

Spatial and temporal variability of the Black Sea suboxic zone

Brian T. Glazer^{a,1}, George W. Luther III^{a,*}, Sergey K. Kononov^b,
Gernot E. Friederich^c, Robert E. Trouwborst^a, Alexander S. Romanov^b

^aCollege of Marine Studies, University of Delaware, Lewes, DE 19958, USA

^bMarine Hydrophysical Institute, Kapitanskaya 2, Sevastopol 99011, Ukraine

^cMBARI, 7700 Sandholdt Road, Moss Landing, CA 95039, USA

Received 1 August 2005; accepted 26 March 2006

Available online 6 September 2006

Abstract

We coupled an in situ electrochemical analyzer to a CTD to conduct high-resolution, real-time profiling of redox species across the oxic–anoxic transition zone of the Black Sea water column. Voltammetry was performed using gold–amalgam working electrodes to measure simultaneously soluble oxygen and sulfur species ($\text{H}_2\text{S}/\text{HS}^-$, S_x^{2-} , S_8) at a resolution of greater than one measurement per meter. In situ data agreed with measurements made in an on-deck voltammetry flow cell coupled to a pump profiling system, and from water samples collected with conventional CTD rosette bottle casts. In situ voltammetric analyses provided rapid redox information, thus enabling more accurate targeting of specific geochemical features by the CTD rosette package. We observed much less lateral oxygen injection from the Bosphorus in 2003 (less than 95 km from Bosphorus) than in 2001 (up to 150 km). This difference can be attributed to variability in physical processes including seasonal temperature and wind variations between winter conditions (2003) and early summer conditions (2001). Furthermore, suboxic zone thickness varied basin-wide, exhibiting changes in the depth of oxygen extinction (minimum detection limit = 3 μM) and sulfide onset (minimum detection limit = 30 nM). The density surface for oxygen extinction was more variable than the density for the onset of sulfide. Vertical shifts in oxygen extinction and sulfide onset also were observed at the western central gyre station for seven profiles measured over 21 days in 2003.

© 2006 Elsevier Ltd. All rights reserved.

Keywords: In situ voltammetry; Oxygen; Sulfide; Suboxic; Black Sea; Redox

1. Introduction

Oxygen and sulfide were thought to coexist in the transition from oxic to sulfidic waters in the Black Sea (Sorokin, 1983; Faschuck and Ayzatullin, 1986), until 1988 when a suboxic zone with

nondetectable levels of O_2 and H_2S was observed (Murray et al., 1989). Suggestions that observations of the coexistence of oxygen and sulfide were an artifact of atmospheric contamination with oxygen during sampling were made as early as 1975 (Grashoff, 1975), but accuracy of sampling and analytical methods were not great enough to prove this point prior to 1988. Similarly, the assumption that the sulfide inventory and budget are at steady state has been challenged in recent years (Murray et al., 1989; Kononov et al., 1999; Kononov and

*Corresponding author. Fax: +1 302 645 4007.

E-mail address: luther@udel.edu (G.W. Luther III).

¹Current address: Department of Oceanography, University of Hawaii, Honolulu, HI 96822, USA.

Murray, 2001). The upward flux of sulfide at the depth of its onset was considered to be equal to its production rate in the anoxic layer, and therefore oxidation of sulfide was assumed to take place at the lower boundary of oxic waters where oxygen diffusing downward formed a layer with co-existing oxygen and sulfide (Konovalov et al., 2001).

The vertical stratification of the Black Sea is determined by low-salinity surface waters of river origin overlying high-salinity deep waters of Mediterranean origin, resulting in a sharp permanent pycnocline that inhibits exchange between surface and deep waters. In the case of the Black Sea, a vertical transition between oxic and anoxic waters is likely to have existed for over the past 7000 years (Lane-Serff et al., 1997; Arthur and Dean, 1998), since post-glacial saline Mediterranean waters broke through a land barrier and flooded the isolated freshwater Black Sea basin, possibly as fast as 0.1–1 m/day (Ryan et al., 1997), setting up a permanent pycnocline. Temporal and spatial variations of the pycnocline are shaped by physical hydrodynamics of the basin and seasonal effects. Winter convection, direct intrusions with Mediterranean waters, and boundary current mixing contribute to ventilation of the pycnocline (Gregoire and Stanev, 2001). The structure of the oxic/anoxic transition as demonstrated recently by Murray et al. (1995) and Konovalov et al. (2003) excludes oxygen as the primary oxidant for sulfide because of the presence of the suboxic zone. Alternative explanations have included oxidation of sulfide by nitrate or iron(III) or manganese(III,IV) hydroxides (Luther et al., 1991; Murray et al., 1995; Konovalov et al., 2003). Konovalov and Murray (2001) also pointed out that O_2 injected into the sulfide layer by the Bosphorus Plume could account for a significant fraction of the upward flux of sulfide.

The balance between sulfide production in the water column and sulfide oxidation at the base of the suboxic zone has an important feedback for the whole Black Sea ecosystem (Neretin et al., 2001). The temporal and spatial variability of the suboxic zone can thereby tell us much about the relative stability of the Black Sea sulfide budget as well as oxidation processes. Furthermore, variability in seasonal mixing and Mediterranean inflow and outflow through the Bosphorus Strait can play a crucial role in the salinity, water budget, and chemical composition of the Black Sea water column (Ozsoy and Unluata, 1997; Neretin et al., 2001).

Traditional methods for water sampling and subsequent analyses include bottle casts on a CTD rosette, which induces water mixing during upward or downward motion through the water column. Furthermore, water samples are collected in vertically oriented bottles, which integrate waters over a vertical distance of greater than a meter. In 1988, a pump profiling system was deployed in the Black Sea (Codispoti et al., 1991) to provide continuous vertical profiling capability, but, again, mixing may be induced through turbid pumping of water from depth to the ship's lab through 200 m of nylon tubing, or reactions may occur as a result of particulate adhesion to the tubing walls. Modern deployable voltammetric analyzers coupled to Au/Hg electrodes recently have been used to characterize O_2 , H_2O_2 , H_2S , S_x^{2-} , soluble S_8 , Fe(II), Fe(III), aqueous FeS, Mn(II) in salt marsh (Bull and Taillefert, 2001), continental shelf sediments and coastal bays (Luther et al., 1999), microbial mats (Glazer et al., 2002), and hydrothermal vents (Luther et al., 2001). Such sensors are capable of making real time, in situ measurements, independent of sample manipulation, thus providing unprecedented vertical resolution for redox profiling.

This work presents data on spatial and temporal variability of the suboxic zone based on in situ voltammetric measurements of O_2 and H_2S with detection limits of $3 \mu M$ and $30 nM$, respectively. Data were collected during a Black Sea cruise on the R/V *Knorr* (April 14–May 16, 2003) enabling comparison of the distributions in the southwest, west central, central, and eastern stations, as well as temporal fluctuations at the west central station. Additionally, broad seasonal comparisons are made between sampling during summer conditions during 2001 and winter conditions during 2003. We used coupled CTD and in situ voltammetry data to demonstrate the existence of partially oxidized sulfur intermediates at depths near the onset of H_2S and lateral intrusions of oxygen-enriched waters into suboxic and anoxic layers.

2. Methods

The R/V *Knorr* occupied various stations within the Black Sea during Voyage 172-legs 7, 8 and 9, between 14 April and 16 May, 2003. Data were collected to provide new insight and comparisons to the previous major US Black Sea expeditions, conducted in 2001 (R/V *Knorr* Voyage 162-16 &

162–17, May–June) and in 1988 (R/V *Knorr* Voyage 134–10, April–July) (Murray, 1991). The participants, station locations and hydrographic and nutrient data for the 2001 and 2003 cruises are available on the web at: www.ocean.washington.edu/cruises/Knorr2001 and www.ocean.washington.edu/cruises/Knorr2003.

