxic (chemocline) zone coincides with the vertically stable layer[9,10] (pycnocline) in which the water density increases in parallel with the salinity. The depth of the pycnocline and of the associated suboxic hydrochemistry varies both seasonally and from one part of the Black Sea to another depending on the circulation and the intensity of eddies[7-11]. Comparison of depth profiles at limited locations is therefore unlikely to define long-term changes in the hydrochemistry of the fertile waters of the Black Sea. But diffusion and mixing in the Black Sea is rapid along equal-density (isopycnal) surfaces and much slower in the vertical direction[10,11]. Consequently, chemical concentrations in the suboxic zone and the upper anoxic layer plotted against density, rather than depth, may be expected to give individually similar density profiles, independent of seasons and location. Codispoti *et al.*[7] demonstrated this for nitrate concentrations measured in 1988. Here we extend their observations to include the dissolved oxygen, hydrogen sulphide and nutrient data collected during the 1969 *Atlantis II*[12], 1988 *Knorr*[13] and 1991 *Bilim* (our own unpublished data) research cruises throughout the Black Sea or within the Turkish Exclusive Economic Zone.

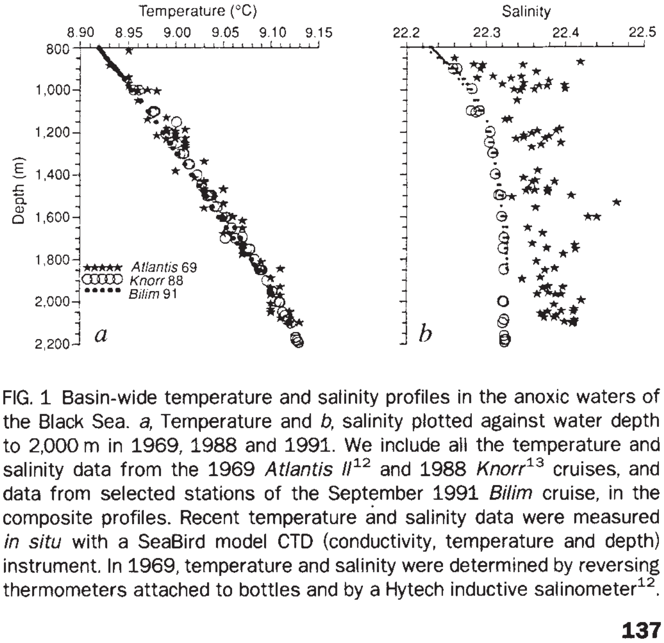

FIG. 1 Basin-wide temperature and salinity profiles in the anoxic waters of the Black Sea. *a*, Temperature and *b*, salinity plotted against water depth to 2,000 m in 1969, 1988 and 1991. We include all the temperature and salinity data from the 1969 *Atlantis II*[12] and 1988 *Knorr*[13] cruises, and data from selected stations of the September 1991 *Bilim* cruise, in the composite profiles. Recent temperature and salinity data were measured *in situ* with a SeaBird model CTD (conductivity, temperature and depth) instrument. In 1969, temperature and salinity were determined by reversing thermometers attached to bottles and by a Hytech inductive salinometer[12].

In plotting data from different cruises it has been necessary to check the consistency of the density (σ_t) values. Our test for consistency has been the assumption that at depths below 1,000 m, temperatures and salinities have remained constant during recent decades. Figure 1 shows this to have been true to within ±0.01 °C of temperatures measured since 1969. Salinities for 1969, however, were always higher than recent data by an average of 0.065 ± 0.02 (33 measurements below 1,700 m). Corrected σ_t values (obtained by using measured temperatures, subtracting 0.065 from the observed salinities and using an equation of state[14] which, in itself, reduces σ_t values by 0.05 units) are, in total, about 0.1 σ_t units smaller than the values reported by Brewer[12]. Such a difference, not previously noticed[3,7], produces an artificial discrepancy between density profiles from the uncorrected data of 1969 and recent observations.

