Variations in the chemistry of the Black Sea on a time scale of decades (1960–1995)

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Abstract

We use data collected on 52 cruises from 1960 to 1995 to analyze the decadal variability in basic chemical properties (oxygen, sulfide, nitrate, phosphate and silicate) throughout the water column of the Black Sea. This analysis reveals some new features in the recent evolution of the chemical structure of the Black Sea: an increase in the inventory of sulfide and nutrients in the anoxic zone, a decrease in the inventory of oxygen in the upper layer, and variations in the thickness of the sub-oxic zone. These changes suggest that an increase in the flux of sinking particulate organic matter (POM) has perturbed the biogeochemistry of the Black Sea. The flux balance that controlled the distribution of nutrients before the early 1970s has been modified due to intensive eutrophication. That has led to an increase in the inventory of nutrients in the anoxic zone due to an increased flux of POM. This increased flux of POM increased the rate of sulfate reduction and created an imbalance in the sulfide budget. As a result, sulfide concentrations have increased in the anoxic zone over the past 20 to 25 years. Additional anthropogenic changes are reflected in the distributions of nitrate and oxygen. Climate related and anthropogenic changes in the sources and sinks of these compounds appear to be equally important for causing variations in their inventory. Unlike oxygen and nitrate, the budget of sulfide depends primarily on the flux of sinking POM and the intensity of the lateral flux of oxygen contained in the Bosporus plume. More than 50% of sulfide production appears to be oxidized by the lateral ventilation flux of oxygen. Thus, different processes govern the dynamics of the upper and lower boundaries of the sub-oxic zone. Variations in the upper boundary of suboxic zone depend on consumption of oxygen by the flux of sinking POM, while the lower boundary is controlled by the balance between the upward flux of sulfide within the anoxic zone and the lateral flux of oxygen associated with the Bosporus plume. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Though chemical distributions in the Black Sea and their controlling biogeochemical processes have been discussed in detail, the possibility of long-term changes in the basic chemical structure has not been resolved. The question of decadal scale variability needs to be understood (Ivanov and Oguz, 1998; Besiktepe et al., 1999) to give insight into the variable nature of the oxic/anoxic environment in the Black Sea and to provide a scientifically sound background for environmental analysis, simulation, forecast and management.

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Temporal variations in the distribution of oxygen and sulfide over the past century have been investigated since the first known publication by Andrusov (1890) and continue to be one of the most intriguing questions about the evolution of the biogeochemical structure in the Black Sea. The possibility of rapid shoaling of the onset of sulfide was proposed by Faschuk et al. (1987) and Murray et al. (1989) and countered by Bezborodov and Eremeev (1990), Vinogradov (1991) and Buesseler et al. (1994). Recently, Konovalov et al. (1999a,b) demonstrated that oscillations in the depth of onset of sulfide can be as large as a few tens of meters and occur on a century time scale. These oscillations were explained by changes in the thermohaline structure of the water column rather than by changes in the inventory of sulfide. It has been argued that the density of onset of sulfide (rather than the depth of onset) has been at steady state (Tugrul et al., 1992; Vinogradov and Nalbandov, 1990; Murray et al., 1995; Konovalov et al., 1999a,b).

Inventory of sulfide in the anoxic layer of the Black Sea has been assumed to be at steady state (Skopintsev, 1975; Bezborodov and Eremeev, 1990) because of the inference that the 5000-year evolution of this oxic/anoxic ecosystem has resulted in a precise redox balance. Discovery of a sub-oxic zone by Murray et al. (1989) made the cycling of oxygen and sulfide in the Black Sea even more complicated. Murray et al. (1995) suggested that the sub-oxic zone be defined as the layer where oxygen varied from less than 2 to 10 μM and sulfide was less than 5 nM and neither oxygen nor sulfide exhibited any perceptible vertical gradients. The presence of the suboxic zone implies that direct reaction between oxygen and sulfide does not occur. An attempt to calculate an oxidation–reduction budget of the oxic/anoxic transition layer (Murray et al., 1995) raised many questions about the budgets of oxygen and sulfide. The oxidation of the upward flux of sulfide (both its site and oxidant) remains unresolved.

Various changes in the Black Sea environment have been attributed to anthropogenic impact. Increasing anthropogenic impact has lead to degradation of the marine ecosystem (Mee, 1992). The 2- to 3-fold increase in nitrate concentration in the layer of the main pycnocline (Codispoti et al., 1991; Tugrul et al., 1992) and the 10-fold decrease in silicate concentration in the upper oxygenated layer (Cociasu et al., 1996) originate from eutrophication and dam construction over the last three decades. New data by Man'kovsky et al., (1998) show that water transparency improved in the 1990s, which may indicate a recent reduction in the intensity of eutrophication.

The inventory of nutrients in the anoxic layer of the Black Sea has also been assumed to be at steady state, but this has not been verified. The increase in eutrophication has caused an increase in primary production (Vedernikov and Demidov, 1997; Stelmakh et al., 1998).

In this study, we discuss temporal trends in the distributions and inventories of oxygen, sulfide, nitrate, ammonia, phosphate and silicate in the oxic and anoxic layers of the Black Sea from 1960 to 1995. We compare these trends with relevant changes in biological and biogeochemical processes. We then try to verify the observed trends with some simple calculations and distinguish between the climate and man-induced processes responsible for their origin.

2. Data

The data listed in Table 1 are from the cruises of the Marine Hydrophysical Institute, National Academy of Sciences of Ukraine (MHI, NASU), and two US expeditions to the Black Sea (R.V. ATLANTIS, 1969, and R.V. KNORR, 1988). These data have been used to analyze (i) temporal changes in the distribution of nutrients and the inventories of nitrate, ammonia, silicate, phosphate, oxygen and

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Notes to Table 1:

(1) ML—R.V. Mikhail Lomonosov, AV—R.V. Academician Vernadskiy, and PK—R.V. Professor Kolesnikov are research vessels of Marine Hydrophysical Institute (MHI), National Academy of Sciences of the Ukraine; R.V. ATLANTIS and R.V. KNORR—research vessels of Woods Hole Oceanographic Institution (WHOI).

(2) Numbers in the columns from "O_2" to "NH_4" represent the number of measurements. For temperature and salinity (column "T,S"), this value is equal to "ALL" and means that all data available for study was used in the work.

Table 1
General information on the data sets used in this study

N	O_2	H_2S	NO_3	PO_4	SiO_4	NH_4	T,S	Time	R.V.
1	787	538					ALL	Oct., 1960	ML-09
2	258	114					ALL	Aug.–Sept., 1964	ML-16
3	382	364	333	574	637	592	ALL	Mar.–Apr., 1969	ATLANTIS
4	571	501					ALL	July–Aug., 1972	AV-06
5	303	212					ALL	Mar.–Apr., 1973	AV-07
6	218	229					ALL	Nov., 1973	AV-08
7	43		29	41	43		ALL	Apr., 1976	ML-30
8	190			183			ALL	Dec., 1976	AV-14
9	218	202					ALL	Mar., 1977	AV-14/1
10							ALL	June, 1977	AV-15
11	372	350					ALL	Feb., 1978	ML-33
12	263	470					ALL	July–Aug., 1978	ML-35
13	359						ALL	Nov., 1980	AV-23
14							ALL	Mar.–Apr., 1982	AT-03/1
15							ALL	July–Aug., 1982	AT-04
16							ALL	Sept., 1982	AT-05/1
17	248	225					ALL	May–June, 1983	AV-27
18							ALL	Aug., 1983	PK-06/2
19	129	194					ALL	June–July, 1984	AV-29
20							ALL	June–Sept., 1984	PK-09
21		231					ALL	Sept., 1984	ML-43/1
22	253	389					ALL	Oct.–Nov., 1984	ML-43/2
23							ALL	Mar., 1985	PK-11
24	479	710					ALL	June–July, 1985	ML-44/1
25	107	100					ALL	Oct., 1985	ML-44/4
26							ALL	Oct., 1985	AV-31
27	405	444					ALL	June–July, 1986	AV-34
28	380	448					ALL	Nov.–Dec., 1986	PK-14/2
29							ALL	Nov.–Dec., 1987	PK-17/2
30	945	1001					ALL	Mar., 1988	ML-49/1
31	408	463					ALL	Apr., 1988	AV-37/1
32	83	6959	3055	8229	8412	8652	ALL	Apr.–June, 1988	KNORR
33	619	365	180	438			ALL	Apr.–May, 1988	PK-18
34							ALL	Aug., 1988	PK-19
35	655	438	27	646			ALL	Nov., 1988– Mar., 1989	PK-20
36	1511	991					ALL	Apr.–May, 1989	PK-21
37							ALL	May, 1988	AV-37/3
38	628	296					ALL	June–July, 1989	PK-22
39							ALL	Aug.–Sept., 1989	PK-23
40	607	581	101	633			ALL	Nov.–Dec., 1989	ML-51
41	2438	2666	407	548	567		ALL	Sept.–Nov., 1990	ML-53a
42		353					ALL	June–July, 1991	PK-27
43	1398	1161	605	709			ALL	Sept.–Oct., 1991	PK-28
44	1524	1386	1104	1396	385		ALL	Nov.–Dec., 1991	ML-54
45							ALL	March, 1992	TR-09
46	1441	1014		1613	1018		ALL	July–Aug., 1992	PK-29
47	167	153		221	67		ALL	Sept.–Nov., 1992	ML-55
48	827	336	449	861	853		ALL	Apr., 1993	PK-30
49	243	64	189	228	220		ALL	Nov., 1993– Jan., 1994	PK-31
50	466	138	547	662	582		ALL	May, 1994	GIDROOPTIK
51	695	459	606	918	957		ALL	Dec., 1994	PK-32
52	811	190	711	816	835		ALL	Mar.–Apr., 1995	PK-33
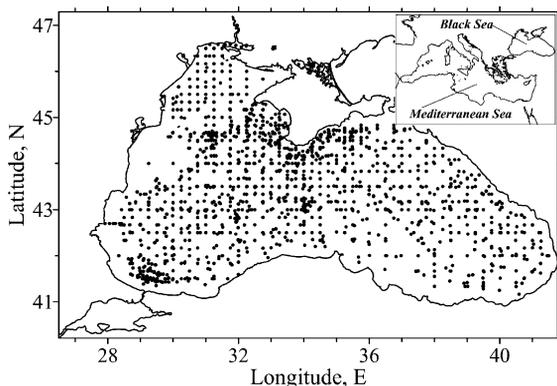
Fig. 1. The Black Sea and positions of station used for analysis of long-term variations in the basic chemical properties from 1960 to 1995. (Coast line—from the US Defense Mapping Agency—World Vector Shoreline; "The GEBCO Digital Atlas published by the British Oceanographic Data Center on behalf of IOC and IHO, 1994"—Bathymetry data).

sulfide and (ii) the possible reasons for these changes. The quantity of different kinds of data is shown in Table 1. The locations of stations can be seen in Fig. 1. The individual data sets can be obtained from S.K. Konovalov (MHI).

Since the raw data appear to be noisy because of coarse spatial and vertical resolution and due to temporal and spatial variability of different frequencies, average profiles were reconstructed for these calculations and analysis. When not specifically indicated, the mean values were calculated for density intervals of $\Delta\sigma_t = 0.1$ for the data sets of individual cruises. The sigma-t scale was used, rather than depth, in order to exclude uncertainties related to variations in the depth of the main pycnocline and chemocline as done previously by Vinogradov and Nalbandov (1990), Codispoti et al. (1991) and others.

3. Results

3.1. Hydrological structure

The thermohaline structure and processes responsible for its temporal variation have been discussed in many publications. Until recently, support was only provided for the following observations (Mamayev et al., 1994): (a) seasonal changes could

be detected only for the surface waters and Cold Intermediate Layer (CIL); (b) the inventory of salt in these two upper layers and the volume of these layers was constant; (c) T–S properties of the deep waters were in steady-state on a time scale of centuries. Residence time of the deep water (Skopintsev, 1975; Ostlund and Dyrssen, 1986; Boudreau and LeBlond, 1989) and of conservative chemical elements in the anoxic zone (Skopintsev, 1975) were estimated to be in the range of ~1000–6000 years. This value was derived from the volume of the deep Black Sea (~5×10^5 km^3) that would be replaced by Mediterranean waters coming in through the Bosporus strait (~100–300 km^3 per year). Murray et al. (1991), however, showed that the residence time of deep waters is far shorter than previously reported because the waters of the Bosporus entrain waters of the CIL and are injected into the Black Sea at different depths depending on the entrainment ratio (Murray et al., 1991; Buesseler et al., 1991; Ozsoy et al., 1995; Lee et al., in press; Samodurov and Ivanov, 1998). The residence time increases from a few years for the layer of the main pycnocline (Unluata et al., 1990; Buesseler et al., 1991) to several hundred years for the deepest layer (Murray et al., 1991).

