Vol. 294: 95–107, 2005 | MARINE ECOLOGY PROGRESS SERIES Mar Ecol Prog Ser | Published June 9

Long-term variability of vertical chlorophyll *a* and nitrate profiles in the open Black Sea: eutrophication and climate change

Oleg A. Yunev[1,*], Snejana Moncheva[2], Jacob Carstensen[3,4]

[1]Institute of Biology of the Southern Seas, National Academy of the Sciences of Ukraine, Nakhimov Av. 2, Sevastopol 99011, Ukraine

[2]Institute of Oceanology, Bulgarian Academy of Sciences, Varna 9000, Bulgaria

[3]National Environmental Research Institute, Roskilde 4000, Denmark

[4]Joint Research Centre, Ispra 21020, Italy

ABSTRACT: The objective of this study was to investigate long-term trends in the subsurface summer phytoplankton community and their underlying mechanisms in relation to nutrient enrichment of the open Black Sea. We analysed parameters describing the summer chlorophyll *a* (chl *a*) and annual mean nitrate depth distribution in terms of their maximum concentration and its depth, the mean nitrate gradient for the layer between the 2 maxima, and Secchi depth. Investigating the entire period from 1964 to 1996 did not reveal any direct relationship between the nitrate and phytoplankton levels. The nitrate level in the open Black Sea increased until 1984/85, corresponding with general increases in anthropogenic riverine nutrient inputs to the sea. Thus, the average maximum nitrate concentration and the nitrate gradient for all depth profiles increased between 1969 and 1984 and then remained constant. Despite the early increase in nitrate characteristics, the maximum in the chl *a* profile remained unaltered from 1964 to 1984. After the mid-1980s, the magnitude of the chl *a* profile gradually increased to 1991 and peaked with an exceptionally high concentration in 1992. In this same period there were only moderate fluctuations in the nitrate profile characteristics. The change of the summer phytoplankton biomass levels since 1984/85 coincided with an intensification of the Rim Current and the associated transport of nitrate to the euphotic zone. Prior to 1984/85 strong stratification and a deep halocline resulted in nitrate accumulation only, whereas uplifting of the halocline, combined with intensified advective currents, increased the transport of nitrate to the euphotic zone during the summer. This resulted in an associated increase in phytoplankton production and biomass in the following period. While this study shows that the open Black Sea, like the coastal regions, has been impacted by eutrophication, the response is different from the coastal region due to the different physical characteristics of the open waters.

KEY WORDS: Chlorophyll profile · Nitrate profile · Secchi depth · Open Black Sea · Long-term variability · Eutrophication

Resale or republication not permitted without written consent of the publisher

INTRODUCTION

According to recent reports of the Group of Experts on Scientific Aspects of Marine Pollution (GESAMP) and the European Environment Agency (EEA), among all man-made impacts, the most important in terms of large-scale biological and ecological consequences is cultural eutrophication (EEA 2001, GESAMP 2001). This process plays a key role in the ecosystem with substantial ramifications for its structure and functioning. Nutrient enrichment primarily affects the phytoplankton community followed by responses of other biological constituents of the ecosystem. In the Black Sea, the signs of eutrophication became apparent in

*Email: yunev@sevcom.net

© Inter-Research 2005 · www.int-res.com

the coastal areas of the north-western and western parts during the late 1960s/early 1970s, mainly by increases in the frequency and magnitude of algal blooms (Mee 1992, Bodeanu 1993, Zaitsev 1993, Zaitsev & Aleksandrov 1997, Petranu et al. 1999, Moncheva et al. 2001).

In contrast to the coastal areas, there was no evidence of any shifts in the plankton and fish communities of the open Black Sea attributed to eutrophication during the 1960s to mid-1980s (Vinogradov et al. 1999, Kideys et al. 2000, Yunev et al. 2002). However, some changes in the vertical distribution of oxygen, sulfide, nitrate, ammonia and particularly silicate were observed (Tugrul et al. 1992, Konovalov et al. 1999a,b, Konovalov & Murray 2001). Considerable changes in the pelagic ecosystem at a basin-wide scale did become apparent in the second half of the 1980s and the beginning of the 1990s. These have been discussed rather widely in the scientific literature during the last decade (Besiktepe et al. 1999, Konovalov & Murray 2001, Yunev et al. 2002). Both regional anthropogenic impacts (increased water pollutants, eutrophication, overfishing, and an outbreak of the alien predator *Mnemiopsis leidyi*, etc.) and changes in the atmospheric and hydrological regimes of the basin related to large-scale climatic oscillations have been reported as possible causes for the changes in the Black Sea pelagic ecosystem after the second half of the 1980s (Niermann et al. 1999, Vinogradov et al. 1999, Kideys 2002, Yunev et al. 2002).

The first detailed investigation of long-term trends (from 1964 to 1996) in phytoplankton characteristics — surface chlorophyll *a* (chl *a*), depth-integrated primary production (DIPP), and phosphate concentration averaged for the upper 0–25 m layer of the deep open Black Sea (>1000 m) — revealed an increase solely in chl *a* during the warm months (May to September), and only for the period 1988 to 1992 (Yunev et al. 2002). Furthermore, significant correlations were found between surface chl *a* and DIPP for different seasons (despite limited DIPP data available), suggesting that the observed patterns in the long-term variability of surface chl *a* in the open Black Sea were likely to be valid for DIPP as well. In contrast, during the same 3 decades, no trends in phosphate concentrations within the upper 0 to 25 m layer throughout the year were evident. Hence, no significant relationship in interannual variations of summer surface chl *a* and phosphates within the upper euphotic layer was found. Most likely, this could be related to the formation of the seasonal thermocline at the beginning of warm months, which prevents the penetration of the nutrient-rich water from the intermediate layer into the surface layer.

However, it appeared to us that improved knowledge might be gained by examining the depth distribution of nutrients, especially the depth of the maximum concentration and the summer subsurface chl *a* peak. The latter is formed with the initiation of the seasonal thermocline and plays an important role in the productivity of the open regions because it includes 80 to 90 % of the total chl *a* within the euphotic layer (Yunev 1994, Vedernikov & Demidov 1997, Yuneva et al. 1999a). Moreover, the summer subsurface chl *a* concentration in the thermocline layer is comparable to that observed in the surface layer during the winter–spring phytoplankton bloom, when chl *a* reaches its highest concentrations (Vedernikov & Demidov 1997, Yunev et al. 2002).

So far, no attempts have been made to evaluate the importance of these subsurface peaks for mediating increased nutrient delivery into 'new production' in the open Black Sea. In addition, there have been few studies on nutrient limitation in the Black Sea. Yayla et al. (2001) found that nitrogen was the potential limiting nutrient of the open part during the warm period of 1998–1999, while phosphorus is still the limiting nutrient in coastal regions with high riverine inputs. Based on these investigations and the general belief that nitrogen ultimately limits primary production in marine systems, we focused on nitrate profiles in the present study. Nitrate concentrations of the open Black Sea are usually low in the euphotic zone, increase to a maximum approximately coincident with the upper boundary of the suboxic zone, and decrease to zero within the suboxic/sulfide zone interface (Codispoti et al. 1991, Tugrul et al. 1992, Konovalov et al. 1997). Thus, a vertical flux of nitrate from the halocline may provide the only important nitrogen source in the open sea to supply phytoplankton in the euphotic layer and support 'new production'.

