Fluxes and budget of sulphide and ammonia in the Black Sea anoxic layer

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Abstract

Using data on average distribution, and applying profiles of the vertical velocity and turbulent diffusivity derived from a stationary one-dimensional model of ventilation of the Black Sea, we calculate and discuss the fluxes and production/consumption rates of ammonia and sulphide in the anoxic layer of the Black Sea in the 1960s and 1990s. The results reveal that sulphide, in terms of its flux and production/consumption rate, is not equivalent to ammonia. The existence of a lateral flux of oxygen, as we believe, associated with the Bosphorus downflow is the basic reason making the difference. Both ammonia and sulphide are of biogenic origin, but a significant part of sulphide is oxidised within the upper 150–250 m layer of the anoxic zone, while ammonia, possessing a higher red-ox potential, is oxidised in the vicinity of the onset of sulphide. The calculated sulphide consumption rate, which is derived from the observed vertical profiles, varies insignificantly for the 1960s and 1990s. The rate of sulphide production derived from the published data on the rate of primary production, sulphate reduction, ammonia oxidation and flux of sinking POM was close to the calculated consumption rate of sulphide in the 1960s, but considerably exceeded it in the 1990s. This suggests that sulphide inventory might increase by the 1990s. The rate of possible changes in the inventory of sulphide is less than 1% per year for the layer above 1000 m, suggesting a slow pace of temporal change for sulphide. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

More than 92% of the Black Sea is occupied by an anoxic zone. Until recently, the inventory and budget of sulphide were considered to be at steady-state (Skopintsev, 1975). Recent data on temporal variations in the chemical structure of the entire water column (Murray et al., 1989; Konovalov et al., 1999; Konovalov and Murray, 2001) suggests that those features are a response to an increase in the input of nutrients over the last three decades. The assumption that the sulphide budget is at steady-state has been questioned.

The anoxic layer of the Black Sea has been investigated for more than a century starting with the first known published paper in 1890 (Andrusov, 1890). The sulphide has a biogenic (microbiological) origin, i.e. its production occurs due to anaerobic respiration of organic matter (Sorokin, 1982). Geological sources of sulphide are considered negligible.

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The upward flux of sulphide at a depth of its onset was considered to be equal to its production rate in the anoxic layer. According to this concept, oxidation of sulphide should take place at the upper boundary of the anoxic layer where oxygen diffusing from the oxycline formed a layer of co-existence of oxygen and sulphide, the so-called "C-layer" (Volkov et al., 1990; Bezborodov and Eremeev, 1993). Sulphide production and consumption were considered reaching a balance over past several millennia. The residence time of sulphide was estimated to be over 1000 years. Changes in the inventory of sulphide were considered plausible on the time scale of centuries to millennia (Skopintsev, 1975). The total production and oxidation of hydrogen sulphide were estimated to be 4.3×10^6 and 7.0×10^6 ton year^{-1}, respectively. These values were considered to be equal, bearing in mind the uncertainties in the data (Bezborodov and Eremeev, 1993).

Recent publications have challenged this concept. Murray et al. (1991), Buesseler et al. (1991) and Ozsoy et al. (1993) showed that the Bosphorus inflow mixes with the cold intermediate layer waters, and the mixture ventilates the main pycnocline and, thus, the anoxic zone. The entrainment ratio of the Black Sea ambient water to Bosphorus inflow has been estimated to range from 3.3 to 11.5. Such ventilation scheme suggests that the residence time increases from a decade for the upper part of the anoxic zone to hundreds and maybe thousands years for the near bottom layer (Murray et al., 1991; Unluata et al., 1990). This means that the layer of the main pycnocline and the upper part of the anoxic zone, in particular, is a highly dynamic system where lateral fluxes may play an important role in maintaining the observed chemical structure.

Buesseler et al. (1991) used data on iron, manganese, suspended matter and Chernobyl Cs below the oxic/anoxic interface to illustrate the role of the Bosphorus in lateral ventilation of the main pycnocline and anoxic layer. Ivanov et al. (1998a) showed that the lateral flux of oxygen in the lower pycnocline may be more important than its vertical flux. Recent publications on the structure of the oxic/anoxic transition layer (Murray et al., 1989; Murray et al., 1995) and temporal changes in the chemical structure of the oxic and anoxic layers (Codispoti et al., 1991; Cociasu et al., 1996; Konovalov and Mur-

ray, 2001) have challenged the former hypothesis of a stagnant and balanced anoxic zone. Murray et al. (1995) demonstrated that the structure of the oxic/anoxic transition zone rules out the possibility of direct interaction between oxygen and sulphide because the downward flux of oxygen expires 20 to 50 m above the onset of sulphide. To solve the puzzle, they suggested a number of processes that might be responsible for oxidation of sulphide in the absence of oxygen. These include oxidation of sulphide by nitrate or by oxi-hydroxides of iron (III) and manganese (III, IV).

Reported changes in the chemical structure of the oxic and anoxic layer (Codispoti et al., 1991; Cociasu et al., 1996; Konovalov and Murray, 2001) have raised even more serious questions about budgets and balances for oxygen, nutrients and sulphide. The increase in the inventory of nitrate in the oxic layer and of other nutrients and sulphide in the anoxic layer, as well as dramatic changes in the inventory of oxygen, silicate and ammonia in the oxic layer, clearly demonstrates that fluxes and budgets of basic substances (elements) vary due to changes in the loading of nutrients into the sea. These alterations suggest that the ratio of the rates of production to consumption of sulphide, in particular, vary for certain periods. Moreover, changes on the time scale of 10 to 30 years reflect both climate-dependent variations in the intensity of ventilation and human-dependent variations in the intensity of eutrophication. Altogether, the existence and rate of changes in the inventory of sulphide and nutrients in the anoxic layer demonstrate that the budget of sulphide cannot be assumed steady-state a priory and should be investigated in the framework of different approaches.

