

Oxygen, nitrogen and sulphide fluxes in the Black Sea

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Manuscript received: 19 August 1999; accepted in revised form: 27 April 2000

Abstract

The fluxes and production/consumption rates of oxygen, nitrate, ammonium and sulphide are estimated in the paper utilising results of the 1.5-dimensional stationary model of vertical exchange in the Black Sea (SAMODUROV & IVANOV, 1998). The profiles of the vertical flux and rate of production/consumption of these substances have revealed a number of intriguing features in the biogeochemical nature of the Black Sea. An approximate redox balance of the counter-fluxes of nitrate and ammonium into the sub-oxic zone has been revealed confirming that intensive denitrification may be the primary loss of nitrogen in the Black Sea. A low ratio of the nitrate stock to the flux of nitrate from the oxycline confirms the possibility of prominent changes in the distribution of nitrate on the time scale of a year. The ratio of the nitrate to oxygen vertical flux has revealed a lack of nitrate in the oxycline above the nitrate maximum. The lateral (related to the "Bosporus plume") flux of oxygen in the layer of the main pycnocline appears to be very important for the existing biogeochemical structure of the Black sea water column being the reason of sulphide consumption inside the anoxic zone and changes in the ammonium-sulphide stoichiometry of the anoxic zone, the primary reason of the existence of the sub-oxic layer and the basic reason of relative stability of the sulphide onset.

Keywords: Black Sea, Flux, Oxygen, Nitrogen, Sulphide.

Introduction

The presence of the anoxic layer that occupies over 90% of the Black Sea waters (SKOPINTSEV, 1975) is the main reason of the strong theoretical and practical interest to various questions on the balance and budget of oxygen and sulphide in this basin. Interestingly, discussing the possibility of notable changes in the depth of sulphide onset during recent decades (BEZBORODOV *et al.*, 1993; SKOPINTSEV, 1975; SOROKIN,

1982), oceanographers have never considered a hypothesis that would a *priori* assumed that the existing oxygen/sulphide balance can be destroyed in a decade. The reason of the observed changes in the sulphide onset has been related to the processes that might be responsible for changes in the water budget (MURRAY *et al.*, 1989; BEZBORODOV *et al.*, 1993; KONOVALOV *et al.*, 1999). The existing balance of oxygen and sulphide has

been assumed as the result of the Black Sea evolution over the last 5 to 7 thousand years (SKOPINTSEV, 1975; BEZBO-RODOV *et al.*, 1993). In this manner, any conspicuous changes in the distribution of oxygen and sulphide are expected to occur on a millenium scale. The redox balance is usually assumed to calculate the budget of sulphide by adjusting the amount of its production and consumption in the Black Sea (BEZBORODOV *et al.*, 1993). This method is based on the measurements of sulphide production (SOROKIN, 1982; LEIN *et al.*, 1991) and oxidation (MILLERO, 1991) rates. The approach suffers from various analytical difficulties that cause very big uncertainty (BEZBORODOV *et al.*, 1993; SOROKIN, 1982). BEZBORODOV *et al.* (1993) assumed 100% of the actual value to be the real error. Besides, this method usually does not take into consideration other basic elements like nitrogen, for example, obviously related to the budget of sulphide and oxygen. Calculations and analysis of the fluxes of the basic elements throughout the water column have never been performed before in spite of the fact that these fluxes primarily reflect the sulphide budget and form the existing biogeochemical structure. The reason is that average profiles of oxygen, sulphide and other substances can be plotted and digitised precisely, but the needed vertical profiles of the vertical diffusion coefficient and vertical velocity have not been available until recently (SAMODUROV & IVANOV, 1998). This work is aimed to calculate fluxes of oxygen, sulphide, nitrate and ammonia through a combination of the most precise data on the distribution of these properties in the Black Sea with the newly published data on the vertical diffusion coefficient and vertical velocity (SAMODUROV & IVANOV, 1998).

The presumed balance of oxygen and sulphide is mainly based on the hypothesis of the mass balance (SKOPINTSEV, 1975). The balance for heat and salt in the Black Sea

has never been actually proved, but it is implicitly supported by the data on the water flux through the Bosphorus and fresh water loads, (SKOPINTSEV, 1975). This balance seems to be feasible because of the long evolution of the Black Sea and slow changes in the mass, salt and heat fluxes. That is not true for basic biogeochemical properties of the Black Sea because their budgets depend on the intensity of primary biological processes. These processes demonstrate a dramatic increase in their intensity. The primary production in the central part of the sea has increased by a factor of 3 to 4 over the last 30 years (SOROKIN, 1962; SOROKIN, 1964; STELMAKH *et al.*, 1998). From this fact, one can reach a conclusion on an increase in the "export" production and in the flux of sinking particulate organic matter (POM) into the anoxic layer of the Black Sea. In turn, that should cause an increase in the sulphide production, as well as in the inventory of other basic elements, such as carbon dioxide, ammonium, phosphate and silica. Keeping in mind that the rate of sinking POM is on the order of hundred meters per day (LORENZEN, 1983) the possibility of fast changes in the budget and in basic chemical structure throughout the water column seems to be plausible. This appears to be intriguing when the data on the prominent temporal changes of the basic biogeochemical structure (KONOVALOV *et al.*, in press), including oxygen, sulphide, nitrate and ammonia, are compared with the commonly accepted hypothesis on the steady oxygen/sulphide balance in the Black Sea. For this reason, the question on the budget and possible changes in the budget of basic biogeochemical properties has turned to be very important. However, before the entire budget of the basic biogeochemical properties, of oxygen, sulphide and nitrogen, in particular, will be reconstructed in its complexity, the possibility to calculate fluxes of these elements for individual layers of

water, as well as their production and consumption rates, is extremely important and fruitful. This work presents an attempt to calculate the oxygen, nitrogen and sulphide fluxes in and beneath the main pycnocline of the Black Sea, to reveal the intensity of production and consumption rates of these elements in specific layers and to gain insight into the nature of the sulphur, nitrogen and oxygen cycling in the Black Sea.

Materials and Methods

Data

Average vertical profiles of oxygen and sulphide (Fig.1a) were obtained by fitting

the data from a number of cruises that were carried out in the Black Sea from the late 1980's to middle 1990's. Namely, data of KNORR cruise (1988) and 11 cruises carried out by the Marine Hydrophysical Institute from 1990 to 1995 were used to calculate the averaged profiles. These cruises provided data for the most typical weather conditions of the annual cycle. A typical cruise stations network covered the Black Sea on a grid of 20x20 nautical miles. Keeping in mind that oxygen data below the middle pycnocline ($\sigma_t=15.5$) suffered from systematic errors until the early 1990's, only the latest high quality data from the basin wide international cruises were used to calculate the average profile of oxygen in the