To make the following discussion of the vertical distribution of properties and processes in the water column easier, we provide a short description of the main physical and chemical properties in terms of sigma-t values. The Cold Intermediate Layer, which is formally bounded by 8 °C isotherms, is usually located above $\sigma_t \sim 15.2$–15.8 with its core at $\sigma_t \sim 14.5$–14.6. The main pycnocline is located between $\sigma_t \sim 14.5$ and 16.5 and is separated into the upper and lower part at $\sigma_t \sim 15.5$. It is generally accepted that the onset of sulfide is currently located at the depth of $\sigma_t \sim 16.2$. The oxycline is on average located between $\sigma_t \sim 14.4$–14.6 and $\sigma_t \sim 15.6$–15.9, which is between the core of the CIL and the upper boundary of the suboxic layer. The suboxic layer is located between the lower boundary of the oxycline ($\sigma_t \sim 15.6$–15.9) and onset of sulfide ($\sigma_t \sim 16.2$).

Temporal variations in temperature and salinity can be easily recognized in water with $\sigma_t < 16.5$ (Fig. 2). This is much deeper than the lower boundary of the CIL ($\sigma_t \sim 15.2$–15.8), which has been suggested as the limit to the depth where the influ-
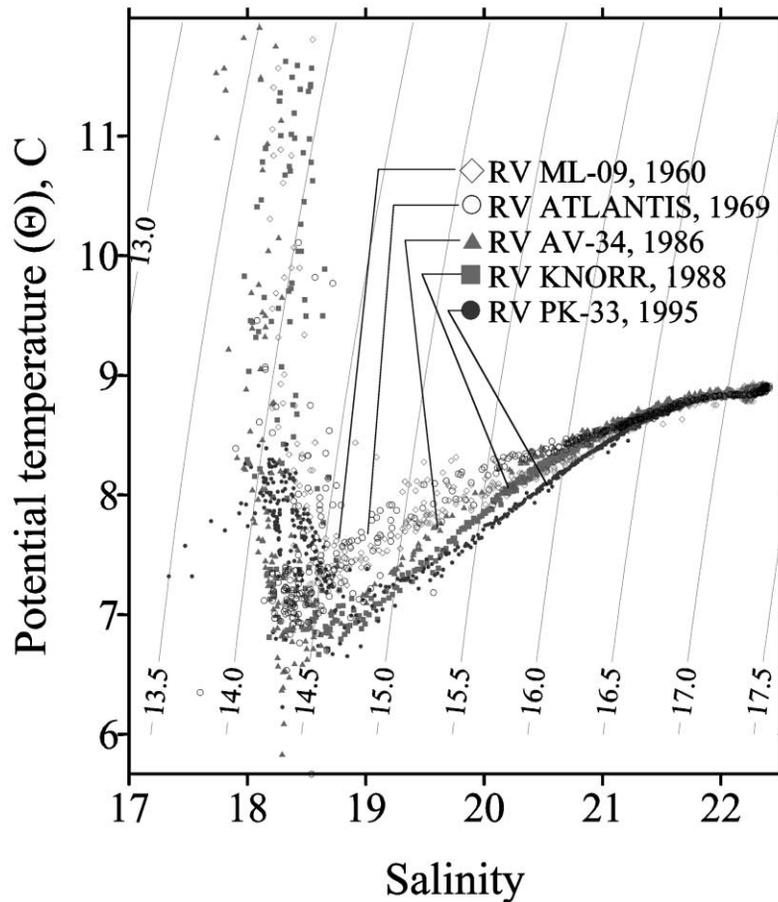
Fig. 2. T–S diagrams of the Black Sea waters for different years derived from data collected on the ML-09, 1960; ATLANTIS, 1969; AV-34, 1986; KNORR, 1988 and PK-33, 1995 (Table 1).

ence of convective ventilation can be detected (Mamayev et al., 1994; Filipov, 1968). This variability extends well into the upper layers of the sulfide zone which begins at about $\sigma_t = 16.2$. The data in Fig. 2 suggest that the temperature of the CIL and upper sulfide zone has generally decreased from 1960 to 1995. Because the only source of cold water to the CIL is the surface water of the Black Sea (the Bosporus inflow is warmer, 11 °C), these variations reflect variable ventilation of surface water into the CIL and the main pycnocline on decadal or shorter time scales (Ivanov et al., 1998a,b).

The most common view is that the waters of the CIL are renewed from the surface every year (Tolmazin, 1985; Ovchinnikov and Popov, 1987).

Ivanov et al. (1997) demonstrated that different layers of CIL are renewed in different proportion depending on the winter weather conditions. Lee et al. (in press) used chlorofluoromethane data from the 1988 R.V. KNORR cruise to calculate the average residence time of 2 years for the CIL waters. Ventilation of the deeper part of the main pycnocline takes place mainly due to intrusive mixtures of the Bosporus plume and the CIL (Buesseler et al., 1991; Ozsoy et al., 1995; Lee et al., in press; Ivanov et al., 1998a,b).

The response of the Black Sea to variable climate conditions can be seen in Fig. 3. Lower values of temperature in the upper pycnocline and CIL ($\sigma_t \sim$ 14.5–15.5, salinity < 20, temperature < 8 °C) were
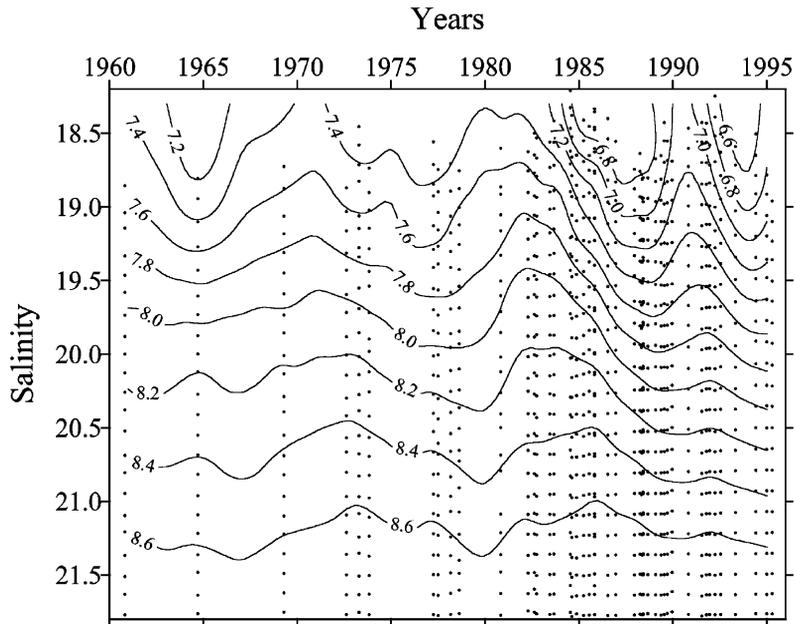
Fig. 3. Temporal variations in temperature versus salinity in the Black Sea.

observed in years following the coldest winter weather conditions. According to Belokopitov (1998), unusually cold winters occurred in 1964, 1972, 1976, 1985, 1993. The trends in Fig. 3 demonstrate some delay in the response of the lower pycnocline ($\sigma_t \sim 15.5$–16.5, salinity > 20). This can be best seen from 1985 to 1995 because, for this period, the more extensive data resolve variations in T,S-properties on a scale of years. The extremely severe winter of 1984–1985 resulted in a steep decrease in the mean temperature in the core of CIL (Fig. 4b). It took the signal 2–3 years to reach the depth of the upper boundary of oxic/anoxic transition zone ($\sigma_t \sim 15.6$–15.8, salinity ~ 20.0–20.5) and 4–6 years to reach the sulfide onset ($\sigma_t \sim 16.2$, salinity ~ 21) (Fig. 3). This time scale is consistent with the data of Buesseler et al. (1991), who demonstrated that the signal of surface water labeled with Chernobyl tracers (^{134}Cs/^{137}Cs) reached the depth of the upper part of anoxic zone 2 years after the accident at the Chernobyl nuclear power station. Ivanov et al. (1998a,b) recently analyzed temporal and spatial dynamics of the distribution of temperature, salinity and oxygen in the main pycnocline. They demonstrated that ventilation of the deeper layers of the main pycnocline (below $\sigma_t \sim 15.5$) starts in the area of anticyclonic circulation at the periphery of the central gyres and then spreads to the cyclonic domain region. These data confirmed the role of entrainment of CIL into Bosporus strait inflow for ventilation of the main pycnocline, oxic/anoxic transition zone, and the upper part of the sulfide bearing waters.

In addition to oscillations in temperature and salinity on a time scale of years, some decadal scale climate-induced changes in these properties are revealed in the data of Figs. 3 and 4b. While temperature scattered randomly around an average value of 7.57 ± 0.18 °C at $\sigma_t = 14.5$ before the middle 1980s, there was a pronounced decrease after that time to 6.82 ± 0.14 °C at $\sigma_t = 14.5$. In general, a decrease in temperature of the CIL and the oxycline reflects more intensive ventilation (more intensive winter mixing and a higher downward flux of cold surface water) and, consequently, an increase in the flux of oxygen into these layers. This means that climate-induced intensity of ventilation of the CIL and the main pycnocline should result in perturbations to the geochemical distributions as well. This ventilation has been more intense since the middle of the 1980s.
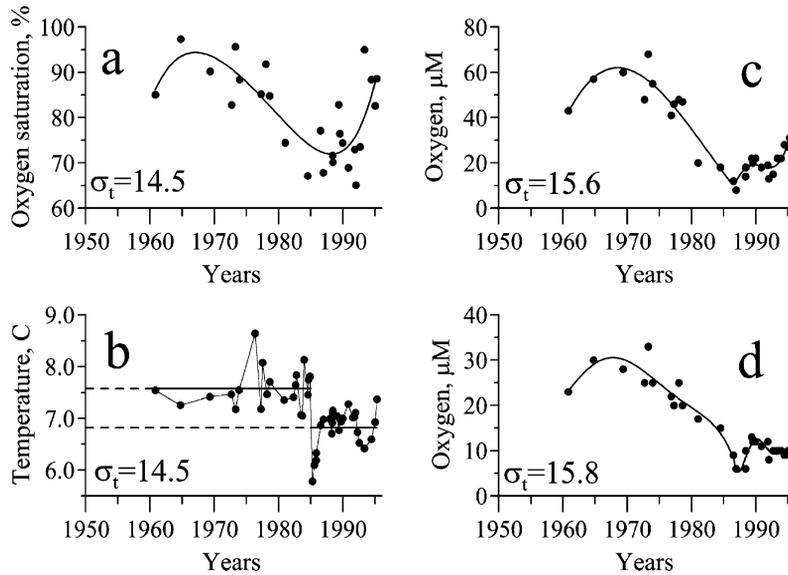
Fig. 4. Oxygen saturation (a) (%) and temperature (b) (°C) at $\sigma_t = 14.5$, oxygen concentration (μM) at 15.6 (c) and 15.8 (d). (Points are average values for individual cruises listed in Table 1. Horizontal lines at (b) represent the average values of temperature for periods of 1960 to 1985 and 1985 to 1995).

3.2. Oxygen

The low downward flux of oxygen in the Black Sea is due to the presence of the strong main pycnocline. As a result, oxygen disappears at a depth where it is consumed faster than it can be replaced due to vertical and lateral fluxes. The vertical profile of oxygen in the Black Sea (Fig. 5a) consists of an upper layer, where water is 90–110% saturated with oxygen, the layer of the oxycline where the oxygen concentration decreases to low values, and the oxic/anoxic transition zone where oxygen goes to zero.