The deployment package consisted of two separate instruments coupled to a protective stainless steel cage. The voltammetric analyzer was linked directly to a dedicated Seabird Microcat to provide temperature, salinity, and density. On-deck flow-through water samples (and corroborative CTD measurements) were provided by the pump profiler-CTD system developed by the Monterey Bay and Aquarium Institute (MBARI) (Codispoti et al., 1991). In situ voltammetric analyses were collected via an electrochemical analyzer built into a pressure housing by Analytical Instrument Systems, Inc. (AIS), powered by an internal rechargeable 12 V DC battery. The internal computer communicated with another aboard the ship via a 300-m RS 232 cable and was controlled by an operator or programmed to continuously perform voltammetric measurements. A separate 1-m cable was used to make connections between the working, reference, and counter electrodes and the pressure housing. This cable accommodated up to four different working electrodes that were used via an internal multiplexer, the counter electrode, and two inputs for the

reference electrode so that it could be grounded to ensure signal integrity.

The working electrodes were solid-state gold–amalgam (Au/Hg) prepared in polyethyletherketone (PEEK™) tubing, sealed with epoxy, and were calibrated for O₂, H₂S, and Mn(II) prior to deployments (Luther et al., 1999). The potential and detection limits for redox reactions that occur at the Au/Hg electrode surface are listed in Table 1. The reference electrode was also solid-state, prepared by oxidizing a 500-μm silver wire in 3 M KCl to make a AgCl coating. 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 1000 mV/s. Prior to each scan, conditioning was performed at –0.9 V for 5 s, where none of the chemical species are electroactive (Brendel and Luther, 1995), and then a 2 s deposition at –0.1 V. Potential scan direction was from positive to negative for linear sweep voltammetry (LSV). Cyclic voltammetry (CV) scans were from positive to negative and then back to positive. These conditions provided a detection limit of 30 nM for H₂S and about 3 μM for O₂, as determined by linear regression of known standards. Such low detection levels allowed for in situ identification of irregular multi-layer vertical structure for chemical species, which cannot be detected by traditional methods. Because voltammetric scans could be performed

Table 1

Selected measurable redox reactions occurring at the 0.1 mm Au/Hg electrode surface vs. the 0.5 mm Ag/AgCl reference electrode

		$E_p (E_{1/2})$ (V)	MDL (μM)
1a	$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$	–0.30	3
1a	$H_2O_2 + 2H^+ + 2e^- \rightarrow H_2O$	–1.2	5
2a	$HS^- + Hg \rightarrow HgS + H^+ + 2e^-$	Adsorption onto Hg < –0.60	
2b	$HgS + H^+ + 2e^- \rightarrow HS^- + Hg$	~–0.60	<0.05
3a	$S^0 + Hg \rightarrow HgS$	Adsorption onto Hg < –0.60	
3b	$HgS + H^+ + 2e^- \leftrightarrow HS^- + Hg$	~–0.60	<0.1
4a	$Hg + S_x^{2-} \leftrightarrow HgS_x + 2e^-$	Adsorption onto Hg < –0.60	
4b	$HgS_x + 2e^- \leftrightarrow Hg + S_x^{2-}$	~–0.60	<0.1
4c	$S_x^{2-} + xH^+ + (2x-2)e^- \leftrightarrow xHS^-$	~–0.60	<0.1
5	$Mn^{2+} + Hg + 2e^- \leftrightarrow Mn(Hg)$	–1.55	5

Oxygen data were collected by linear sweep voltammetry. Cyclic voltammetry was employed in the absence of oxygen to better measure sulfur species. Potentials can vary with scan rate and concentration. When applying potential from a positive to negative scan direction, sulfide and S(0) react in a two step process: adsorption onto the Hg surface, and reduction of the HgS film. Polysulfides, if present, react in a three-step process: adsorption onto the Hg surface, reduction of the HgS_x film, and reduction of the S(0) in the polysulfide. Increasing scan rate separates electrode reactions 4b and 4c into two peaks because reaction 4c is an irreversible process. Increasing scan rate shifts this signal. MDL = minimum detection limit.

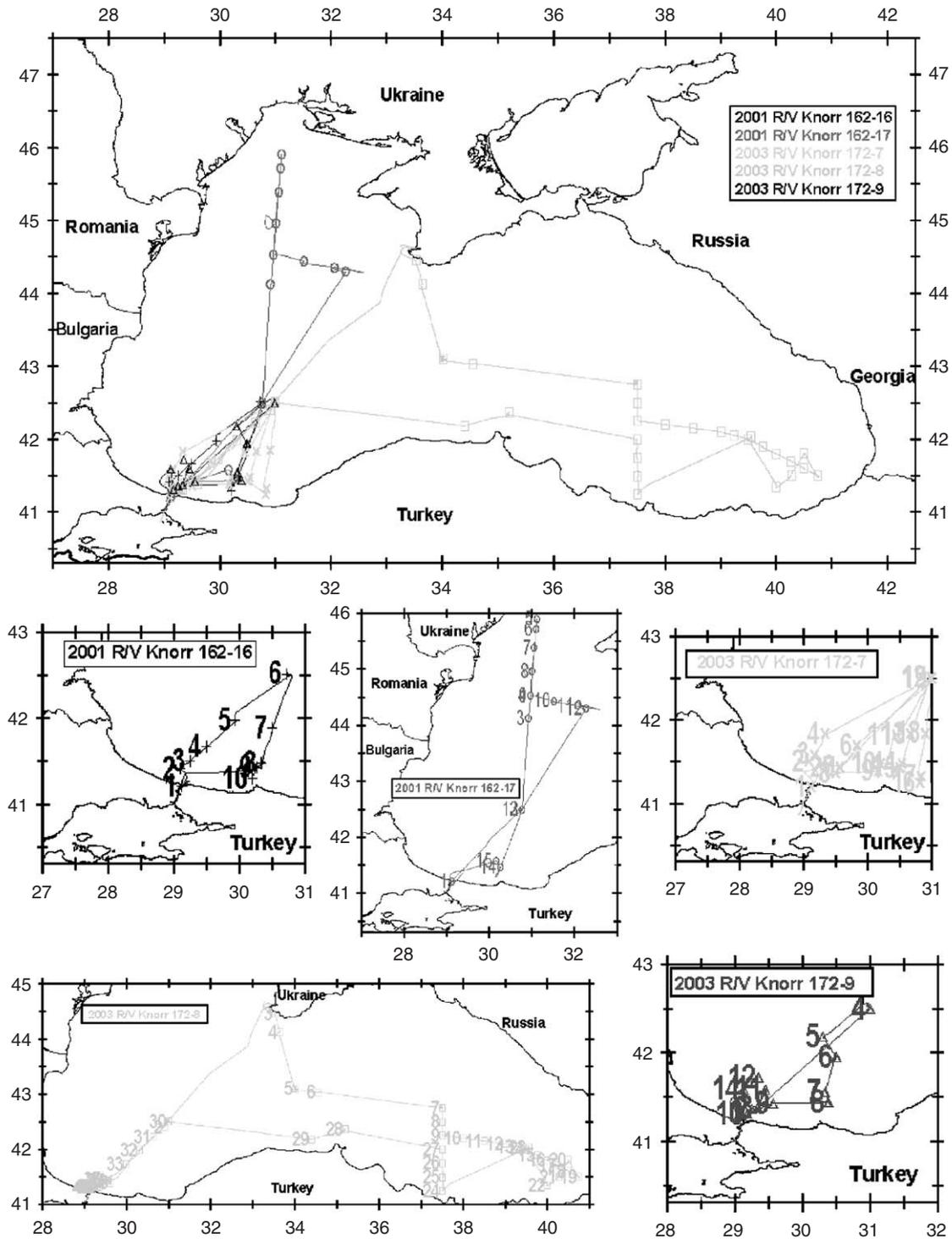


Fig. 1. Maps of Black Sea depicting cruise tracks and stations locations for R/V *Knorr* cruises discussed in text. Top panel depicts overview of all five cruise tracks and sampling stations. Middle row (left to right) gives station locations and names for 162-16, 162-17 (2001), and 172-7 (2003). The bottom panels (left–right) give station locations and names for 172-8, and 172-9.