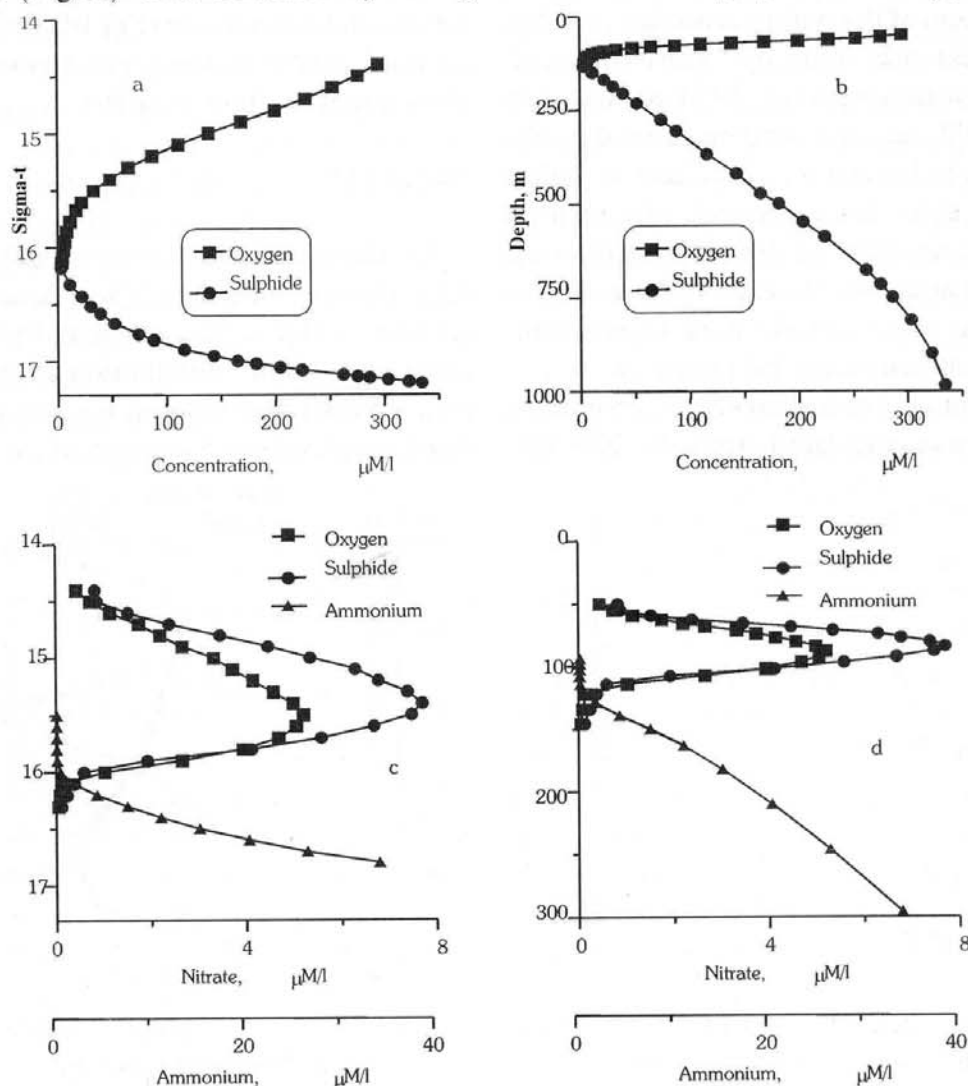


Fig. 1: Average profiles of oxygen, sulphide, nitrate and ammonium in the Black Sea water column versus sigma-t (a and c) and versus depth (b and d).

vicinity and inside the suboxic zone. The number of measurements usually exceeded several thousand for every parameter and was enough to filter short-term and spatial variations in distribution of these properties. Basic questions of data quality (precision, reproducibility and resolution) were discussed in (IVANOV *et al.*, 1998a). Random errors for the chemical properties have never exceeded 10 per cent. These data are of the best available quality and, even if not sufficient for some kinds of analysis, estimates of the fluxes and rates based on these data are less uncertain than the existing estimates of the *in situ* sulphide production or flux of sinking POM. Sigma-t scale was used to diminish the effect of spatial variability in the position of the main pycnocline as it had been previously done by CODISPOTI *et al.*, 1991; VINOGRADOV *et al.*, 1990; KONOVALOV *et al.*, 1997; etc. The average vertical profile of sigma-t (Fig.2a) was obtained by fitting the data from the basin wide international cruises from 1990 to 1993 (IVANOV *et al.*, 1998a). Latter, the average vertical profiles of oxygen and sulphide were drawn using the data of Figure 1a and Figure 2a.

The average vertical profile of ammonium (Fig.1c) was calculated from the KNORR

cruise (1988) data set. No other data on the ammonium distribution in the Black Sea were available for the last decade. Fortunately, the profile of ammonium for the layer below $\sigma_t = 16.0$ does not exhibit any noticeable seasonal variations. Hence, this profile (Fig.1c) may be considered as a good estimate of the average distribution of ammonium in the Black Sea.

Two average profiles of nitrate (Fig.1c) were calculated using the data of the KNORR cruise and data collected in the 1990's. These profiles differ in maximum values of nitrate concentration due to conspicuous seasonal and intra-annual variability (CODISPOTI *et al.*, 1991; KONOVALOV, 1994). The average vertical profiles of nitrate and ammonium (Fig.1d) were reconstructed exactly in the same manner as for oxygen and sulphide (Fig.1b).

The model

1.5-dimensional stationary model of vertical exchange in the Black Sea, based on the solution of the inverse problem for temperature and salinity distribution in the Black Sea, with the known input for salt and heat, (look for details in SAMODUROV & IVANOV,

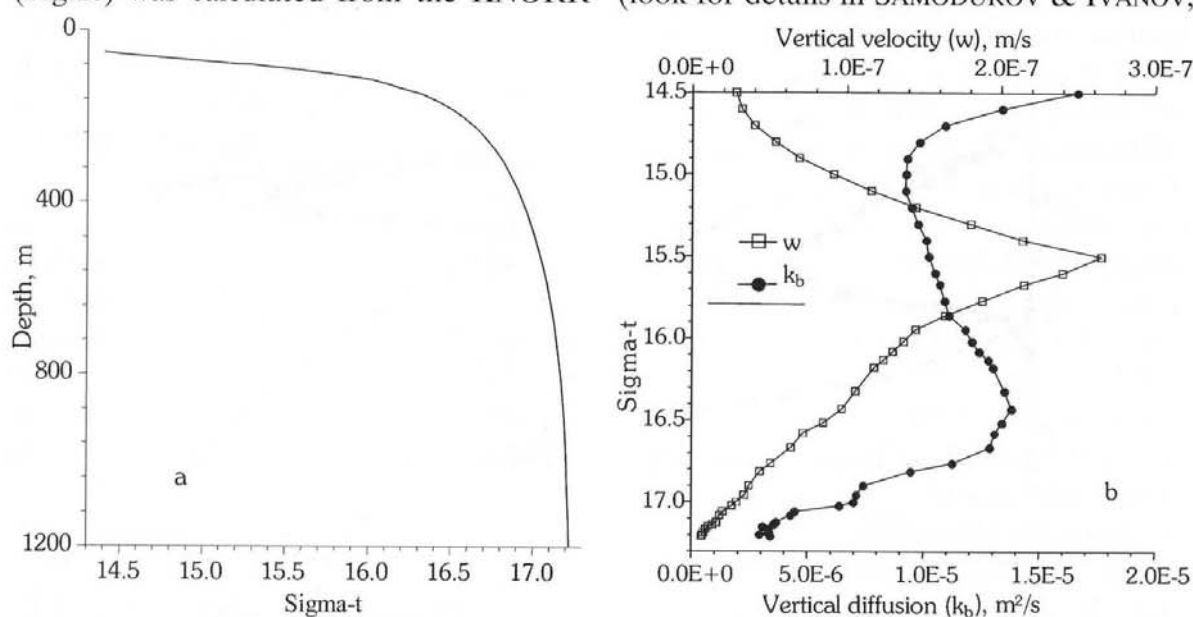


Fig. 2: The average profile of the density (a) and of the vertical diffusion coefficient and vertical advective velocity (b) in the Black Sea water column.

1998) has been used to calculate the mean profiles of diffusion coefficient and vertical velocity (Fig.2b). The hypothesis of stationarity in regard to hydrological conditions seems to be reasonable at least for the salt and water budgets because the in-flux and out-flux of salt through the Bosphorus strait are well-balanced (UNLUATA *et al.*, 1990) and no notable trends in the sea level are observed (AL'TMAN *et al.*, 1991). Being applied to calculate the fluxes of biogeochemical substances, the model has no influence on the thermohaline structure of the Black Sea water column. The model simulates entrainment of the Black Sea waters to the Mediterranean inflow at the stage of the "Bosphorus plume" formation and diffusion of the plume through the formation of isopycnal intrusions within the ambient waters starting from a certain depth level (Fig.3a). This scheme fits recently obtained data on ventilation of the Black Sea pycnocline and anoxic layer (BUESSELER *et al.*, 1991; MURRAY *et al.*, 1991; OZSOY *et al.*, 1993; IVANOV *et al.*, 1998b). It also agrees with other models of ventilation of the Black Sea waters (LEE *et al.*, 1999). The effective residence times for different layers derived from this model and from the box

model published by LEE *et al.* (1999), which is calibrated using data on chlorofluoromethanes, appear to be quite close (Fig.3b). It is worth mentioning that the applied model reveals that the main part of the "Bosphorus plume" is trapped in the layer of the main pycnocline flushing mainly the upper 500 m layer of the sea. A small fraction of the plume reaches the bottom layer stabilising the benthic homogeneous layer. This makes a difference between this and other models (SKOPINTSEV, 1975; BOUDREAU *et al.*, 1989), which predominantly assumed flushing of the bottom layer. An important premise that needs to be outlined from the very beginning is related to the origin of oxygen fluxes. We distinguish between the vertical flux (the sum of diffusive and advective components) and lateral flux that occurs due to penetration of oxygenated water of the plume into the ambient waters of the pycnocline. The process of the formation of the "Bosphorus plume" means entrainment of the Black Sea waters with rather high oxygen concentrations. The "Bosphorus plume" that is a mixture of 3.3 (MURRAY *et al.*, 1991) or 7 - 11 (BUESSELER *et al.*, 1991) to 10 (SAMODUROV & IVANOV, 1998) parts of the Black Sea water per one