The significance of a subsurface phytoplankton population for primary production has been reported for other European seas, most of them shallow compared to the open Black Sea. An example is the Kattegat, where the subsurface phytoplankton population contributes substantially to primary production, particularly to 'new production' immediately after the spring bloom in March (Richardson & Christoffersen 1991). This subsurface production also has repercussions for the sedimentation of particulate organic matter and oxygen depletion in the bottom waters of the Kattegat (Jørgensen & Richardson 1996).

In this study, we present data on the long-term variability of summer subsurface chl *a* and deep nitrate peaks in the open Black Sea, focusing on the possible role of eutrophication and climatic changes as underlying mechanisms of this variability. The aim is to test a conventional hypothesis for the open Black Sea, common for eutrophication studies of freshwater and marine systems, that there is a link between the environmental stressors (assessed by nutrient concentrations or fluxes) and biological responses (such as phytoplankton biomass by means of chl *a* concentrations). The trends were investigated from the onset of eutrophication within the shelf region (end of the 1960s). It was hypothesized that specific events related to eutrophication within the western and NW Black Sea shelf during the 1970s and 1980s could be traced to the deeper part and to the drastic changes of the pelagic ecosystem observed in the 1980s and 1990s.

MATERIALS AND METHODS

Chl *a* and nitrate profiles, as well as water transparency measured as Secchi depth (Z_d, m) were analyzed for temporal variations. The data sets of these variables are relatively large (352 and 639 profiles of chl *a* and nitrate, respectively, and 455 Z_d measurements) of the open (>200 m) Black Sea (Fig. 1) covering the period from 1964 to 1996 (Table 1). The data in the present study originated from 3 sources: (1) the database set up within the framework of the NATO TU Black Sea Project (TU-BS DB), (2) the Department of Ecological Physiology of Phytoplankton at the Institute of Biology of the Southern Seas (Sevastopol, Ukraine) and (3) the Institute of Oceanology, Bulgarian Academy of Sciences (Varna).

Chl *a* in the Black Sea was measured using 2 methods (spectrophotometrical and fluorometrical) as discussed

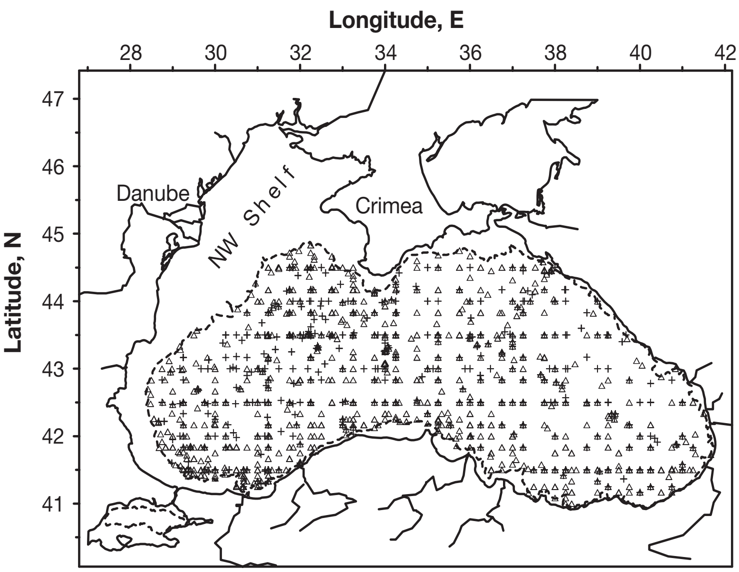

Fig. 1. The location of stations in the open Black Sea (>200 m, dotted line), where chl *a* (+) and nitrate (Δ) profiles were sampled from 1964 to 1996

Table 1. Data used in this study to examine temporal variations in chl *a*, nitrate (NO_3) profiles and Z_d in the open Black Sea

Year	Month	Variable	Data source[a]
1964	Aug, Sep	Chl, Z_d	IBSS DB
1969	Mar, Apr	NO_3	TU-BS DB
1972	Jul, Aug	Z_d	TU-BS DB
1976	Apr	NO_3	TU-BS DB
1978	Jul, Aug	Z_d	TU-BS DB
	Sep	Chl	TU-BS DB
1980	Aug, Sep	Chl, NO_3	IBSS DB
1982	Jul, Aug	Chl	IBSS DB
1983	Sep	Chl	IBSS DB
1984	Apr, May	Chl, NO_3, Z_d	TU-BS DB
	Jul, Sep	Z_d	TU-BS DB
	Jun, Jul	Z_d	TU-BS DB
	Sep	Chl, Z_d	IBSS DB
1985	Jun, Jul	Z_d	TU-BS DB
	Jul, Sep	Z_d	TU-BS DB
	Sep	Chl, Z_d	TU-BS DB
1986	May, Jul, Sep	Chl, NO_3	TU-BS DB
	May, Jun	Chl, Z_d	TU-BS DB
1987	Apr, May, Jul	NO_3	TU-BS DB
1988	May, Jun, Jul	NO_3	TU-BS DB
	Jun	Z_d	TU-BS DB
	Mar, Apr	NO_3	TU-BS DB
	Apr, May	NO_3	TU-BS DB
	Aug, Sep	Chl, NO_3	TU-BS DB
1989	Jan, Apr, Nov	NO_3	TU-BS DB
	May	Z_d	TU-BS DB
	Aug, Sep	Z_d	TU-BS DB
	Jun	Chl	TU-BS DB
	Jul, Aug, Sep	Chl , NO_3, Z_d	TU-BS DB
	Nov, Dec	NO_3	TU-BS DB
1990	Feb, Apr, Sep	Chl, NO_3	TU-BS DB
	Sep, Oct	Chl, NO_3, Z_d	TU-BS DB
1991	Mar, Apr	NO_3	TU-BS DB
	Jun	Chl, Z_d	TU-BS DB
	Jun, Sep	Chl, NO_3	TU-BS DB
	Aug	Chl, NO_3, Z_d	TU-BS DB
	Sep	Chl	BUL DB
	Sep	Chl, NO_3, Z_d	TU-BS DB
	Nov, Dec	NO_3	TU-BS DB
1992	Jul	Chl	BUL DB
	Jul	Chl, Z_d	TU-BS DB
	Jul	Chl, NO_3, Z_d	TU-BS DB
	Jul	Z_d	TU-BS DB
	Sep, Oct	Chl, NO_3, Z_d	TU-BS DB
1993	Apr	NO_3	TU-BS DB
	Apr	NO_3	TU-BS DB
	Apr, Aug, Dec	Chl, NO_3, Z_d	TU-BS DB
	Nov	NO_3	TU-BS DB
1994	Apr, May	NO_3, Z_d	TU-BS DB
	May	Z_d	TU-BS DB
	Nov, Dec	NO_3	TU-BS DB
1995	Mar, Apr	NO_3	TU-BS DB
	Mar, Apr	NO_3	TU-BS DB
	Jul, Aug	Chl	BUL DB
1996	Sep	Z_d	TU-BS DB
	Sep	Chl	TU-BS DB