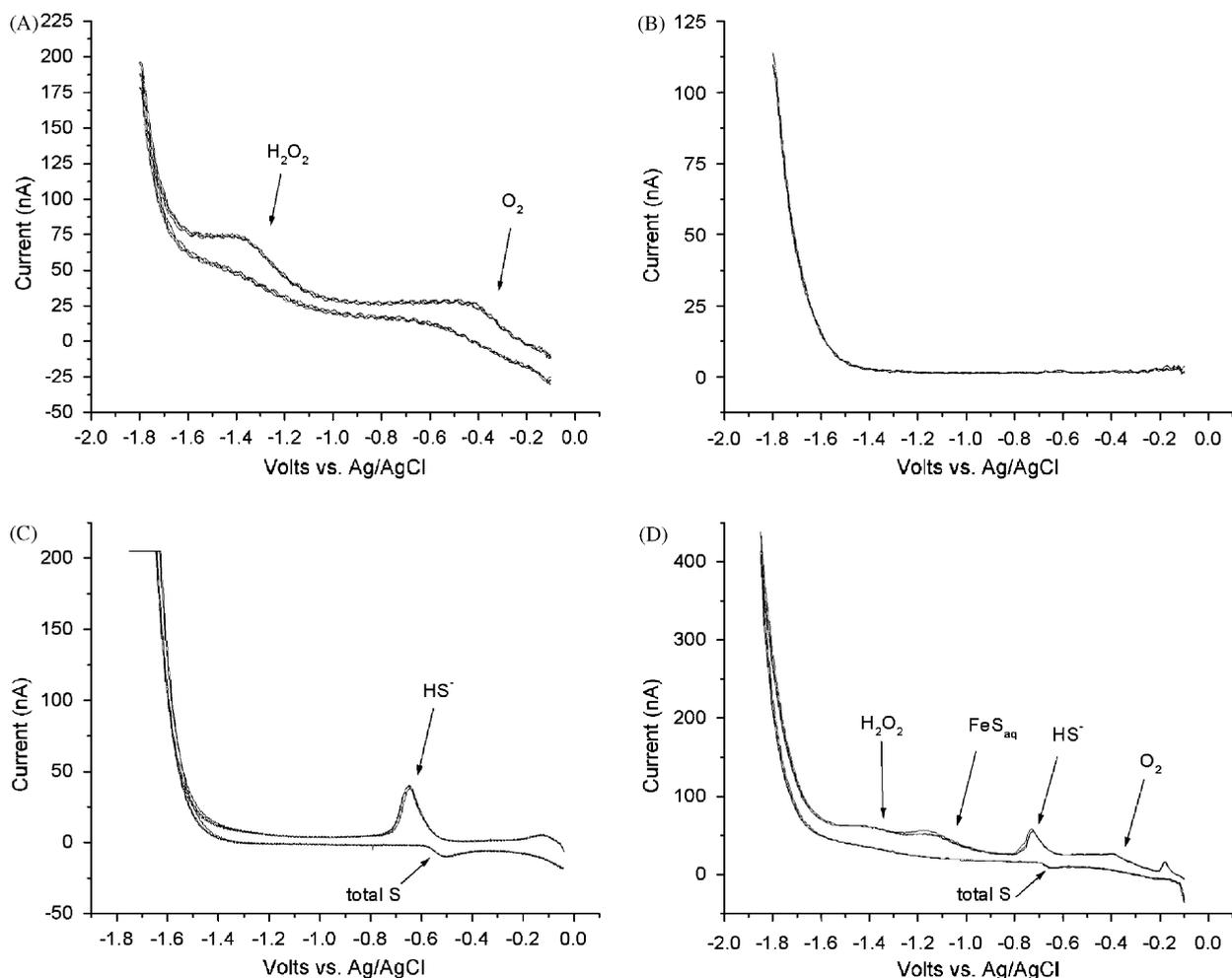


Fig. 2. Three replicate representative in situ voltammograms depicting: (A) presence of only oxygen, with subsequent reduction to peroxide at electrode surface, in upper water column; (B) no detectable oxygen, manganese, iron, or sulfur in the suboxic zone; (C) presence of only HS^- below the initial sulfide onset; (D) coexistence of oxygen, sulfide, FeS_{aq} , as observed at hydrothermal vents (e.g., Luther et al., 2001).

every 9 s or less, measurements were made approximately every 0.8 m, based on the descent rate of the MBARI-AIS package through the water column.

Aboard ship, a DLK-60 electrochemical analyzer (AIS, Inc.) controlled similar solid-state Au/Hg working, Ag/AgCl reference, and Pt counter electrodes within a flow cell (Luther et al., 2002) attached to the pump profiling outflow. Typical conditions were a potential scan range from -0.1 to -1.8 V using LSV or CV modes at 1 or 4 V/s. The working electrode was conditioned at -0.9 V for 2 s to clean the Au/Hg surface, and then a deposition step at -0.1 V for 5–20 s was performed. These conditions provided the low detection limit of 3 nM for H_2S and about 3 μM for O_2 .

Bottle casts were conducted immediately after the in situ profiles. Water samples from discrete samples were analyzed by Winkler titrations for O_2 (detection limit $\sim 3 \mu\text{M}$) and by iodometric titration for H_2S (detection limit $\sim 3 \mu\text{M}$) and voltammetry (detection limit ~ 3 nM) for H_2S .

3. Results and discussion

The R/V *Knorr* occupied 82 stations in the southwest (SW), west central (WC), central (C), and eastern (E) Black Sea between 14 April and 16 May 2003 (Fig. 1). In situ voltammetric data were obtained for 20 profiles of the suboxic transition zone between upper oxic and deeper sulfidic waters.

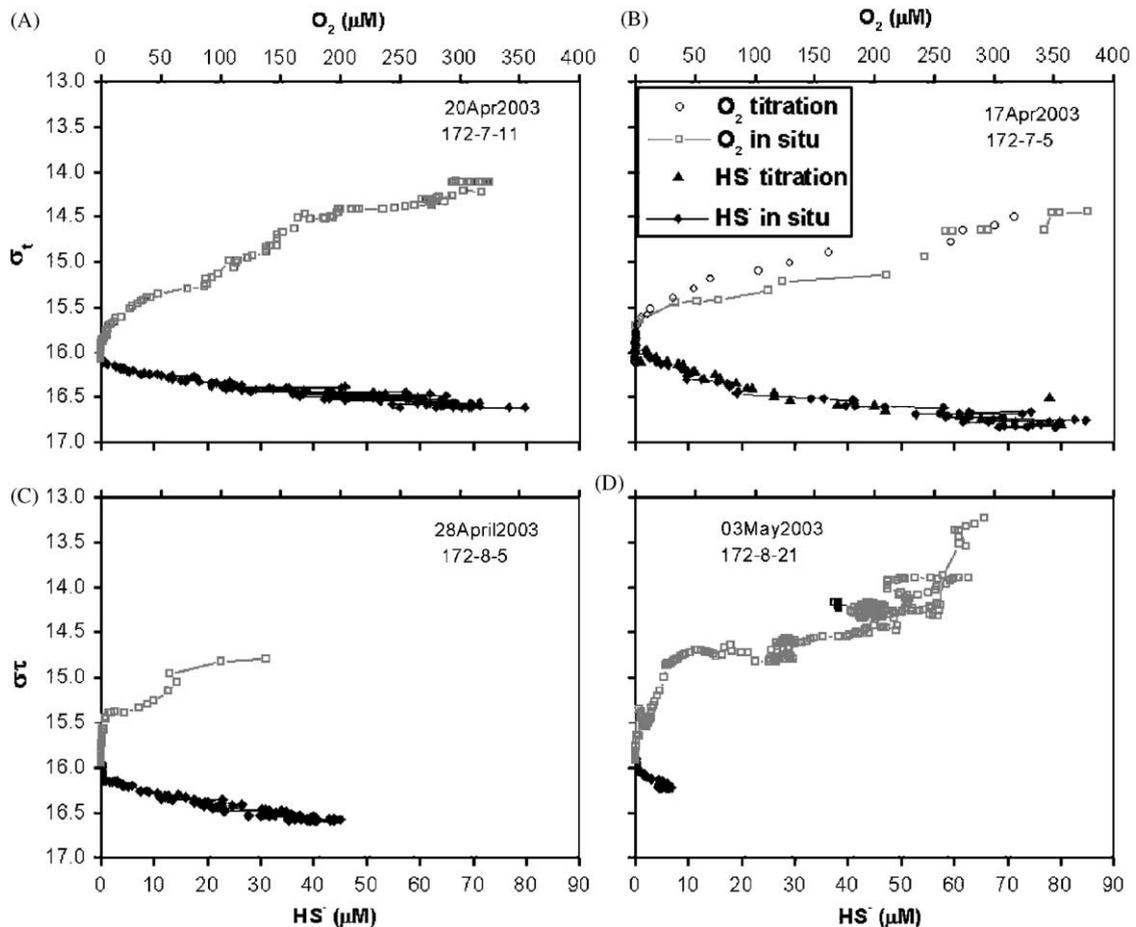


Fig. 3. Representative profiles of oxygen and sulfide for each major geographic area of the Black Sea during the 2003 cruise (R/V *Knorr* 172-7, -8, -9): (A) 172-7-11 (south west), (B) 172-7-5 (west central), (C) 172-8-5 (central), (D) 172-8-21 (eastern). Note the overall good agreement between in situ voltammetry and traditional titrations in B. Disparity is most likely due to depth offsets between in situ profiling casts and bottle casts.