The distribution of oxygen in the surface layer, above the oxycline, depends mainly on primary production, gas exchange and the solubility of oxygen, which depends on the temperature and salinity of the water (Konovalov et al., 1997). Thus, it shows significant seasonal variations in this layer. Year-to-year and long-term variations in the distribution of oxygen have only been considered for the layer of the oxycline (Ivanov et al., 1998a,b). Long-term variations in the average distribution of oxygen are significant for the layer below the core of the CIL ($\sigma_t \sim$ 14.5) including the oxycline ($\sigma_t \approx$ 15.6) and sub-oxic

zone ($\sigma_t \approx$ 15.8) (Figs. 4c,d and 6). Average oxygen concentrations for all of these layers decreased steadily from the middle 1970s to 1986 (Fig. 4). The lowest concentrations of oxygen in the oxic zone were detected in the middle 1980s to the beginning of the 1990s. Both the concentrations (Figs. 4c,d), and oxygen saturation (Fig. 4a) demonstrated a sharp decline in the inventory of oxygen.

Additional distinct features were changes in the structure of the oxycline and the appearance of large oscillations in the oxygen distributions from 1960 to 1995 (Fig. 6). Variations in the depth of the main pycnocline, the Cold Intermediate Layer (CIL) and other T,S-dependent properties of the Black Sea have been excluded by utilization of the density (σ_t) scale. Since these properties are plotted versus density, variations in the distribution of oxygen reflect changes in the main sources and sinks of oxygen in individual isopycnal layers of water, rather than hydrographic changes. They occur on a time scale of years and show that rapid changes can occur in the inventory of oxygen.

Seasonal and spatial variations in the thickness of the suboxic zone were recently discussed by Konovalov et al. (1997). The thickness of the suboxic
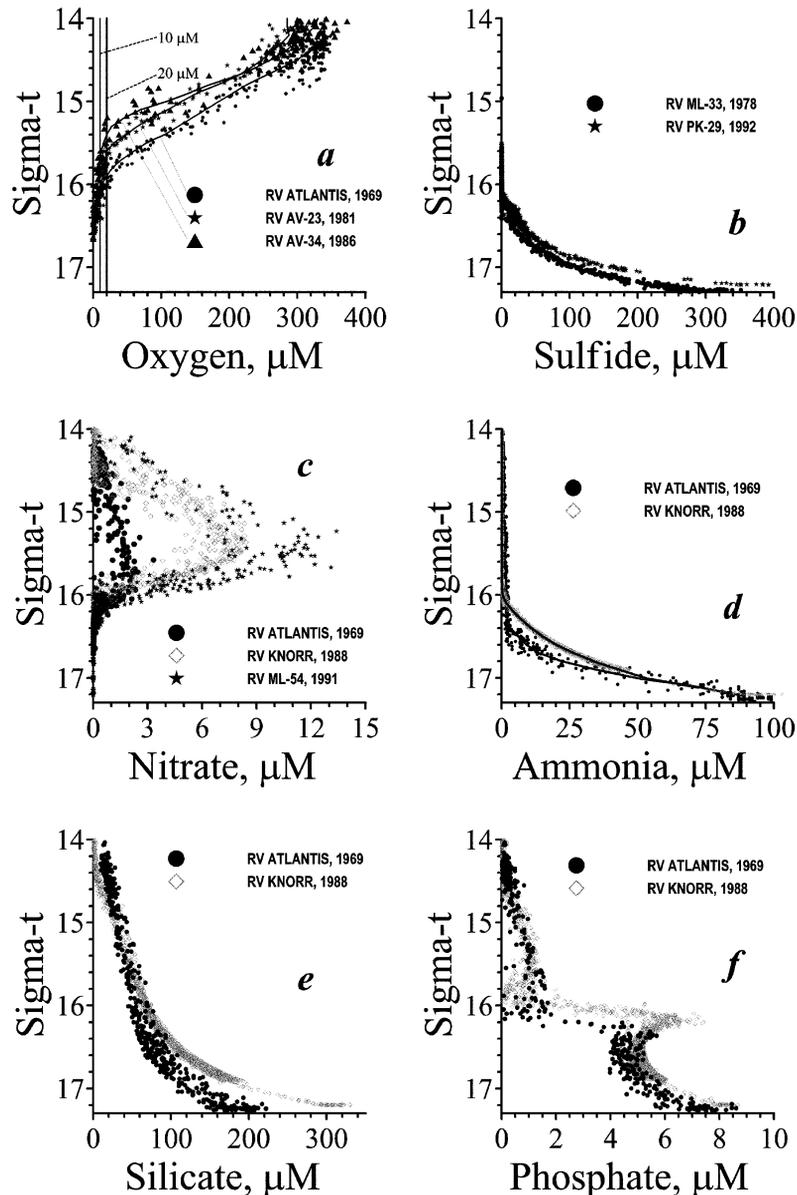
Fig. 5. Distribution of oxygen (a), sulfide (b), nitrate (c), ammonia (d), silicate (e), and phosphate (f) (µM) versus sigma-t scale for different years. (Solid line profiles at (a) and (d) represent an average distribution of oxygen and ammonia derived from individual cruise data sets).

zone varied from 20 to 70 m equivalent to a density difference of $\Delta \sigma_t = 0.3$ to 0.8. The primary reason for these variations remains unclear, but there is a negative linear correlation between the thickness of the suboxic zone and concentration of phosphate at its local minimum at $\sigma_t \sim 15.95$, which suggests that it might be related to respiration of particulate or-

ganic matter. For example, in April 1993 (cruise #30 of R.V. "Professor Kolesnikov", Table 1) that correlation ($n = 86$, $r = 0.64$) was highly ($p < 0.01$) significant (Taylor, 1982).

Long-term variations in the structure of the sub-oxic zone have never been discussed. Initially, Murray et al. (1989) suggested that the sub-oxic zone
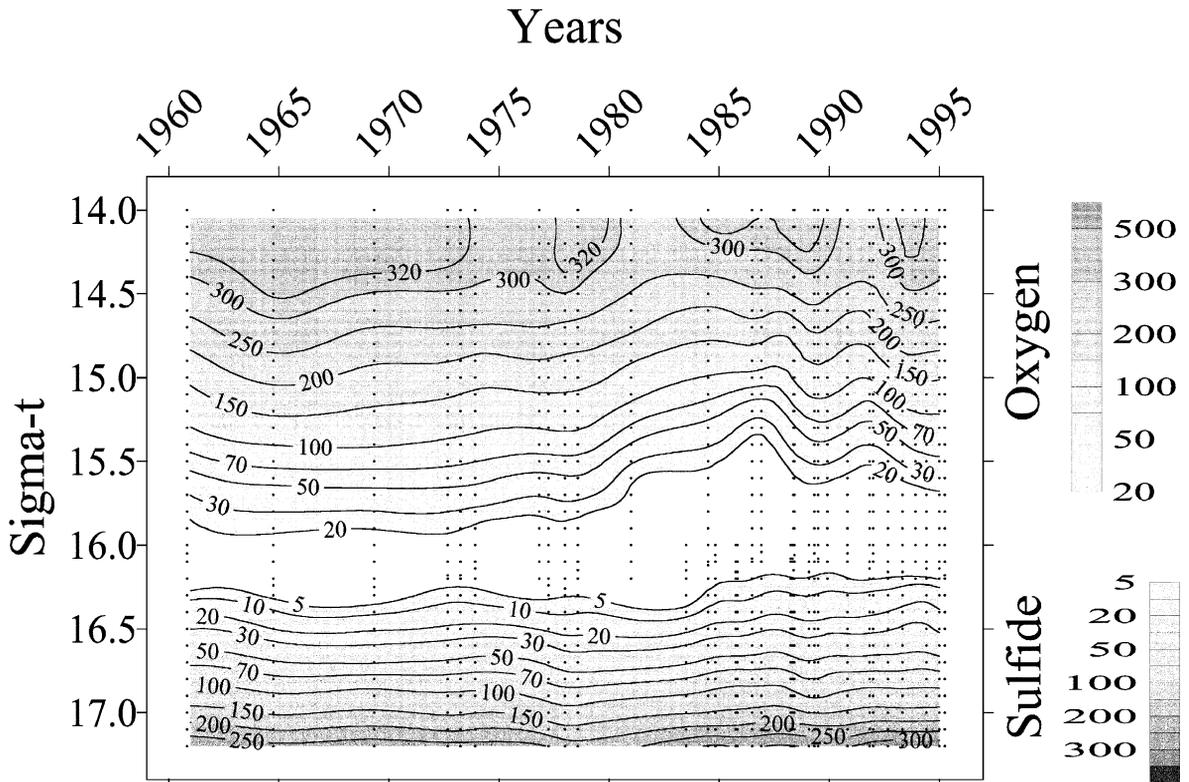
Fig. 6. Distribution of oxygen and sulfide (μM) versus sigma-t scale in the Black Sea.

was a new feature in the chemical structure of the Black Sea that had formed due to either a change in the fresh water balance or due to intensive eutrophication of the sea. Unfortunately, the quality of available data is not sufficient to trace the thickness of the suboxic zone before 1988. Analytical errors for oxygen data obtained before 1988 may exceed 100% for concentrations less than 10 μM (Novoselov, 1989; Broenkow and Cline, 1969). In addition, the depth of 5 nM sulfide can be obtained from the relatively new method of voltametric analysis (Luther et al., 1991) but not from the volumetric (Novoselov and Romanov, 1985) or spectrophotometric (Cline, 1968) determinations used earlier. On the other hand, the average difference between the position of the 10 and 20 μM oxygen iso-surfaces is as much as $\Delta \sigma_t \sim 0.1$ (Fig. 5a). The density difference for 5 nM and 5 μM of sulfide is equal to $\Delta \sigma_t \sim 0.05$. At a concentration of 20 μM oxygen or 5 μM sulfide, analytical error does not exceed 50% (Novoselov, 1989;

Novoselov and Romanov, 1985). The boundaries of the suboxic zone (10 μM oxygen and 5 nM sulfide) were arbitrarily chosen by Murray et al. (1995) based on the structure of the 1988 data from the R.V. KNORR cruise. In this analysis, we want to interpret a larger historical data base, thus it is more convenient for us to define an oxic/anoxic zone as where the oxygen concentration is less than 20 μM and the sulfide concentration does not exceed 5 μM (Fig. 6).

The presence of an oxic/anoxic zone by this definition from 1960 to 1995 (Fig. 6) supports the idea of Buesseler et al. (1994) and Murray et al. (1995) that the suboxic zone has been a permanent feature of the Black Sea. On average, the oxic/anoxic transition zone varied insignificantly and occupied a $\Delta \sigma_t$ of 0.4 in the 1960s. Starting in the middle 1970s, this increased to $\Delta \sigma_t \sim 0.9$ in 1986. About two thirds of this variation resulted from changes in the structure of the oxycline and the location of the upper boundary (20 μM of oxygen), while only 1/3

was due to oscillations in the position of 5 μM sulfide. The upper boundary of the oxic/anoxic layer shoaled from the depth of $\sigma_t \sim 15.9$ in the 1960s to $\sigma_t \sim 15.4$ in 1986 (Fig. 6). This situation partly reversed in the late 1980s and the middle 1990s, and there is some ambiguity about current trends.

3.3. Sulfide

The spatial and interannual variations in the location of the first appearance of sulfide appear to be small when viewed on the density (sigma-t) scale (Vinogradov and Nalbandov, 1990; Saydam et al., 1993). However, the depth of sulfide onset oscillates over a few tens of meters on the time scale of a century (Konovalov et al., 1999a).

Data in Fig. 6 confirm that the density of the onset of sulfide has varied little (see also Vinogradov, 1991; Tugrul et al., 1992). There may be a small upward shift in the position of this boundary in the 1980s. Unfortunately, vertical sample resolution in chemical profiles has never been better than $\Delta\sigma_t = 0.1$, except for the data from the 1988 R.V. KNORR cruise, when it was close to $\Delta\sigma_t = 0.01$–0.02 at the depth of sulfide onset (Codispoti et al., 1991), and the cruises after 1992, when vertical resolution at the depth of sulfide onset was equal to $\sigma_t = 0.05$.