In this paper, we extend application of the 1-D model of vertical exchange in the Black Sea (Samodurov and Ivanov, 1998; Ivanov and Samodurov, 2001) to the analysis of fluxes, production/consumption and budgets of sulphide and ammonia. Assuming, after Konovalov and Murray (2001), that changes in the average vertical distribution of sulphide and ammonia in the late 1960s and 1980s result from eutrophication, we analyse a possibility of alterations in the budget of sulphide and a possibility of a balance between production and consumption of sulphide.

2. Data and methods

2.1. Data

The average ammonia versus sigma-t profiles for the upper 1000 m were drawn by fitting the data of the R.V. ATLANTIS (1969) and KNORR (1988) cruises (Fig. 1b). Other data on ammonia distribution in the Black Sea are rare and have poor vertical and horizontal resolution. Sorokin (1982) discussed an average profile of the vertical distribution of ammonia, recalculating the data after Skopintsev (1975). Actually, the data published by Skopintsev (1975) consisted of less than a score 10-point vertical profiles for the period from the early 1920s to the early 1960s. Sapozhnikov (1990) summarised all available data to demonstrate (a) the presence of two local

minima in the vertical profile at a depth of 10–30 and 70–100 m and (b) a plain increase of the ammonia concentration that reaches 100 μM in the near bottom layer. No hypotheses were suggested to explain these features. Data on the distribution of ammonia were not supported with data on T, S properties and the distribution of sulphide. Temporal changes in the distribution of ammonia were not discussed. These data were important to investigate basic features of the vertical distribution of ammonia, but could hardly be utilised to calculate the profiles, fluxes, rates of production and consumption and ammonia/sulphide ratio discussed in this paper. Fortunately, seasonal fluctuations play a minor role in modifying the structure of the lower ($\sigma_t > 15.5$) pycnocline (Ivanov et al., 1998a). Hence, we neglect effects of seasonal variability for the anoxic layer
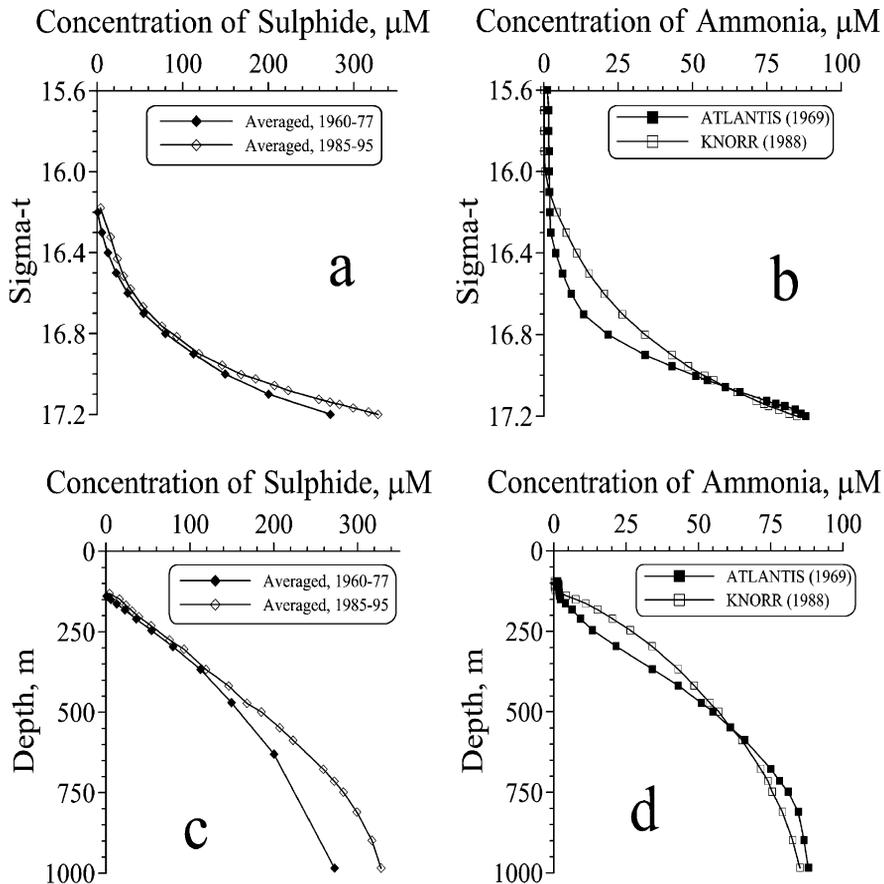

Fig. 1. The average profiles of the distribution of sulphide and ammonia versus density (a, b) and depth (c, d).

and consider that the R.V. ATLANTIS II (1969) and KNORR (1988) ammonia profiles adequately describe average distribution of ammonia in the Black Sea. The average profiles of sulphide (Fig. 1a) were drawn using the data from a number of cruises over the period from early 1960s to late 1970s and from late 1980s to early 1990s. The quality of the data and the reasons of the observed alterations in the basin-average distribution of sulphide and ammonia were discussed by Konovalov and Murray (2001).

The average profiles of ammonia and sulphide versus depth (Fig. 1c–d) were recalculated from the corresponding concentration versus sigma-t profiles using data on the average density stratification drawn from the results of several basin-wide surveys conducted in early 1990s (Ivanov et al., 1998b). The average positions of specific sigma-t surfaces are as follows: 15.80–106, 16.00–118, 16.20–136, 16.30–146, 16.40–165, 16.50–186, 16.60–211, 16.70–247, 16.80–294, 16.90–367, 16.95–412, 17.00–472, 17.05–540, 17.10–630 and 17.20–984 m.