[a]TU-BS DB: database collected within the NATO TU-Black Sea Project; IBSS DB: data from the Department of Ecological Physiology of Phytoplankton of the Institute of Biology of Southern Seas (Sevastopol, Ukraine); BUL DB: data from the Institute of Oceanology, Bulgarian Academy of Sciences (Varna, Bulgaria)

in detail by Yunev et al. (2002), where a comparison of the 2 methods was carried out. The result of that comparison allowed us to pool the chl *a* data obtained by the 2 methods and use them as a single data set without any further correction. Nitrate analytical techniques, determination of Z_d measurements, and the criteria for the integrated use of data sampled by different Black Sea riparian countries are given in the reports of the Institute of Marine Science (Erdemli, Turkey), and the TU-BS DB chemical and bio-optical expert groups (Konovalov et al. 1994, Ivanov et al. 1998).

We analysed chl *a* and nitrate profiles by estimating 2 parameters: the maximum value of each profile (C_m, mg m^{-3} and N_m, µM) and the depths at which the maximum values were found (Z_m^C and Z_m^N, m) (Fig. 2A). Due to irregular chl *a* sampling with depth and the lack of continuous *in situ* fluorometer measurements for the selection of the maximum concentration depth in most of the early cruises, many profiles had insufficient vertical resolution for us to assign a depth of maximum concentration based on the measurements alone. We resolved this problem by approximating the vertical chl *a* profiles using a general equation proposed by Lewis et al. (1983) for computing chl *a* concentration (C) as a function of depth Z:

$$C(Z) = C_b + C_m \exp\left[-(Z - Z_m^C)^2/(2\sigma^2)\right] \quad (1)$$

where C_b is the background concentration over which a Gaussian curve is superimposed with a maximum value given by C_m, occurring at depth Z_m^C, and having a thickness controlled by σ^2 (Fig. 2A). The parameters of Eq. (1), C_m and Z_m^C, were determined by least-squares regression, provided that at least 5 observations were available and distributed around the peak of the profile. The coefficient of determination (R^2) and the standard error (SE) were calculated for each of the fitted Gaussian curves.

A statistical evaluation of the unimodal Gaussian curve to the vertical distributions of summer chl *a* profiles showed some variation in their goodness-of-fit (Fig. 2B). However, all fitted curves had R^2 values of 0.85 and above, and low standard errors, thus showing a reasonable fit of the measured profiles. It should be noted that the modified Gaussian curve applied in our study has been successfully used for describing the vertical distribution of chl *a* in stratified oligotrophic subtropical and equatorial deep ocean regions in remote sensing investigations (Morel & Berton 1989, Platt et al. 1991). It has also shown good results in the study of seasonal features of chl *a* vertical distribution

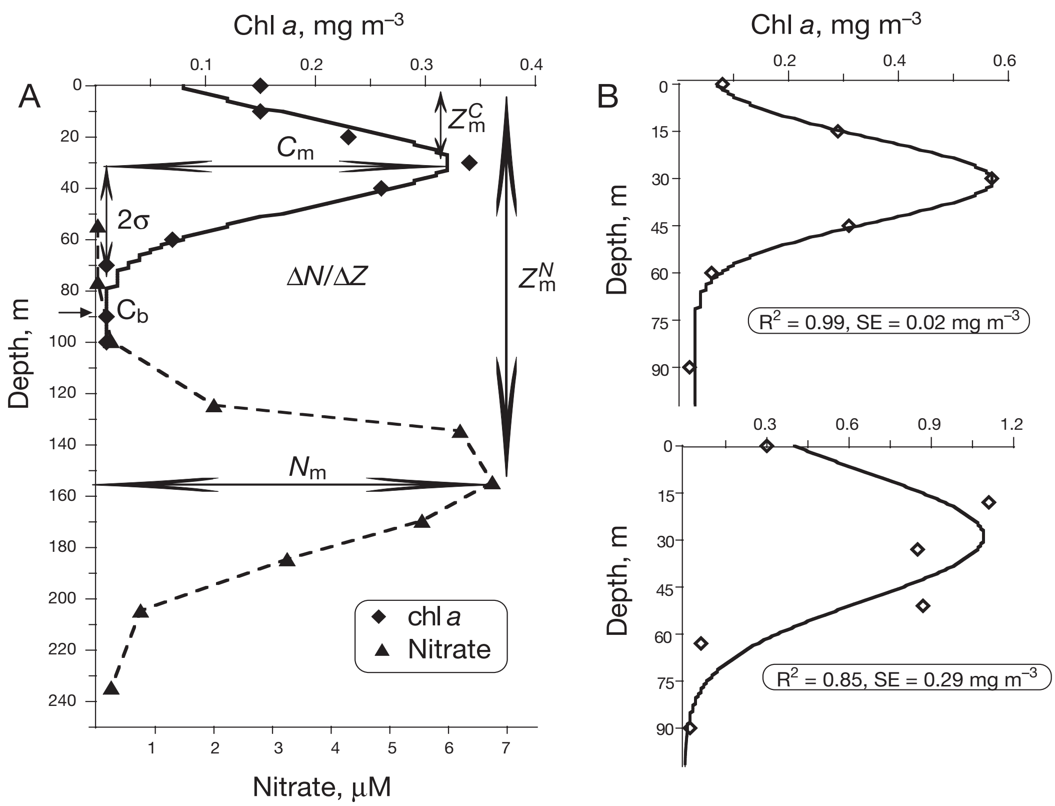

Fig. 2. (A) Typical summer chl *a* and annual mean nitrate vertical profiles in the open Black Sea. Parameters of the estimated Gaussian curve used for fitting the chl *a* (continuous line) and sampling nitrate (dashed line) profiles are indicated. Parameter explanations are given in the text. (B) Vertical chl *a* profiles estimated from *in situ* measurements (◇) showing the best (upper panel) and worst (lower panel) fit

in the Black Sea, the eastern Mediterranean and the Arabian Sea (Yunev 1994, Yunev et al. 1999).

In contrast to chl *a*, nitrate profiles were reconstructed based on sampling which was generally done at fixed depths in earlier studies, or at fixed σ_t in recent cruises (Konovalov et al. 1999b). We compared the nitrate concentrations found by sampling at the standard depths with those found by sampling at the standard σ_t values using measurements obtained with a pump sampler giving 1 m vertical resolution during a 1988 RV 'KNORR' cruise. The results showed very good agreement between all approaches.

