

Lateral injection of oxygen with the Bosphorus plume—fingers of oxidizing potential in the Black Sea

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Abstract

Saline and warm Mediterranean water flowing through the Bosphorus Strait maintains a permanent pycnocline with vertical separation of oxic (O₂), suboxic (absence of O₂ and H₂S), and anoxic (H₂S) zones in the Black Sea. The stable suboxic zone implies restricted vertical mixing of the upper oxic and lower anoxic layers and limited vertical flux of oxygen that cannot balance the upward flux of sulfide. We report data that directly confirm massive lateral injections (>200 km from the Bosphorus) of oxygen-enriched waters of the Bosphorus plume, created by the mixing of shallow, cold, intermediate-layer Black Sea water with Mediterranean water. These plume waters are laterally injected into the oxic layer and, more importantly, into the suboxic and anoxic layers over several small vertical scales (“fingers” of ~5 m) at water densities (σ_t) from 15.0 to 16.4. O₂ injection oxidizes Mn(II) to Mn(III,IV), which then oxidizes H₂S. The onset of H₂S detection occurs in deeper waters in the southwest (>170 m; $\sigma_t \approx 16.4$) relative to the west central Black Sea (110 m; $\sigma_t \approx 16.2$) and coincides with increased MnO₂ and S₈ formation in the southwest.

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A permanent pycnocline formed by an increase in salinity (Anderson et al. 1988) or a decrease in temperature (Scranton et al. 2001) with depth is a natural barrier, inhibiting vertical fluxes, including the downward flux of O_2 . In fjords, bays, large inland seas such as the Black and Baltic Seas, and large oceanic basins such as the Cariaco, water stratifies, resulting in weaker vertical mixing. Thus, slow diffusion of O_2 across the pycnocline occurs and might be insufficient to account for the rates of redox processes and organic matter oxidation observed (Murray et al. 1995), leading to suboxic and, finally, anoxic (sulfidic) conditions beneath the pycnocline (Richards 1965; Anderson et al. 1988; Murray et al. 1995; Pers and Rahm 2000; Scranton et al. 2001; Stunzhas 2002; Yakushev et al. 2002).

In 1988, a suboxic zone (where O_2 and H_2S are at trace or undetectable levels and thus have no significant gradient, Murray et al. 1989) was discovered in the central Black Sea. This zone dramatically limits the possible advective and diffusive vertical fluxes of O_2 to the onset of H_2S , which occurs at an average water density (σ_t or $\sigma\text{-}t$) of 16.2. The oxic-anoxic system of the Black Sea has existed for seven millennia (Ryan et al. 1997; Arthur and Dean 1998) and even intensive anthropogenic eutrophication from the 1970s to 1980s had little effect on the vertical onset of H_2S versus $\sigma\text{-}t$ (Konovalov et al. 1999; Konovalov and Murray 2002). Several hypotheses were suggested to explain the stability of the H_2S onset and, in particular, to determine what electron acceptors directly oxidize H_2S (Lewis and Landing 1991; Luther et al. 1991; Tebo 1991; Murray et al. 1995).

For the Black Sea, Mediterranean water entering through the Bosphorus Strait (32-m water depth at the sill) does not reach the deep water (~50–2,200 m water depth) as an unmodified water mass (Ozsoy et al. 1991). Instead, the more saline Bosphorus outflow of Mediterranean water entrains the less saline Black Sea cold, intermediate-layer (CIL) water in the upper part of the main pycnocline. Depending on how it is calculated, the ratio of the entrained waters of the Mediterranean and Black Sea varies from 3 (Murray et al. 1991) to 10 (Ivanov and Samodurov 2001), resulting in a total flux of water to the deep Black Sea of up to 3,000 $\text{km}^3 \text{yr}^{-1}$. This water mixture creates a plume that is injected into the stratified water column of the Black Sea to form anomalies in temperature, salinity (Murray et al. 1991; Ozsoy et al. 1991), and activity of ^{137}Cs (Buesseler et al. 1991). These intrusions can be traced to a water depth of 500–700 m (Oguz and Rozman 1991; Ozsoy et al. 1991) and provide the flux of salt that maintains the main pycnocline. These intrusions also should provide injections of O_2 and other dissolved substances (Buesseler et al. 1991). Previous limited observations in the southwest Black Sea suggest suppression and distortion of the upper part of the H_2S onset at a few individual locations near the Bosphorus Strait (Bezborodov and Eremeev 1993; Basturk et al. 1998).

Hydrographic properties (Murray et al. 1991), radionuclide measurements (Buesseler et al. 1991; Ozsoy et al. 1991), and subsequent modeling of several data compilations (Konovalov et al. 2000; Stanev et al. 2001; Konovalov and Murray 2002) suggest that lateral flux of Mediterranean waters into the southwestern Black Sea might be important for lateral ventilation of the pycnocline and oxidation of H_2S .