Though the onset of sulfide has been stable there have been consistent temporal variations in the concentration of sulfide within the anoxic zone at different depths and density surfaces (Fig. 7) (Konovalov et al., 1999b). Some of these changes may be due to analytical artifacts. For example, the sharp increase in sulfide concentration from 1980 to 1985 may be the result of changes in the type of sampling bottles used. Metallic samplers were used before 1980, while only plastic samplers were used after that time. On average, sulfide concentrations were 17% higher when plastic samplers were used (Brewer and Murray, 1973; Novoselov and Romanov, 1985). This means that the sulfide distributions in the Black Sea from 1960 to 1995 must be interpreted separately for the periods before and after 1980. Sulfide concentrations increased after 1985 (Fig. 7). Methods of sampling and analysis did not vary for that period. The linear correlation coefficients (r) for the time trend of data collected after 1985 (Fig. 7) range from 0.71 to 0.80 (for $n = 10$ to 19) depending on sigma-t/depth. The percentage probability that the trend is random ranges from $< 0.1\%$ to 1.5% (Taylor, 1982) suggesting significant temporal variations in the distribution of sulfide within the anoxic zone. While the trend is statistically significant and consistent with the other changes triggered by eutrophication of the Black Sea over the last 30 years, more data are needed to quantitatively estimate of this trend.
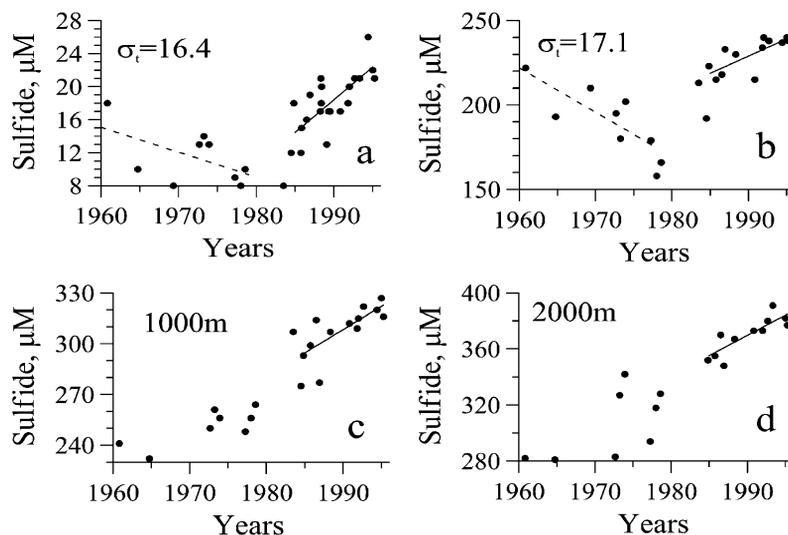
Fig. 7. Variations in the concentration of sulfide at $\sigma_t = 16.4$ (a), $\sigma_t = 17.1$ (b), 1000 m (c) and 2000 m (d) from 1960 to 1995.

3.4. Nitrate and ammonia

Distribution of nitrate in the Black Sea (Fig. 5c) reveals an increase in concentration from $\sigma_t \sim 14.2$–14.5 towards a maximum at $\sigma_t \sim 15.4$–15.7 and a decrease in deeper water until the detection limit is reached above the depth of the onset of sulfide (Codispoti et al., 1991; Tugrul et al., 1992; Kono-

valov et al., 1997). Tugrul et al. (1992) compared the results of a few cruises (R.V. ATLANTIS, 1969; R.V. KNORR, 1988; R.V. BILIM, 1991) and identified a two- to three-fold increase in nitrate concentration and an upward shift in the position of the nitrate maximum from $\sigma_t \sim 15.7$–15.9 to $\sigma_t \sim 15.3$–15.5 for the period of 1969 to 1991. They suggested that these changes were due to alterations in the structure
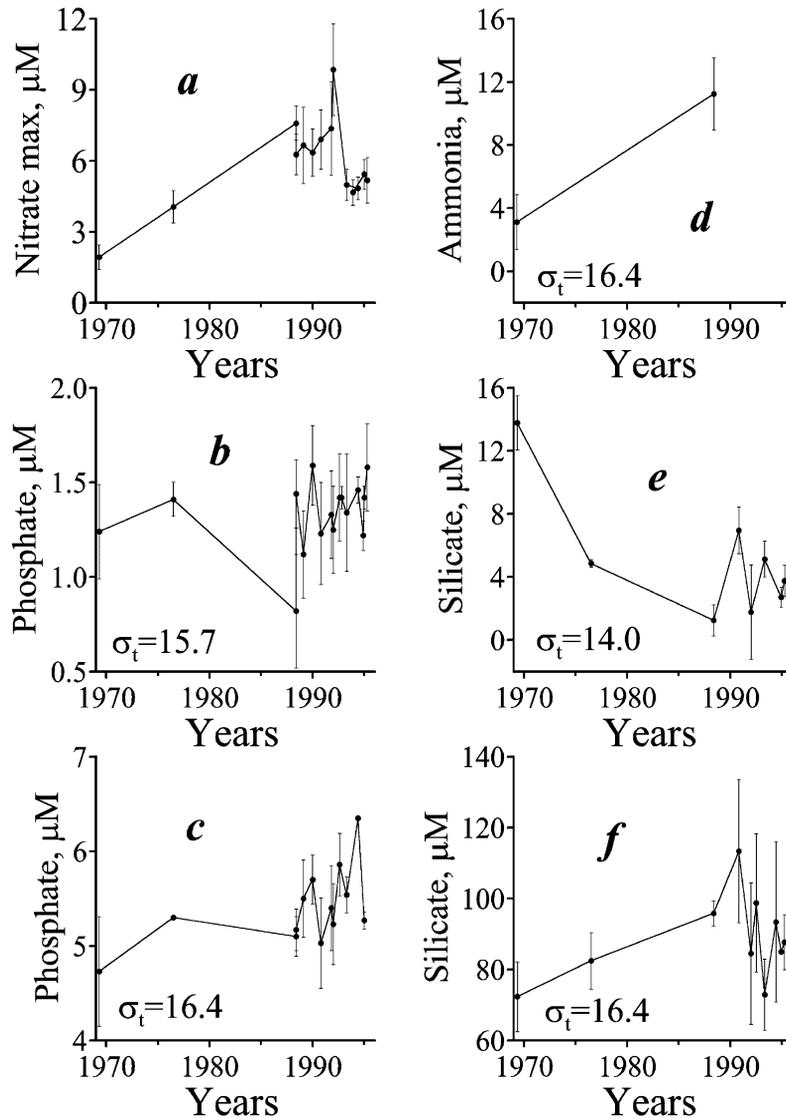
Fig. 8. Variations in the concentration (average values for individual cruises listed in Table 1) of nitrate (a), phosphate at $\sigma_t = 15.7$ (b) and $\sigma_t = 16.4$ (c), ammonia at $\sigma_t = 16.4$ (d) and silicate at $\sigma_t = 14.0$ (e) and $\sigma_t = 16.4$ (f) from 1969 to 1995. (Data on nitrate concentration from the nitrate maximum (σ_t varied from 15.4 to 15.7 depending on year) were used to plot (a)).

of the phytoplankton community dominating the nitrogen and silicate cycles in the upper layer of the Black Sea.

The average maximum concentration of nitrate increased from ~ 2 μM in 1969 to ~ 6 μM in the 1990s (Fig. 8a). This increase is consistent with the increase in the inorganic nitrogen input from the Danube River (Cociasu et al., 1996). However, the changes in the distribution of nitrate are more complex than a simple increase. The average maximum concentration of nitrate oscillated by 1.5- to 2-fold from 1988–1991 to 1995, a period when data were available to resolve year-to-year variations. An attempt to calculate the budget of nitrate in the main pycnocline (Konovalov et al., in press) reveals that the annual flux of nitrate out of the layer between $\sigma_t = 14.5$ and $\sigma_t = 16.2$ is roughly equal to the inventory of nitrate. This means that the residence time of nitrate in the layer of the main pycnocline is fairly short (1 to 3 years) and small changes in the fluxes could result in substantial changes in the nitrate concentrations on a time scale of years.

The oscillations in the distribution of nitrate from 1988 to 1995 (Fig. 8a) correlate positively with changes in temperature of the main pycnocline (Fig. 3): an increase in the mean temperature corresponds to an increase in the nitrate concentration and vice versa. There is also a correlation between nitrate and oxygen in the layer of the main pycnocline (Fig. 9a). The average Nitrate/AOU ratio (Fig. 9b) agrees with the Redfield stoichiometry (16/138) within 6%.

There are also significant changes in the ammonia concentrations in the Black Sea (Fig. 5d). Since there are only two cruise data sets available for analysis, we cannot resolve any sub-scale features of these changes. Still, between 1969 (R.V. ATLANTIS) and 1988 (R.V. KNORR), the average concentration of ammonia decreased from about 0.5 to 0.2 μM in the oxic layer ($\sigma_t < 16.0$) and increased by up to twofold in the sulfide containing waters ($\sigma_t > 16.2$). The highest increase was observed in the layer from $\sigma_t = 16.2$ to 16.7 (Figs. 5d and 8d). Unfortunately, lack of data from the R.V. KNORR cruise for ammonia in waters deeper than $\sigma_t \sim 16.8$ (Fig. 5d) and the absence of reliable ammonia data for all other cruises makes it impossible to make conclusive statements about changes in the deep water.

3.5. Inorganic phosphate

The profile of phosphate (Fig. 5f) has the most complicated structure of the profiles of the basic chemical properties (Brewer and Murray, 1973; Murray et al., 1995). It is generally assumed that the so-called "phosphate's pumps and shuttles" processes involving Mn and Fe cycling between oxidized and reduced forms (Shaffer, 1986), are responsible for the extremes in the phosphate profile. The extremes (minimum at $\sigma_t \sim 15.95$ and maximum at $\sigma_t \sim 16.20$) display distinct spatial and temporal variations (Konovalov et al., 1997). Thus, in April, 1993, the concentration of phosphate at the depth of local minimum ($\sigma_t = 15.95$) varied from 0 to 2.5
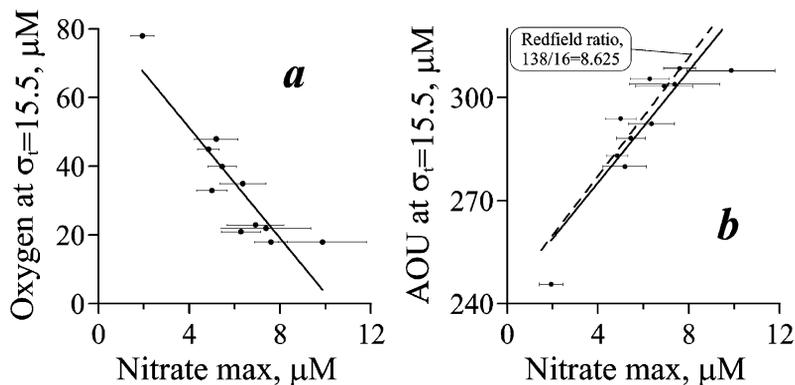
Fig. 9. Nitrate maximum versus oxygen concentration (a) and versus AOU (b) at $\sigma_t = 15.5$. (Average values for individual cruises listed in Table 1 were used to plot this figure).

μM and the concentration of phosphate at the depth of lower maximum ($\sigma_t = 16.20$) varied from 5 to 7.7 μM (Konovalov et al., 1997). For this reason, the depths of $\sigma_t = 15.70$ (rather than $\sigma_t = 15.95$) and $\sigma_t = 16.40$ (instead of $\sigma_t = 16.20$), which are supposedly not affected by seasonal and other meso-scale processes, have been chosen to trace the long-term changes in phosphate distributions in the Black Sea (Fig. 8b–c). The data at these densities (Fig. 8b–c, see also Fig. 5f) demonstrate that changes were not greater than 10–20% between 1969 and the 1990s. While these observed changes are consistent with increased eutrophication of the Black Sea, the range of these changes is close to the random scatter in the data.