Density stratification in the Black Sea may be considered stationary on a long-term scale (decades to centuries) notwithstanding the concerns of Murray et al. (1989). This assumption is partially confirmed by published data on the balance of salt fluxes in the Bosphorus (Unluata et al., 1990). Hydrographic data do not show any trends for the past 75 years for the pycnocline layer or the near surface layers (Altman and Simonov, 1991; Ivanov et al., 2000). At the same time, climate-driven variability on a decadal scale is a characteristic feature for the Black Sea (Ivanov et al., 2000), and density stratification for certain periods may be quite different. However, as a first-order approximation, we neglect these changes because the range of variations of the chemical structure of the water column is apparently an order of magnitude larger than the range of changes in the density stratification.

Uncertainties in the vertical distribution of sulphide originating from different methods of sampling and a lack of data on ammonia distribution in the deep layer (Konovalov and Murray, 2001) make calculations of fluxes and production/consumption rates of ammonia and sulphide doubtful and limit our analysis to the layer above 1000 m.

2.2. Model

A one-dimensional stationary (steady-state) model of vertical exchange in the Black Sea, based on the solution to the inverse problem for temperature and salinity, with the known inputs for salt and heat (Samodurov and Ivanov, 1998; Ivanov and Samodurov, 2001), has been used to reveal the basin-average vertical distribution of turbulent diffusivity, $k(z)$, and vertical velocity, $w(z)$ (Fig. 2a,b). The latter parameters are needed to calculate fluxes and production/consumption rates.

A detailed description of the model can be found in (Ivanov and Samodurov, 2001). A brief description of basic approaches and assumptions, however, will be given in this paragraph for the sake of completeness. The model suggests the balance of heat, mass of salt and mass of water and takes into account the bottom geothermal heat flux as an additional, in addition to the Bosphorus inflow, source of
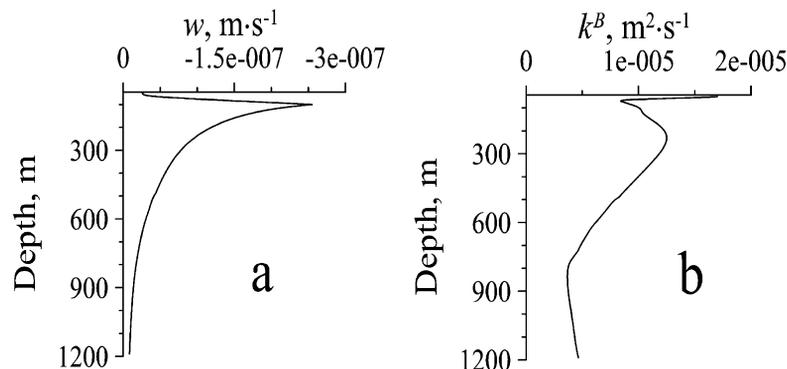

Fig. 2. The profile of the vertical velocity (a) and coefficient of turbulent duffusivity (b) calculated within the framework of the model.

heat for the Black Sea. The uppermost 50-m layer of the sea, where seasonal changes are essential, is excluded from the consideration. The lower boundary of the upper layer, z^*, is thus set at a depth of the upper boundary of the Bosphorus inflow. Since the Black Sea is characterised by steep continental slopes, it is suggested that the boundary mixing processes take place in a basin with the vertical boundaries and plane bottom.

Two different domains are distinguished within the basin, representing (i) the plume and (ii) interior of the basin itself. The plume associated with the inflow is formed due to entrainment of the Black Sea ambient water to the Bosphorus effluent. The volume of the plume is considered small compared with the volume of the interior part of the sea. The influence of the plume on the interior is set in the form of

boundary conditions as a source or sink of water distributed over the vertical. At $z = z^*$ a source of salty and warm water is set describing the Bosphorus undercurrent with the known transport and thermohaline properties. The volume transport, through the principal of continuity, determines vertical velocity in the interior domain. Conditions at the bottom are characterised by the absence of water and salt fluxes across the bottom and by a value of the geothermal heat flux.

In the vertical, the system of the plume and interior consists of three layers. The solution is thus sought for each layer. The conditions of continuity of heat, salt and water fluxes hold at the boundaries between the layers. In the first layer, $z^* \leq z \leq z_0$, where the plume forms, ambient Black Sea waters are entrained to the inflow. The position for z_0 has
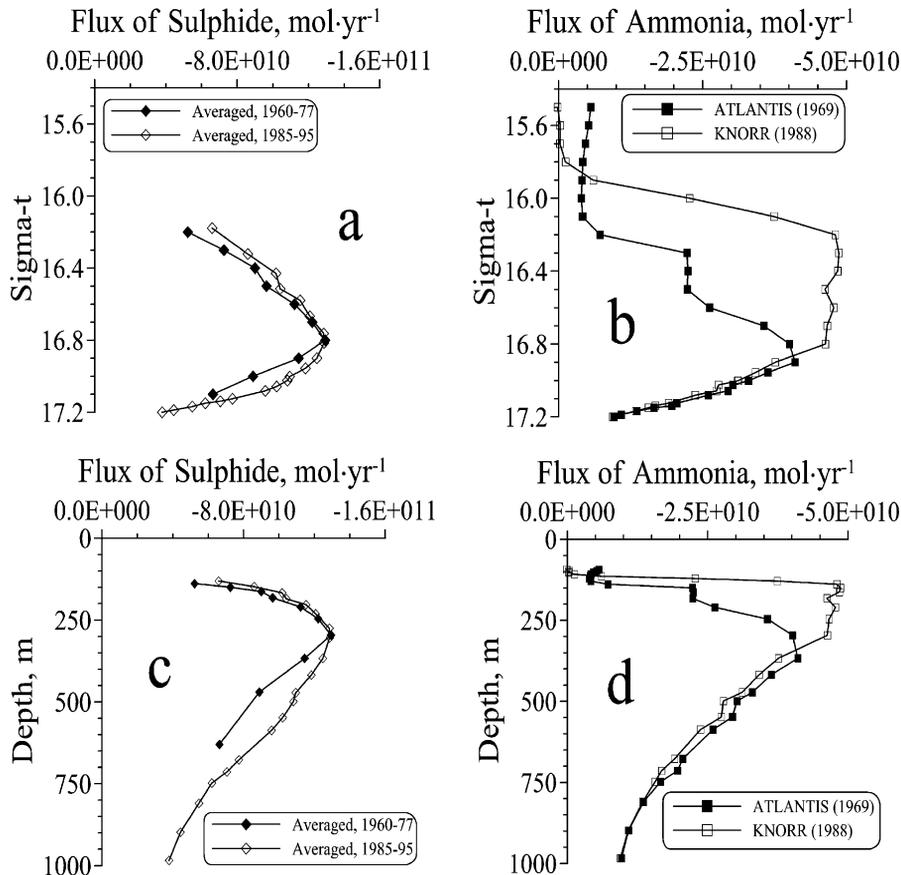