Indirect evidence of lateral ventilation has been presented for other stratified marine systems (Anderson et al. 1988; Pers and Rahm 2000; Scranton et al. 2001), but the chemical constituents contained within the lateral intrusions and their reactivity with sulfide have not been documented. In fact, lateral injection of oxygen has been considered to be a peculiar event, which does not affect the redox budget of an oxic-anoxic marine system (Neretin et al. 2001). Also, Yakushev et al. (2002) indicate that the vertical fluxes of the major oxidizers and reducers are in balance and that lateral flux might be unimportant.

Here, we report coupled conductivity, temperature, and depth (CTD) and in situ voltammetry data from the Black Sea cruise on the R/V *Knorr* (23 May–9 June 2001) that directly confirm massive lateral intrusions of oxygen-enriched waters into the suboxic and anoxic layers of the southwestern Black Sea. We trace the influence of lateral injection at least 200 km into the center of the Black Sea. Layers of lateral intrusions of oxygen-enriched waters (of only a few meters thickness) intensify the introduction of oxygen into the suboxic and anoxic zones, which oxidizes Mn(II) to Mn(III,IV), which then oxidizes H_2S .

Methods

The electrodes and in situ electrochemical analyzer (DLK-SUB-II, Analytical Instrument Systems) were mated to the frame of the CTD-pump profiler system developed by Codispoti et al. (1991) to measure temperature, salinity, and density. The in situ analyzer consists of a pressure case, which encloses the voltammetry hardware linked to an IBM-compatible computer. Power is provided by an internal rechargeable 12-VDC battery. The internal computer communicates with another aboard the R/V *Knorr* via a 300-m RS-232 cable and is controlled by an operator in the lab. A separate 1-m cable was used to make connections between the working, counter, and reference electrodes and the pressure housing. This cable had four inputs for working electrodes, which are controlled via a multiplexer. One input is for the counter electrode, one for the reference electrode, and one for grounding the reference electrode to insure signal integrity. The working electrodes are solid-state gold-amalgam (Au/Hg) and were prepared in polyethyletherketone (PEEK[®]) tubing (Luther et al. 2001a). The reference electrode was Ag wire oxidized in 3 M KCl to make an AgCl coating. This Ag/AgCl reference was used as a solid-state electrode. The counting electrode was made of platinum (Pt). Potentials for chemical species measured in situ and onboard ship with the same reference electrode were comparable, so no pressure effects were observed. Scan rates were 1 V s^{-1} .

Before each scan, conditioning was performed at -0.9 V for 5 s where none of the chemical species are electroactive (Brendel and Luther 1995), which was followed by a 5-s deposition step at -0.1 V to detect low concentrations of H_2S . Potential scan direction is from positive to negative for linear sweep voltammetry (LSV). The experimental procedure of electrochemical cleaning prior to scanning potential made each scan independent of the influence of the previous scan. Thus, voltammetry provides the ability to (1) detect

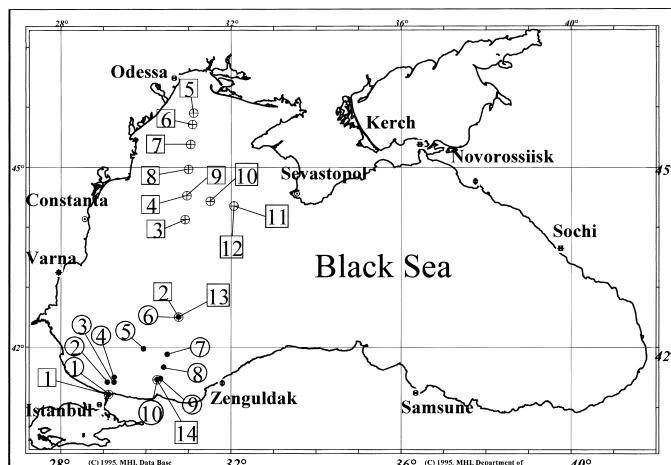


Fig. 1. Black Sea station locations (Leg 1, 23–31 May 2001 [numbers in circles] and Leg 2, 1–9 June 2001 [numbers in squares]).

oxygen and sulfide in the same scan without interference, if present and (2) resolve the oxygen and sulfide profiles at a submeter scale (0.8 m). For cyclic voltammetry (CV), the potential scan is positive, to negative, and back to positive. These conditions provided a detection limit of 30 nmol L^{-1} for H_2S and $\sim 3 \text{ } \mu\text{mol L}^{-1}$ for O_2 and permit the identification and tracing of the irregular multilayer vertical structure (*see below*), which cannot be resolved using traditional discrete sample bottle methods. The electrodes are calibrated according to the procedures in Brendel and Luther (1995) and Luther et al. (2002) for a variety of parameters, including temperature and water flow.