These data documented the existence and extent of the suboxic zone across the four geographic zones targeted (SW, WC, C, E), confirmed oxygen injection into the southwest Black Sea via the Bosphorus plume, and provided insightful comparisons for temporal comparisons at the WC station, and for overall comparison to data collected in 2001 (Glazer et al., 2006) (Fig. 2).

3.1. Basin-wide suboxic zone thickness and vertical location

Twenty in situ voltammetric profiles were made during the 2003 R/V *Knorr* cruise. In situ voltammetry is ideal for profiling the Black Sea oxic–anoxic transition because of its capability for making real-time, in situ simultaneous measure-

ments of oxygen and sulfur species. In no profiles were oxygen and sulfide observed to co-occur (Figs. 2 and 3), and the onset of the sulfidic zone was always overlain by a suboxic zone, but its vertical location was variable (Table 2). Overall the thickness of the suboxic zone did not vary significantly among the geographic areas (SW, WC, C, E) studied (Table 2). However, oxygen extinction depths and their corresponding density surfaces did significantly vary between regions (Fig. 3, Table 2, Table 3). The O_2 extinction averaged 108 m (σ_t 15.73) for SW, 56 m (σ_t 15.56) for WC, 67 m (σ_t 15.68) for C, and 142 m (σ_t 15.59) for E. A comparison of oxygen extinction depth for 2003 vs. 2001 reveals that in the SW region, O_2 was found at a significantly shallower density in 2003, but depth was not significantly different (Table 4),

Table 2
Suboxic zone thickness in terms of σ_t and depth (m)

Station	Date	O ₂ disappearance		H ₂ S onset		Suboxic zone	
		σ_t	Depth	σ_t	Depth	σ_t	Depth
172-8-7	1-May-03	15.54	86.3	16.06	116.5	0.52	30.2
172-8-21	3-May-03	15.75	172	16.02	188	0.27	16
172-8-22	3-May-03	15.48	169	> 15.82	> 177	> 0.34	> 81
<u>172-8-5</u>	<u>28-Apr-03</u>	<u>15.73</u>	<u>67.36</u>	<u>16.09</u>	<u>84.64</u>	<u>0.36</u>	<u>17.3</u>
<u>172-8-5b</u>	<u>29-Apr-03</u>	<u>15.64</u>	<u>66.3</u>	<u>16.09</u>	<u>86.02</u>	<u>0.55</u>	<u>19.7</u>
172-7-5	17-Apr-03	15.65	64.82	16.0	77.29	0.35	12.47
172-7-12	21-Apr-03	15.63	63.07	15.93	75.53	0.30	12.46
172-8-2	26-Apr-03	15.55	55.11	16.0	77.93	0.45	22.82
172-8-30	7-May-03	15.66	53.71	16.13	79.35	0.47	25.64
172-8-30b	8-May-03	15.53	50.51	16.11	78.66	0.58	28.15
172-9-4	11-May-03	15.37	49.203	16.15	88.69	0.78	39.48
<i>172-7-11</i>	<i>20-Apr-03</i>	<i>15.88</i>	<i>81.95</i>	<i>16.13</i>	<i>104.2</i>	<i>0.25</i>	<i>22.25</i>
<i>172-7-13</i>	<i>21-Apr-03</i>	<i>15.97</i>	<i>88.56</i>	<i>16.12</i>	<i>102.5</i>	<i>0.15</i>	<i>13.94</i>
<i>172-7-14</i>	<i>22-Apr-03</i>	<i>15.94</i>	<i>142</i>	<i>16.12</i>	<i>158.5</i>	<i>0.18</i>	<i>16.50</i>
<i>172-7-17</i>	<i>23-Apr-03</i>	<i>15.77</i>	<i>147.1</i>	<i>16.1</i>	<i>167.6</i>	<i>0.33</i>	<i>20.5</i>
<i>172-7-18</i>	<i>23-Apr-03</i>	<i>15.66</i>	<i>70.6</i>	<i>16.10</i>	<i>102</i>	<i>0.44</i>	<i>31.4</i>
<i>172-7-20</i>	<i>24-Apr-03</i>	<i>15.81</i>	<i>145.2</i>	<i>16.05</i>	<i>158.5</i>	<i>0.24</i>	<i>13.3</i>
<i>172-8-34</i>	<i>9-May-03</i>	<i>15.67</i>	<i>142.8</i>	<i>16.11</i>	<i>179.6</i>	<i>0.44</i>	<i>36.8</i>
<i>172-9-5</i>	<i>12-May-03</i>	<i>15.13</i>	<i>48.68</i>	<i>16.09</i>	<i>86.74</i>	<i>0.96</i>	<i>38.06</i>

In situ data were acquired by voltammetry from the electrochemical analyzer coupled to an onboard Seabird Microcat (detection limits of 3 μ M for O₂ and 30 nM for H₂S). Normal typeface represents eastern (E) stations, underlined are central (C), bold are west central (WC), and italicized are southwest (SW).

indicating that 2003 winter conditions had suppressed lateral O₂ injection and therefore O₂ fingering did not penetrate as deep in 2003 as in 2001. The opposite was true for the WC, with the O₂ extinction occurring at a significantly shallower depth, but not lesser density (Table 4). Apparently denser waters were shallower in the water column in 2003 due to colder winter conditions (there was more than 1 °C difference in CIL between 2001 and 2003, as observed in Fig. 6A–C).

In contrast, while the onset depth of sulfide was significantly variable across the Black Sea, no pairwise comparison between geographic locations for density surface of H₂S onset was significantly different (Fig. 3, Tables 2 and 3). The sulfide onset averaged 132 m (σ_t 16.10) for SW, 80 m (σ_t 16.05) for WC, 85 m (σ_t 16.09) for C, and 152 m (σ_t 16.04) for E. Furthermore, a comparison of H₂S onset depths for 2003 vs. 2001 reveals that for the SW, the depth of H₂S onset was significantly less in 2003 yet the density was not significantly different (Table 4), again indicating that colder waters were shallower in the water column in 2003. For the WC, density

was not significantly different between 2001 and 2003, but H₂S onset was significantly shallower in 2003, again indicating that more dense waters were higher in the water column (Table 4), as related to temperature. Gregg and Yakushev (2005) showed that during winter conditions of 2003 surface ventilation of the Black Sea's cold intermediate layer (CIL) occurred in the west central gyre region. Its important to note that the physical effect that winter conditions have on upper water column temperature does not affect the overall chemistry (i.e. the ~1 °C difference observed in the CIL was not enough of a change to affect kinetics, but was significant to the vertical location of chemical species at a given density surface).