In addition to estimating the maximum values of summer chl *a* and nitrate profiles (C_m and N_m), we also calculated the summer mean nitrate concentration gradient with depth ($\Delta N/\Delta Z$) for the layer between the 2 maxima (Fig. 2A):

$$\Delta N/\Delta Z = N_m/(Z_m^N - Z_m^C) \quad (2)$$

It was assumed that variations in $\Delta N/\Delta Z$ could be related to changes in the C_m level in the open Black Sea because the vertical flux of nitrate from its peak (described as a sum of advective and turbulent transports) is the only source of 'new' nutrients (Konovalov et al. 2000) and, consequently, 'new production' in the euphotic zone (Dugdale & Goering 1967, Richardson 1996).

Spatial differences in the hydrodynamic regimes of the open Black Sea may prove to be very important for understanding temporal variations in chl *a* and nitrate profiles (Kushnir et al. 1999, Yuneva et al. 1999a,b). Unfortunately, the circulation of the Black Sea is very complex and variable. It is characterized by an interconnected series of cyclonic eddies and subbasin scale gyres which vary in size and shape across the basin and with depth. These features also display a substantial seasonal and interannual variability, which makes it impossible to select fixed stations or regions with well-defined hydrodynamic regimes (Oguz et al. 1994, 1998, Ozsoy & Unluata 1997, Oguz & Besiktepe 1999). A further complication is that the data in the present investigation were collected during different cruises with differing objectives. They were also collected in various Black Sea regions as parts of transects, polygons, or at specific stations.

In order to deal with these complexities and limitations, we subdivided all profiles into 3 distinct groups corresponding to different hydrodynamic regimes. Temporal variations of chl *a* and nitrate profiles were examined for each of these groups separately. The depth location of density σ_t = 16.2 ($Z_{\sigma16.2}$), the lower boundary of the aerobic layer, was used as an indicator of hydrodynamic activity for characterizing the profiles (Bezborodov & Eremeev 1993, Murray et al. 1995). We assumed that a σ_t = 16.2 located at depths between 80 and 120 m was indicative of a cyclonic gyre, while a σ_t = 16.2 at depths of 160 to 200 m indicated an anticyclonic eddy. Profiles with σ_t = 16.2 located at depths between 120 and 160 m were considered characteristic of a convergent regime.

Before averaging the profile characteristics over time and space, we wanted to investigate the spatial variation in chl *a* profiles with respect to the hydrodynamic regime and the seasonal variation in nitrate profiles. In order to do this, we subdivided the chl *a* data into 2 distinct quasi-stationary periods, 1986 to 1989 and 1990–1991, i.e. periods exhibiting relatively stable values of the parameters investigated and relatively high data coverage. The seasonal variations in the profile characteristics were investigated for nitrate only, since the chl *a* profiles were relatively constant in the warm months (Yunev 1994). Z_d data were similarly averaged for the quasi-stationary warm months of May to September based on the results from Mankovsky et al. (1996) and Vladimirov et al. (1999).

RESULTS

The chl *a* profiles, characterized by the estimated parameters C_m and Z_m^C, were not related to the depth distribution of $Z_{\sigma16.2}$ within the short periods of 1986 to 1988 and 1990–1991 (Fig. 3). Both of these periods

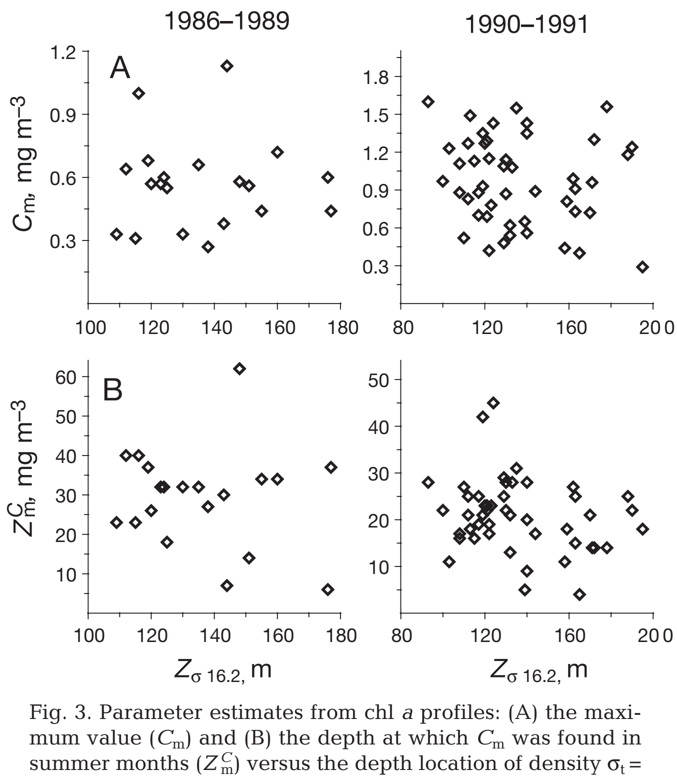

Fig. 3. Parameter estimates from chl *a* profiles: (A) the maximum value (C_m) and (B) the depth at which C_m was found in summer months (Z_m^C) versus the depth location of density σ_t = 16.2 ($Z_{\sigma16.2}$) during 2 quasi-stationary periods (left and right panel, respectively)

also had moderate interannual variations of surface chl *a* (Yunev et al. 2002). Consequently, spatial variation in the summer chl *a* profiles could be neglected as the profile parameters were unrelated to the different hydrodynamic regimes indicated by the varying depths of σ_t = 16.2 Also, there was no distinct seasonal pattern in the maximum concentration of nitrate (N_m) or for its depth location (Z_m^N) during the quasi-stationary period at the end of the 1980s and the beginning of the 1990s (Konovalov et al. 1999b) (Fig. 4). This is important because it means that annual mean values of the nitrate profile parameters can be used for studying their long-term changes, irrespective of differences in the times of sampling between years.

The subsurface chl *a* peak in warm months for the entire open Black Sea revealed clear long-term trends (Fig. 5A). From 1964 to 1983, maximum chl *a* levels were low and stable, with a mean value of 0.4 ± 0.14 mg m^{-3}. Beginning about 1984, maximum chl *a* values began increasing at a rate of 0.09 mg m^{-3} yr^{-1} to 1.12 ± 0.57 mg m^{-3} in 1991. The subsurface chl *a* maximum then increased to an exceptionally high value in 1992 of 3.08 ± 2.16 mg m^{-3} (due to unusually high values measured in July) before decreasing sharply. After 1992, C_m stabilized at 0.57 mg m^{-3}. Unfortunately, there are no suitable data available after 1996.