A DLK-60 Electrochemical Analyzer (Analytical Instrument Systems) and a solid-state Au/Hg working electrode, Ag/AgCl reference electrode, and Pt counter electrode were used for pump profiling voltammetric analysis with a flow cell in the pumped flow stream aboard ship (Luther et al. 2002). Typical conditions were a potential scan range from -0.1 to -1.8 V using LSV, CV, or both modes at 1 or 4 V s^{-1} or both. The working electrode was conditioned at -0.9 V for 2 s to clean the surface of the Au/Hg electrode, then a deposition step at -0.1 V for 20 s was performed. These conditions provided the low detection limit of 3 nmol L^{-1} for H_2S and $\sim 3 \text{ } \mu\text{mol L}^{-1}$ for O_2 . Vertical resolution for this system was about 1.5 m .

Water samples from discrete 24×10 -liter rosette bottle casts were analyzed by Winkler titrations for O_2 (detection limit $\sim 3 \text{ } \mu\text{mol L}^{-1}$) and by iodometric titration (detection limit $\sim 3 \text{ } \mu\text{mol L}^{-1}$) and voltammetry (detection limit $\sim 3 \text{ nmol L}^{-1}$) for H_2S .

Dissolved Mn was determined on filtered (0.2 – $0.4 \text{ } \mu\text{m}$) samples by the formaldoxime method (Brewer and Spencer 1971). Oxidized particulate Mn was determined by reducing the particulate Mn from the filters in 0.1% hydroxylamine and then measuring Mn(II) by the formaldoxime method.

S_8 was measured on filtered ($0.2 \text{ } \mu\text{m}$) samples by converting all $\text{S}(0)$ to thiosulfate by reaction with sulfite (Luther et al. 1991). Bottle casts were taken immediately before or after the in situ profiles or at both times.

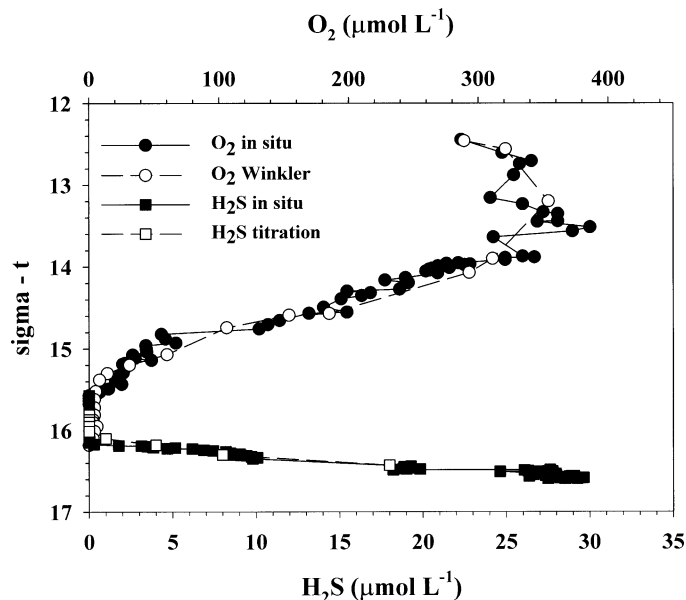


Fig. 2. Comparison of O_2 and H_2S data determined by titrations and voltammetry from Leg 2, Sta. 2 on two separate casts.

Details and data for the 2001 R/V *Knorr* Black Sea voyage 162, Legs 16 and 17 (J. W. Murray, chief scientist), are available on the Web site at www.ocean.washington.edu/cruises/Knorr2001.

Results and discussion

High-resolution vertical chemical profiles for O_2 and H_2S were performed at stations in the northern, central, and southern regions of the western Black Sea (Fig. 1). Some stations (Leg 1, Sta. 6 and Leg 2, Stas. 2 and 13 in the central part of the sea and several stations on Legs 1 and 2 in the southern part of the sea) were reoccupied to resolve synoptic processes (7–10 d) on a basin-wide scale. To obtain high-resolution profiles of O_2 and H_2S , as well as other partially oxidized sulfur intermediates, in situ voltammetric analyses (Luther et al. 2001a) and pump profiling (Codispoti et al. 1991) with a shipboard voltammetric cell (Luther et al. 2002) were used in the upper 200 m of the water column with a vertical resolution of 0.8 m for in situ analyses and 1.5 m for pump profiling. These techniques were coupled with a CTD to obtain temperature, salinity, and density data and to provide more chemical information than the use of an in situ oxygen sensor alone (Stunzhas 2000). Figure 2 shows O_2 and H_2S data from a station in the center of the western gyre with a well-developed suboxic zone, where variability is low, and demonstrates that there is good agreement for data obtained by standard titrations and in situ voltammetry, even though the titration data are from a separate bottle cast. The results of Winkler titration and voltammetric analyses from the same bottle (data not shown) indicate an excellent inter-comparison. Analyses of samples from traditional rosette sampling methods cannot resolve the vertical structure of the distribution of O_2 (e.g., Fig. 3c). This makes high-resolution voltammetric profiling extremely useful for the investigation