Fig. 3. The flux of sulphide and ammonia versus density (a, b) and depth (c, d).

been selected using T, S data for the past 70 years (Ivanov et al., 2000), which reveal the absence of lateral sources of heat and salt in the depth range 60–100 m (sigma-t $\approx$ 14.9–15.7), and set at 100 m. The inflow thus entrains the cold intermediate water (CIW) rich in oxygen.

The intermediate layer, $z_0 \leq z \leq z_b$, models the layer where the plume disintegrates with the formation of isopycnal intrusions of plume water into Black Sea ambient water. In this layer, the properties are transported from the plume into the interior together with the volume of the plume, $w_z \Delta z$. Redistribution of the volume of the plume over the intermediate layer occurs under an assumption of a linear density distribution in the plume itself.

The third layer, $z_b \leq z \leq z_H$, represents the bottom homogeneous layer (BHL) with the known thermohaline characteristics. A small part of the plume penetrating into BHL is essential to maintain stationarity of the system. It balances the outward flux of salt across the upper BHL boundary. This flux of salt can be calculated with certain accuracy because the exchange across the upper BHL boundary is controlled by double diffusion (Murray et al., 1991; Eremeev et al., 1997).

One-dimensional transport equations for heat and salt are used to describe processes of vertical exchange in the interior domain. The equations are inferred by means of horizontal averaging of the relevant three-dimensional transport equations. The vertical profiles of $w(z)$ and $k(z)$ derived from the model are explicitly non-linear (Fig. 2). The basin-average vertical velocity increases from $w^* = -2.55 \times 10^{-8}$ m s^{-1} at z^* to $w_0 = -2.55 \times 10^{-7}$ m s^{-1}
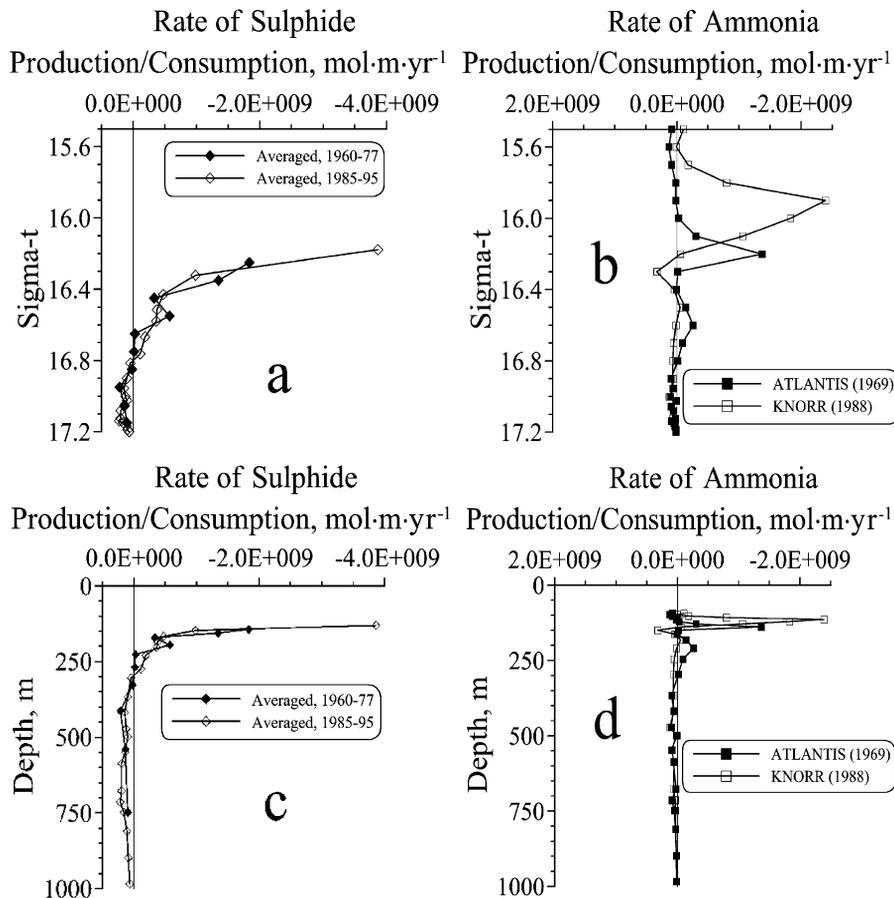

Fig. 4. The rate of production/consumption of sulphide and ammonia versus density (a, b) and depth (c, d).

at z_0 and then declines exponentially to about -6.8×10^{-9} m s^{-1} at z_b (Fig. 2a). There is a minimum in the vertical profile of $k(z)$ at about 70 m and maximum at about 200 m (Fig. 2b).

The results are sensitive to a value of the volume transport of Bosphorus undercurrent. The published values of this estimate varies in a broad range. We used the estimate for q_B ($q_B = 300$ km^3 year^{-1}) published by Unluata et al. (1990) and adopted in western publications. However, Altman and Simonov (1991) summarised published data and estimated the transport of the Bosphorus inflow by the value of 174 to 229 km^3 year^{-1}. If the latter estimates are correct, the vertical velocity and mixing coefficient derived from the model were overestimated. However, the general structures of $w(z)$ and

$k(z)$ does not depend on q_B. As it has been shown in Ivanov and Samodurov (2001) the form of $w(z)$ and $k(z)$ is not sensitive to input parameters, and this is essential for the flux estimates of the solutes. As it will turn out in the next section, the conclusions of the paper are based on the comparison of the form of the profiles of vertical fluxes for sulphide and ammonia rather than on the estimates of the flux values.