No pairwise comparison of geographic regions showed a significantly different thickness for the suboxic zone in terms of depth or density for 2003 (Table 3), and there were also no significant differences among comparisons between 2001 and 2003 suboxic zone thicknesses for the SW and WC (Table 4). This suggests that the suboxic zone of the Black Sea is a permanent feature acting as a barrier

Table 3

Comparisons of in situ voltammetry suboxic zone profiles among stations from the eastern, central, west central, and southwest Black Sea, 2003

Comparison	Parameter	<i>p</i> -Value
C-WC	O ₂ disappearance (σ_t)	0.0774
	O ₂ disappearance (m)	0.0052
	H ₂ S onset (σ_t)	0.1789
	H ₂ S onset (m)	0.0146
	Suboxic thickness (σ_t)	0.4024
	Suboxic thickness (m)	0.1471
E-WC	O ₂ disappearance (σ_t)	0.3054
	O ₂ disappearance (m)	0.1691
	H ₂ S onset (σ_t)	0.3791
	H ₂ S onset (m)	0.1457
	Suboxic thickness (σ_t)	0.2912
	Suboxic thickness (m)	0.4827
SW-WC	O ₂ disappearance (σ_t)	0.0743
	O ₂ disappearance (m)	0.0042
	H ₂ S onset (σ_t)	0.1176
	H ₂ S onset (m)	0.0026
	Suboxic thickness (σ_t)	0.1716
	Suboxic thickness (m)	0.4581
SW-C	O ₂ disappearance (σ_t)	0.3435
	O ₂ disappearance (m)	0.0110
	H ₂ S onset (σ_t)	0.0995
	H ₂ S onset (m)	0.0043
	Suboxic thickness (σ_t)	0.2913
	Suboxic thickness (m)	0.0867
SW-E	O ₂ disappearance (σ_t)	0.2975
	O ₂ disappearance (m)	0.3626
	H ₂ S onset (σ_t)	0.1071
	H ₂ S onset (m)	0.3473
	Suboxic thickness (σ_t)	0.4518
	Suboxic thickness (m)	0.4559
E-C	O ₂ disappearance (σ_t)	0.3928
	O ₂ disappearance (m)	0.1917
	H ₂ S onset (σ_t)	0.1211
	H ₂ S onset (m)	0.1562
	Suboxic thickness (σ_t)	0.3696
	Suboxic thickness (m)	0.3190

p-Value results from two-sample *t*-test assuming unequal variances and $\alpha = 0.05$. Significant differences are in boldface, and indicate statistically different parameters (e.g., the density surface for H₂S onset did not vary between the central and west central, but the depth did).

between the coexistence of oxygen and sulfide, the thickness of which does not significantly vary between regions or seasonal conditions (summer conditions of 2001 vs. winter conditions of 2003).

It is important to note, however, that these statistical tests should only be a guideline to suggest general trends between 2001 and 2003 (summer vs. winter conditions) and we observed changes in the

Table 4

Comparisons of in situ voltammetry suboxic zone profiles between 2001 and 2003 for the SW and WC stations from the Black Sea

Comparison	Parameter	<i>p</i> -Value
SW 2001 vs. 2003	O ₂ disappearance (σ_t)	0.0340
	O ₂ disappearance (m)	0.0839
	H ₂ S onset (σ_t)	0.3014
	H ₂ S onset (m)	0.0001
	Suboxic thickness (σ_t)	0.1267
	Suboxic thickness (m)	0.1364
WC 2001 vs. 2003	O ₂ disappearance (σ_t)	0.1657
	O ₂ disappearance (m)	0.0045
	H ₂ S onset (σ_t)	0.3014
	H ₂ S onset (m)	0.0001
	Suboxic thickness (σ_t)	0.1787
	Suboxic thickness (m)	0.2176

p-Value results are from two-sample *t*-tests assuming unequal variances and $\alpha = 0.05$. Significant differences are in boldface.

suboxic zone structure on smaller time scales. During the R/V *Knorr* cruise 172-7, -8, -9, we revisited the west central station repeatedly to provide a time series data set for suboxic zone variability over a period of 1 month. We measured differences in oxygen penetration in terms of depth and density (Fig. 4A and B, Table 2). The shoaling of the oxygen penetration depth through time (most likely attributable to decreasing physical mixing associated with the shift from winter to spring) is shown in Fig. 4A. We also observed a relatively constant sulfide onset depth over a 3-week period, however the onset occurred at deeper density surfaces through time (Fig. 4C and D, Table 2). Also of particular interest are the unusually high sulfide concentrations on 17 and 21 April. The comparatively large amount of noise can be attributed to rough sea state and subsequent rapid movement of the deployment package; but the absolute concentrations are indeed higher than in later profiles, as corroborated by volumetric titrations (Fig. 3B). In essence, we see the development of a thicker, more stable suboxic zone as downward mixing of surface waters and the CIL that coincide with winter conditions gives way to more stable spring conditions with thicker suboxic zones, as observed in 2001 (Glazer et al., 2006).

3.2. Bosphorus plume dynamics

The Black Sea offers a unique environment for studying ventilation dynamics because of the

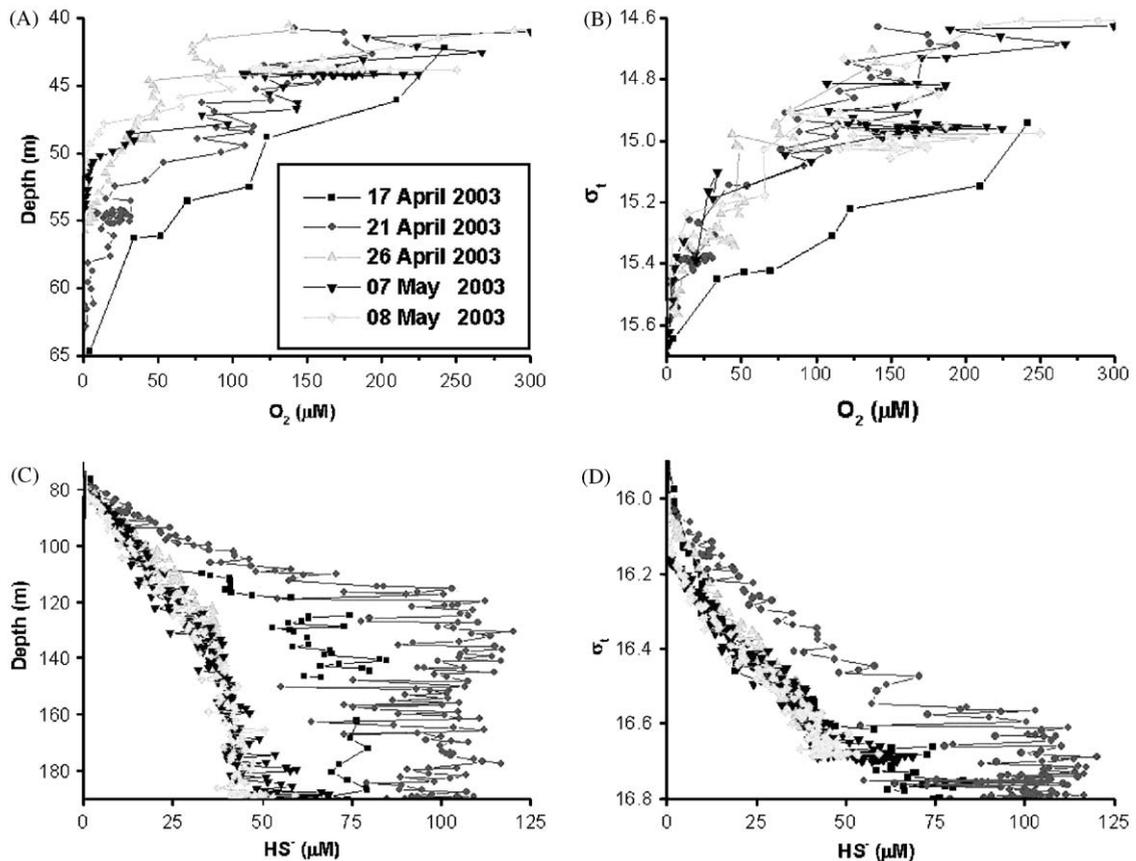


Fig. 4. Time series of profiles for the west central station between 17 April and 08 May 2003. Depth profiles are given on the left (panels A & C) and density on the right (panels B & D).

extremely sharp salinity difference with the neighboring basin (Mediterranean surface waters are ~ 36 vs. ~ 18 for the Black Sea), very well-defined vertical stratification (surface salinity of ~ 18 vs. 21.5 at ~ 300 m), and highly variable bathymetry (shallow shelf of ~ 50 m changing to 2000 m within 10–50 km) (Stanev et al., 2001). Furthermore, implications of oxidation of suboxic or anoxic Black Sea waters by Mediterranean inflow are extremely significant to basin-wide redox biogeochemistry.