Previous workers[3,5,7-9] have naturally attempted to define the upper and lower boundaries of the oxic-anoxic interface by examining the depth profiles of dissolved oxygen (O_2) and hydrogen sulphide (H_2S), whose concentrations in this zone are low and can be measured accurately only by special techniques[5,7]. From changes observed in depth profiles at a single station in the central Black Sea, Murray *et al.*[4] suggested that the anoxic interface had risen by 30 m since 1969, whereas basin-wide comparison of the depths of the anoxic interface seemed to indicate that changes in this boundary had been insignificant in recent decades[5]. Here we discuss this problem using composite profiles of sulphide plotted against density (Fig. 2). Hydrogen sulphide concentrations from the high-resolution data of the 1988 *Knorr* cruise[13] increase smoothly with density, indicating that similar sulphide concentrations follow similar density surfaces throughout the basin (Fig. 2*b*). A concentration of $[H_2S] = 10$ μM was observed consistently at $\sigma_t = 16.32$. The composite profiles from the 1969 and 1991 data are much scattered at each given density surface (Fig. 2*a*, *c*), strongly suggesting that sampling and analytical techniques were inadequate. The profile for 1991 is relatively consistent with that of 1988, whereas the 1969 profile coincides with recent profiles only at larger sulphide concentrations below the $\sigma_t = 16.4$ surface (or 30 m from the sulphidic boundary). A hydrogen sulphide concentration of 10 μM was not reached in 1969 until $\sigma_t =$ 16.35-16.40, but the large scatter in the 1969 profile, by as much as 20 μM at a given density surface, strongly suggests that the detection of sulphide at larger values of σ_t was inaccurate by the equivalent of more than 0.05 σ_t units (or 10 m in depth) probably because of the incomplete recovery of sulphides from samples that were stored until analysis[12].

To clarify this problem further we have examined the phosphate concentrations, whose profile within the anoxic transition (redox) zone is dominated by redox processes[7,15,16]. The phosphate profiles show two maxima[7-9,15,16]; the upper, broad maximum occurs at similar depths to the nitrate maximum whereas the deeper, larger maximum is formed at depths within the anoxic transition zone at which the sulphide concentrations first exceed 3 μM. The composite profiles of phosphate shown in Fig. 3*a* and *b* demonstrate that the phosphate concentrations in the suboxic-anoxic transition zone increase by at least an order of magnitude from a minimum value at $\sigma_t = 15.9$-16.0 to a maximum at $\sigma_t = 16.20$-16.25. The location of the sharp increase in the concentrations coincides with similar features observed in the Fe^{2+} and Mn^{2+} profiles[17,18], suggesting that redox processes involving iron and manganese are important in the vertical transport of phosphate and in the formation of the deeper phosphate maximum[15,16]. The σ_t values corresponding to these characteristic features and which coincide with those locating the suboxic-sulphidic interface[7-9,15,16] have remained constant since 1969, so the redox potentials defining the anoxic interface have remained at this chemical depth since 1969.

The hydrochemistry of the fertile upper layer which all the living resources inhabit is more likely to be affected by recent changes in the Black Sea ecosystem than is the anoxic lower layer. Murray *et al.*[4], comparing the depth profiles of oxygen from the central Black Sea, suggested that the oxygenated upper layer has become shallower because of the formation of a relatively thick (few 10 m), oxygen-deficient zone (termed here the suboxic zone, where $[O_2] < 10$ μM and $[H_2S] < 3$ μM) at the oxic-anoxic interface. The oxygen profiles in Fig. 3 show that discussions of the development of the suboxic zone are hampered by the scatter in the data. Nevertheless, in 1969, oxygen concentrations throughout the Black Sea exceeded 10 μM down to at least the $\sigma_t = 16.0$ surface, whereas in 1988 and in 1991, oxygen decreased to suboxic concentrations (<10 μM) by the $\sigma_t = 15.6$-15.7 surfaces in the Turkish Exclusive Economic Zone. In recent years, the suboxic zone therefore seems to have spread towards the surface by ~0.3 σ_t units relative to its position in 1969 or by at least 20 m with respect to the $\sigma_t = 16.0$ surface. Confirmation that the shift has been caused by long-term changes in the system is provided by a similar upward shift in the depth of the nitrate maximum, formed as the result of nitrification and denitrification[7-9], at depths where oxygen concentrations diminished below 10 μM at all seasons throughout the Black Sea. The nitrate profiles shown in Fig. 3*c* and *d* demonstrate that the maximum concentrations have remained stationary at $\sigma_t = 15.3$-15.5 since 1988, whereas in 1969, the maximum was established between the $\sigma_t = 15.7$ and 15.9 surfaces.