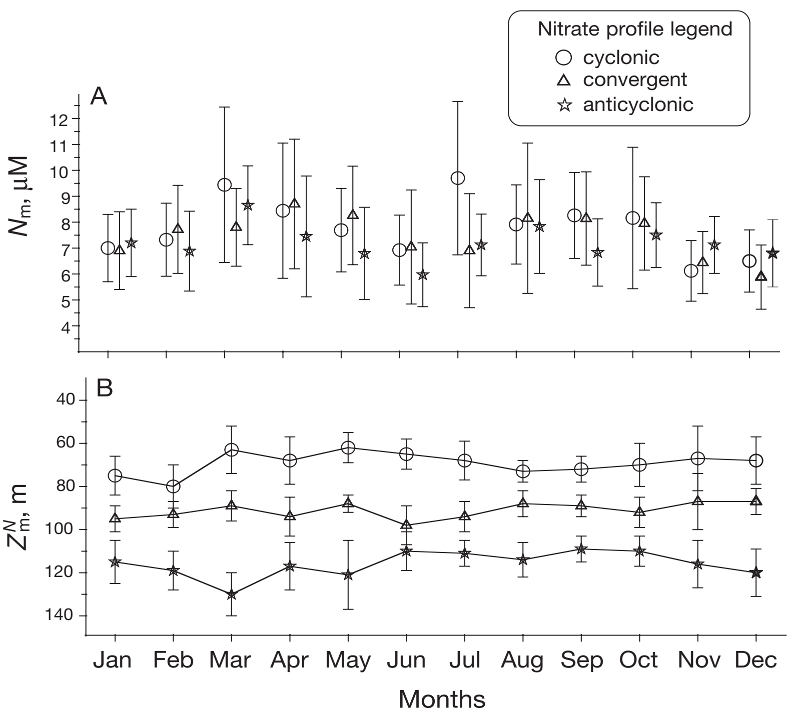

Fig. 4. Seasonal variation of nitrate profile parameters: (A) the maximum value (N_m) and (B) the depth at which N_m was found (Z_m^N) on stations with different hydrodynamic regimes in the open Black Sea during 1988 to 1991. Error bars show the standard deviations

Trends in 0 to 100 m depth-integrated chl *a* (DIChl, mg m^{-2}) (Fig. 5AA), a commonly used integral characteristic of vertical chl *a* distribution in the sea, were very similar to those of C_m, with a mean value of 19.3 mg m^{-2} from 1964 to 1983 which increased steadily at a rate of 1.8 mg m^{-2} yr^{-1} from 1984 to reach 35.1 mg m^{-2} in 1991. This parameter also peaked sharply in 1992 at 78.6 mg m^{-2} before falling to an average of 20.8 mg m^{-2}, approximately to the level of the 1960s and 1970s.

The trends of N_m for cyclonic, anticyclonic, and convergent profiles were very similar in timing and magnitude (Fig. 5B). N_m increased gradually at a rate of +0.40 µM yr^{-1} from 1.9 ± 0.5 µM in 1969 up to 7.72 ± 1.5 µM in 1984. It remained at about this level until 1992, then decreased to an average of 4.98 ± 0.75 µM (1993 to 1995).

Interannual variations in the depth location of C_m and N_m, as well as in the N_m values, resulted in a characteristic long-term trend for the mean nitrate depth gradient in the layer between the 2 maxima (Fig. 5C). From 1969 to 1984, the levels of $\Delta N/\Delta Z$ increased steadily from 0.03, 0.02 and 0.01 µM m^{-1} up to 0.23, 0.13 and 0.09 µM m^{-1} (approximately 8-fold) for cyclonic, convergent and anticyclonic profiles, respectively. After 1991, $\Delta N/\Delta Z$ values decreased approximately by a factor of 2: down to 0.08, 0.06 and 0.04 µM m^{-1} in 1992 to 1995, correspondingly for cyclonic, convergent and anticyclonic profiles.

The depth location of C_m and Z_d had comparable step changes coinciding almost around the same years (Fig. 5D,E). The first shift of the 2 depth variables was observed in 1978 and remained relatively constant up to 1985–1986. The next major shift occurred in 1988–1989. The lowest value of Z_m^C (~17.5 m) was observed in 1992 and the lowest value of Z_d (~6 m) in 1991. During the end of the study period (1993 to 1996) there was a shift in Z_d down to 12 m, whereas the subsurface chl *a* maximum stayed at about 20 m.

Combining the trends of Z_d (Fig. 5E) with the characteristics of the chl *a* profiles (Fig. 5A,D), declines in water transparency after 1985 were associated mainly with the magnitude of the C_m (63%) (Fig. 6A, line 1). Variations in Z_d before 1985 were, on the other hand, linked to the depth location of the subsurface chl *a* maximum in the water column (67%) (Fig. 6B, line 3). The relationships between the chl *a* profile parameters and Secchi depth were calculated by excluding the data for 1992 because of abnormally high chl *a* values (3.08 ± 2.16 mg m^{-3}).