In 2003, we confirmed lateral injection of O_2 into the suboxic zone ($\sigma_t > 15.4$) with high resolution in situ voltammetric measurements at Stations 172-7-17 and 172-7-20 (Fig. 5A and B vs. depth and 5C and D vs. density). Station 172-7-17 exhibited three small oxygen injections in the oxic layer (Fig. 5A and C; 1–3 m thick as opposed to the 5–10 m thick injections observed in 2001), and a 10-m thick deficiency in the sulfidic layer, suggesting a major oxidation event between 163 and 175 m (σ_t of

16.0–16.1). Station 172-7-17 is approximately 65 km SE of Station 162-16-9 where a prominent injection was observed in 2001. We did not observe injection any farther into the interior than Station 172-7-20 (Fig. 1), which was approximately 92 km less than observed in 2001. In contrast to 172-7-17, Station 172-7-20 did not have any evident oxygen injection into the suboxic zone, but we did observe a sharp decrease in sulfide concentration below the initial onset (Fig. 5B and D) between 176 and 190 m (σ_t of 16.30–16.38).

Previous observations suggested that the Bosphorus plume spreads in an ageostrophic manner (taking a northwest track on the shelf as opposed to deflecting to the right as expected in the northern hemisphere), explained by topographically controlled flow directed through a submarine channel (Latif et al., 1991; Oguz and Rozman, 1991). Plume detection on the continental slope is difficult because entrainment and mixing with Black

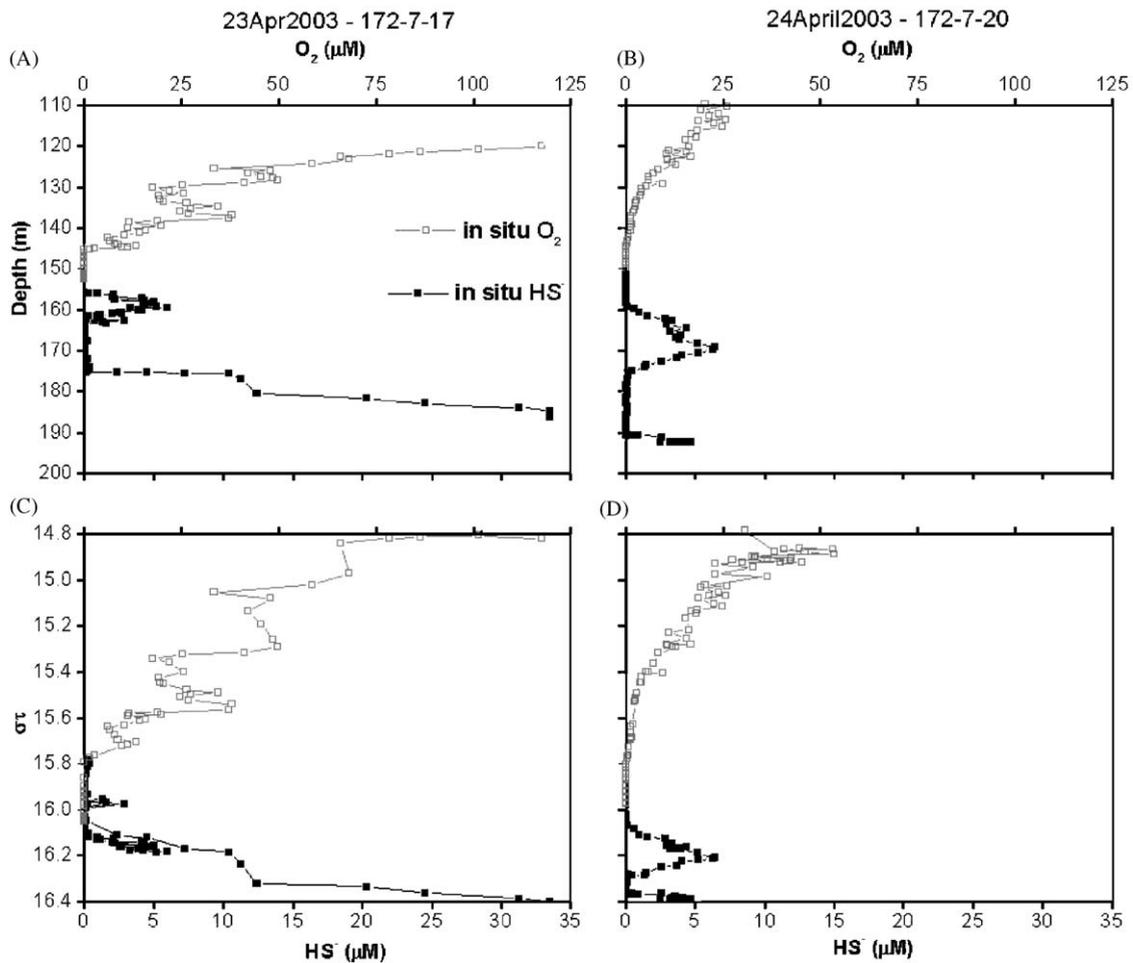


Fig. 5. (A) and (B) Profiles of oxygen and sulfide vs. depth for 23–24 April 2003 in the southwest Black Sea. Note presence of a second, deeper suboxic zone, presumably caused by a lateral injection of oxygen between 165 and 175 m at Station 17, and 178–190 m at Station 20. (C,D) Same profiles of oxygen and sulfide vs. density for 23–24 April 2003. Here, the second, deeper suboxic zone, is located between 16.3 and 16.38 at Station 17, and 16.0–16.1 at Station 20.

Sea waters (Oguz and Rozman, 1991; Gregg and Ozsoy, 1999) result in a thin layer at the bottom. However, lateral oxygen injection via the Bosphorus plume recently has been shown to exist up to 150 km northeast of the entrance to the Bosphorus (Konovalov et al., 2003; Glazer et al., 2006), satisfying geostrophic constraints once the plume reaches the continental slope and Coriolis force dominates transport. Models of Bosphorus plume inflow have predicted that plume thickness should be roughly 3 m in thickness upon reaching the continental slope (Stanev et al., 2001). Independent physical observations (temperature and salinity) have observed plume thickness to be roughly 2 m in this area (Latif et al., 1991). Our measurements of oxygen and sulfide suggest slightly thicker effluent (<5 m) farther into the Black Sea, but can be considered to

agree generally with the lower resolution techniques measuring physical vs. chemical parameters). Another major difference between our observations and those of Latif et al. (1991) and the predictions of Stanev et al. (2001) is that our observations are chemical and physical measurements from water-column data, while their data map the plume along the shelf bottom (<50 km out from Bosphorus entrance) based on only physical measurements and do not consider entrainment.