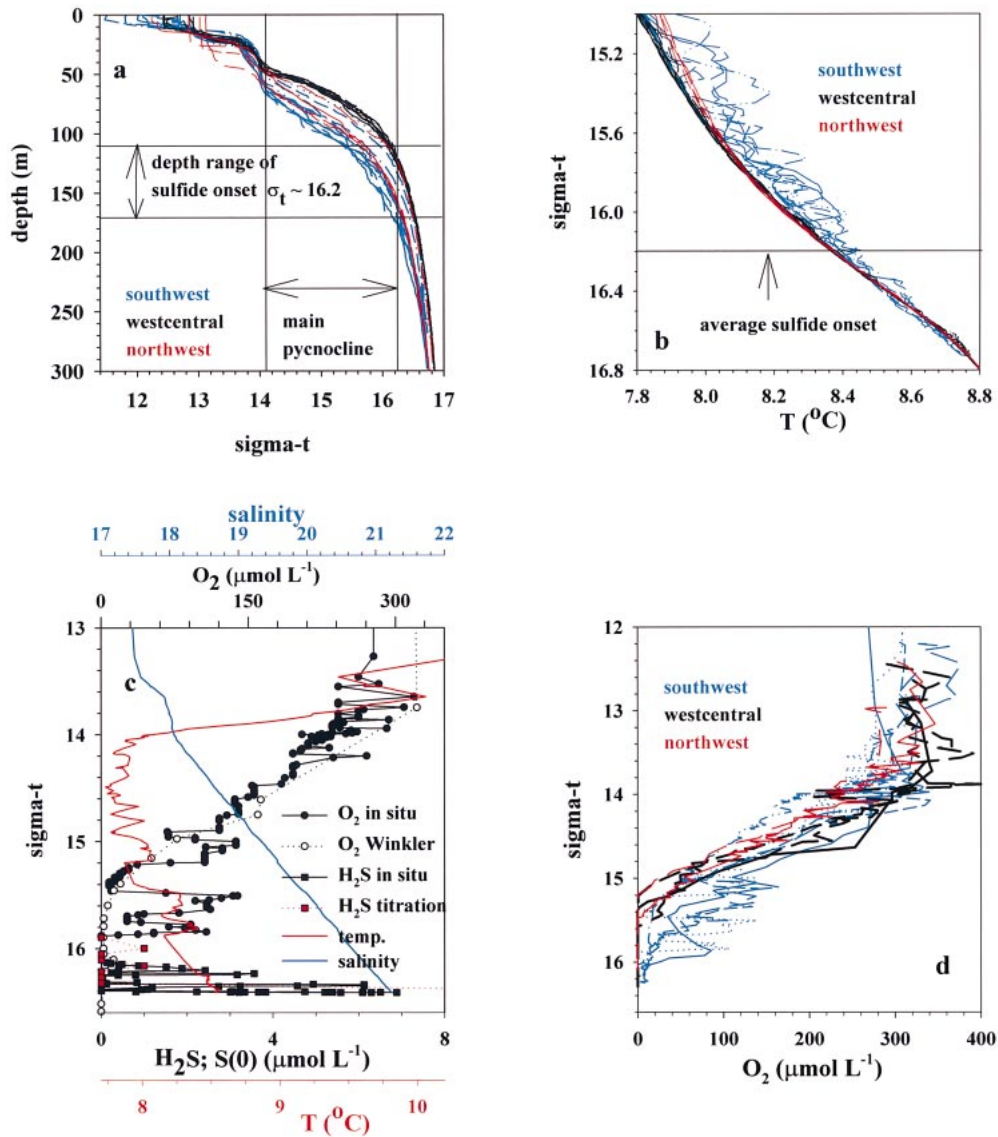


Fig. 3. (a) Depth versus density (σ_t) plot showing the main pycnocline. The H_2S onset (vertical reference lines) occurs at an average σ_t of ~ 16.2 , but the depth of H_2S onset varies within the basin (horizontal reference lines). (b) Temperature versus σ_t profiles show intrusions into the southwest Black Sea. (c) σ_t versus high-resolution in situ voltammetric O_2 and H_2S data coupled with temperature and salinity data from the CTD on the pump profiler for Sta. 9 (Leg 1; 29 May 2001). Winkler and iodometric titration data for O_2 and H_2S , respectively, are also given (note O_2 increases parallel to temperature increases). (d) O_2 data from in situ and pump profile voltammetry versus σ_t profiles show lateral injection of O_2 into the southwest Black Sea.

of lateral intrusions and other irregularities in the distribution of chemical properties at a (sub)meter scale.