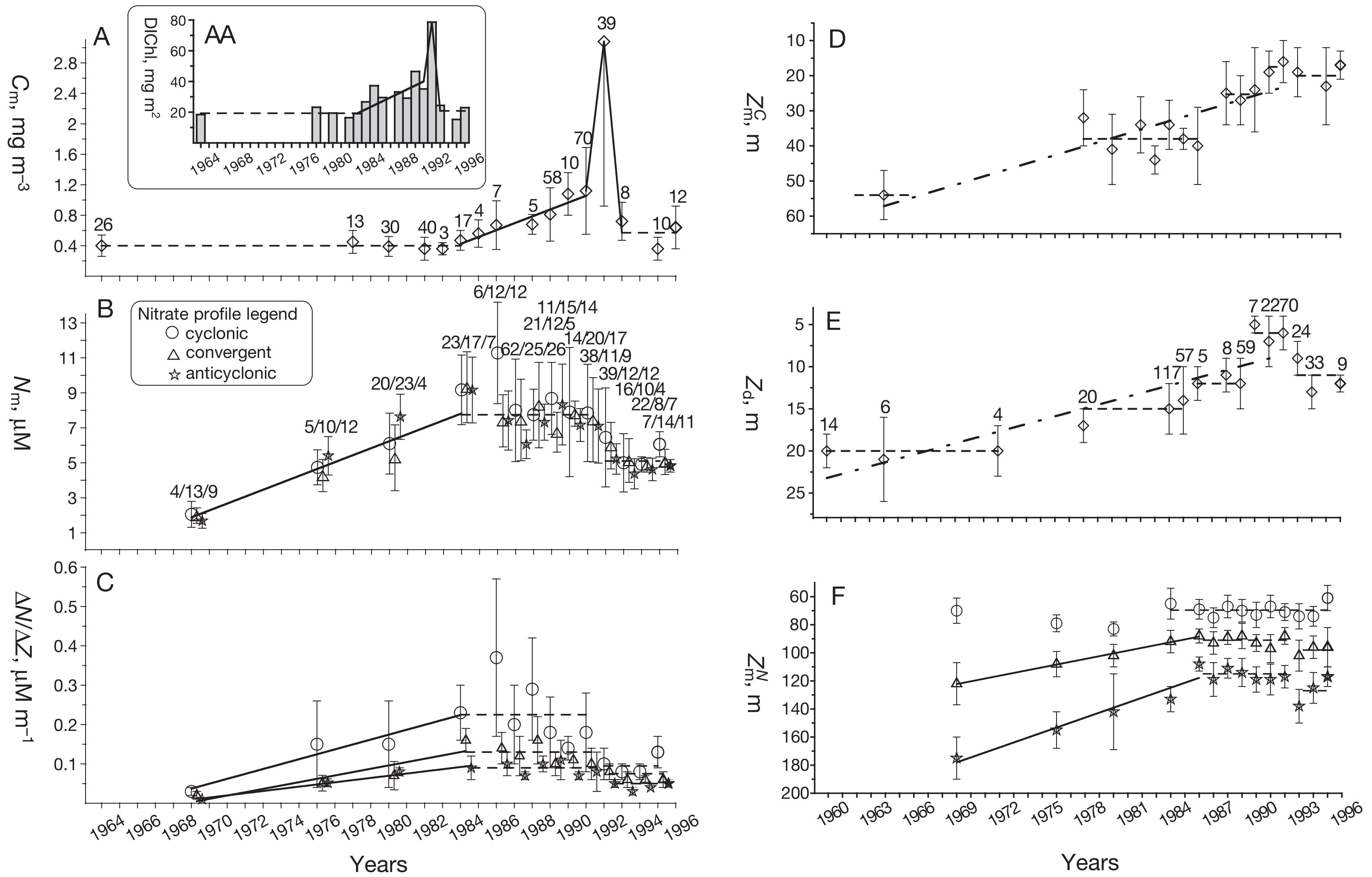

Fig. 5. Long-term variability: (A) in the maximum value of summer chl *a* profile (C_m); (AA) in 0–100 m depth-integrated chl *a* (DIChl); (B) in the maximum value of annual mean nitrate profile (N_m); (C) in the summer mean nitrate concentration gradient with depth for the layer between chl *a* and nitrate maxima ($\Delta N/\Delta Z$); (D) in the depth at which C_m was found (Z_m^C); (E) in water transparency measured as Secchi depth (Z_d); and (F) in the depth at which N_m was found (Z_m^N). Dashed lines indicate quasi-stationary periods for the different parameters. Unbroken lines show: (A,AA) a steady increase of C_m and DIChl from 1984 to 1991 and sharp increase in 1992, as well as an abrupt decrease in 1993; (B) a steady increase of N_m from 1969 to 1984; (C) a steady increase in $\Delta N/\Delta Z$ of cyclonic, convergent and anticyclonic profiles from 1969 to 1984; and (F) a steady decrease in Z_m^N of convergent and anticyclonic profiles from 1969 to about 1986. Dash dot lines (D,E) show *a* steady decrease of Z_m^C and Z_d, correspondingly, from 1960s to the beginning of the 1990s. Standard deviations are marked by the error bars, and in A, B and E the number of measurements used for averaging are given

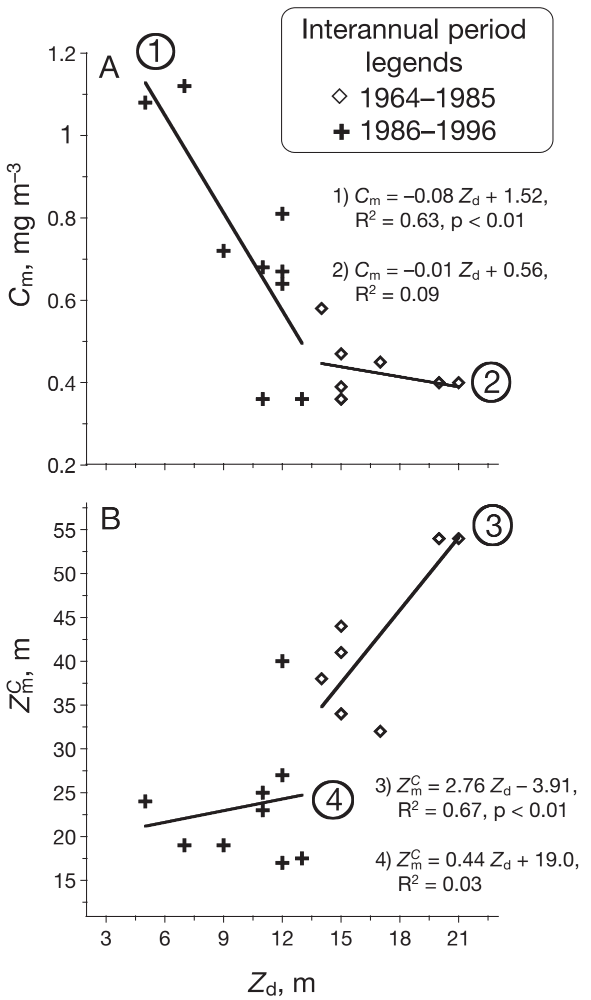

Fig. 6. Summer mean chl *a* profiles parameters: (A) the maximum value (C_m) and (B) the depth at which C_m was found (Z^C_m) versus summer mean Secchi depth (Z_d) in the open Black Sea during different interannual periods

The trends of Z^N_m were more pronounced in anticyclonic and convergent profiles (Fig. 5F). Z^N_m gradually shoaled from 175 and 122 m in 1969 up to 115 and 91 m in 1986 to 1992 for the anticyclonic and convergent profiles, respectively. The location of the nitrate maximum was shifted slightly downwards in 1993 to 1995 under both hydrodynamic regimes. The cyclonic profiles, on the other hand, did not reflect any major changes over the entire study period.

Thus, the available data from the open Black Sea did not reveal any significant direct relationship between interannual changes in nitrate profile characteristics (concentration in maximum and mean gradient of the upper part of the peak) and chl *a* concentrations in the summer subsurface peak, either for the period before the mid-1980s (intensive eutrophication within the shelf region), or for the period of dramatic changes in the pelagic ecosystem revealed at the end of the 1980s and the beginning of the 1990s.

DISCUSSION

Long-term trends of phytoplankton and nutrients

While eutrophication in the Black Sea coastal regions has been well documented since the beginning of 1980s for nutrients and phytoplankton (e.g. see references in Cociasu et al. 1996 and Bodeanu et al. 1998), studies showing expanding eutrophication in the open Black Sea are far fewer, more recent, and relate only to hydrochemistry (Konovalov et al. 1999a,b, Konovalov & Murray 2001). These studies show that there was an increase in the sulfide content of the anoxic zone and a rather abrupt decrease of annual mean oxygen concentration below the core of the cold intermediate layer (CIL), particularly in the oxycline, between the mid-1970s and the 1980s. Interannual variations in the vertical distribution of annual mean oxygen and sulfide were mirrored by corresponding changes in the v ertical distribution of annual mean nutrients, especially nitrate and silicate, during 1975 to 1985 (Tugrul et al. 1992, Konovalov & Murray 2001).

Based on these observations, Konovalov & Murray (2001) proposed that the increased nutrient load since the early 1970s (Cociasu et al. 1996, Humborg et al. 1997) had resulted in an intensification of primary production in the open Black Sea with a consequent increase in sinking particulate organic matter (POM) flux in the 1970s to 1980s (Luther et al. 1991), and an increase in oxygen demand from remineralisation. These changes of chemical properties would thus document the development of eutrophication in the open Black Sea since the mid-1970s, a pattern similar to that observed in coastal regions.