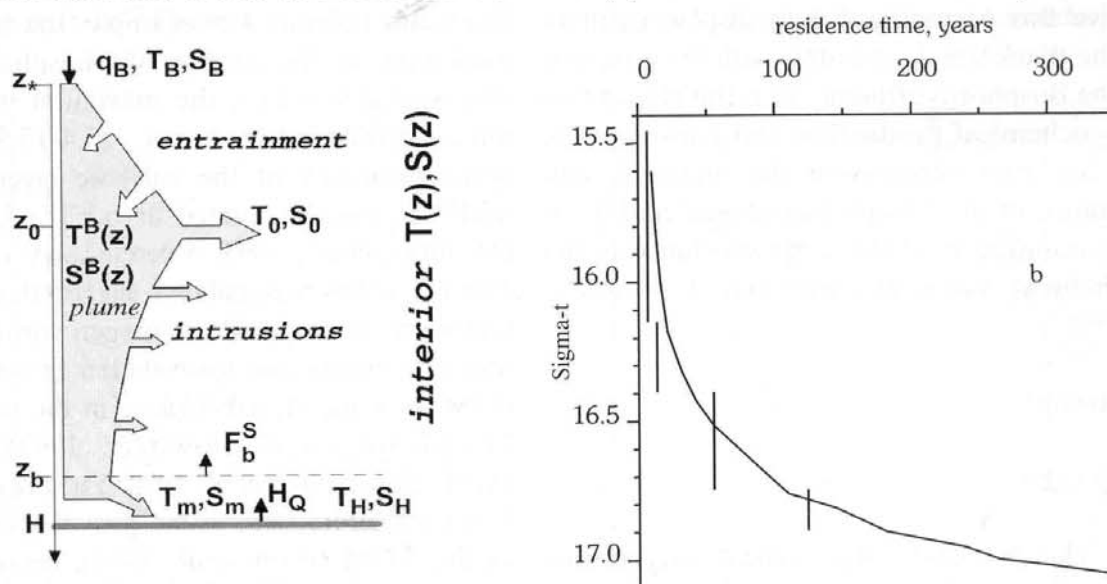


Fig. 3: The scheme of evolution of the Bosphorus plume (reproduced from SAMODUROV & IVANOV, 1998) (a) and the effective residence time for water at different depths of the Black Sea (b) derived from the applied model (solid line) and from the model of LEE *et al.*, 1999 (vertical bars).

part of the Mediterranean water should contain oxygen on the order of about hundred micromoles per litre. Considering 300 km³ per year to be an optimal estimate of the water influx (OZSOY *et al.*, 1995) the total volume of the "Bosphorus plume" equals about 2,000 to 3,000 km³ per year. Being trapped in the layer of the main pycnocline, these waters are responsible for the lateral flux of oxygen. It seems plausible, and that will be estimated quantitatively below, that this lateral flux of oxygen, which has always been ignored, plays an important role in oxygen/sulphide interaction and, consequently, in the sulphide budget.

The vertical flux of any of the considered substances has been calculated from Equation 1, while the profile of the production/consumption rate has been derived from Equation 2.

$$\text{Total Flux} = -k \frac{\partial C}{\partial z} + w C \quad (1)$$

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

where k is the vertical diffusion coefficient and $-k \frac{\partial C}{\partial z}$ is the diffusive flux, w is the vertical velocity and, hence, $w C$ is the advective flux occurring due to displacement of the Black Sea deep waters with the waters of the Bosphorus effluent, R is the rate of biogeochemical production and consumption, C_b is concentration of the analysed substance in the "Bosphorus plume" and C is concentration of the same substance in the ambient water (SAMODUROV & IVANOV, 1998.)

Results

Oxygen

The profile of the vertical oxygen flux (Fig.4a) and oxygen consumption rate (Fig.4b) is consistent with the average profile of oxygen (Fig.1a) and the profiles of the

vertical diffusion coefficient and vertical velocity (Fig.2b). The advective flux is always directed upward (negative values) and it reveals a broad maximum at the depth of the core of the main pycnocline, where the regime of entrainment is changed for the regime of the formation of isopycnal intrusions. The diffusive flux of oxygen (Fig.4a) is directed downward and exceeds the vertical advective flux 8 to 10 times. For this particular reason, the profile of the total vertical flux of oxygen appears to be very close in the form and values to the profile of its diffusive flux. The maximum value at $\sigma_t=14.8$ is the result of very high vertical gradient of oxygen in this layer of water. The first derivative of the total vertical flux with respect to depth is an estimate of the rate of production and consumption of oxygen (Fig.4b). It demonstrates the presence of two different layers. The rate of production exceeds the rate of consumption above $\sigma_t=14.8$ but oxygen is predominantly consumed beneath $\sigma_t=14.8$. It is worth mentioning that the negative extreme of the oxygen production/consumption rate appears at $\sigma_t=15.1$ (Fig.4b). This sigma-t value does not correspond to any of the known features of the biogeochemical structure of the Black Sea water column. For example, the upper maximum in the profile of phosphate is observed at $\sigma_t=15.5$, the maximum in the nitrate profile is found at $\sigma_t \sim 15.4-15.5$, the upper boundary of the sub-oxic layer (10 mM/l) is usually situated at $\sigma_t=15.65$, etc. (MURRAY *et al.*, 1995, VINOGRADOV *et al.*, 1990). It is thus reasonable to suggest that this maximum in the profile of oxygen consumption rate occurs due to oxidation of sinking POM, as it usually takes place in the ocean. Indeed, oxygen (KONOVALOV, 1997) and POM (BURLAKOVA *et al.*, 1992; YILMAZ *et al.*, 1998) concentrations, as well as the flux of sinking POM (KARL *et al.*, 1991), decreases dramatically from the lower part of the euphotic layer to the upper part of the anoxic zone. This should cause relevant decrease in

the rate of oxygen consumption. On the other hand, the revealed decrease in the oxygen consumption rate above $\sigma_t=15.1$ is apparently the result of production of oxygen that overcomes its consumption in the euphotic layer.

The lateral flux of oxygen is proportional to the volume entrained from or trapped in an individual layer. This flux appears to be a "sink" of oxygen above $\sigma_t \sim 15.5$ and a "source" of it in the deeper layers (Fig.3a). By definition, this flux of oxygen equals an additional consumption / production of oxygen in a specific layer of water. The fraction of the total oxygen flux into the sub-oxic layer determined by the lateral flux increases with increasing depth reaching 100 per cent at the sulphide onset. Keeping in mind that the vertical flux of oxygen becomes negligibly small few meters above the anoxic zone (MURRAY *et al.*, 1995), the lateral flux of oxygen appears to be a unique and extremely important source of oxygen for the anoxic zone. Indeed, the vertical flux of oxygen at the upper boundary of the sub-oxic zone ($\sigma_t \sim 15.85$ in the 1990's) does not exceed $5 \cdot 10^{10}$ M/year. Assuming that this flux of oxygen is specifically spent for oxidation of sulphide one can see that it is only a small part of the lateral flux of oxygen into anoxic zone, which is about $25 \cdot 10^{10}$ M/year.