3.3. Summer conditions vs. winter conditions

During the R/V *Knorr* cruises 162-16 and -17, the Black Sea exhibited typical stratification for stagnant summer conditions with very little variability of temperature for a given density surface

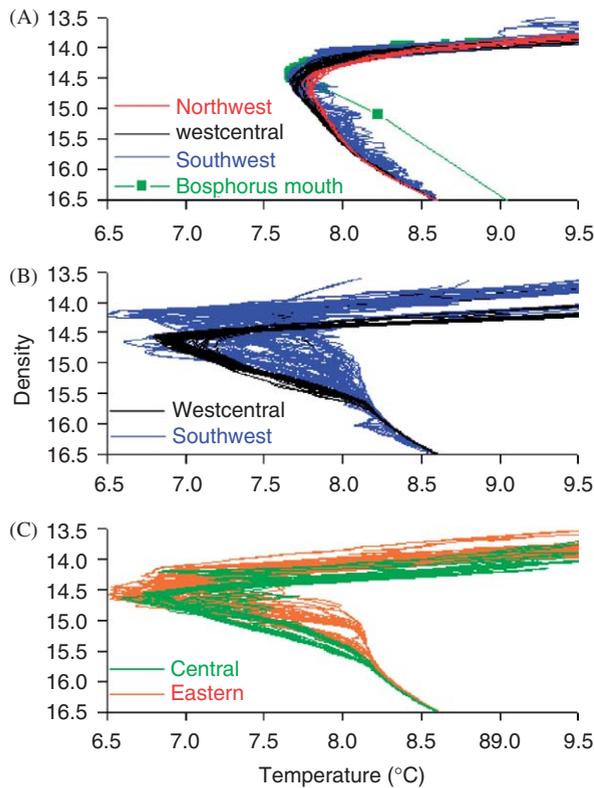


Fig. 6. (A) Density vs. temperature profiles for major regions of western Black Sea from R/V *Knorr* 162-16 & -17, 2001. Note very little basin-wide σ_t variation near the surface, as well as warmer intrusions caused by Bosphorus inflow in the southwest (blue) and no such intrusions in the west central (black) and northwest (red). (B,C) depict similar profiles from R/V *Knorr* 172-7, -8, -9, 2003. The winter conditions of 2003 are further illustrated here as prominent variance in near-surface σ_t variation. Again, the southwest is markedly more variable than the other regions due to Bosphorus inflow, and much more variable than observed in 2001.

throughout the (warmer, summer) CIL, but with significant evidence for lateral injection within the southwest (Fig. 6A, adapted from Konovalov et al., 2003). Temperature profiles vs. density are more variable in the southwestern Black Sea than in the west central or northwest, as a result of influence from Bosphorus inflow. Conversely, during R/V *Knorr* cruise 172-7, -8, and -9, we observed significantly more evidence for vertical mixing as reflected by the larger variability in temperature on a given density surface throughout the (cooler, winter) CIL, as compared with 2001 (Fig. 6B— σ_t 14.0–15.0 for SW and 14.5–15.5 for WC; and Fig. 6C— σ_t 14.5–15.5 for C and 14.0–15.0 for E).

Based upon the intrusions observed under summer conditions (2001), it is clear that warmer saltier

influxes of the Mediterranean waters can penetrate the southwest Black Sea intermediate waters between roughly σ_t of 15.0 and σ_t 16.25 (Fig. 6A). The Mediterranean water flowing into the Black Sea is continually modified by turbulent entrainment across the shelf region, as it mixes with colder ambient oxygen-rich water from the CIL ($\sigma_t \approx 14.5$). The ratio of entrainment flux (of parts of Mediterranean water to parts of CIL) over the shelf has been estimated to be 3–11.5 (Murray et al., 1991; Buesseler et al., 1991; Latif et al., 1991; Konovalov et al., 2003). Due to entrainment, the plume can become cooler than the interior waters and be observed in the depth range from 100 to 500 m (Ozsoy et al., 1993; Ivanov and Samodurov, 2001).

In contrast to the warmer lateral intrusions found in 2001, the intrusions that we observed in 2003, as well as overall southwest temperature variations with density ($\sigma_t < 15.5$) were all cooler than ambient central basin waters (Figs. 6B and 7). This phenomenon may be explained by Bosphorus inflow entrainment with colder CIL waters during winter because of a cooling effect caused by ventilation of the CIL that is not found during summer conditions (Gregg and Yakushev, 2005).

4. Conclusions

The Black Sea anoxic zone is governed by complex biogeochemical cycling that has occurred over thousands of years and by the formation of deep water, which is a fundamental issue to the physical oceanography of the Black Sea (Stanev et al., 2001). Investigation of the suboxic layer that buffers the transition between oxic and sulfidic waters is paramount to understanding these redox cycles; however, progress in chemical understanding has been limited until recently because chemical instrumentation lacked the required vertical resolution capability. In situ voltammetric profiling is an ideal method for resolving the boundaries of the suboxic zone through better detection limits, rapid response times, and unprecedented vertical resolution.

Our data suggest that lateral oxygen injection via the Bosphorus can occur under both summer and winter conditions, and can be correlated with temperature. Entrainment of Mediterranean inflow from the Bosphorus with the CIL has a strong effect on the lateral intrusions, explaining why lateral injections into the southwest Black Sea are generally warmer than ambient central basin waters under

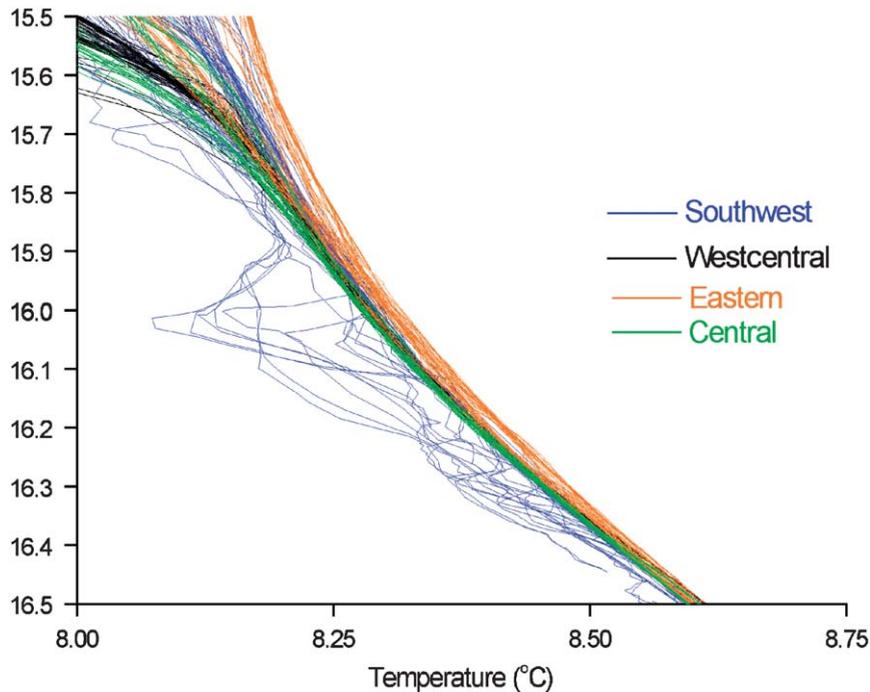


Fig. 7. Density vs. temperature profiles for all sampled regions of the Black Sea from R/V *Knorr* 172-7, -8, and -9, 2003, focusing on temperature anomalies between σ_t 15.5 and 16.5. Note cooler intrusions into the southwest below σ_t 15.75 and no intrusions for the west central, central, and eastern Black Sea.

summer conditions and generally colder than ambient central basin waters under winter conditions. Furthermore, colder CIL temperatures in 2003 vs. 2001 indicate that winter conditions ventilate the CIL with colder surface waters.

Another important observation is the difference in density surfaces between lateral injections located at Stations 172-7-17 and 172-17-20, sampled within a day of each other (Fig. 5C and D). Evidence for injections at different density surfaces signifies the variation in the entrainment of the CIL, resulting in injections occurring at different vertical positions throughout the southwest, depending on the ratio of Mediterranean to Black Sea waters. Other physical processes may cause differences in outflow rates from the Bosphorus or mixing, which also would affect overall plume thickness and volume. Physical features such as eddies, filaments and jets can influence the variability of water sampled vs. time at a given location in the central gyre. Bottom contours also can affect fingering, as multiple channeling of the plume as it crosses the shelf could result in various entry points into the water column after the shelf break. Additionally, many physical constraints govern the potential flow pattern of the

plume once it reaches the continental shelf break, as the Black Sea rim current, the Coriolis Force, or small eddies can alter its course.

Acknowledgments

We thank the crew and captain of the R/V *Knorr* for their help. This work was funded by grants from the National Science Foundation to G.W.L. (OCE-0096365), B.M.T. (OCE-0221500 and EAR-9725845), and James W. Murray (OCE-9906656), as well as the US Civilian Research and Development Foundation to S.K.K., A.S.R., and G.W.L. (UG2-2080).