3.6. Silicate

Tugrul et al. (1992) and Humborg et al. (1997) demonstrated that silicate concentrations in the surface waters of the Black Sea decreased by an order of magnitude from 1969 (R.V. ATLANTIS cruise) to 1988 (R.V. KNORR cruise). They suggested that these changes were due to reduction in the input of silicate from the Danube river from 800×10^3 t year^{-1} in 1959–1960 (Almazov, 1961) to the present value of $(230–320) \times 10^3$ t year^{-1} (Cociasu et al., 1996; Humborg et al., 1997) due to dam construction in the early 1970s. The observed decrease in silicate inventory in the oxic layer was correlated with alterations in the Black Sea ecosystem that included substitution of diatoms for non-diatom species in the phytoplankton community (Humborg et al., 1997; Tugrul et al., 1992). Changes in the distribution of silicate in the anoxic zone have never been discussed.

The data in Figs. 5e and 8e confirm the decline of the silicate concentration in the oxic waters from the early 1970s to the 1990s (Tugrul et al., 1992; Humborg et al., 1997). At the same time, these data show that the concentration of silicate in the anoxic water has increased by a factor of two (Fig. 8f). Considering that the thickness of the anoxic layer is 2000 m, this increase in the inventory of silicate seems to be too high to reflect real changes in the inventory of dissolved silicate. No analytical or methodological problems appear to exist for the data sets used in this work. The increase in silicate concentrations in the

anoxic zone from the late 1960s to the late 1980s is based on data from three to four cruises (Fig. 8f). The data since 1991 have been obtained by the same analytical procedure which was inter-calibrated during the CoMSBlack and NATO "TU-Black Sea" International Programs (Ivanov et al., 1998a,b). The percentage probability of the linear correlation (Taylor, 1982) between the distribution of silica at $\sigma_t = 14.0$ (Fig. 8e) and $\sigma_t = 16.4$ (Fig. 8f) does not exceed 50% ($n = 8$, $r = 0.27$), if all data are taken into consideration, but this value increases to 95% ($n = 7$, $r = 0.75$), if the data for September–November of 1990 (the R.V. MIKHAIL LOMONOSOV cruise #53a, Table 1) are ignored. The opposing temporal trends in the silica concentrations of the oxic and anoxic layers may represent real variations in the downward flux of biogenic silica.

4. Discussion

4.1. Trends

4.1.1. Oxygen

The absence of perceptible vertical gradients of oxygen at the depth of sulfide onset and the presence of distinctive vertical gradients of sulfide means that the downward flux of dissolved oxygen cannot be the direct sink for the upward flux of sulfide. Brewer and Murray (1973) suggested that sulfide can be oxidized in the absence of oxygen. Later, Murray et al. (1995) suggested a number of possible chemical or biogeochemical processes to increase the flux of oxygen through the suboxic zone. They estimated that the downward gradient of oxygen calculated as electron accepting equivalents at the upper boundary of the sub-oxic zone (52.8×10^{-3} mol e$^-$ m^{-4}) is about 10 times larger than the upward gradient of electron donors gradient from sulfide at the lower boundary (5.1×10^{-3} mol e$^-$ m^{-4}). In order for oxygen to be the direct oxidant of sulfide one has to assume rapid shifts in the position of the oxic/anoxic transition zone or some unrealistic physical processes that make the vertical oxygen and sulfide fluxes balance. The observed increase in thickness of the oxic/anoxic transition zone from $\Delta \sigma_t = 0.4$ in the 1960s to $\Delta \sigma_t = 0.9$ in 1986 (Fig. 6) is due to the upward shift in the position of the oxycline by about

$\Delta \sigma_t = 0.35$, while the relevant downward shift in the position of sulfide onset does not exceed $\Delta \sigma_t = 0.15$. This suggests that the amount of oxygen consumed considerably exceeds the equivalent amount of sulfide consumed in this layer.

Oxidation of sinking particulate organic matter is the most likely process responsible for changes in the oxygen distribution. It is known that 75% to 95% of the primary production of particulate organic matter is regenerated in the oxic layer (Deuser, 1971; Lein and Ivanov, 1991; Karl and Knauer, 1991). The oxycline is located at 30–60 m in the central basin restricting the inventory of oxygen available for respiration. The increase in primary production (Stelmakh et al., 1998; Vedernikov and Demidov, 1997) and the accompanying increased flux of POM (Luther, 1991) that took place in the 1970–1980s should have resulted in an increase of the amount of oxygen consumed by oxidation of sinking POM and an upward shift in the position of the oxycline and the upper boundary (20 μM of oxygen) of the oxic/anoxic transition zone (Fig. 6).

The effect of the increase in the flux of sinking POM should be seen better in the deeper layers of the oxycline, because the upper layer is ventilated more intensively with oxygen. On the other hand, the sinking rate of POM is probably slower and its residence time is longer in the layer of the oxycline due to the increased vertical density gradient in the main pycnocline. Indeed, the concentration of oxygen decreased by a factor of 2 in the CIL (Fig. 4a) and by factor of 5 in the layer of the main pycnocline (Fig. 4c,d) from the beginning of the 1970s to the middle of the 1980s.

The concentrations and saturation of oxygen decreased prior to the middle 1980s and then started to increase after that time (Figs. 4a and 6). Nitrate (Fig. 8a) and silicate (Fig. 8e,f), which are the end-products of oxidation of POM, have opposite trends for the periods before and after the middle 1980s. There appear to be two periods in the recent evolution of the Black Sea when the oxygen concentration in the oxycline was a function of the climate-dependent intensity of ventilation (Fig. 10). An inverse linear correlation of temperature and oxygen concentration was observed before 1975 and after 1985. The percentage probability that temperature and oxygen were uncorrelated was equal to 10% ($n = 5$, $r = 0.8$) be-
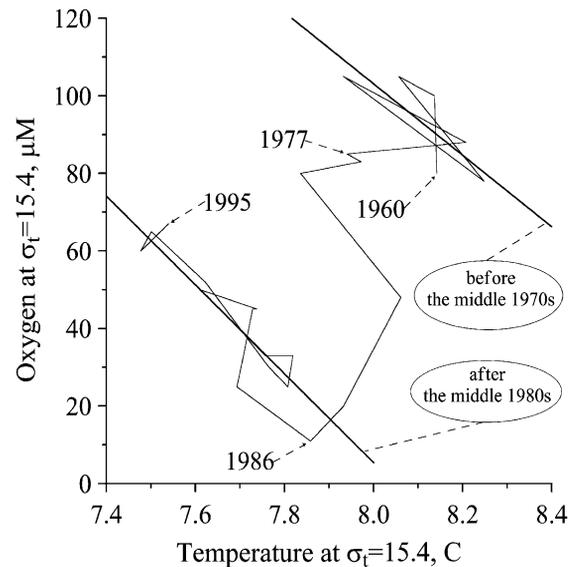
Fig. 10. Variations in oxygen concentration versus temperature in the layer of the main pycnocline ($\sigma_t = 15.4$). (Average values for individual cruises listed in Table 1 and liner fit for the periods before 1975 and after 1985).

fore 1975 and it was less than 0.1% ($n = 15$, $r = 0.9$) after 1985 (Taylor, 1982). The oscillations in the distribution of oxygen for those periods reflect climate-induced changes in the Black Sea ecosystem.

From the middle 1970s to the middle 1980s, the oxygen concentration decreased in spite of the fact that the temperature was significantly lower in 1986 than in 1975 (Fig. 10). Both the concentration of oxygen and the oxygen saturation showed a dramatic decrease during that decade (Fig. 6). Based on this, we suggest that changes in the Black Sea ecosystem and POM flux should be attributed to anthropogenic impact rather than to climate-induced variations. The increase in the amount of nutrients added to the sea (Cociasu et al., 1996; Humborg et al., 1997) caused an increase in primary production, an increase in the flux of sinking particulate organic matter, and an increase in the amount of oxygen consumed to oxidize this organic matter.

Oscillations in temperature (Fig. 3) and oxygen (Fig. 6) after 1986 are very important for understanding the present-day state of the Black Sea. On one hand, the inverse linear correlation between temperature and oxygen (Fig. 10) confirms the balance of sinks and sources of oxygen after 1985. On the other

hand, the present-day balance is achieved due to an increase in the flux of oxygen that resulted from the cold weather conditions in 1984–1985 and 1992–1993 (Fig. 3). The Black Sea ecosystem has not returned to the state of the 1960s, but it has been balanced with an increased flux of sinking particulate matter and oxygen.

4.1.2. Nutrients

To confirm the proposed role of POM in the budget of oxygen in the Black Sea, variations in the distribution of oxygen (Fig. 6) should be mirrored by related changes in the distribution of nutrients. Indeed, the temporal increase of nitrate in the oxic zone (Figs. 5c and 8a) and the increase of ammonia in the anoxic zone (Fig 5d and 8d) reflect the increase in the inventory of inorganic nitrogen from the late 1960s to the early 1990s. The value of the observed Nitrate/AOU ratio (Fig. 9b) agrees well with the Redfield value, supporting the hypothesis that most of the oxygen consumed in the oxycline is used for oxidation of sinking organic matter. This can help explain why temporal variations are more pronounced at the upper boundary than at the lower boundary of the oxic/anoxic zone (Fig. 6). The upper boundary reflects the balance between the vertical flux of oxygen and particulate organic matter, while the lower boundary is dominated by the upward flux of reduced substances from the anoxic zone, by the downward vertical flux of iron(III) and manganese(III,IV) oxy/hydroxides and nitrate and, as we will show later, by the lateral flux of oxygen from the ventilating waters of the Bosphorus plume.

The ratio of nitrate to AOU at $\sigma_t = 15.5$ (Fig. 9b) and dramatic increase in the inventory of nitrate from the late 1960s to the early 1990s (Figs. 5c and 8a) support the important role for POM in determining the basic chemical structure of the Black Sea. Only an increased flux of sinking POM can cause both the observed increases in nitrate in the main pycnocline (Fig. 5c) and ammonia in anoxic waters (Fig. 5d). Actually, the inventories of all nutrients increased from 1969 to 1988 (Fig. 11b–f), while the oxygen inventory decreased dramatically (Fig. 11a).

The changes in the distribution of silicate and phosphate in anoxic waters of the Black Sea have not been previously identified. The temporal variations in the distribution of silicate (Figs. 5e and 8e–f) confirm the 10-fold decrease in concentration of silicate reported for the oxic layer (Tugrul et al., 1992), and reveal a dramatic increase in the inventory of silicate in the anoxic zone from 1969 to 1991, followed by a slight decrease after 1991. We suggest that the opposing trends in the silicate concentrations in oxic (Figs. 8e and 11b) and anoxic (Figs. 8f and 11b) layers are the result of extensive downward transfer of silica in the form of sinking diatom-generated POM. If true, the depletion of silicate in the oxic layer could be the result of activation of diatom species of phytoplankton, rather than silicate limitation (Tugrul et al., 1992; Humborg et al., 1997), due to an increase in the amount of nitrate and phosphate from coastal sources in the late 1970s and 1980s. Some of the silica may originate from shelf sediments. Friedl et al. (1998) identified large benthic fluxes of nutrients from the sediments in the northwest shelf. In summary, our understanding of silica cycling and the dynamics of silica transformation in the Black Sea is still poor.

Observed changes in phosphate agree well with both the general scheme of increased eutrophication of the Black Sea as well as changes in the distribution of nitrate and ammonia. The changes in the distribution of phosphate from 1969 to 1988 (Fig. 11d) reveal slight depletion in the upper layer above $\sigma_t = 14.8$ and accumulation in the deeper layer, below the suboxic zone. The depletion in the inventory of phosphate in the upper layer can be explained by river input of excess inorganic nitrogen that exceeds the stoichiometric amount of phosphate. Changes in the inventories of phosphate and inorganic nitrogen inside the anoxic zone are consistent with the Redfield P:N ratio of 1:16. The increase in concentration of nitrate (Fig. 11f) and decrease of ammonia (Fig. 11e) in the layer above $\sigma_t = 14.5$ may be evidence of an increase in "new" production and an indication of changes in nutrient limitation for primary production from nitrogen to phosphorus.