Nitrate concentrations (Fig. 3*c* and *d*) in the oxic layer, which is thus becoming shallower, have increased at least two- to threefold from concentrations of 2-4 μM in the 1960s (refs 8, 9, 19) to 7-9 μM by 1991 (refs 7, 20). The ratio of nitrogen in the form of $NH_3 + NO_3$ to phosphorus in the form of PO_4 in the oxic layer between the $\sigma_t = 15.0$ and 15.7 surfaces shows

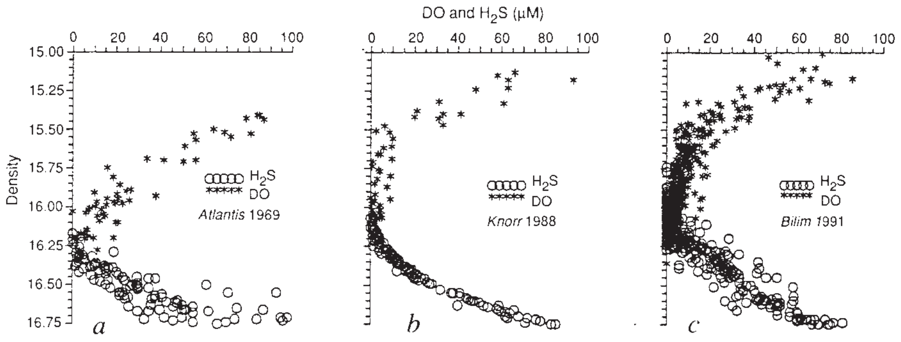

FIG. 2 Composite profiles of dissolved oxygen (DO) and hydrogen sulphide in the oxic-anoxic transition zone of the Black Sea relative to density (σ_t). *a*, Historical profiles of dissolved oxygen and hydrogen sulphide from 30 stations of the March-April 1969 *Atlantis II* Black Sea cruise. *b*, Recent composite profiles from five oxygen and 12 sulphide stations of the June-July 1988 *Knorr* cruise in the Turkish Exclusive Economic Zone. *c*, Latest profiles from 46 stations of the September 1991 *Bilim* cruise in this zone. Oxygen was determined by Winkler titration[12,13,20] except for the 1988 *Knorr* data below 20 μM, which were obtained by colorimetry[7]. Sulphide data for 1969 were determined manually by colorimetry in samples from bottle casts, stored before analysis by adding preservative[12]. The high-resolution sulphide data for 1988 were produced by a multichannel autoanalyser coupled to a continuous pumping system[7,13]. The latest data from the 1991 *Bilim* cruise were measured by iodimetry[20] in the subsamples from a 12-bottle Rozette attached to a CTD.

that the N/P ratio beneath the euphotic zone (where only 0.1% of the surface light penetrates), which is lower than the Redfield value for the oceans (N/P = 16 by mole), has varied only between 6 and 8 since the 1960s (refs 7, 9, 21). The ratio, dominated by both ammonia and nitrate until 1975, has become nitrate-dependent since 1980. But the N/P ratio evident from the *Atlantis II* 1969 data was as low as 2–3 because of the underestimation of ammonia[22] (Fig. 3*e*). This figure also shows that there has been a net loss of inorganic nitrogen in the bottom of the suboxic zone in recent years. Silicate concentrations in the surface waters of the Black Sea have decreased by an order of magnitude since 1969 (refs 6–9, 20), with a lesser decrease in the concentrations in the lower oxic layer extending down to the $\sigma_t = 15.7$ surface (Fig. 3*f*). The present concentrations, as low as 0.3 μM in summer[21], may be limiting the growth of diatoms. Alterations in the ecosystem of the Black Sea have therefore been observable since the 1970s with concurrent changes in the biochemical processes dominating nitrogen and silicate cycles in the upper layer. □