Lateral processes—Profiles of physical and chemical properties from the southwestern and northwestern shelf regions differ significantly from the west central parts of the Black Sea in the upper 200 m, as shown for density (Fig. 3a). Thus, the onset of H_2S at an average σ_t value of 16.2 occurs near 110 m in the central part of the sea but at >170 m near the southwest shelf break (Fig. 3a). There is little change in the onset of H_2S with σ_t in the center of the Black Sea, where isopycnal and cross-isopycnal fluxes are not ex-

posed to lateral variations in chemistry. In the southwestern Black Sea, plots of physical and chemical properties versus density reveal lateral injection (Figs. 3b,c,d, 4). Temperature profiles plotted versus density (Codispoti et al. 1991; Tugrul et al. 1992) (Fig. 3b) are more variable in the southwestern Black Sea than in the northwestern and central regions. Maximum values in the temperature profiles from the southwestern region (Figs. 3b, 4b,d) reveal the presence of intrusions of the warmer and saltier Bosphorus plume waters into the main pycnocline as far inward as Stations 5, 6, and 7 (>200 km for Leg 1; Fig. 1).

Only lateral intrusions of the Bosphorus plume waters can

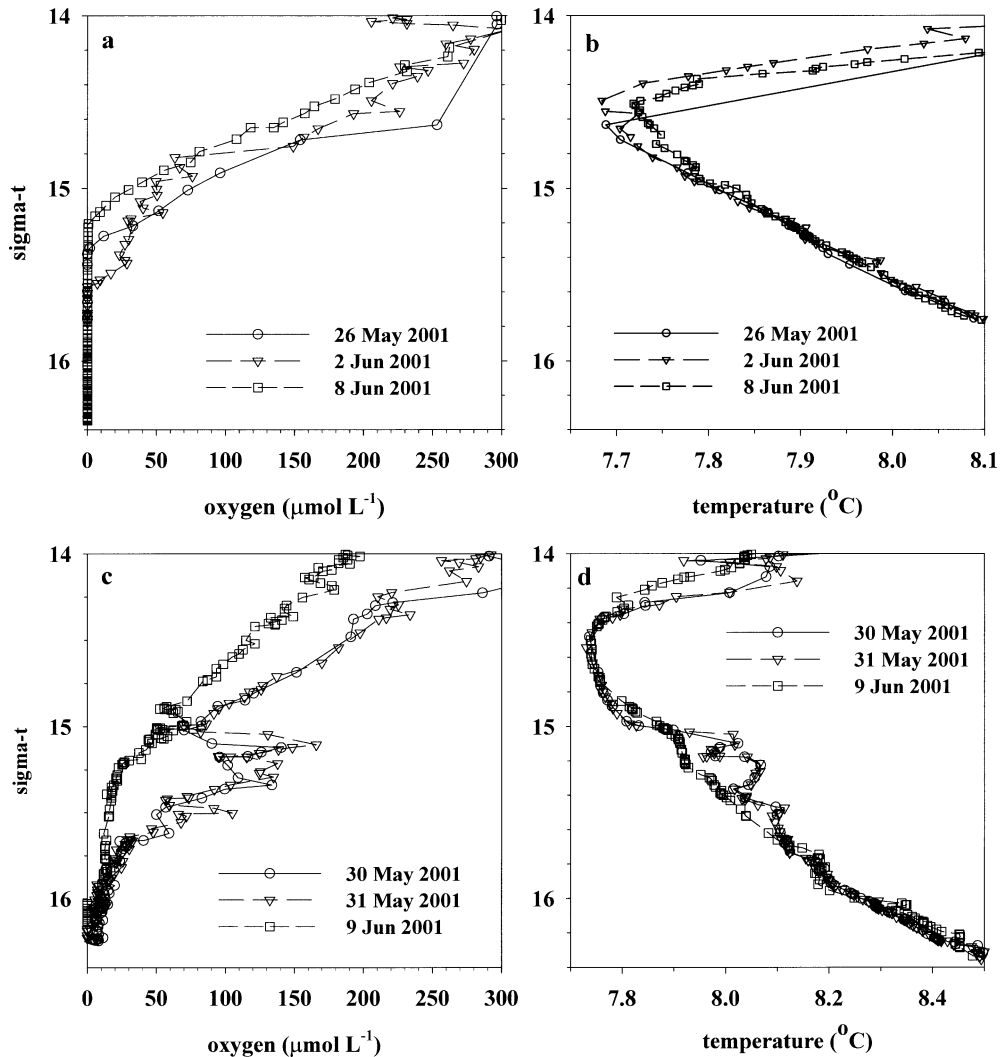


Fig. 4. Synoptic changes for (a) O_2 and (b) temperature in the west central station (Leg 1, Sta. 6; Leg 2, Stas. 2 and 13) and synoptic changes for (c) O_2 and (d) temperature in the southwestern stations (Leg 1, Sta. 10; Leg 2, Sta. 14).

be the source for both warmer and saltier waters of the main pycnocline, which is overlain by the CIL. The waters of the CIL are not only colder compared to the deeper layers, but they are also less saline. Thus, the O_2 increases observed are associated with positive anomalies in both temperature and salinity. Although intrusions were traced in individual profiles in 2001 