4.1.3. Sulfide

There have been two different trends in the distribution of sulfide in the anoxic zone of the Black Sea over the past decades (Fig. 7). There were significant increases in sulfide concentrations in the late 1980s and early 1990s (Taylor, 1982). We can estimate the increase in sulfide that could be produced by an
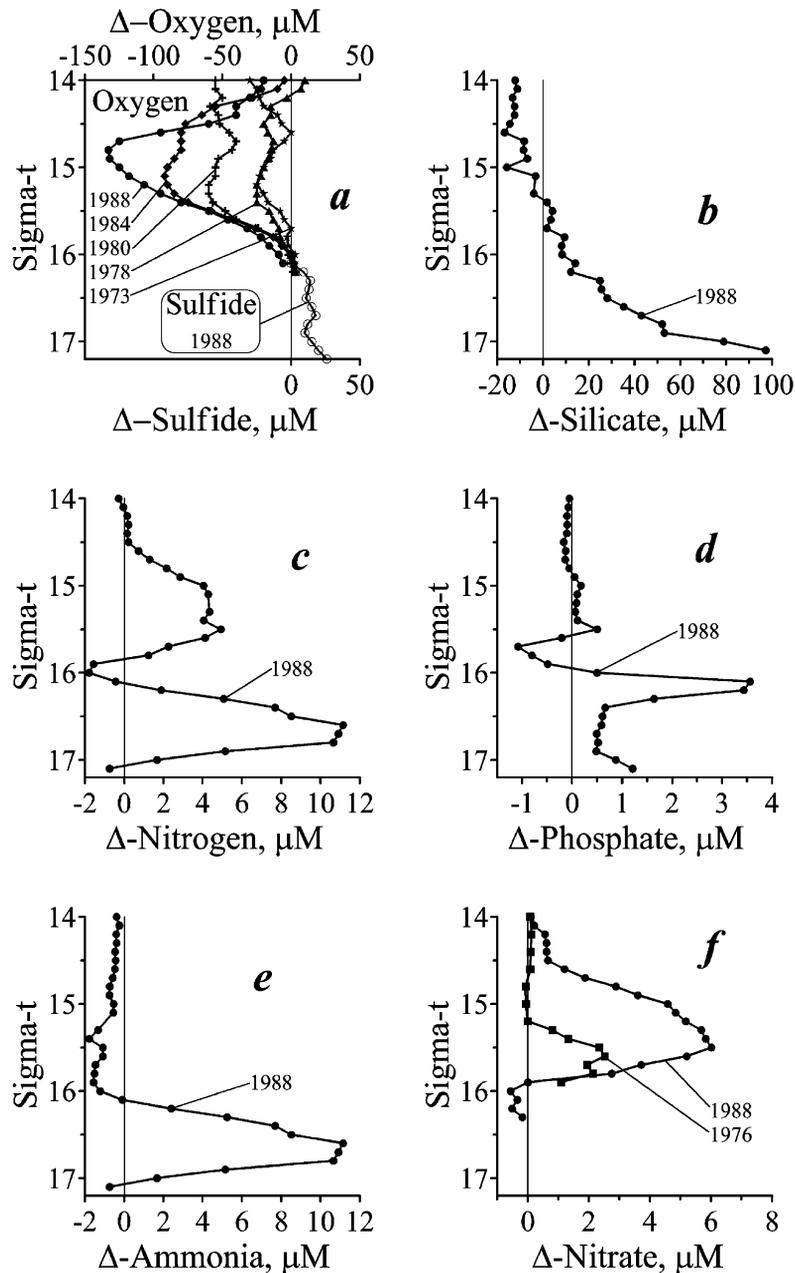
Fig. 11. Changes in vertical profiles of oxygen and sulfide (a), silicate (b), inorganic nitrogen (c), phosphate (d), ammonia (e), and nitrate (f) after 1969 (R.V. ATLANTIS) cruise. (Data collected on the KNORR, 1988; AV-29, 1984; AV-23, 1980; ML-35, 1978; ML-30, 1976; AV-08, 1973 cruises (Table 1) were used to plot the figure. Positive values mean an increase in the concentrations and negative values mean a decrease in the concentrations from 1969 to 1988 or another year after 1969).

increase in the POC flux due to an increase in primary production. Assuming that the average primary production (Table 2) was equal to 300 g C m^{-2} $year^{-1}$ for the late 1980s (Lein and Ivanov, 1991) and 100 g C m^{-2} $year^{-1}$ for the 1960s (Sorokin, 1962, 1964), that 5% to 25% of the newly

Table 2
Primary production in the central part of the Black Sea

The average rate of primary production (g C m^{-2} year^{-1})	The source of data
40 (from 18 to 110)	Sorokin (1962, 1964)
200–250	Sorokin (1982)
113	Stelmakh et al. (1998)
140	Vedernikov and Demidov (1997), the average data for 1978 to 1992
210 and 123	Karl and Knauer (1991), for two different locations
300	Lein and Ivanov (1991)

produced POM could reach the anoxic layer (Deuser, 1971; Lein and Ivanov, 1991; Karl and Knauer, 1991), that the area of anoxic zone is close to 3×10^{11} m^2 and that its depth is equal to 2×10^3 m, the potential increase in the annual production of sulfide could be as high as 0.2 to 1.0 μM year^{-1}. The actual value for different layers of the anoxic zone can be even higher because the intensity of sulfide production clearly varies with depth (Lein and Ivanov, 1991). The average annual increase derived from the linear trends (Fig. 7) ranged from 0.8 to 2.2 μM year^{-1}.

The commonly accepted hypothesis that the distribution of sulfide in the anoxic zone is at steady state is based on the assumption that all the sources and sinks of sulfide have been perfectly balanced over the long evolution of the Black Sea (Skopintsev, 1975; Sorokin, 1982; Bezborodov and Eremeev, 1993). The calculation given above suggests that a threefold increase in the primary production over the past two to three decades (Sorokin, 1962, 1964; Lein and Ivanov, 1991; Stelmakh et al., 1998) and an increase in the flux of POM to the anoxic zone could perturb the balance of sulfide production and consumption and result in an increase in the inventory of sulfide on relatively short time scales.

It is also possible that changes in the concentration of oxygen in the CIL could result in an increase of the flux of oxygen into the anoxic zone associated with the waters of the Bosporus plume (Murray et al., 1991). In addition, temporal changes in the intensity of redox processes are easily derived from data on changes in the distribution of inorganic nitrogen (Fig. 11c) and variations in the thickness of oxic/anoxic transition zone (Fig. 6). All these data to-

gether suggest that variations in sulfide (Fig. 7) rather than a steady state distribution should be recognized as typical.

4.2. Stoichiometry and budget

4.2.1. Nutrients

Stoichiometry of chemical reactions in the Black Sea and other anoxic basins has been discussed in a number of publications (Richards, 1965; Scranton et al., 1987; Anderson et al., 1988; Goyet et al., 1991; Zhang and Millero, 1993; Yao and Millero, 1995). The following set of equations was used in all these publications to calculate theoretical ratios of chemical properties (AOU, total alkalinity, carbonate alkalinity, nitrate, ammonia, phosphate, sulfide) in oxic (Eq. (1)) and anoxic (Eq. (2)) waters.

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 138O_2$$
$$= 106CO_2 + 16HNO_3 + H_3PO_4 + 132H_2O \quad (1)$$

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 53SO_4^{2-}$$
$$= 106HCO_3^- + 53H_2S + 16NH_3 + H_3PO_4. \quad (2)$$
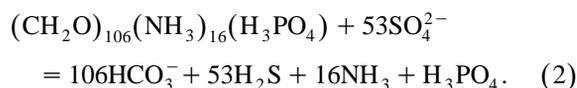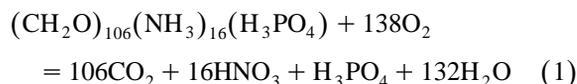
Stoichiometry of the Black Sea anoxic zone derived from the 1988 R.V. KNORR data was summarized by Yao and Millero (1995). They suggested, in particular, that Ammonia:Sulfide = 0.23 (theoretical value (T.V.) 0.30) and C:N:P = 255:25:1 (T.V. 106:16:1). The ratio of silica to nitrogen for diatoms in other ocean areas averages 1.05 but can range from 0.41 to 4.38 (Brzezinski, 1985; Dunne et al., 1999).

The data from the individual cruises used in this analysis have strong linear correlations between the concentrations of the various nutrients and sulfide. Correlation coefficients (r) are rarely less than 0.8, and are usually higher than 0.95. This is consistent with nutrients and sulfide having the same source which is from respiration of sinking POM. Though the correlations are good, the ratios of nutrient to sulfide differ considerably from the values derived from Eq. (2). To make this problem more complicated, these ratios demonstrate significant variations from 1969 to 1995. The ratio of phosphate to sulfide varies by 10–20% while the ratio of silicate to sulfide varies twofold. There is only one consistent explanation for these changes in the ratio of nutrients

to sulfide. It is the systematic difference between the distribution of sulfide observed before 1980 and after 1985 (Brewer and Murray, 1973; Novoselov and Romanov, 1985). This can explain less than 20% of the observed changes. A higher differences suggest the presence of processes that can change the C:N:P:S ratio on the time scale of decades.

Yao and Millero (1995) analyzed data for different anoxic basins to demonstrate that the nutrient/sulfide ratios rarely agreed with the ideal values derived from Eq. (2). The C:N:P:S ratio is only close to the theoretical value (106:16:1:53) in the anoxic zone of the Cariaco Trench. The C:N:P ratio is as much as 155:16:1 in Framvaren Fjord, Norway (Zhang and Millero, 1993; Yao and Millero, 1995). Yao and Millero, (1995) suggested that about 30% of the sulfide produced in Framvaren was removed by processes of oxidation, precipitation of pyrites, degassing and incorporation into organic matter. We suggest that the prominent temporal variations in the nutrient/sulfide ratios from 1969 to 1995 in the Black Sea result of changes in chemical structure induced by eutrophication and/or changes in the intensity of ventilation of the main pycnocline and anoxic zone.

In order to simplify the observations, we have applied stoichiometric analysis to the changes in chemical properties for a specific period (Fig. 11), rather than to the data from any individual cruise. This method eliminates the influence of the initial chemical structure, so that changes in chemical properties over shorter periods of time can be compared in a quantitative manner. Using this approach, variations in oxygen, sulfide and nutrients from 1969 (R.V. ATLANTIS) to 1988 (R.V. KNORR) fit well with the hypothesis of increased eutrophication shown below.

(1) An increase in the input of nutrients results in an increase in primary production and, consequently, in the export flux of POM. An input of nitrate, that exceeds the stoichiometric amount of phosphate and silicate (N:P as 16:1 and Si:N as 1.05:1), depletes the inventory of ammonia (Fig. 11e), silicate (Fig. 11b) and phosphate (Fig. 11d) in the upper layer and increases the flux of these nutrients into the deeper layer.

(2) The increase in the flux of POM causes a decline in the inventory of oxygen (Fig. 11a) in the

layer beneath the euphotic zone, and leads to an increase in the inventory of nutrients (Fig. 11b,d,f) due to oxidation of the sinking POM. The more rapid decrease in oxygen with depth results in a thicker suboxic zone (Fig. 6).

(3) The increased flux of POM into the anoxic zone results in an increase in nutrients and sulfide (Fig. 11a) concentration.

The stoichiometry of these changes (Fig. 12) confirms the biogenic origin of the variations in inorganic nitrogen (ammonia, nitrite, and nitrate), phosphate and silicate. Variations in the ratio of $\Delta P/\Delta N$ and $\Delta Si/\Delta N$ in the layer above $\sigma_t \sim 14.8$ (Fig. 12a,b) reflect cycling of nutrients in euphotic zone. The $\Delta P/\Delta N$ ratio in the oxycline ($\sigma_t < 15.8$) and anoxic zone ($\sigma_t > 16.2$) coincides with the theoretical ratio in POM (1:16) (Fig. 12b). The profile of the $\Delta Si/\Delta N$ ratio (Fig. 12a) also suggests a biogenic control for changes in the distribution of silicate (Fig. 11b). This ratio varies slightly in the water column confirming the primary role of POM in the present evolution of the Black Sea chemical structure. Dramatic variations in the ratio of $\Delta P/\Delta N$ and $\Delta Si/\Delta N$ in the oxic/anoxic transition zone ($\sigma_t \sim$ 15.8 to 16.2) reflect the presence of additional sources and sinks of phosphate and nitrogen, such as the metal oxide (Mn, Fe) cycling (Shaffer, 1986), and loss of nitrogen due to denitrification (Murray et al., 1995).