Summarising, the applied physical inverse model for the Black Sea provides input parameters for the determination of the upward advective transport, which occurs in the interior part due to the existence of the Bosphorus inflow, and vertical diffusive transport.

The vertical flux of any chemical substance can be calculated from Eq. (1), while the profile of the
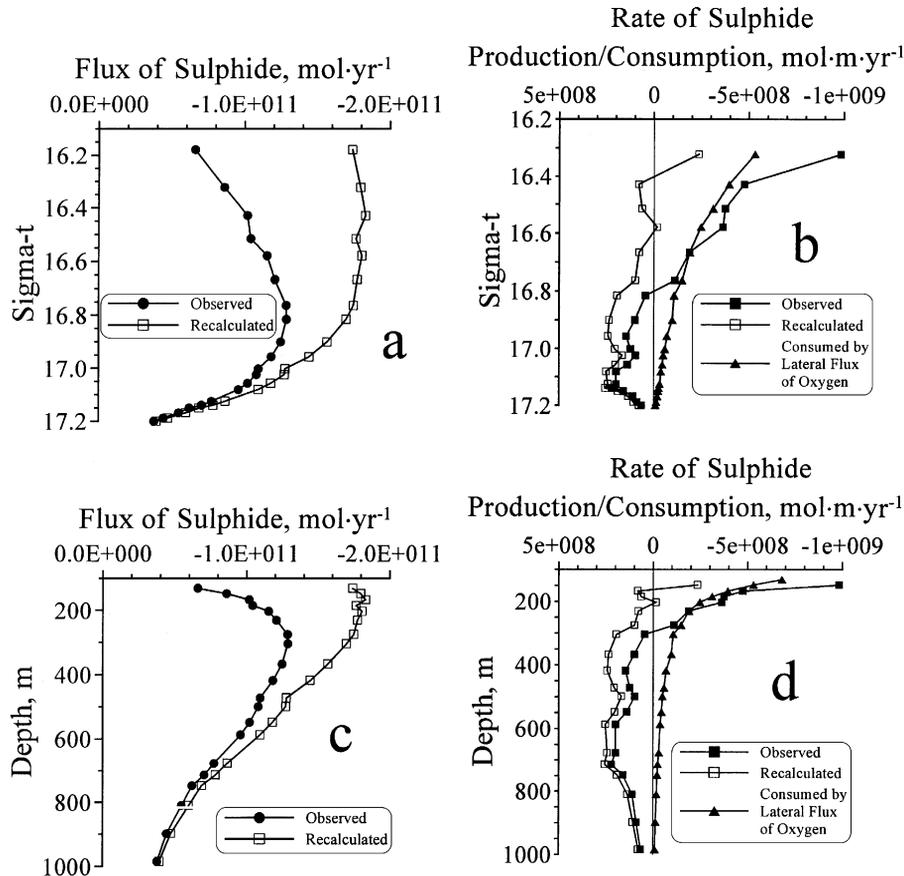
Fig. 5. The flux and production/consumption of sulphide in the 1990s versus density (a, b) and depth (c, d) calculated from the average profiles of sulphide and recalculated with respect to the lateral flux of oxygen.

production/consumption rate can be calculated from Eq. (2).

$$\text{Flux} = -k\frac{\partial C}{\partial z} + wC \qquad (1)$$

$$R = \left(\frac{\partial}{\partial z}\left(-k\frac{\partial C}{\partial z}\right) + w\frac{\partial C}{\partial z}\right) - (C_b - C)\frac{\partial w}{\partial z} \qquad (2)$$

where R is the rate of biogeochemical production/consumption, C_b is the concentration of the analysed substance in plume water and C is the concentration of the same substance in ambient water. The unknown functions, the flux(z) and $R(z)$, are calculated directly from Eqs. (1) and (2) and will be analysed in Section 3. For sulphide and ammonia, $C_b = 0$. For oxygen, C_b is an average concentration for the volume of the Black Sea entrained waters and the Bosphorus inflow. This value appears to be close to 130 μM for the average profile of oxygen from late 1980s to early 1990s.

The vertical axis is directed downward. So, negative values of vertical velocity (Fig. 2a) and fluxes of sulphide and ammonia (Fig. 3) mean that they are directed upward. Negative values of the rate of consumption/production (Fig. 4) mean that the rate of consumption exceeds the rate of production.

The approach suggests that the calculated fluxes for sulphide and ammonia represent "actual" mean fluxes for a period of averaging, contrary to estimates of the rates of production/consumption. The latter are "fictitious" or equilibrium production/consumption rates for a period of averaging since they do not comprise production/consumption that leads to transient increase/decrease in a concentration. This is because, as a general statement, the observed vertical profiles of solutes represent a transient state of the Black Sea.

It is worth mentioning that the vertical distribution of the lateral flux of oxygen (Fig. 5b,d) is consistent with the concepts of Murray et al. (1991) and Ozsoy et al. (1993) and results of Buesseler et al. (1991). The Bosphorus inflow entrains the waters of the Cold Intermediate Layer (CIL), which are enriched with oxygen, and then the major part of the plume is trapped within 500 m of the water column.