as narrow, local anomalies with an increase in temperature, a decrease in temperature with an increase in salinity could occur depending on the relative temperatures of the Mediterranean and Black Sea CIL waters. Overlaying all profiles shows influx of the Bosphorus plume waters throughout the main pycnocline. The intensity of these intrusions decrease with increasing density, but can be traced to depths with densities as large as $\sigma_t \approx 16.6$ (~ 200 m) (Fig. 3b). Similar intrusions are not observed in the north-west shelf area.

Ivanov and Samodurov (2001) analyzed averaged basin-wide T-S diagrams and possible mixing ratios on a time scale of decades and showed that an average mixing ratio of 10

occurs at an average density of $\sigma_t = 15.7$ and an average depth of 100 m, which is a boundary between net entrainment versus net intrusion. The actual depth at the boundary of net entrainment and net intrusion can vary from 90 to 110 m, and the density at 100 m varies spatially from $\sigma_t < 15.0$ to $\sigma_t > 16.0$ (Fig. 3a). Thus, intrusions of the Bosphorus plume can be detected at any given station at density values deeper than about $\sigma_t = 15.0$, as we observed during the 2001 KNORR cruise (Fig. 3b). The origin of this value is the lower boundary of the CIL at $\sigma_t = 15.0$.

For the deep Black Sea from 50 to 2,200 m, the ventilating Bosphorus plume water must be a mixture of one part Bosphorus outflow of Mediterranean origin and three parts CIL ($\sigma_t = \sim 14.5$; Murray et al. 1991). But the entrainment ratio varies with depth, and with waters ventilating the main pycnocline ($\sigma_t = 15.0$ – 16.5), it can be closer to 1:10 (Buesseler et al. 1991; Ivanov and Samodurov 2001; Stanev et al. 2001). This means that the concentration of dissolved O_2 in the Bosphorus plume should reach 100–150 $\mu\text{mol L}^{-1}$ (Ko-