In order to evaluate the potential of POM to change the budget of nutrients and sulfide in the anoxic zone of the Black Sea on a time scale of decades, we need to estimate the increase in inventory of nutrients and compare these values with published data on the river input of these elements. To calculate the total input of nutrients into the Black Sea from 1969 to 1988, we used data for the annual input of nutrients from the Danube (Table 3). We assumed that data from Almazov (1961) are appropriate for the period of the 1969 R.V. ATLANTIS II cruise, and that data from Cociasu et al. (1996) can be applied to the period of the 1988 R.V. KNORR cruise. Based on data of Cociasu et al. (1996), we also hypothesize a linearly increasing trend for the input of nutrients (which is unlikely to be true). Considering that the Danube was the main ($\sim$ 50–70%), but not the only source of nutrients (Kubilay et al., 1995), we increased the calculated
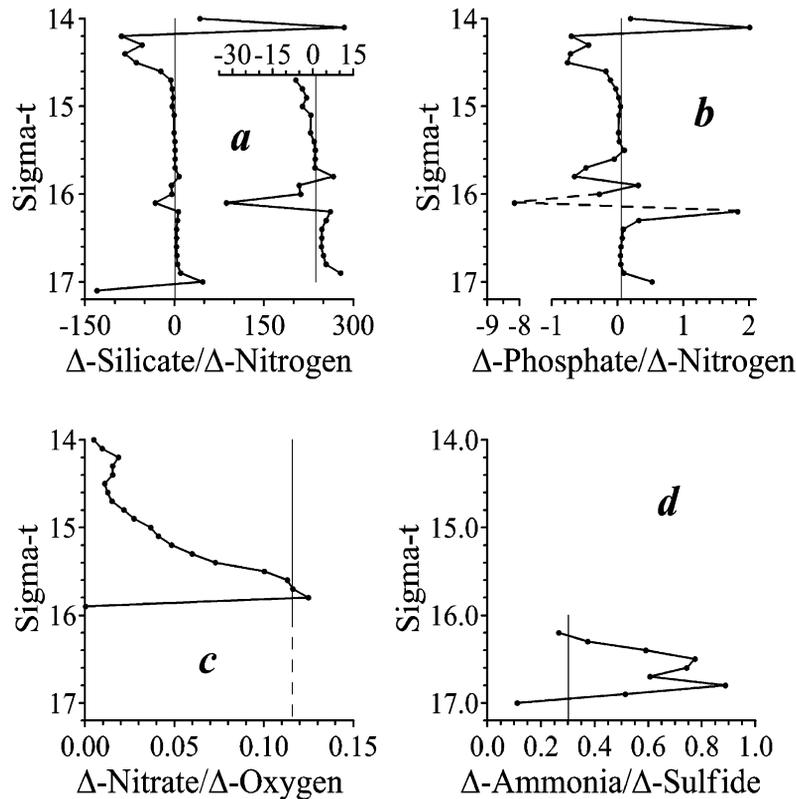
Fig. 12. Stoichiometry of changes in nutrients, oxygen and sulfide distribution in the Black Sea waters based on the differences in profiles of these properties between R.V. KNORR (1988) and R.V. ATLANTIS (1969). (Vertical lines represent the ratio derived from Eqs. (1) and (2) or published elsewhere).

values by a factor of 2 to make a rough estimate of the total riverine input of nutrients to the Black Sea. This enabled us to calculate both the total input of nutrients over the 19 years between the R.V. AT-LANTIS II (1969) and R.V. KNORR (1988) cruises and the increase (decrease for silica) in the input of nutrients (Table 3).

To estimate changes in the inventory of nutrients in the Black Sea from 1969 to 1988, we have the average depths for individual values of sigma-t (Table 4) derived from the recent CoMSBlack and TU-Black Sea cruises conducted in 1990 to 1995. The changes in the average vertical distribution of nutrients were calculated as the difference between

Table 3
Data on the budget of nutrients in the Black Sea

Nutrients	The input from the Danube in the 1960s (t/year)	The input from the Danube in the 1990s (t/year)	The ratio of the input in the 1990s to the 1960s	The input from the Danube from 1969 to 1988 (mol) (A)	The total input from 1969 to 1988 (mol) (as twofold of A)	The increase in the input (mol) (B)	The observed increase in inventory (mol) (C)	The ratio of C to B
DIN	1.4×10^5	7.0×10^5	5	5.7×10^{11}	11.4×10^{11}	7.5×10^{11}	8.0×10^{11}	~ 1.07
PO_4	0.12×10^5	0.25×10^5	~ 2	0.1×10^{11}	0.2×10^{11}	0.07×10^{11}	1.3×10^{11}	~ 18
SiO_4	7.9×10^5	2.5×10^5	~ 0.3	3.5×10^{11}	7.0×10^{11}	–	9.1×10^{12}	?

Table 4
Average depth of individual sigma-t surfaces

Sigma-t	Depth (m)	Area (km^2)
14.30	41.0	381607.6
14.40	50.0	372521.5
14.50	54.4	368079.4
14.60	63.0	359397.1
14.70	65.0	357377.9
14.80	70.4	351926.3
15.00	76.5	345767.9
15.20	82.0	340215.3
15.40	88.5	333653.1
15.60	96.0	326081.3
15.80	106.0	321598.7
16.00	118.0	320710.0
16.20	136.0	319376.9
16.30	146.0	318636.3
16.40	165.0	317229.3
16.50	186.0	315674.1
16.60	211.0	313822.6
16.70	247.0	311156.6
16.80	294.0	307675.8
16.90	367.0	302269.7
16.95	412.0	298937.1
17.00	472.0	294493.6
17.05	540.0	289813.8
17.10	630.0	283950.0
17.15	748.0	
17.20	984.0	141576.0

the average concentrations in 1988 and 1969 (Fig. 11). The inventory of inorganic nitrogen increased by 8.0×10^{11} mol (Table 3). This value differs only by 7% from the increase in the input of nitrogen in the Black Sea from 1969 to 1988 (7.5×10^{11} mol). Acknowledging the uncertainties of these calculations, we suggest that a significant amount of the additional nitrogen discharged into the Black Sea from 1969 to 1988 accumulated in the water column in the form of ammonia and nitrate. These calculations suggest that the nitrogen budget may have been balanced before the late 1960s, but was disturbed in the 1970s and the inventory of nitrogen increased on average by 0.42×10^{11} mol year^{-1} from 1969 to 1988.

Unlike inorganic nitrogen, the calculations of the increase in the inventories of phosphate and silicate raise a number of questions. The $\Delta N / \Delta P$ molar ratio for the layer of $\sigma_t = 16.4$ to 16.9, which is assumed to be the layer of the most intensive pro-

cesses of POM respiration and sulfate reduction, is equal to 17.6 and differs from theoretical value (16) by only 10%. The total increase in the inventory of phosphate in the layer $\sigma_t = 14.5$ to 17.1 is equal to 1.3×10^{11} mol. This value exceeds the calculated input of phosphate to the sea (0.2×10^{11} mol) by a factor of 6.5 and increase in the input of phosphate (0.078×10^{11} mol) by a factor of 18. We can speculate about possible explanations of this observation. One possibility is that an additional amount of phosphate could be discharged into the sea from coastal sources other than rivers. These are fertilizer producing plants or fertilizer containing waters from the agricultural regions of the Black Sea coast. Fluxes of nutrients from the sediments of the northwestern shelf (Friedl et al., 1998) might also supply a large amount of dissolved inorganic nutrients. These fluxes and their direction depend on the redox potential of the sediments and the bottom water, which, in turn, is a function of the flux of POM. Suboxic and even anoxic conditions in the bottom water of the northwest shelf appear to be a regular phenomena for the period of the 1980s–early 1990s (Faschuk, 1995) and provide favorable conditions for an intensive flux of nutrients from the sediments into the water. The data are too very limited to estimate the flux but Friedl et al. (1998) suggested that it may be as large as the input of nutrients from the Danube. The discrepancy between the increase in the input and inventory of nutrients is even more prominent for silicate. The increase in the inventory of silicate in the layer $\sigma_t = 14.5$ to 17.1 (9.1×10^{12} mol) is 6.5 times higher than the calculated river input (7.0×10^{11} mol). Humborg et al. (1997) suggested that there has been a threefold decrease rather than an increase in the flux of silicate associated with river input.

4.2.2. Oxygen and sulfide

The variations in ΔNitrate/ΔOxygen and ΔAmmonia/ΔSulfide (Fig. 12c–d) reveal new and unexpected features about oxygen and sulfur cycling in the Black Sea. The ratio of ΔNitrate/ΔOxygen was close to the expected Redfield value (16:138) for only the narrow oxycline layer of $\sigma_t = 15.4$ to 15.7 (Fig. 12c) which corresponds to the region of the nitrate maximum (Fig. 5c). Both ΔNitrate/ΔOxygen (Fig. 12c) and Nitrate/AOU (Fig. 9b) demonstrate

that temporal variations in nitrate and oxygen in this layer are due to oxidation of POM. The decrease in ΔNitrate/ΔOxygen deeper than $\sigma_t = 15.7$ can be explained by nitrate reduction in the sub-oxic layer (Murray et al., 1995). The low values of ΔNitrate/ΔOxygen in the layers shallower than $\sigma_t = 15.4$ have no simple explanation, but are probably due to biological processes. The values of ΔSilicate/ΔNitrogen and ΔPhosphate/ΔNitrogen (Fig. 12a and b) are consistent with regeneration of POM. Thus, there must be some process for uptake of nitrate that does not affect the concentration of oxygen or for consumption of oxygen without release of nutrients. The decrease in oxygen (-1.7×10^{12} mol) in the layer between $\sigma_t = 14.5$ and 16.0 is 2.9 times higher than the value (5.84×10^{11} mol) expected based on the increase in nitrate (6.77×10^{10} mol). This discrepancy may be due to the "bacteria loop" and oxidation of DOM and POM that has a low nitrogen content. Karl and Knauer (1991) investigated microbial production and particle flux in the upper layer of the Black Sea and concluded that particle desaggregation, dissolution and hydrolysis could be potentially important mechanisms contributing to the loss of sinking particulate organic matter below the euphotic layer.

Another important conclusion derived from the stoichiometric data is that the average ΔAmmonia/ΔSulfide ratio is much higher than the expected value (16:53) for the upper part of anoxic zone (Fig. 12d). The observed increase in the inventory of sulfide from 1969 to 1988 in the anoxic layer from $\sigma_t = 16.2$ to 17.0 was equal to 1.36×10^{12} mol. But this value should have been 1.82 times higher or 2.47×10^{12} mol, if calculated from Eq. (2) using the increase in inventory of ammonia. The amount of missing sulfide is close to 1.11×10^{12} mol.

The only known source of ammonia in the anoxic zone of the Black Sea is respiration of the sinking POM (Eq. (2)). The values of C:N ratio in POM reported for the Black Sea range from 7.5 to 9.6 (Burlakova et al., 1997; Yilmaz et al., 1998). Karl and Knauer (1991) reported that the mean C:N ratio of the suspended particulate matter was 7.8 ± 2.3 but that the mean C:N ratio of the sinking particulate matter was 14.1 ± 2.0. A high C/N ratio would result in a deficiency in ammonia compared to the value based on Eq. (2), rather than an excess.

Thus, we hypothesize that some chemical processes are responsible for consuming or removing of sulfide within the anoxic zone. Yao and Millero (1995) investigated a similar problem in the anoxic waters of Framvaren Fjord, Norway. As possible sulfide sinks they proposed (i) oxidation of sulfide inside the anoxic zone due to the flux of oxygen saturated waters into the fjord over the sill, (ii) precipitation of sulfide in the form of FeS_2, (iii) degassing of hydrogen sulfide and (iv) incorporation of sulfide into organic matter. Degassing of hydrogen sulfide is not possible because the maximum concentration of sulfide is much lower than the solubility value and the sulfide layer does not contact the atmosphere. Incorporation of sulfide into organic matter is not likely to be the process responsible for the sulfide sink that exceeds production of sulfide because organic matter appears to be basically a source, rather than sink of sulfide in the anoxic zone of the Black Sea. Muramoto et al. (1991) reported that the sinking flux of iron sulfide in the Black Sea is as much as 10 mmol m^{-2} $year^{-1}$. Assuming the area of the deep part of the Black Sea is 3×10^{11} m^2, the total amount of sulfide removed in the form of iron sulfide over 19 years (from 1969 to 1988) would be 5.7×10^{10} mol. This can only explain 5% of the sulfide deficiency (1.1×10^{12} mol).