References

- Arthur, M.A., Dean, W.E., 1998. Organic-matter production and preservation and evolution of anoxia in the Holocene Black Sea. *Paleoceanography* 13 (4), 395.
- Brendel, P.J., Luther III, G.W., 1995. Development of a gold amalgam voltammetric microelectrode for the determination of dissolved Fe, Mn, O_2 , and S(-II) in porewaters of marine and freshwater sediments. *Environmental Science and Technology* 29 (3), 751–761.

- Buesseler, K.O., Livingston, H.D., et al., 1991. Mixing between oxic and anoxic waters of the Black Sea as traced by Chernobyl cesium isotopes. *Deep-Sea Research Part II: Topical Studies in Oceanography* 38 (Suppl. 2A), S725–S745.
- Bull, D.C., Taillefert, M., 2001. Seasonal and topographic variations in porewaters of a southeastern USA salt marsh as revealed by voltammetric profiling. *Geochemical Transactions* 13, 173.
- Codispoti, L.A., Friederich, G.E., Murray, J.W., Sakamoto, C.M., 1991. Chemical variability in the Black Sea: implications of data obtained with a continuous vertical profiling system that penetrated the oxic–anoxic interface. *Deep-Sea Research Part II: Topical Studies in Oceanography* 38, S691–S710.
- Faschuck, D.Y., Ayzatullin, T.A., 1986. A possible transformation of the anaerobic zone of the Black Sea. *Oceanology (Russian)* 26, 171–178.
- Glazer, B.T., Cary, S.C., Hohmann, L., Luther III, G.W., 2002. In situ sulfur speciation using Au/Hg microelectrodes as an aid to microbial characterization of an intertidal salt marsh microbial mat. In: Taillefert, M., Rozan, T.F. (Eds.), *Environmental Electrochemistry: Analyses of Trace Element Biogeochemistry*. American Chemical Society, Washington, DC.
- Glazer, B.T., Luther III, G.W., et al., 2006. Documenting the suboxic zone of the Black Sea via high-resolution real-time redox profiling. *Deep-Sea Research II*, this issue [doi:10.1016/j.dsr2.2006.03.011].
- Grashoff, K., 1975. The hydrochemistry of landlocked basins and fjords. In: Riley, J.P., Skirrow, G. (Eds.), *Chemical Oceanography*. Academic Press, New York.
- Gregg, M.C., Ozsoy, E., 1999. Mixing on the Black Sea shelf north of the Bosphorus. *Geophysical Research Letters* 26 (13), 1869.
- Gregg, M.C., Yakushev, E., 2005. Surface ventilation of the Black Sea's cold intermediate layer in the middle of the western gyre. *Geophysical Research Letters* 32 (13), L03604.
- Gregoire, M., Stanev, E., 2001. Ventilation of Black Sea anoxic waters. *Journal of Marine Systems* 31 (1–3).
- Ivanov, L.I., Samodurov, A.S., 2001. The role of lateral fluxes in ventilation of the Black Sea. *Journal of Marine Systems* 31 (1–3), 159–174.
- Kononov, S.K., Ereemeev, V.N., et al., 1999. Climatic and anthropogenic variations in the sulfide distribution in the Black Sea. *Aquatic Geochemistry* 5 (1), 13–27.
- Kononov, S.K., Murray, J.W., 2001. Variations in the chemistry of the Black Sea on a time scale of decades (1960–1995). *Journal of Marine Systems* 31, 217–243.
- Kononov, S.K., Ivanov, L.I., Samodurov, A.S., 2001. Fluxes and budget of sulphide and ammonia in the Black Sea anoxic layer. *Journal of Marine Systems* 31 (1–3), 203–216.
- Kononov, S.K., Luther III, G.W., Friederich, G.E., Nuzzio, D.B., Tebo, B., Murray, J.W., Oguz, T., Glazer, B.T., Trouwborst, R.E., Clement, B.G., Murray, K.J., Romanov, A.S., 2003. Lateral injection of oxygen with the Bosphorus plume-fingers of oxidizing potential in the Black Sea. *Limnology and Oceanography* 48 (6), 2369–2376.
- Lane-Serff, G.F., Rohling, E.J., Bryden, H.L., Charnock, H., 1997. Postglacial connection of the Black Sea to the Mediterranean and its relation to the timing of sapropel formation. *Paleoceanography* 12 (2), 169–174.
- Latif, M.A., Ozsoy, E., Oguz, T., Unluata, U., 1991. Observations of the Mediterranean inflow into the Black Sea. *Deep-Sea Research Part II: Topical Studies in Oceanography* 38 (2), S711–S723.
- Luther III, G.W., Church, T.M., Powell, D., 1991. Sulfur speciation and sulfide oxidation in the water column of the Black Sea. *Deep-Sea Research Part II: Topical Studies in Oceanography* 38, S1121–S1138.
- Luther III, G.W., Reimers, C.E., Nuzzio, D.B., Lovalvo, D., 1999. In situ deployment of voltammetric, potentiometric, and amperometric microelectrodes from a ROV to determine dissolved O₂, Mn, Fe, S(-2), and pH in porewaters. *Environmental Science and Technology* 33, 4352–4356.
- Luther III, G.W., Rozan, T.F., Taillefert, M., Nuzzio, D.B., Di Meo, C., Shank, T.M., Lutz, R.A., Cary, S.C., 2001. Chemical speciation drives hydrothermal vent ecology. *Nature* 410 (6830), 813–816.
- Luther III, G.W., Bono, A.B., Taillefert, M., 2002. A continuous flow electrochemical cell for analysis of chemical species and ions at high pressure: laboratory, shipboard and hydrothermal vent results. In: Taillefert, M., Rozan, T.F. (Eds.), *Environmental Electrochemistry: Analyses of Trace Element Biogeochemistry*. American Chemical Society, Washington, DC, pp. 54–73.
- Murray, J.W., 1991. The 1988 Black Sea Oceanographic Expedition: introduction and summary. *Deep-Sea Research* 38, S655–S662.
- Murray, J.W., Jannasch, H.W., Honjo, S., Anderson, R.F., Reeburgh, W.S., Top, Z., Friederich, G.E., Codispoti, L.A., Izdar, E., 1989. Unexpected changes in the oxic–anoxic interface in the Black Sea. *Nature* 338, 411–413.
- Murray, J.W., Top, Z., Ozsoy, E., 1991. Hydrographic properties and ventilation of the Black Sea. *Deep-Sea Research* 38, S663–S689.
- Murray, J.W., Codispoti, L.A., Friederich, G.E., 1995. Oxidation–reduction environments: the suboxic zone in the Black Sea. In: Huang, C.P., O'Melia, C.R., Morgan, J.J. (Eds.), *Aquatic Chemistry: Interfacial and Interspecies Processes*, vol. 244. American Chemical Society, Washington, DC, pp. 157–176.
- Neretin, L.N., Volkov, I.I., et al., 2001. A sulfur budget for the Black Sea anoxic zone. *Deep-Sea Research Part I* 48 (12), 2569–2593.
- Oguz, T., Rozman, L., 1991. Characteristics of the Mediterranean underflow in the southwestern Black Sea continental shelf/slope region. *Oceanologia Acta* 14 (5), 433–444.
- Ozsoy, E., Unluata, U., 1997. Oceanography of the Black Sea: a review of some recent results. *Earth-Science Reviews* 42 (4), 231–272.
- Ozsoy, E., Unluata, U., et al., 1993. The evolution of Mediterranean water in the Black Sea: interior mixing and material transport by double diffusive intrusions. *Progress in Oceanography* 31, 275–320.
- Ryan, W.B.F., Pitman III, W.C., Major, C., Shimkus, K., Moskalenko, V., Jones, G.A., Dimitrov, P., Gorur, N., Sakine, M., Yuce, H., 1997. An abrupt drowning of the Black Sea shelf. *Marine Geology* 138, 119–126.
- Sorokin, Y.I., 1983. The Black Sea. In: Ketchum, B.H. (Ed.), *Ecosystems of the World 26: Estuaries and Enclosed Seas*. Elsevier, Amsterdam.
- Stanev, E.V., Simeonov, J.A., et al., 2001. Ventilation of Black Sea pycnocline by the Mediterranean plume. *Journal of Marine Systems* 31 (1–3), 77–97.