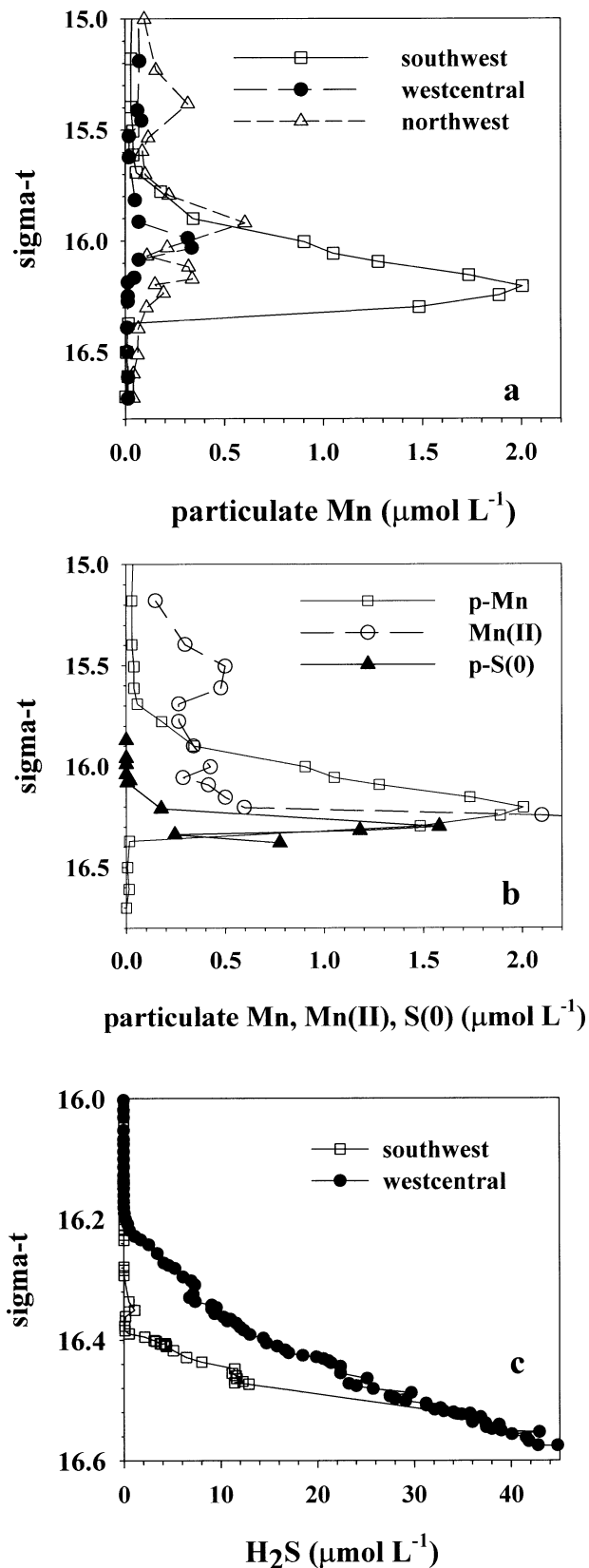


Fig. 5. (a) Particulate Mn(III,IV) versus sigma-t data; massive formation of particulate Mn in waters of a higher density in the southwest shows the effects of the lateral injection of O_2 . (b) Dis-

novalov and Murray 2002). Thus, maxima were detected in the distribution of O_2 (Fig. 4c) that coincide with small temperature increases ($<0.4^\circ\text{C}$) (Fig. 4d), confirming that intrusions of the warm, salty Bosphorus plume generate an intensive lateral flux of O_2 into the oxic, suboxic, and anoxic layers of the pycnocline (Figs. 3c, 4). Thus, salinity, temperature, and O_2 are all excellent tracers of lateral intrusions. However, O_2 is best because salinity of the Bosphorus plume differs from the ambient Black Sea waters by less than a few percent, and temperature differs by less than 0.4°C , whereas the difference for O_2 exceeds $100 \mu\text{mol L}^{-1}$. Moreover, smaller temperature increases ($<0.1^\circ\text{C}$) track decreases in H_2S concentration after O_2 was not detectable. Thus, oxidation of H_2S must have occurred.

Both direct voltammetric profiling of O_2 (Figs. 3c,d, 4) and temperature data (Figs. 3b, 4) demonstrate that lateral ventilation from the Bosphorus is not just a local event but is a fundamental physical process affecting the oxic-anoxic balance of the Black Sea. Unlike previous results (e.g., Ozsoy et al. 1991; Bezborodov and Eremeev 1993; Basturk et al. 1998), this high-resolution voltammetric profiling demonstrates the ability to trace the lateral intrusion of O_2 into the oxycline layer, as well as the suboxic and anoxic zones of the Black Sea. Clear evidence of lateral injection can be traced at least 200 km from the Bosphorus (Leg 1, Stas. 5, 6, and 7; Fig. 1).

The vertical and spatial structure of intrusions should be highly variable and trace synoptic changes. O_2 disappearance varies with σ_t or depth over 6 d at the west central station (Fig. 4a) and might be due to O_2 lateral injection because temperature changes on 2 June (Fig. 4b) correlate with small O_2 changes below $\sigma_t = 15$. However, "fingering" is not as obvious as in Fig. 3c. On a 24-h basis, some variability in fingering at southwest locations correlates with temperature changes (30 and 31 May; Fig. 4c,d). However, on a 10-d time scale, there can be great variability even though O_2 disappearance occurs at the same σ_t or depth.