3. Results

The average profile of ammonia (Fig. 1b,d) does not exhibit any extremes below the middle part of the pycnocline layer ($\sigma_t \sim 15.5$). Its concentration increases with depth from very low values in the suboxic layer (~ 0.2 μM at $\sigma_t = 15.95$) to ~ 100 μM in the bottom layer. The general shape was the same both for 1969 and 1988 but the depths of rapid increase in ammonia concentration (the ammonia onset) and the average concentrations in the upper part of the anoxic layer were different for these decades. The ammonia onset was located at $\sigma_t = 16.4$ in 1969 and shifted upward to $\sigma_t = 16.0$ in 1988. Concentrations of ammonia also increased in the upper part of the anoxic layer above $\sigma_t = 17.1$. This increase can be easily detected in the figure of the vertical distribution of ammonia published by Sapozhnikov (1990), who plotted data from the R.V. ATLANTIS (1969) and VITYAZ (1988) cruises but did not discuss the difference in these data to any extent. Konovalov and Murray (2001) suggested that the changes in the average profiles of ammonia occurred due to intensive eutrophication that began in the middle 1970s.

The profiles of ammonia flux (Fig. 3b,d) and ammonia production/consumption rates (Fig. 4b,d) are consistent with the commonly accepted hypothesis that production of ammonia occurs through microbial respiration of sinking particulate organic matter. The flux increases from 1000 m towards the onset of sulphide, confirming that production of ammonia occurs throughout the water column. This flux decreases dramatically due to oxidation of ammonia in the suboxic layer. For example, the upward flux of ammonia in 1988 decreased to 2% of its maximum value 30 m above the sulphide onset (Fig. 3d).

The difference between the average distributions of ammonia in the 1960s and 1980s predetermines different profiles of the flux and production/consumption rate (Fig. 3b,d and Fig. 4b,d). Briefly, the depth where the flux of ammonia expired or reached its lowest value was different: $\sigma_t \sim 15.8$ in 1988 and $\sigma_t \sim 16.2$ in 1969 (Fig. 3b). The flux of ammonia reached about the same maximum value of 4.8×10^{10} mol year^{-1} but it occurred at $\sigma_t \sim 16.3$ in 1988 and much lower in 1969. The flux of ammonia decreased

at greater depths in consistency with the idea of its production within the water column. The most prominent changes were observed in the rate of ammonia oxidation. The maximum rate located shallower in 1988 and it was 2.5 times higher than the maximum value in 1969 (Fig. 4b).

Sulphide was considered for a long time as an equivalent of ammonia in terms of production and distribution within the water column. It was assumed that sulphide is produced in the bottom layer (Sorokin, 1982) or in the entire anoxic water column (Lein and Ivanov, 1991) and oxidised at the upper boundary of the anoxic zone ("C-layer") or at the depth of sulphide onset (Volkov et al., 1990; Bezborodov and Eremeev, 1993). The similarity of the profiles of sulphide and ammonia was considered as a confirmation of similar processes governing their production and consumption. However, detailed examination reveals that the vertical profile of sulphide is linear above a depth of 600 m while the profile of ammonia is convex (Fig. 1). Previously, Bezborodov and Eremeev (1993) pointed out that the vertical profile of sulphide is linear above 600 m, but did not suggest an explanation.

The profile of the vertical flux of sulphide (Fig. 3a,c) clearly demonstrates the difference between the cycling of sulphide and ammonia. A decrease in the flux of sulphide commences much deeper than the onset of sulphide. The sulphide flux reaches a maximum value at $\sigma_t \sim 16.8$ (~ 300 m). There is no change in the location of this maximum from the 1960–1970s to 1980–1990s. The flux of sulphide decreases downward below this depth similar to the flux of ammonia. This confirms the results of Lein and Ivanov (1991) pointing out that production of sulphide takes place mainly in the water column above 1000 m. The flux of sulphide at about 300 m is about three times larger than that at 1000 m (Fig. 3c). However, there is a difference between the profiles of the fluxes deeper than $\sigma_t \sim 16.8$ that may reflect temporal changes in the distribution and production of sulphide or changes in sampling technique as discussed by Konovalov and Murray (2001). The value of the maximum flux (Fig. 3a,c) is confirmed by results of calculations based both on the average profiles (Fig. 1a,c) and profiles from specific cruises, like the 1969 R.V. ATLANTIS or 1988 R.V. KNORR cruises. The decrease in the flux of sulphide that

commences about 150 m below the sulphide onset reveals that sulphide is consumed within the anoxic zone rather than at the depth of its onset. Konovalov and Murray (2001) reached the same conclusion by analysing stoichiometry of changes in the distribution of sulphide and ammonia from the 1960s to 1990s. They suggested that the lateral flux of oxygen generated by intrusions of water from the Bosphorus plume is responsible for different behaviour of sulphide and ammonia in the upper part of anoxic zone. The calculated vertical profile of this flux of oxygen (Fig. 5b,d) demonstrates an "exponential" decrease of this source of oxygen with depth. This confirms that oxidation of sulphide inside the upper anoxic zone should result in the registered non-conservative behaviour of sulphide and shift of the maximum flux of sulphide from the onset of sulphide to the deeper layer (Fig. 3a,c).

The upward flux of sulphide in the vicinity of the onset of sulphide ($\sigma_t = 16.2$) was equal to $\sim 6.9 \times 10^{10}$ mol year^{-1} for the 1990s and $\sim 5.2 \times 10^{10}$ mol year^{-1} for the 1960s (Fig. 3a,c). This is the amount of sulphide supposedly to be oxidised in the suboxic zone. The maximum flux of sulphide is close to 12.9×10^{10} mol year^{-1} at $\sigma_t \sim 16.8$ (Fig. 3a), which is about 2 to 2.5 times higher than that value. This suggests that 50% to 70% of sulphide production is oxidised inside the anoxic layer rather than at the depth of sulphide onset.

The data in Fig. 3a suggest an insignificant increase in the flux of sulphide at every depth shallower than $\sigma_t \sim 16.8$ from the 1960s to 1990s. The similar increase in the flux of ammonia (Fig. 3b) is prominent. Unlike for ammonia, consumption of sulphide exceeds its production in a thick layer. As a result, temporal variations in the rate of sulphide consumption are less evident than changes in the rate of ammonia oxidation from the 1960s to 1990s (Fig. 4).