Nitrate

The profiles of the advective, diffusive and total vertical fluxes of nitrate (Fig.5a) reveal the main features that match an expected picture based on distribution of nitrate (Fig.1c). Since maximum concentration is at $\sigma_t \sim 15.6$, the diffusive flux is directed upwards above $\sigma_t \sim 15.6$ and it is directed downwards below this density level (Fig.5a), and the vertical advective flux reaches maximum at $\sigma_t \sim 15.5$ (Fig.5a). A slight upward shift in the position of the extreme in the advective flux is due to the profile of the vertical velocity. Unlike the diffusive flux, the advective flux is directed upward throughout the water column. The ratio of the vertical advective to diffusive flux of nitrate is much higher than the same ratio for oxygen. As the result, the vertical advective flux plays an important role increasing the total flux of nitrate above $\sigma_t = 15.6$, but diminishing it beneath $\sigma_t = 15.6$ and shifting the layer of "zero-flux" from $\sigma_t = 15.5$ to 15.7 (Fig.5a).

While the data on vertical diffusive, advective and total fluxes of nitrate (Fig.5a) primarily confirm the expected scheme of nitrate fluxes in the pycnocline, the first derivative of the total vertical flux (Fig.5b) that is an estimate of production / consump-

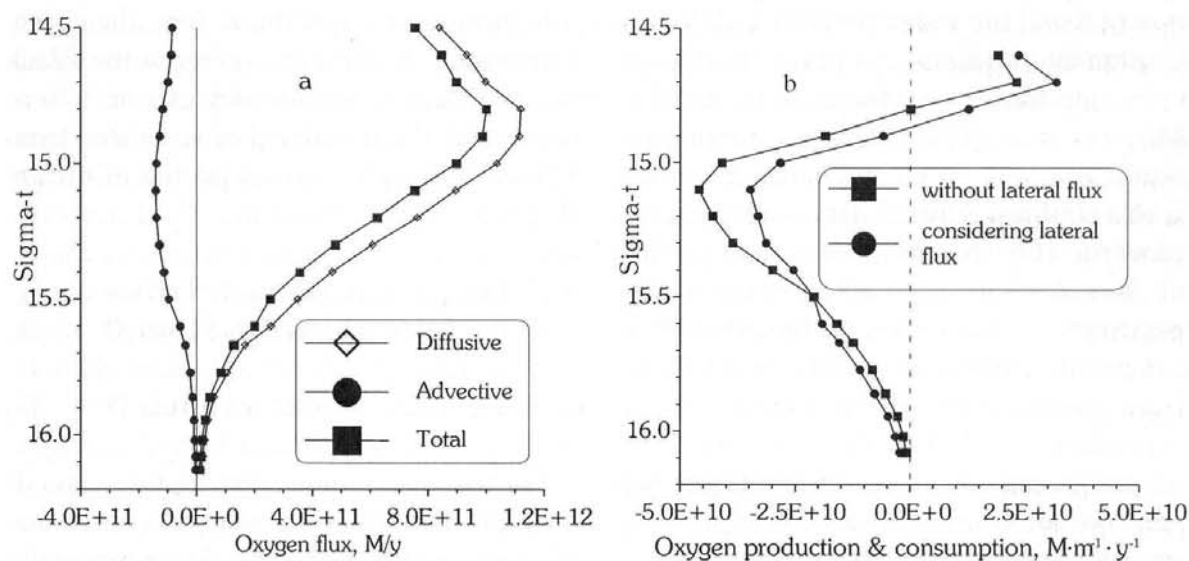


Fig. 4: The profiles of the vertical oxygen flux (a) and oxygen consumption rate (b).

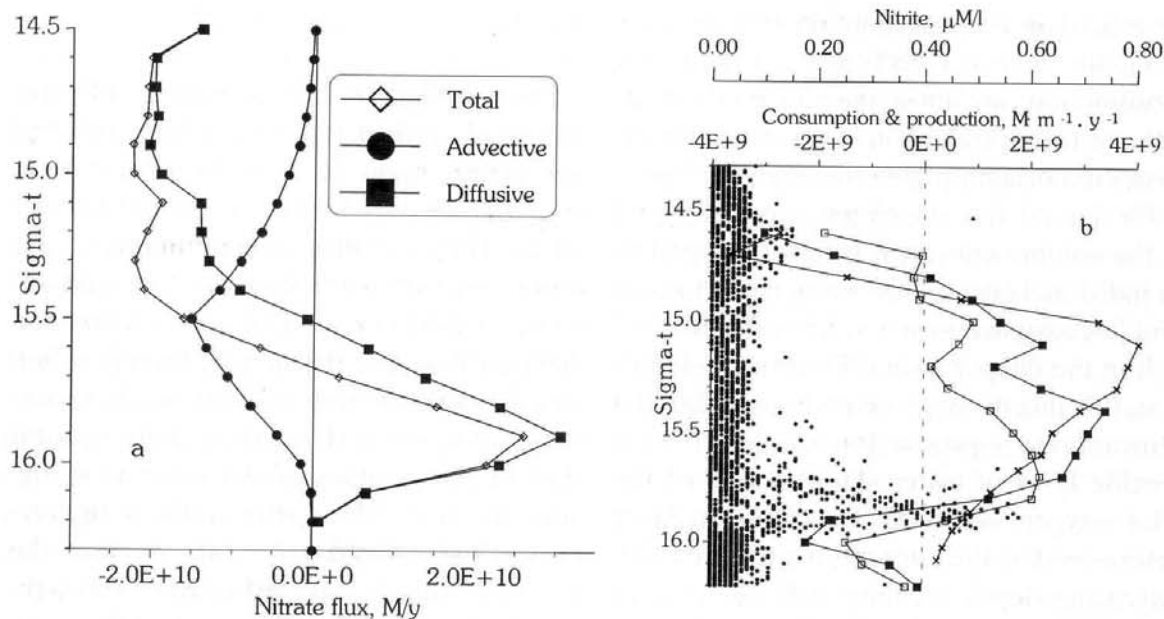
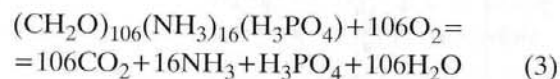


Fig. 5: The profiles of the vertical nitrate flux (a) and nitrate production rate derived from the nitrate fluxes (full squares for 1988, empty squares for 1990's) and oxygen consumption rate (crosses) comparing to the vertical distribution of nitrite (small dots) (b).

tion rate of nitrate reveals some unexpected phenomena. Negative values of the first derivative above $\sigma_t = 14.8$ and beneath $\sigma_t = 15.8$ indicate the layers where consumption of nitrate overcomes its production. This can be explained easily because the upper layer (above $\sigma_t = 14.8$) is situated next to the euphotic zone and the lower layer (beneath $\sigma_t = 15.8$) is a part of the suboxic zone. The nitrate uptake by phytoplankton seems to be an evident reason of its consumption above $\sigma_t = 14.8$ and the redox processes of denitrification and utilisation of nitrate in the suboxic zone have been discussed in detail by MURRAY *et al.* (1995). This consumption of nitrate above $\sigma_t = 14.8$ and beneath $\sigma_t = 15.8$ is also confirmed by the data on distribution of nitrite (Fig.5b), an intermediate product of the redox nitrogen cycling in any marine environment. Interestingly, the nitrate consumption/production profile recalculated from oxygen data (if we assume that in accordance with Equation 3 and 4 the nitrate production is equal to 16/138 of oxygen consumption) confirms consumption of nitrate above $\sigma_t = 14.8$ (fig.5b). However, neither location of the extremes of oxygen

consumption and nitrate production, no intensities of these extremes match each other beneath $\sigma_t = 14.8$. The maximum of oxygen consumption is observed above the maximum of nitrate production. Besides, oxygen consumption exceeds nitrate production in the layer $\sigma_t = 14.9$ to 15.4 and beneath $\sigma_t = 15.8$, but it is close to nitrate production in the layer of nitrate maximum from $\sigma_t = 15.5$ to 15.7 . Even the form of the profile of the first derivative of nitrate vertical flux arises questions on the basic hypotheses of nitrogen cycling in the Black Sea pycnocline, because any extremes have never been discussed and/or suggested from a smooth average vertical profile of nitrate (Fig.1c).