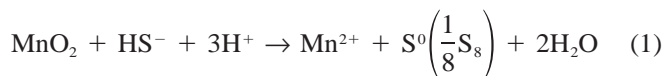
Redox processes—Lateral influx of O_2 associated with the Bosphorus plume must dramatically affect the redox budget of the system and result in changes in the distribution of the main reduced redox species (H_2S , Mn^{2+} , and NH_4^+). The vertical profile of particulate oxidized manganese, the primary end-product of oxidation of dissolved Mn^{2+} , also reveals remarkable spatial differences in the intensity of manganese cycling (Fig. 5a). The maximum concentration of particulate manganese was three- to sixfold higher in the southwestern than in the northern and central part of the sea. The distribution of dissolved Mn^{2+} reveals the expected opposite trend (data not shown). Although the major onset of dissolved Mn^{2+} was traced at about $\sigma_t = 15.8$ – 15.9 in the northwest and west central part of the sea, it was suppressed to $\sigma_t =$

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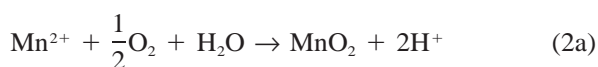
dissolved Mn^{2+} , particulate Mn(III,IV), and particulate S(0) from hydrocast bottle samples at Sta. 10 (Leg 1) in the southwestern Black Sea. (c) H_2S versus sigma-t data from the central and southern stations shows a H_2S loss resulting from O_2 lateral injection.

16.2–16.3 in the southwest part, but with the observation of one smaller maximum at $\sigma_t < 16.2$ (Fig. 5b).

Manganese cycling in oxic–anoxic marine systems is tightly coupled with sulfide–elemental sulfur–sulfate cycling (Luther et al. 1991). MnO_2 can serve as an oxidant for H_2S after dissolved Mn^{2+} is oxidized to particulate Mn(III,IV) (Tebo 1991) above the anoxic layer and sinks into the sulfidic zone (Eq. 1).



Moreover, Mn^{2+} can also catalyze the oxidation of H_2S by O_2 when Mn^{2+} and O_2 coexist in the same water mass (Luther et al. 1991) (Eq. 2a,b).



As shown in Fig. 5c, the intensity of sulfide oxidation increases in the southwestern part of the sea as the Bosphorus plume provides intensive lateral influx of O_2 both above and below the H_2S onset (Fig. 3c,d). Particulate Mn (Fig. 5a,b) extends to the H_2S zone consistent with O_2 oxidizing Mn^{2+} to Mn(III,IV), which in turn oxidizes H_2S to polysulfides and S_8 . Polysulfides (data not shown) were detected at the H_2S onset by both in situ and pump profiling voltammetry methods (Rozaan et al. 2000; Luther et al. 2001b). In addition, Fig. 5b shows that particulate S_8 [plotted as $\text{S}(0)$] overlaps with Mn(III,IV) and has a maximum slightly deeper than the Mn(III,IV) maximum ($\sigma_t = 16.2$). The particulate $\text{S}(0)$ and Mn(III,IV) are nearly equal in concentration, as expected from Eq. 1. Because O_2 and H_2S do not coexist as σ_t increases (e.g., Fig. 3b), these data demonstrate that Mn(III,IV) phases are the direct oxidants of H_2S in the western Black Sea and that O_2 is the ultimate oxidant via Mn catalysis (Eq. 3a,b).

Because the O_2 , H_2S , and Mn^{2+} layers reveal an irregular multilayer (fingering) vertical structure (Figs. 3c,d, 5b), the H_2S onset occurs at a higher density in the southwestern Black Sea (Fig. 5c). For southwestern stations, the permanent H_2S onset occurs at $\sigma_t \approx 16.4$ (higher than the average basin-wide σ_t of 16.2). Because of the pump profiler's cable length, we were unable to obtain in situ voltammetric H_2S profiles below the depth of 200 m, which corresponds to $\sigma_t \approx 16.5$. Still, CTD data (e.g., Fig. 3b) revealed small anomalies in the distribution of temperature that suggest H_2S oxidation, resulting from the lateral flux of O_2 , and formation of Mn(III,IV) phases can be prominent inside the anoxic zone as deep as $\sigma_t \approx 16.6$ –16.7.

The lateral flux of O_2 with the intrusions of the Bosphorus plume into the interior of the Black Sea (>200 km) significantly intensifies consumption of H_2S . This process is of large enough magnitude, because both the volume of the plume and the oxygen concentration appear large, to affect the basin-wide distribution of sulfide: up to 70% of the total sink for sulfide is potentially a result of oxidation by the lateral flux of oxygen in the Black Sea (Konovalov et al. 2000).

Our data directly prove that Bosphorus plume intrusions introduce lateral flux of oxygen into deeper waters of the Black Sea. Thus, lateral ventilation might be equal to or more important than other physical processes in bringing oxidants into anoxic waters, which would then significantly affect the overall redox budget and lead to an imbalance in the observed rates of redox processes on the basis of vertical processes alone (Murray et al. 1995). Lateral processes could also be responsible for the presence of local maxima of oxygen above the onset of sulfide in the Cariaco Basin (Scranton et al. 2001), the Chesapeake Bay (Luther et al. 2002), and the revealed deficit of sulfide in the upper anoxic zone of Framvaren Fjord (Norway) (Anderson et al. 1988).

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