Oxygen injected during deep water formation could consume sulfide. Most of the waters of the Bosporus plume are injected into the Black Sea above 500–800 m (Ozsoy et al., 1993). This is in good agreement with the vertical distribution of sulfide and ammonia in the upper part of the anoxic zone (Fig. 13). Indeed, the ratio of ammonia to sulfide expected from Eq. (1) is observed at the depth of $\sigma_t = 16.9$, which is about 150 m deeper than the onset of sulfide. The observed ratio has a typical exponential profile confirming that the waters of the Bosporus plume are mainly trapped in the upper 400–500 m layer of the sea.

To estimate the flux of oxygen delivered with the waters of the Bosporus plume, we assumed that the volume of water incoming through the Bosporus strait is 312 km^3 $year^{-1}$ (Unluata et al., 1990). We assumed that the Bosporus inflow entrains CIL in the average ratio 1:3.3 (Murray et al., 1991). This is a lower estimate because waters that ventilate shallower depths have higher ratios. We estimate that the
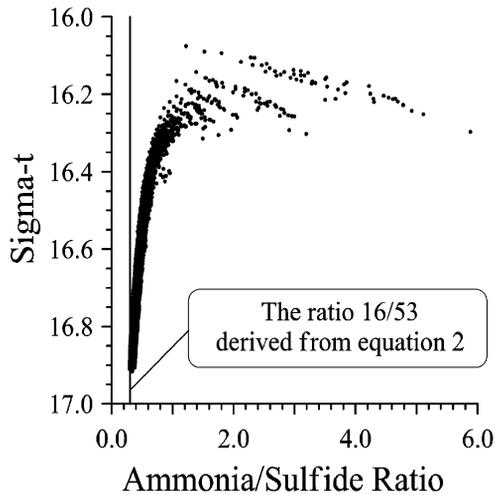
Fig. 13. The ratio of ammonia to sulfide derived from data collected on the R.V. KNORR (1988).

oxygen concentration in the Bosporus plume is 200–300 μM. This value is based on the fact that the waters of Marmara Sea, with an oxygen concentration of about 50 μM, are mixed with CIL waters with oxygen concentrations in the range of 250–350 μM. The total amount of oxygen predicted to be injected into the anoxic layer by the Bosporus plume over 19 years would be $(5.1–7.6) \times 10^{12}$ mol. This is a lower limit for the reasons stated above. This oxygen flux potentially could oxidize $(2.5–3.8) \times 10^{12}$ mol of sulfide, assuming that sulfide is oxidized to sulfate. Usually, $S°$ is the product when HS^- is oxidized by O_2 but past work has shown that the concentrations of $S°$ are low in the anoxic zone (e.g., Luther et al., 1991).

For comparison, we have calculated the upward flux of sulfide from the anoxic to the suboxic zone. These calculations are based (i) on the vertical velocity and coefficient of turbulent diffusion derived from a 1-D model that takes into account the Bosporus plume (Samodurov and Ivanov, 1998; Ivanov and Samodurov, 2001), and (ii) the average profile of sulfide. The upward flux of sulfide at $\sigma_t = 16.2$ over 19 years is equal 1.1×10^{12} mol for the area of the deep part of the sea. We find that the amount of sulfide consumed in 19 years in both the suboxic $(1.1 \times 10^{12}$ mol) and anoxic zone $(1.1 \times 10^{12}$ mol) is similar to the oxygen flux from the Bosporus plume, which could consume $(2.5–3.8) \times 10^{12}$ mol

of sulfide during the same period. The reason the location of the upper and lower boundary of oxic/anoxic transition zone (Fig. 6) are uncorrelated is because they are controlled by different processes. While oxygen in the oxycline is consumed by oxidation of sinking POM, consumption of sulfide depends mainly on lateral ventilation of the main pycnocline by waters of the Bosporus plume.

The increase in inventory of ammonia shallower than $\sigma_t = 17.0$ is equivalent to an increase in inventory of sulfide of 1.3×10^{11} mol year^{-1}. Taking into consideration that about 60% of the sulfide is produced in the upper layer of the anoxic zone (Lein and Ivanov, 1990), we estimate that the total increase in the annual sulfide production in the Black Sea is equal to $(1.3–2.2) \times 10^{11}$ mol year^{-1}. Lein and Ivanov (1991) suggested the total annual production of sulfide was $(6.2–7.8) \times 10^{11}$ mol year^{-1}. The data published by Sorokin (1982) are three to five times lower suggesting a total production of $(1.2–2.4) \times 10^{11}$ mol year^{-1}. We suggest that this increase in the rate of sulfate reduction may be due to the increase in POM production due to eutrophication from the 1960s to the late 1980s.

Some data for ^{14}C primary production are listed in Table 2. The most distinctive feature of this data set is the threefold increase in the rate of primary production in the central part of the sea. Sorokin (1964) suggested the value of 109 g C m^{-2} year^{-1} as an average value for the entire area of the Black Sea. But, in fact, the typical rate of primary production published by Sorokin (1964) for the central part of the sea was 0.05–0.2 g C m^{-2} day^{-1} (18–73 g C m^{-2} year^{-1}) with an average value of 40 g C m^{-2} year^{-1}. Some of the difference may be due to improvements in methods but the following calculation suggests that the increase may be real.

One approach for estimating the changes in primary production is based on data for the increase in the input of inorganic nitrogen into the Black Sea (Cociasu et al., 1996). We assume that (1) the river input of inorganic nitrogen has increased by 8×10^{10} mol year^{-1}, (2) the C:N uptake ratio is equal to 106:16, (3) primary production is nitrogen limited, (4) 40% of the POC is produced in the central area of the sea (Sorokin, 1962, 1964; Skopintsev, 1975), and (5) the export flux of nitrogen to the anoxic zone is 10% to 15% of the nitrogen primary production.

Based on these assumptions, the potential increase in primary production in the central regions could reach $(15–21) \times 10^{11}$ mol C year^{-1}. This figure is close to the difference between the present-day primary production $((28.3–35.1) \times 10^{11}$ mol C year$^{-1})$ in the deep part of the sea (Stelmakh et al., 1998; Vedernikov and Demidov, 1997) and the historical value $(10 \times 10^{11}$ mol C year$^{-1})$ derived from the data of Sorokin (1964).

The rates of sulfide production derived from published data on sulfate reduction, flux of sinking POM, primary production and the changes in chemical structure of the Black Sea water column proposed here are listed in Table 5. In order to calculate these sulfide production rates, we used the following data and assumptions:

1. The area of the deep part of the Black Sea is equal to 3×10^{11} m^2.
2. The average flux of POC consumed in the Black Sea anoxic zone is equal to 2.5×10^{11} mol year^{-1} (Deuser, 1971), 3.6×10^{11} mol day^{-1} (Karl and Knauer, 1991), 0.6×10^{11} to 2.0×10^{11} mol year^{-1} (Muramoto et al., 1991).
3. The flux of POM to the anoxic zone is equal to 10% to 15% of total primary production.
4. Finally, Albert et al. (1995) have estimated sulfide production to be $(0.24–1.61) \times 10^{11}$ mol year^{-1} in the water column and $(1.41–1.59) \times 10^{11}$ mol year^{-1} in the sediments.

Thus, we calculated the basin integrated values of primary production, the flux of POM to the anoxic

zone and the rate of sulfate reduction by multiplying the published values per meter squared by the area of the deep sea. The flux of POM to the anoxic zone was calculated to be 10% to 15% of the published values of basin integrated primary production. The flux of POM to the anoxic zone was recalculated to the rate of sulfide production according to Eq. (2).

Considering all the uncertainties involved in these calculations, the agreement between these different estimates is good. These estimates support the argument that there has been a significant increase in the rate of sulfide production due to the response of the Black Sea ecosystem to intensive eutrophication.

Comparing the rates of sulfide production, that vary from $(1.2–2.4) \times 10^{11}$ mol year^{-1} in the 1960s to $(1.8–7.8) \times 10^{11}$ mol year^{-1} in the late 1980s– early 1990s (Table 5), with the amount of sulfide that can be oxidized by oxygen originated from the Bosporus plume, $(1.3–2.0) \times 10^{11}$ mol year^{-1}, we can see that there should have been a balance or even some decline in the inventory of sulfide in the 1960s, and an increase in the inventory of sulfide in the 1980s. The field data reveal exactly these trends in sulfide distribution (Fig. 7). Thus, the difference between the rates in the 1960s and 1980s may represent different periods in the recent evolution of the Black Sea environment: the period before the beginning of intensive eutrophication and the period of intensive eutrophication. A main feature of the recent period is a significant imbalance in the budget of nutrients, oxygen and sulfide in the Black Sea. To stabilize the present-day situation and, in particular, to balance the budget of sulfide, the amount of nutrients (primarily of nitrogen) discharged into the

Table 5
Sulfide production in the Black Sea

Sulfide production in 1960s (mol year^{-1})	Sulfide production in 1980s (mol year^{-1})	Type of data	Source of data
$(1.25–1.75) \times 10^{11}$		10–15% of primary production	Sorokin (1962, 1964)
	$(3.5–6.5) \times 10^{11}$		Vedernikov and Demidov (1997), Stelmakh et al. (1998)
$(1.2–2.4) \times 10^{11}$		The rate sulfate reduction	Sorokin (1982)
	$(6.2–7.8) \times 10^{11}$		Lein and Ivanov (1991)
	$(1.65–3.20) \times 10^{11}$		Albert et al. (1995)
1.25×10^{11}		Flux of POC in anoxic zone	Deuser (1971)
	1.8×10^{11}		Karl and Knauer (1991)
	$(0.6–2.0) \times 10^{11}$		Muramoto et al. (1991)

Black Sea should be decreased by two to fivefold. The reported decrease in discharge of nutrients from the Danube River (Cociasu et al., 1996; Humborg et al., 1997) that provides up to 60–80% of the total input of nutrients, is minor compared to previous increases in the input of these substances. Keeping in mind, that the years favorable for intensive ventilation are quite rare (Belokopitov, 1998; Ivanov et al., 2001), the present-day balance in the Black Sea ecosystem may be easily perturbed during the predicted global warming. For this reason, continued investigations of the Black Sea are extremely important to document the evolution of this perturbed marginal sea.

5. Conclusions

The data on the changes in the distribution and stoichiometry of nutrients, oxygen and sulfide in the Black Sea suggests the following.

(1) The changes in the distribution of these substances are mostly of biogenic origin.

(2) These changes are due to an increase in the input of nutrients into the sea, primarily from rivers.

(3) The increase in the inventory of nitrogen in the water column is roughly equal to the increase in the river input of inorganic nitrogen.

(4) A significant fraction of the nitrogen input is stored in the anoxic water column in the form of ammonia.

(5) The increase in the input of nitrogen that is not supported by an equivalent input of phosphate and silicate results in depletion of these nutrients from the upper layer and their increase in the anoxic zone.

(6) The excess in the increase in inventories of phosphorus and silica suggests other sources, such as benthic fluxes from shelf sediments (Friedl et al., 1998). Focussed studies are needed to investigate the budget and cycling of these nutrients in more detail.

(7) The uncorrelated variations in the location of the upper (O_2) and lower (H_2S) boundary of oxic/anoxic transition zone can be explained by different processes governing these variations. While oxygen in the oxycline is consumed by oxidation of sinking POM, consumption of sulfide depends mainly on input of oxygen associated with lateral ventilation of the main pycnocline by waters of the Bosporus plume.

(8) Up to 70% of the annually oxidized amount of sulfide is consumed inside the anoxic zone due to the flux of oxygen with the Bosporus plume.

Acknowledgements

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