The fact that oxygen consumption exceeds the equivalent nitrate production in the layers above and beneath the nitrate maximum at $\sigma_t \sim 15.4 - 15.7$, but matches it inside of this

layer, has been previously revealed by KONOVALOV *et al.* (in press). This has been derived from the results of analysis of nitrate concentration to AOU (apparent oxygen utilisation) ratio and variations in the distribution of nitrate and oxygen in the Black Sea from 1960 to 1995. KONOVALOV *et al.* (in press) reported that the ratio of nitrate concentration to AOU at $\sigma_t=15.6$ differs from the Redfield's value (16/138) by only 6% and the results of modelling reveal ~8% difference. The fluxes and consumption/production rates, which are primarily responsible for the ongoing evolution of the biogeochemical structure, and that have been derived from the applied model (SAMODUROV & IVANOV, 1998) must simulate the main features of this structure in a realistic manner. This agreement between the results of modelling and analysis of the basic chemical structure perfectly verifies the applied model. At the same time, the results of modelling also reveal some features of nitrogen cycling in the Black Sea that are hardly obtainable otherwise. Unlike the lack of nitrate beneath $\sigma_t=15.8$, that is probably the result of the process of denitrification in the sub-oxic zone (MURRAY *et al.*, 1995), the revealed discrepancy between nitrate production and oxygen consumption above $\sigma_t=15.4$ (Fig.5b) has no apparent explanation. The process of denitrification in the sub-oxic layer has never been investigated in the Black Sea, but it has been explored and discussed in detail for the oxygen deficit layers of the Arabian Sea (NAQVI, 1987) and South Pacific (CODISPOTI *et al.*, 1985), for example. The processes of nitrogen cycling in the upper part of the layer of oxycline above $\sigma_t=15.4$ are traditionally limited to the physical out-flux, flux of sinking POM and bacteria mediated regeneration of nitrogen (Equations 3 and 4). Arguing for this hypothesis, the results of modelling (Fig.5b) clearly demonstrate that the scheme of nitrogen cycling in the upper part of the Black Sea pycnocline is more

complex. In any case, the quality or structure of the data on the distribution of nitrate cannot explain the revealed features of nitrogen cycling. Indeed, similar local extremes of nitrate production are detected (Fig.5b) from KNORR data. It is worth mentioning that the pump-profiling system and analytical procedures used in the KNORR cruise provided measurements with less than two meters vertical resolution (MURRAY *et al.*, 1995).

Ammonium

The average profile of ammonium does not exhibit any extremes (Fig.1c). The ammonium concentration being usually low in the oxygenated layer of the Black Sea experiences a plain growth starting from a depth in the suboxic layer close to the sulphide onset. MURRAY (1995) has reported that concentration of ammonium exceeds 0.2 mM/l at $\sigma_t=15.95$. It reaches ~100 mM/l close to the bottom. The profiles of the vertical flux of ammonium (Fig.6a) and of its consumption rate (Fig.6b) fit the commonly accepted hypothesis on production of ammonium due to respiration of POM in the anoxic zone, the upward flux of ammonia and its oxidation in the vicinity of the sulphide onset. The vertical flux of ammonium slightly increases in the anoxic zone towards the sulphide onset confirming an excess of production over consumption of ammonium in this layer. This flux starts to decrease close to the sulphide onset ($\sigma_t\sim 16.2$) reaching 2% of the initial value 30 meters above that depth. These dramatic changes in the vertical flux correspond to extremely intensive oxidation of ammonium (Fig.6b) close to the depth of sulphide onset, mainly in the sub-oxic layer.

Sulphide

The behaviour of sulphide is usually considered to be similar to ammonium. The

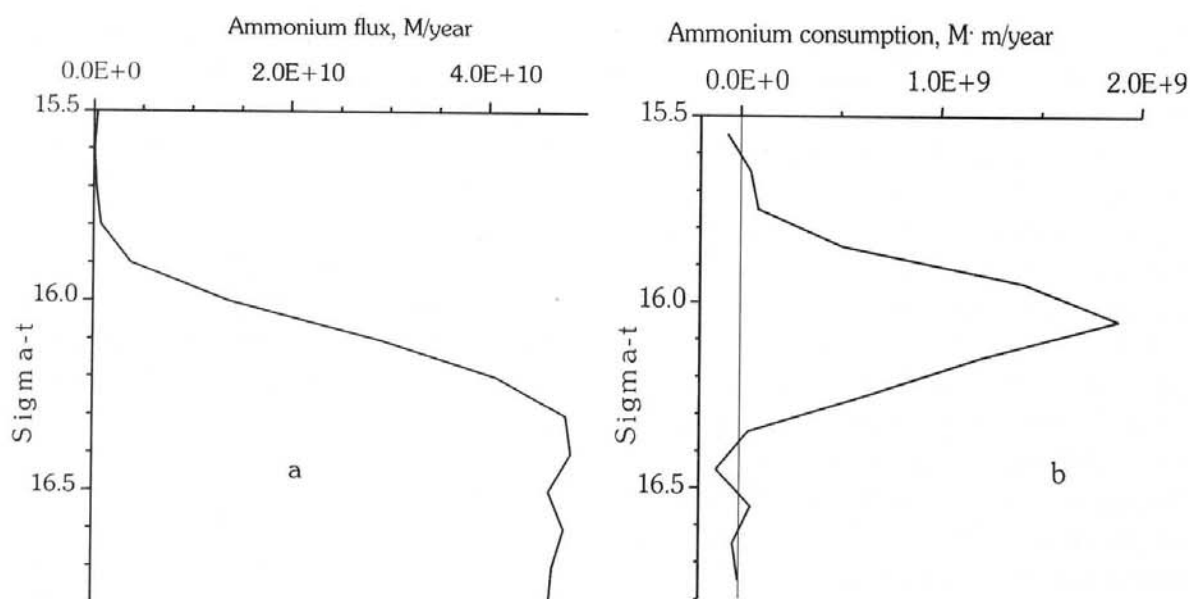


Fig. 6: The profile of the vertical flux of ammonium (a) and ammonium consumption rate (b).

average profile of sulphide (Fig.1a) generally resembles the profile of ammonium (Fig.1c). Bacteria mediated sulphate reduction inside the anoxic zone, limited by the flux of POM, and oxidation of sulphide at the depth of sulphide onset are usually regarded to be the primary processes responsible for sustaining sulphide budget in the Black Sea (BEZBORODOV *et al.*, 1993). Other processes, like geological sources of hydrogen sulphide (BEZBORODOV *et al.*, 1993) or precipitation of sulphide in the form of sulphide of iron (MURAMOTO *et al.*, 1991), while been discussed, have never been considered important for sulphur cycling in the Black Sea. For this particular reason, the profile of the vertical flux of sulphide derived from the model (Fig.7a) appears unexpected. Unlike similar profile for ammonium (Fig.6a) the sulphide profile has a local maximum at $\sigma_t \sim 16.8$. On the average, this sigma-t surface corresponds to a depth of 300-meters (Fig.7a). The rate of sulphide production reveals intensive consumption of sulphide inside the anoxic layer (Fig.7b) rather than at the sulphide onset. The existence of a maximum of the sulphide vertical flux (Fig.7a) actually means that the sulphide consumption rate exceeds the rate of sulphide production

above $\sigma_t \sim 16.8$, which is about 150 meters beneath the sulphide onset. The basic features of the profiles of the sulphide vertical flux and of the first derivative of this flux with respect to depth (Fig.7b) are not sensitive to the choice of the sulphide data set. Data of the cruises carried out in the 1960's to 1980's, as well as data of the KNORR cruise in 1988, which are considered to be of very high quality and high vertical resolution (MURRAY *et al.*, 1995), show similar results confirming the presence of intensive consumption of sulphide within the anoxic zone. This behaviour of sulphide appears to be a natural feature of the Black Sea environment. Actually, the same conclusion on the sulphide consumption within the anoxic zone can be drawn in another way also. The ratio of the ammonium to sulphide concentration must be close to 0.3 (16/53) throughout the anoxic zone according to Equation 5. In reality (Fig. 8), this ratio decreases from a relatively high value at the sulphide onset to the expected value (16/53) at $\sigma_t = 16.9$ thus confirming the presence of some processes that cause consumption of sulphide but not of ammonium.

$$(\text{CH}_2\text{O})_{106}(\text{NH}_3)_{16}(\text{H}_3\text{PO}_4) + 53\text{SO}_4^{2-} = 106\text{HCO}_3^- + 53\text{H}_2\text{S} + 16\text{NH}_3 + \text{H}_3\text{PO}_4 \quad (5)$$