4. Discussion

The vertical profiles of the flux confirm the biogenic origin of sulphide through anaerobic respiration of sinking particulate organic matter (POM). An increase in the flux (Fig. 3) and consumption/production rates (Fig. 4) takes place at the same depths

for both ammonia and sulphide, suggesting these substances are linked through common reaction (Eq. (3)). In addition, the maximum upward flux of sulphide is equal to 12.9×10^{10} mol year^{-1} at $\sigma_t = 16.8$ and the flux of ammonia is equal to 4.6×10^{10} mol year^{-1} at the same depth. The ratio of these fluxes is 0.36, which is within 20% of the 0.3 (16/53) value expected from Eq. (3), assuming the absence of biogeochemical transformations of ammonia and sulphide in the anoxic layer.

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 53SO_4^{2-}$$

$$= 106HCO_3^- + 53H_2S + 16NH_3 + H_3PO_4 \quad (3)$$
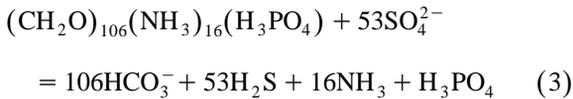
Analysing the profiles of the flux and consumption/production rates of ammonia and sulphide, we get a picture that is different from a usually accepted hypothesis on cycling and budget of these substances. Production of ammonia in the anoxic zone and its consumption in the vicinity of the onset of sulphide (Fig. 4) appear to be the main processes responsible for ammonia cycling in the anoxic zone. The flux of sulphide at the depth of sulphide onset was less than 30% to 50% of the maximum values in the 1960 and 1990s.

Murray et al. (1995) calculated the red-ox budget of the suboxic zone and found that the downward flux of oxygen at the depth of sulphide onset did not exceed 10% of the needed value to balance the upward flux of sulphide. To explain this phenomena, they suggested a complex red-ox process based on oxidation and reduction of manganese. Volkov (personal communication) investigated cycling of manganese in the oxic/anoxic transition zone of the Black Sea and estimated that the flux of manganese could be responsible for oxidation of about 25% of sulphide flux at the depth of sulphide onset. In addition, we suggest that the lateral flux of oxygen originating from the Bosphorus plume is responsible for oxidation of a significant portion of sulphide production inside the anoxic zone.

Assuming the lateral flux of oxygen is consumed for oxidation of sulphide (Fig. 5), one can correct or recalculate the sulphide flux (Fig. 5a,c) and rate of sulphide production (Fig. 5b,d) by increasing the values of sulphide production over the anoxic layer proportionally to the lateral flux of oxygen. The

major difference between the original and corrected values of sulphide production is that the corrected profile (Fig. 5c) reveals production of sulphide throughout the anoxic zone. The corrected consumption of sulphide exceeds its production only in the vicinity of the onset of sulphide, exactly as for ammonia. This result demonstrates the importance of the lateral flux of oxygen in the Black Sea. The lateral flux of oxygen oxidises from 50% to 70% of the total sulphide produced in the anoxic layer. The amount of oxygen penetrating into shallower layers of the main pycnocline exponentially increases opposing upward excursion of the onset of sulphide.

The ratio of the fluxes of ammonia to sulphide (Fig. 6) is another indication of the deficiency in sulphide in the upper part of the anoxic zone. This ratio is twice the expected value at the depth of sulphide onset and decreases to 0.3 at the depth of $\sigma_t = 16.9$, where the lateral flux of oxygen decreases more than 10-fold relative to the flux at the depth of sulphide onset. The usage of the corrected values of the flux of sulphide (Fig. 5a,c) shifts the ratio of the fluxes of ammonia to sulphide much closer to the expected value. Essentially, this profile does not differ from the expected value (0.3) (Fig. 6), keeping in mind the accuracy of the discussed estimates.
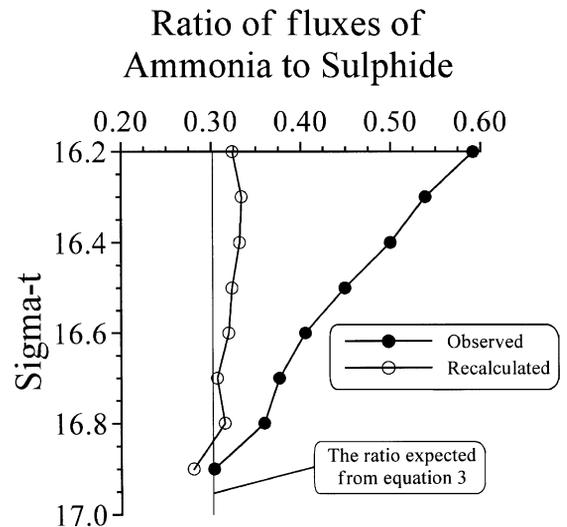

Fig. 6. The ratio of the flux of ammonia to the flux of sulphide derived from the observed distribution of sulphide and to recalculated flux of sulphide in the 1990s.

The corrected rate of sulphide consumption was equal to 18×10^{10} mol year^{-1} in the 1980–1990s and 21×10^{10} mol year^{-1} in the 1960–1970s. The sulphide profile, namely the vertical gradient of sulphide that determines the diffusive flux, did not change much over the 30-year period. The values of the calculated fluxes appeared to be similar, but oxidising capacity of the plume was higher in the 1960–1970s, owing to higher oxygen content in waters entrained to the inflow (Konovalov and Murray, 2001). For a steady-state, the rate of consumption equals the rate of production. These equilibrium production rates for the 1960–1970s and 1980–1990s differed by only 15%.