The lack of an observed increase in summer surface chl *a* and primary production within the period from 1964 to 1986 (Yunev et al. 2002) was believed to be related to the strong summer temperature stratification in the Black Sea, which prevents the penetration of the nutrient-rich water from the intermediate layer into the surface layer. The underlying mechanisms for the observed increase in surface chl *a* after 1986 were not totally clear, although climatic forcing was suggested to have triggered these changes (Yunev et al. 2002).

The present results for the open Black Sea also show a decoupling of nutrient and phytoplankton summer trends (Fig. 5A–C), in contrast to the clear linking of nutrient load to primary production and chlorophyll biomass documented in various marine systems throughout Europe and North America (Jonge et al. 1994, Solic et al. 1997, Allen et al. 1998).

It should be stressed that the increase of the nitrate maximum in the open Black Sea (Fig. 5B) corresponded well with the increase of inorganic nitrogen input from the Danube River (Konovalov et al. 1999b), whereas the chl *a* values in the subsurface maximum (Fig. 5A) and in the surface layer (Yunev et al. 2002) remained moderate. These results are in contrast to the general perception of a direct linear response of the pelagic system to nutrient enrichment. However, among marine ecologists there is growing recognition that physical and biological properties of marine ecosystems may act as a filter that may modulate the response to changing nutrient inputs, often in a nonlinear way (Smetacek et al. 1991, Gray 1992, Nixon 1995, Jørgensen & Richardson 1996, Cloern 2001). Therefore, in order to explain the observed differences in the chl *a* and nitrate profile parameters we will look closer at the circulation and mixing processes that may be influencing phytoplankton responses to nutrient enrichment in the open Black Sea.

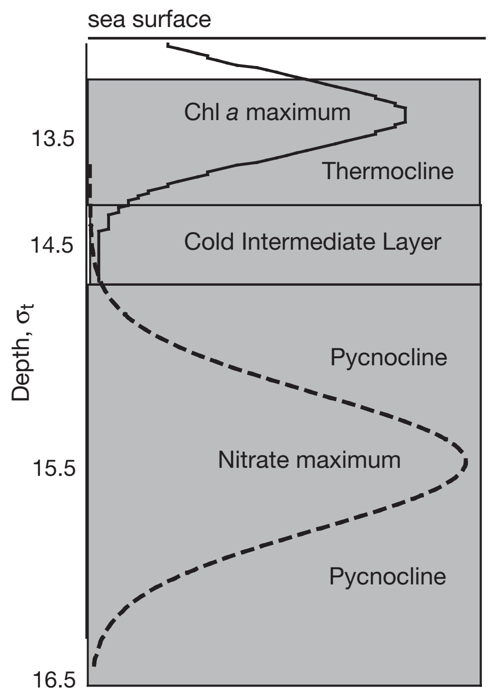

Fig. 7. Typical vertical distribution of chl *a* (unbroken line) and nitrate (dashed line) in the water column of the open Black Sea during warm months versus σ_t. Location of the seasonal thermocline, the cold intermediate layer and the halocline are shown

Physical factors modulating eutrophication responses

The Black Sea constitutes a typical 2-layered stratified system, with an ~100 m thick layer of relatively fresh surface water separated from the underlying water body (~2000 m deep) by a sharp permanent pycnocline located between σ_t ~ 14.5 and 16.5 (Oguz et al. 1993) (Fig. 7). Nitrate concentrations in the open Black Sea typically increase from densities σ_t ~ 14.2 to 14.5 towards a maximum at σ_t ~ 15.4 to 15.7 (Codispoti et al. 1991, Tugrul et al. 1992, Konovalov et al. 1997). In other words, the nitrate concentration starts to increase at the location of the permanent halocline (Fig. 7).

In summer, solar heating of the upper layer initiates a temperature gradient, the thermocline, which effectively isolates the upper part of the euphotic zone from the nutrient-rich underlying domain. In the thermocline, which normally coincides with the lower part of the euphotic zone, the summer subsurface chl *a* maximum is located (Fig. 7). In winter, an isothermal layer down to a depth of 70 to 80 m or deeper, i.e. depths of σ_t ~ 15.2 to 15.8 (Mamayev et al. 1994, Filipov 1968) occurs due to cooling and the subsequent convective mixing. This extends the mixed layer down to the upper part of the nitrate peak (Konovalov & Murray 2001). Another important process during the winter cooling is the formation and replenishment of the permanent CIL, formally bounded by 8°C isotherms, and usually located above σ_t ~ 15.2 to 15.8 with its core at σ_t ~ 14.5 to 14.6 (Tolmazin 1985; Ovchinnikov & Popov 1987). Thus, in summer, the CIL, with minimum core temperatures of ~6°C, is located between the permanent halocline and the seasonal thermocline (Fig. 7).

All of the above features of the Black Sea vertical physical and chemical structures show that the location of the summer subsurface chl *a* maximum corresponds to the seasonal thermocline, and the nitrate maximum corresponds to the permanent halocline. The separation of the halocline and the thermocline by an extensive CIL means that there is a barrier hindering the transport of 'new' nitrates to the euphotic zone. 'New' production in the subsurface chl *a* peak and in the surface layer will result only if there is vertical mixing to transport the nitrates from the halocline to the euphotic zone. Such transport can occur in the open sea by mechanisms of convection, advective currents and wind-driven entrainment as shown in the Kattegat (Møller 1996, Richardson 1996).

In contrast to the Kattegat, however, the transport of 'new' nitrates in the open Black Sea by wind-driven entrainment during summer is highly improbable due to the deep location of the nitrate maximum and the presence of strong vertical gradients. Wind mixing is thus dissipated in the seasonal thermocline. However, there is evidence that the Rim Current in the Black Sea has increased since the middle of the 1980s. For example, the increased mixing of the CIL indicated by decreasing temperatures at σ_t ~ 14.5 (corresponding to the CIL core) since 1985 (Konovalov & Murray 2001), suggests an intensification of the surface circulation. This change of the Rim Current results from low winter temperatures and causes intense water uplift in the centres of the cyclonic cells (Ozsoy & Unluata 1997). This enables the transportation of nitrate across the CIL by both turbulent motion and advection.

The intensification of the Rim Current coincided with the increase of summer chl *a* values in the subsurface maximum beginning around 1984–1985 (Fig. 5A), and subsequently in the surface layer about 1987–88 (Yunev et al. 2002). This corresponding pattern suggests that the intensification of the Rim Current after 1985 has increased the nitrate transport to the euphotic zone and consequently resulted in increasing chl *a* observations. The lack of summer chl *a* trends before the mid-1980s (Fig. 5A, as well as in Yunev et al. 2002) combined with the increasing nitrate inventory (Fig. 5B, as well as in Konovalov & Murray 2001) shows that the nitrate transport was low. Consequently, it could be assumed that summer primary production in the open Black Sea was mainly sustained by remineralized nitrogen prior to the change in 1985.