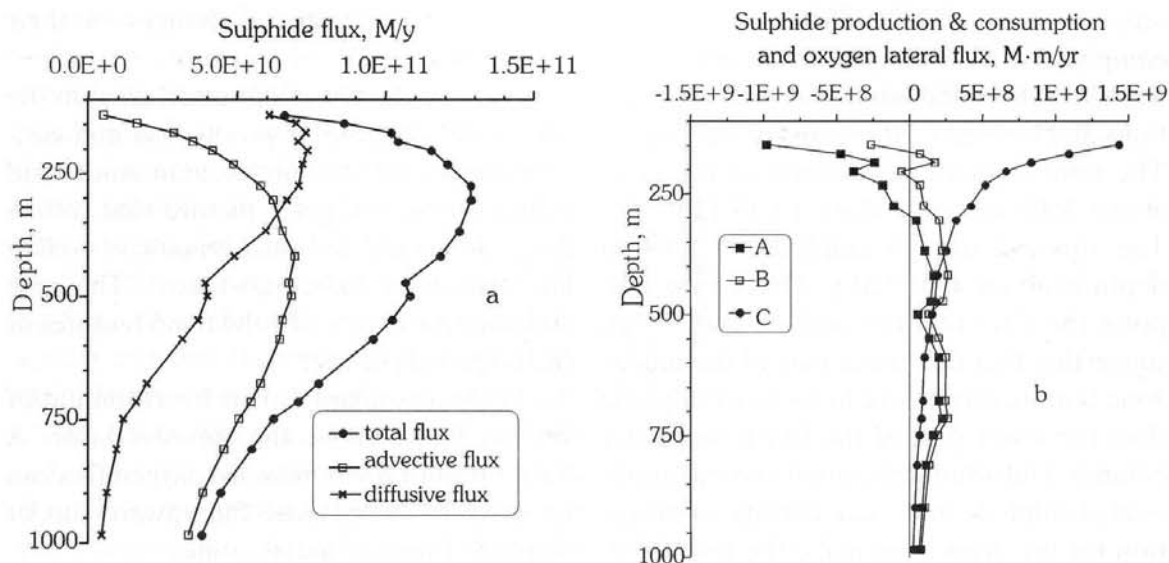


Fig. 7: The profile of the vertical flux of sulphide (a) and the rate of sulphide production (A) comparing to the lateral flux of oxygen (C) and corrected for the lateral flux of oxygen (B) (b).

Comparing the data on the lateral flux of oxygen and sulphide production/consumption rate (Fig.7b) one can easily draw a conclusion about the important role of lateral processes in ventilation of the Black Sea anoxic layer and maintaining the sulphide budget. On the one hand, the upward flux of sulphide in the vicinity of sulphide onset ($\sigma_t=16.2$) equals $\sim 6 \times 10^{10}$ M/y (Fig.7a), so this amount of sulphide is expected to be oxidised through various redox processes at the sulphide onset. On the other hand, the maximum flux of sulphide is close to $14 \cdot 10^{10}$ M/y at $\sigma_t=16.8$ (Fig.7a), or about 2.5-fold of that value. This actually means that $\sim 2/3$ of the sulphide is oxidised inside the anoxic layer rather than at the sulphide onset. It is worthy to note that this value, which is close to $8 \cdot 10^{10}$ M/y for the layer from $\sigma_t=16.2$ to 16.8 (Fig.7a), being compared to the lateral flux of oxygen into the same layer (about $15 \cdot 10^{10}$ M/y), demonstrates an excellent agreement between the results of modelling and data analysis.

Assuming that the lateral flux of oxygen into the anoxic zone is entirely spent for oxidation of sulphide, the rate of sulphide production in the anaerobic layer can be estimated as the difference between the first

derivative of the sulphide vertical flux (consumption/production rate) and lateral flux of oxygen (Fig.7b). This profile seems to be more realistic in terms of fitting the hypothesis of sulphide production in the Black Sea. The form of this profile indicates higher rate of sulphide production in the upper 500-meter layer of the anoxic zone, as it has been demonstrated by LEIN *et al.* (1991) and SOROKIN (1964), who analysed data on the rate of sulphate reduction. The profile of the sulphide production/consumption rate also reveals a sharp increase of sulphide consumption near sulphide onset (Fig.7b). This turns the sulphide behaviour closer to the scheme of ammonium cycling (Fig.6b) in terms of production and consumption. Local extremes in the profile of sulphide production rate can be artefacts because the rate of production, being a function of the second derivative of the concentration with respect to depth, is extremely sensitive to irregularities in vertical distribution of a particular property. So, some minor "errors" in the average profile, which is calculated from the results of observations, may become visible in the profile of the rate of production. On the other hand, these local extremes may also show that the real

scheme of sulphide cycling is even more complicated than the plot discussed in this work, but this demands additional investigations and lies out of the scope of this paper. The total sulphide production in the layer above 1000 meter is close to $15 \cdot 10^{10}$ M/y. The upward flux of sulphide at 1000-m depth is about $4 \cdot 10^{10}$ M/y. This figure supports the data of LEIN and IVANOV, 1991, suggesting that the upper part of the anoxic zone is more productive in terms of sulphide than the lower part of the Black Sea water column. Unfortunately, small vertical gradients of sulphide and weak density stratification for the deep layer make the result sensitive to uncertainties in the average profiles of sulphide (Fig.1a) and coefficients (Fig.2b). Besides, we can say very few on the reduction of sulphide in and the flux of it out of the upper layer of sediments. This sets the limit of this work and demands further investigation of this problem.

Discussion

At this point, before the discussion of the results of calculations, it is necessary to give some general remarks concerning our estimates of the production/consumption rates of chemical substances. The approach implies stationarity of the vertical average profiles of these substances. Besides, it implies that variations in the average profiles on a sub-annual time scale have been effectively filtered. However, if there is a gradual trend in the average concentration the real production/consumption may be quite different from the estimated values. Thus, for the ammonium and sulphide, the calculated production/consumption rates reveal the values valid for a period when their production equals consumption. The recently published data (KONOVALOV *et al.*, 1999) suggest an increase in the average concentrations of sulphide and ammonium. This means that the production rate of these substances discussed in this work is underes-

timated for the rate of changes in their inventories.

Adjusting the above discussed data on the fluxes and the rate of production and consumption of oxygen, nitrate, ammonium and sulphide one can get a picture that differs from the usually accepted scheme of cycling and budget of these substances. The next statements can describe the main features of the obtained picture:

- Oxygen is mainly spent for oxidation of sinking POM above the sub-oxic layer. A minor part of the downward oxygen flux can be spent to compensate the upward flux of sulphide from the anoxic zone.

- The flux of nitrate at the upper and lower boundaries of the oxycline and production of nitrate due to oxidation of sinking POM inside of this layer do not describe the entire scheme of nitrate cycling. The maximum of oxygen consumption is located notably above the maximum of nitrate production revealing a lack of nitrate production versus oxygen consumption. An additional process is responsible for this lack of nitrate in the upper part of the oxycline.

- The vertical counter-fluxes of nitrate and ammonium into the suboxic zone appear to be equivalent. This confirms the existing hypothesis (MURRAY *et al.*, 1995) on effective denitrification, which is responsible for losses of nitrogen in the Black Sea and "zero" up ward flux of nitrogen from the anoxic and suboxic layers.

- The annual nitrate flux out of the pycnocline roughly equals nitrate inventory. This reveals a short turnover time of nitrate and the possibility of fast changes in nitrate inventory caused by small changes in the physical fluxes of nitrate and/or in the rate of nitrate production.

- Sulphide, produced due to bacteria mediated respiration of sinking POM in the anoxic zone, is oxidised both at the sulphide onset and within the anoxic zone. The lateral flux of oxygen into the anoxic layer is responsible for oxidation of sulphide inside

the anoxic zone. The latter process appears to be very important for the sulphide budget and existence of the sub-oxic zone in the Black Sea. It is actually responsible for the depletion of about 2/3 of the totally produced sulphide. Besides, this process of sulphide oxidation inside the anoxic zone explains the existing misbalance in the vertical fluxes of sulphide and ammonium and the known fact that the ammonium to sulphide ratio decreases from a high value at the sulphide onset to the expected value at $\sigma_t=16.9$.