The equilibrium production below 1000 m is 4×10^{10} mol year^{-1}, and is about 20% of the total equilibrium production. The result that most of the production of sulphide occurs above 1000 m is not surprising. Lein and Ivanov (1991) reported that there was more intensive sulphate reduction in the upper part of the anoxic zone. The exponential decrease in the flux of sinking POM (Karl and Knauer, 1991) also suggests more intensive production of sulphide in the upper part of anoxic layer. Interestingly, Albert et al. (1995) demonstrated that: (i) the rate of sulphide production reached a maximum in the upper part of the anoxic layer and decreased dramatically in the deeper layers; (ii) the total production of sulphide in the water column was $\sim 12 \times 10^{10}$ mol year^{-1}; and (iii) there was a local minimum of the rate of sulphide production in the layer from 400 to 500 m. While data of these publications are in agreement with the results of this work, as far as the results of a model based on decade-averaged profiles can be in agreement with results of observations for individual stations, the local extremes in the profile of sulphide production (Fig. 5b,d) suggest that the hypothesis on an exponential decrease of the rate of sulphide production with depth implies a very approximate description of the occurring processes.

The equilibrium sulphide production derived from the model can be compared with the estimates of actual production derived from the data on primary production (Sorokin, 1962; Sorokin, 1964; Vedernikov and Demidov, 1997; Stelmakh et al., 1998), rate of sulphate reduction (Sorokin, 1982; Lein and Ivanov, 1991; Albert et al., 1995), flux of POM into the anoxic zone (Deuser, 1971; Karl and Knauer,

1991; Muramoto et al., 1991) and temporal variations in the distribution of sulphide and ammonia (Konovalov et al., 1999; Konovalov and Murray, 2001).

In the 1980–1990s, the rate of sulphide production derived from the POM flux ($(18–20) \times 10^{10}$ mol year^{-1}) appears to be very close to the estimate given here, 18×10^{10} mol year^{-1}. The data on primary production ($(35–65) \times 10^{10}$ mol year^{-1}) and the rate of sulphate reduction ($(62–78) \times 10^{10}$ mol year^{-1}), however, suggest that the observed production exceeded the equilibrium production by a factor of 2 to 4. Similarly, Konovalov and Murray (2001) used temporal trends in the data to show that the annual production of sulphide increased by $(19–32) \times 10^{10}$ mol year^{-1} from the 1960s to 1990s.

The published values of sulphide production in the 1960s (reviewed in Konovalov and Murray, 2001) did not exceed the calculated rate of the equilibrium sulphide production (21×10^{10} mol year^{-1}). The annual sulphide production was calculated as $(12–17) \times 10^{10}$ mol year^{-1} from the rate of primary production, $(12–24) \times 10^{10}$ mol year^{-1} from the rate of sulphate reduction and 12×10^{10} mol year^{-1} from the flux of sinking POM. The sulphide production in the 1960s was equal to or slightly lower than its equilibrium production derived from the average profile. Altogether, these data suggest that the anoxic zone was at steady-state or was even experiencing a slow decrease in the inventory of sulphide in the 1960s. The period of the 1980–1990s was essentially non-stationary, and the inventory of sulphide was increasing.

Another issue to be addressed is the possible rate of change in the distribution of sulphide. The increase in the average concentrations of sulphide above 1000 m detected from the most precise data of the period from 1985 to 1995 was estimated by a value of 0.5% a year (Konovalov et al., 1999). On the other hand, the sulphide production in the same layer calculated in this work is equal to 14×10^{10} mol year^{-1} and the inventory of sulphide is close to 5000×10^{10} mol. It suggests an increase in the inventory of sulphide of 0.56–0.84% a year provided by the actual rate of sulphide production increased three to four times. These estimates are in good agreement and demonstrate that prominent changes in the distribution of sulphide are possible on the

time scale of decades to centuries because the ratio of the inventory of sulphide to its annual production appears to be a very large value.

5. Conclusions

The lateral flux of oxygen plays an extremely important role in the budget of sulphide in the Black Sea. This flux of oxygen is responsible for oxidation of 50% to 70% of total sulphide consumed in the Black Sea. The lateral flux of oxygen exponentially changes approaching the oxic–anoxic interface and probably plays a significant role in determining the position of sulphide onset. For this reason, the observed shoaling of the ammonia profile was more prominent than for sulphide. The lateral flux of oxygen is the main explanation for the different behaviour of ammonia and sulphide in the upper part of the anoxic zone. The distribution of ammonia is consistent with the commonly accepted hypothesis of its production throughout the anoxic zone and oxidation in the vicinity of the onset of sulphide. Sulphide is also produced throughout the anoxic layer but is oxidised extensively in the upper $\sim$ 150-m layer of the anoxic zone. Oxidation of sulphide inside the anoxic zone changes the ratio of ammonia to sulphide fluxes considerably. The ratio increases towards the depth of sulphide onset. The ratio of ammonia to sulphide fluxes in the deeper layer, where the lateral flux of oxygen is small, differs by less than 20% from the expected ratio, confirming biogenic origin of ammonia and sulphide in the anoxic zone.

The equilibrium production of sulphide changed by about 15% from the 1960–1970s to the 1980–1990s. The rate of sulphide production derived from the data on the rate of primary production, sulphate reduction, ammonia oxidation and the flux of sinking POM was close to the equilibrium production of sulphide in the 1960s, but supposedly increased from the 1960s to 1990s. This figure suggests that the distribution of sulphide was at a steady-state in the 1960s, but it was essentially non-stationary in the 1980–1990s. An increase in the inventory of sulphide took place in the 1980–1990s and is confirmed by other publications.

The possible rate of increase in the average concentrations of sulphide is estimated to be 0.56–0.84% per year for the layer above 1000 m. It suggests a small change in the vertical profile of sulphide because the ratio of the inventory of sulphide to its production is very high.

The comparison of the estimated sulphide consumption rates for the conditions of the 1960–1970s and 1980–1990s allows drawing a conclusion that the equilibrium production of sulphide in the Black Sea is about 20×10^{10} mol year^{-1} for present conditions. The actual production of sulphide should be decreased to this level to alter the tendency on the on-going transition of the Black Sea to a state with a higher anoxic/oxic ratio.

Acknowledgements

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