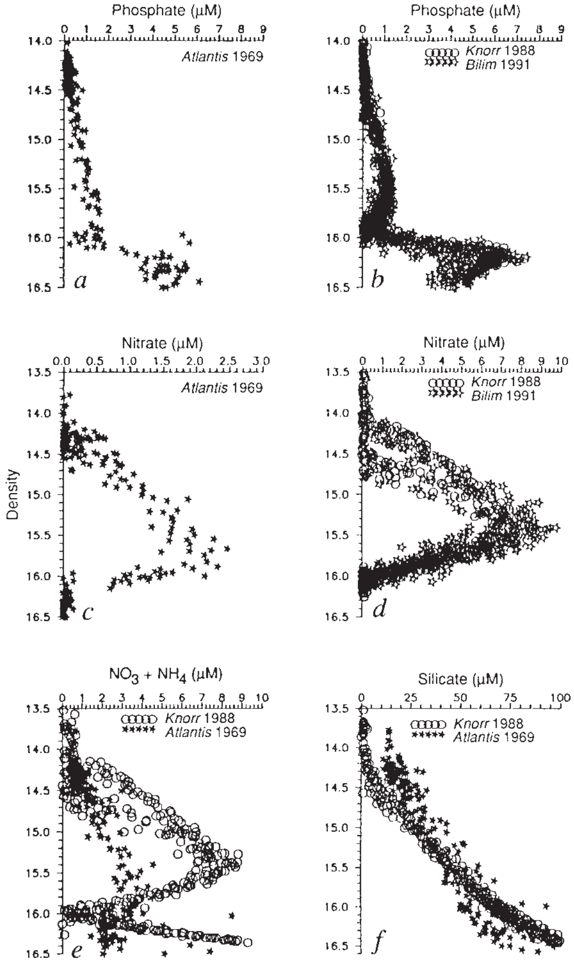

FIG. 3 Basin-wide vertical distribution of nutrients in the upper layer of the Black Sea relative to density. Composite profiles of (*a, b*) phosphate (*c, d*) nitrate in 1969, 1988 and 1991 plotted against σ_t using the data sets from 27 stations of the 1969 *Atlantis II*, 12 stations of the 1988 *Knorr* and 46 stations of the 1991 *Bilim* Black Sea cruises. *e*, Composite profiles of nitrate plus ammonia for 1969 and 1988, showing an inorganic nitrogen deficiency in the lower suboxic zone resulting from denitrification as well as a linear increase in ammonia concentrations with water density in the upper anoxic lower layer. The 1969 data alone show considerable scatter, probably because of analytical artefacts[21]. *f*, Silicate profiles for 1969 and 1988 plotted from the data sets of the same nutrient stations, showing that in 1969 the silicate concentrations in the upper layer down to the suboxic zone were larger than recent values, although values for deep anoxic water appear[12] underestimated by ~30% when compared with those obtained by others[9,13]. In *e* and *f*, no data are given for 1991 because of a lack of ammonia and silicate measurements. The nutrient samples of 1969 and 1991 collected by discrete bottle casts were stored before being autoanalysed by colorimetry[12,20], whereas the 1988 samples were processed immediately by a multichannel autoanalyser coupled to a pump-profiling system[7,14].

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Intense hydrolytic enzyme activity on marine aggregates and implications for rapid particle dissolution

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LARGE, rapidly sinking organic aggregates are an important component of the carbon flux from the ocean's surface to its depths. Marine snow, the main type of large (>0.5 mm) aggregate, is heavily colonized by bacteria in surface waters[1], yet the carbon demand of the attached bacteria is so small that months to years are required to consume the aggregates' carbon[2–5]. This has led to the conclusion that marine aggregates are resistant to degradation by attached bacteria, and thus act as refractory carriers of carbon to the deep ocean. Here we report that aggregates play host to intense activities of hydrolytic enzymes (presumably due to cell surface bound and released enzymes of the attached bacteria), which render the aggregates soluble. Particulate amino acids were hydrolysed rapidly (turnover time 0.2–2.1 days), with very little of the hydrolysate being taken up by the attached bacteria. Our results support the hypothesis[6,7] that such 'uncoupled' hydrolysis is a biochemical mechanism for large-scale transfer of organic matter from sinking particles to the dissolved phase,