The profile of oxygen consumption rate (Fig.4b) demonstrates that maximum oxygen consumption takes place well above the sulphide onset and sub-oxic layer. It occurs in the upper part of the oxycline close to the euphotic layer, where oxygen and POM concentrations are high enough to provide intensive consumption of oxygen. Besides, the total consumption of oxygen in the layer above the sub-oxic zone is as much as $9.3 \cdot 10^{11}$ M/y, while the vertical flux of oxygen into the sub-oxic layer does not exceed $5 \cdot 10^{10}$ M/y. Even the amount of oxygen that is consumed in the layer above the sub-oxic layer ($\sigma_t=15.8$) but below the maximum of nitrate ($\sigma_t=15.5$) appears to be 7-fold of the flux of oxygen into the sub-oxic layer. Actually, this figure fits the data published by KARL *et al.* (1991) suggesting that 95% of POM regenerates in the layer above the sulphide onset. If we recalculate the rate of oxygen consumption and sulphide production into the rate of particulate organic carbon (POC) respiration, we get exactly the same figure (Fig.8). Assuming a steady distribution of oxygen, these data lead to a general conclusion that 95% of the downward oxygen flux must be spent to oxidise sinking POM rather than sulphide and other reduced substances. On the one hand, this makes the Black Sea less unique putting it in a line with other marine basins; on the other hand, this confirms that the Black Sea may be a natural testing laboratory for other marine systems.

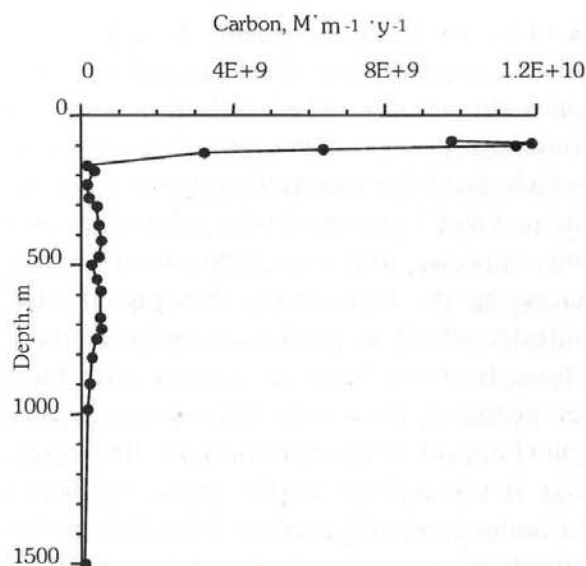


Fig. 8: The rate of carbon respiration calculated from the data of the rate of oxygen consumption and sulphide production.

The maximum rate of oxygen consumption should correspond to the maximum nitrate production if we adopt the hypothesis on oxygen being spent for oxidation of POM. The ratio of carbon to nitrogen for POM in the Black Sea water column does not differ from the Redfield ratio ($106/16 \approx 6.6$) being within the range from 5 to 10 (BURLAKOVA *et al.*, 1992; YILMAZ *et al.*, 1998). So, usually observed changes in the C/N ratio cannot explain the revealed disagreement between the profiles of oxygen consumption (Fig.4b) and nitrate production (Fig.5b). Indeed, to explain the observed ratio of oxygen consumption to nitrate production the C/N ratio in sinking POM should be 6- to 25-fold of the Redfield C/N ratio in the layer from $\sigma_t=15.0$ to 15.2. Keeping this in mind we suggest more complicated nitrogen cycle than the usually accepted scheme, which includes nitrate production due to oxidation of sinking POM and physical out-flux of nitrate.

In a speculative manner we may suggest that the process of oxidation of sinking POM is not accomplished by nitrate production described by Equations 3 and 4. An attempt to suggest that this process is limited to production of ammonium and, for

some reason, it does not go further to nitrate is in evident contradiction with the data on ammonium distribution (Fig.1c). Indeed, the local maximum of ammonium, which should be expected at $\sigma_t \sim 15.1$, cannot be revealed from the existing data. There is no extreme in the distribution of nitrite close to $\sigma_t = 15.1$, also. This means that nitrate, which is produced and consumed through nitrite being an intermediate form of nitrogen, does not experience any biogeochemical transformation in this layer, like it takes place at the upper and lower boundaries of the oxycline (Fig.5b). In this situation, we can only suggest a "bacteria loop" or process of denitrification. Unfortunately, there are no data to verify these suggestions and further investigation is needed to reveal the nature of this process. On the other hand, it seems to be extremely important to parameterise this process, even knowing nothing of its nature, to simulate correctly nitrogen cycling in the Black Sea.

The scheme of nitrate cycling in the oxycline of the Black Sea (Fig.9) provides insight into the nitrogen budget. To build this scheme we have used the upward flux at $\sigma_t = 14.5$ ($2.0 \cdot 10^{10}$ M/y) and downward flux at $\sigma_t = 15.9$ ($2.6 \cdot 10^{10}$ M/y). We have also calculated out-flux ($0.8 \cdot 10^{10}$ M/y) and influx

($0.3 \cdot 10^{10}$ M/y) of nitrate due to formation and dissipation of the Bosphorus plume. The difference ($0.5 \cdot 10^{10}$ M/y) reveals the flux of nitrate into the anoxic zone through lateral induction. Besides, we have estimated the load of inorganic nitrogen into the Black Sea ($\sim 10 \cdot 10^{10}$ M/y) from the data published by HUMBORG *et al.* (1997) and the amount of nitrogen that should be transformed in POM in order to balance the existing budget of nitrate. Briefly, this diagram reveals that the upward and downward fluxes do not differ considerably. The lateral flux of nitrate depletes the stock of nitrate by $0.5 \cdot 10^{10}$ M/y. The total out-flux of nitrate ($5.1 \cdot 10^{10}$ M/y) is close to the amount of nitrate stored in this layer ($\sim 6.0 \cdot 10^{10}$ M). The last figure shows that the balance of nitrate is extremely sensitive to the rate of biogeochemical processes and physical fluxes. As the result, dramatic changes in distribution of nitrate are easily possible on a scale of years. This conclusion fits the data on seasonal and long-term changes published by CODISPOTI *et al.* (1991); KONOVALOV (1994); KONOVALOV *et al.* (1997).

Another interesting conclusion drawn from the scheme of nitrogen cycling (Fig.9) is related to the process of denitrification in the sub-oxic zone (MURRAY *et al.*, 1995).

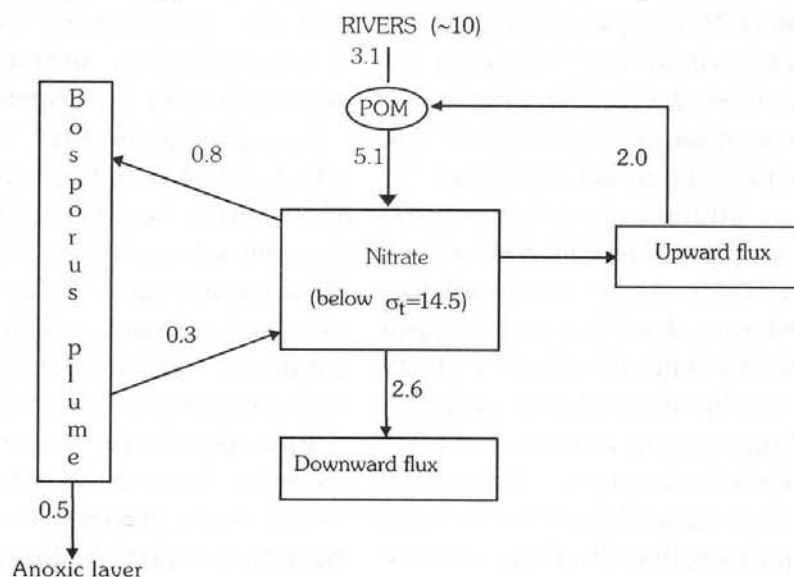


Fig. 9: The scheme of nitrogen cycling in the layer of the main pycnocline (All values should be multiplied by 10^{10} M/y).

The flux of nitrate into the suboxic zone is as much as $2.6 \cdot 10^{10}$ M/y (Fig.9) and the flux of ammonium into the same layer is close to $4.8 \cdot 10^{10}$ M/y (Fig.6a). The ratio of these values being equal to 0.542 differs from the expected ratio of nitrate to ammonium, 3/5 according to Equation 5, by less than 10%. This result may be considered as an indirect confirmation of denitrification that takes place in the sub-oxic zone. This figure also provides necessary information to estimate the intensity of denitrification, and the amount of inorganic nitrogen that must penetrate into the layer of the oxycline and anoxic zone, through the formation, sinking and respiration of POM in order to support steady state distribution of nitrate and ammonium. Thus, about 30% of the river-born nitrogen should go to the layer of the oxycline. The total annual loss of nitrogen from the Black Sea environment due to denitrification equals $7.4 \cdot 10^{10}$ M/y that is actually more than the stock of nitrate in the layer of oxycline. Therefore, the amount of nitrogen that is irreversibly lost from the layer of the main pycnocline appears to be ~75% of the total annual load of inorganic nitrogen into the Black Sea. All together, these data reveal an effective process of elimination of nitrogen from the Black Sea environment providing its ability to resist dramatic eutrophication over the last 20 years. Besides, it demonstrates the possibility of very fast changes in the distribution of nitrate caused by changes in the flux of POM.

Contrary to nitrate (CODISPOTI *et al.*, 1991; KONOVALOV *et al.*, 1997), the distribution of sulphide is usually considered to be in a steady state (BEZBORODOV *et al.*, 1993; SKOPINTSEV, 1975). While the possibility of changes in the sulphide production has been discussed (SKOPINTSEV, 1975), misbalance of the sulphide production and consumption has been always considered as an error of calculations and/or measurements (LEIN *et al.*, 1991; BEZBORODOV *et al.*, 1993).

Interestingly, the basic reason of this stability is expected to be 5,000 to 7,000-year evolution of the oxic/anoxic conditions in the Black Sea that has resulted in adjustment of all processes. Therefore, this hypothesis does not assume a discussion of particular reasons and conditions of the sulphide balance, as well as the possibility of changes in the distribution of sulphide on a shorter time scale. It seems to be strange if dramatic changes in biological and chemical properties of the oxic layer (MEE, 1992; HUMBORG *et al.*, 1997; CODISPOTI *et al.*, 1991) induced by drastic eutrophication over the last 20 years are not accompanied by any changes in biogeochemical structure of the anoxic zone. Actually, recent publications (KONOVALOV *et al.*, 1999; KONOVALOV *et al.*, in press) reveal the presence of changes in the distribution of sulphide and ammonium from 1969 to 1995, as well as relative stability of the sulphide onset over the same period. For this reason, the discussed profiles of the flux and production of sulphide (Fig.7) and oxygen (Fig.4) are extremely important in helping us to gain a new insight into the nature of the anoxic zone of the Black Sea. Thus, the sulphide onset mainly depends on the lateral flux of oxygen because 2/3 of the upward sulphide flux is balanced by the lateral but not vertical flux of oxygen. This seems to be the reason of a broad sub-oxic zone. The sulphide onset and the oxycline poorly depend on each other. While the sulphide onset depends mainly on the lateral flux of oxygen, the oxycline depends on the flux of POM. This means that disappearance of the sub-oxic zone and dramatic changes in the sulphide onset are possible when the sulphide production exceeds the redox equivalent of the lateral flux of oxygen. Keeping in mind that the total lateral flux of oxygen is equal to $33.4 \cdot 10^{10}$ M/y and the current lateral flux of oxygen into the anoxic zone is equal to $25.1 \cdot 10^{10}$ M/y, one can find out that 1.5-fold increase in the sulphide flux can result in

consumption of the entire lateral flux of oxygen and further adverse changes in biogeochemical structure of the oxic/anoxic system of the Black Sea. The flux of sulphide and the rate of sulphide production depend on the primary production. So, 1.5-fold increase in the flux of sulphide cannot be assumed as very high because 3- to 4-fold increase in the primary production has been already detected for the Black Sea over the last 2 decades being the result of drastic increase in the load of nutrients (HUMBORG *et al.*, 1997). Fortunately, the latest data (COCIASU *et al.*, 1997) does not support the idea of the ongoing increase in the load of nutrients.

Variations in the load of nutrients have caused changes in primary production (STELMAKH *et al.*, 1998) and, probably, in export production, as well as in the flux of POM into the anoxic zone. An increase in the stock of sulphide in the deep layer of the Black Sea (KONOVALOV *et al.*, 1999) arises questions on the stationarity of the Black Sea oxic/anoxic system. The calculated production of sulphide equals 19×10^{10} M/y, which fits well the value derived from the data on the flux of POM into the anoxic zone (KARL & KNAUER, 1991) and exceeds

by 50% the sulphide production derived from the data on the flux of POM, the rate of sulphate reduction and primary production published for the 1960's (DEUSER, 1971; SOROKIN, 1982). More recent data (LEIN & IVANOV, 1991) suggest even higher (up to 300%) increase in sulphide production from the 1960's to late 1980's. This might mean that the calculated sulphide production is indeed underestimated for the today situation characterised by the increased level of eutrophication. It is because the sulphide profile is not sensitive to variations in production/consumption rates (the inventory considerably exceeds the rates), the fluxes are not sensitive to changes in the production/consumption rates also.

Another aspect of the issue of sulphide oxidation inside the anoxic zone is related to the ammonium-sulphide stoichiometry. While the results of investigations (Fig.10) reveal striking variation in the ammonium to sulphide ratio, the results of modelling make this phenomenon logistical and clear. Indeed, the lateral flux of oxygen alters the ammonium-sulphide stoichiometry established by the process of sulphate reduction (Equation 5) making the ammonium/sulphide ratio higher depending on the flux of

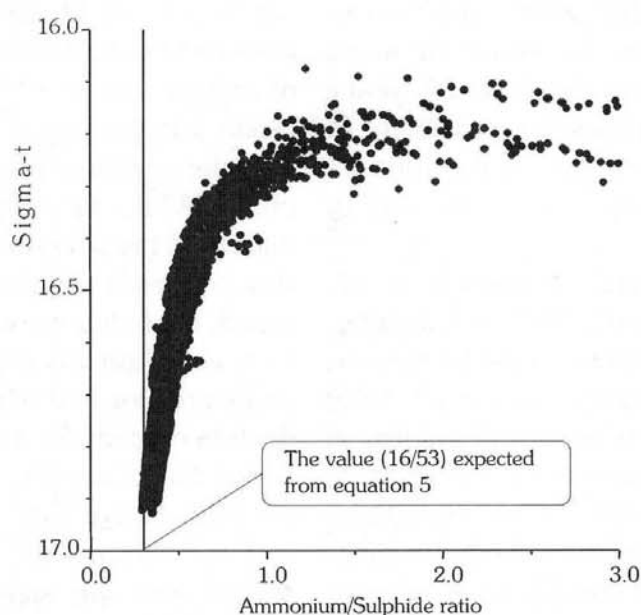


Fig. 10: The ammonium to sulphide ratio in the anoxic zone of the Black Sea derived from the KNORR cruise (1988) data set.

oxygen. As the result, the ammonium/sulphide ratio must decrease from the highest value at the sulphide onset to the expected from Equation 5 value ($16/53=0.3$) at a depth, where the lateral flux of oxygen diminishes to a small amount. The lateral flux of oxygen decreases exponentially ~10-fold from $\sigma_t=16.2$ to 16.9 (Fig.7b), and the ammonium to sulphide ratio behaves similarly (Fig.10). Thus, the lateral flux of oxygen appears to be an important feature of the Black Sea environment responsible for the existence of the sub-oxic zone, and extremely important for the sulphide distribution and for determining the peculiar ammonium-sulphide stoichiometry in the upper 400 m layer of the Black Sea.

Acknowledgements

This work has become possible due to financial support from the INCO Copernicus Project (IC15CT96-113). We wish also to thank all the participants of the KNORR cruise and the cruises in frame of the NATO SFP "TU-Black Sea" project responsible for collecting of the data on the basic physical and chemical properties.

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