Due to the establishment of a thermocline in the summer period, the mechanisms for nutrient transport into the euphotic zone differ fundamentally from the winter period. Therefore, the trends in annual mean nutrient and oxygen levels in the open Black Sea, associated with the development of eutrophication between the mid-1970s to mid-1980s (see Konovalov & Murray 2001 and references therein), were not related to changes in summer chl *a* formation in either the surface or the subsurface maximum layer. We suggest that the increased nitrate level in the halocline during summer is related to the remineralization of increasing amounts of POM sinking after winter–early spring diatom blooms that were gradually increasing in intensity or duration during the 1975–1985 period. However, this must remain a speculation as there are almost no data from before 1986 to show the trends in winter–early spring DIPP, chl *a*, phytoplankton biomass, or community structure.

There are however some peculiar observations that do not fit the suggested hypothesis above. For example, the sharp increase of chl *a* in July 1992, both in the surface (Yunev et al. 2002) and in the subsurface maximum (Fig. 5A) do not agree with an expected gradual increase of the pigment concentration. As specified earlier, this may be due to the abnormally intensive bloom of coccolithophores at basin-wide scale observed in this particular year (Mankovsky et al. 1996, Yilmaz et al. 1998). Although the underlying mechanisms have not been fully clarified, it is suggested that this episode was related, at least to some extent, to the strong cooling event in winter 1991–1992, which precipitated changes in the main halocline structure of the open Black Sea that had considerable impacts for the next several years (Ivanov et al. 1997).

The extreme winter cooling in 1991–92 appears to be linked with the persistent atmospheric anomaly that occurred in the eastern Mediterranean/Black Sea region following the eruption of Mount Pinatubo in the Philippines in June 1991(Ozsoy & Unluata 1997). This event had significant ramifications for many ecosystems, particularly in the northern hemisphere (Halpert et al. 1993). For example, the Pinatubo eruption and the following cold air temperature anomaly in the winter of 1991–1992 stimulated an unusually deep (down to >850 m) vertical mixing in the Gulf of Eilat in the Red Sea, which increased the supply of nutrients to the surface and evoked extraordinarily large algal blooms (Genin et al. 1995).

Other effects of eutrophication

Secchi depth is an indirect indicator of eutrophication in the open Black Sea, because variation in light attenuation is largely related to changes in phytoplankton biomass, size distribution, and species composition (Falkowski & Wilson 1992, Mankovsky et al. 1996, Sanden & Hakansson 1996, Vladimirov et al. 1999, Nielsen et al. 2002). In recent decades changes in nutrient ratios and related effects on the phytoplankton community composition have been also documented (Conley et al. 1993, Dortch et al. 2001, Rousseau et al. 2002). Special emphasis has been placed on the ratio of Si and N because silicate limitation may shift the phytoplankton community from diatoms to non-diatom small-size species.

In the present study, the observed changes in Z_d during different interannual periods (before and after 1985) were associated with changes in different chl *a* profile parameters: the maximum value of summer chl *a* profile (C_m) and the depth at which C_m was found (Z^C_m) (Fig. 6). Evidently, the increase of chl *a* concentration in the surface layer (Yunev et al. 2002) and in the subsurface peaks (Fig. 5A), in the second half of the 1980s until the beginning of the 1990s, made a considerable contribution to the decrease of Z_d — 63% on average (Fig. 6A). At the same time, the alterations in Z_d before the mid-1980s (Fig. 5E) may have been caused by changes in the phytoplankton taxonomic and size structure initiated by drastic modifications of nutrient ratios in the Black Sea during this period. Humborg et al. (1997) documented decreases in the Si:N ratio from 42 in the 1970s to about 2.8 in the mid-1980s, which was related to numerous dam constructions at the Yugoslavia/Romania border.

All these changes might well be responsible for interannual variability of the chl *a* maximum depth location (Fig. 5D) and the significant correlation between Z_d and Z_m^C (Fig. 6B) in the period before 1985–1986. The latter could be explained by the fact that light and nutrient supply are key factors which shape the chl *a* profile during the period of temperature stratification (Kiørboe 1996). However, the suggested changes in the phytoplankton community can only be speculated, because information on the interannual variability of the species composition in the open Black Sea is very limited for both summer and winter before the mid-1980s (Georgieva 1993, Mankovsky et al. 1996).

In the period after 1986, increased nitrate supply to the euphotic zone (as described above), combined with the alteration of Si:N:P ratios to those not optimal for diatom growth, stimulated intense summer blooms of opportunistic non-siliceous phytoplankton — coccolithophores (mainly *Emiliana huxleyi*) and small flagellates — prevailing in certain periods (Mankovsky et al. 1996). This was especially the case in July 1992, when coccolithophores provided 91.4% of the total phytoplankton abundance compared to 45.5% in 1991 (Mankovsky et al. 1996) and only ~20% before 1986 (Georgieva 1993). Thus, the sharp decline in Z_d (especially in 1991) (Fig. 5E) and associated maximal shallowing of Z_m^C in 1992 (Fig. 5D) resulted from multiple, superimposed factors: (1) the significant proliferation of small size phytoplankton species, (2) the increase of chl *a* in the surface layer and in the profile maximum, and (3) metabolites of the invader ctenophore *Mnemiopsis* (Mankovsky et al. 1996), which mass-developed in the Black Sea in the late 1980s (Vinogradov et al. 1999).

So far, all observed changes in the Black Sea ecosystem characteristics after 1992–1993 (in the present study, Fig. 5A–C,E) have been considered signs of an improved ecological state (e.g. Konovalov et al. 1999b, Petranu et al. 1999, Vladimirov et al. 1999, Yunev et al. 2002). The recent findings of Konovalov & Murray (2001), however, provide new important insight for understanding the recent state of the Black Sea. They demonstrated that the current balance in the budgets of nutrients, oxygen, and sulfide was partly related to the increased oxygen flux that resulted from the very cold weather conditions in 1984–1985 and in 1992–1993. This implies that, despite the downtrend of the maximum nitrate and chl *a* levels after the beginning of the 1990s (Fig. 5A–C), the Black Sea ecosystem is quite far from the state it was in during the 1960s. It may have actually entered a stable state with an increased POM sedimentation flux and lower oxygen concentration in the CIL. This state of the Black Sea pelagic ecosystem appears to have become quasi-permanent, since no differences in chl *a* magnitude, seasonal and interannual dynamics have been detected from *in situ* measurements (1993 to 1996) or satellite data (1997 to 2002) (Yunev et al. 2004).

The present study gives some basis to postulate that the recent shifts in the physical, chemical, and biological characteristics of the Black Sea pelagic ecosystem, although having a different nature and manifestation during the periods of 1985 to 1992 and after 1992–93, were probably related more to changes in weather conditions than to changes in anthropogenic forcing. This is contrary to the prevailing mechanisms of the period before the mid-1980s. Consequently, the open Black Sea continues to maintain its high eutrophic state with strong modification of the Si:N:P ratios precipitating potential shifts in the phytoplankton size distribution and species composition.

Acknowledgements. This work was funded by the NATO Science for Peace program, contract CLG-979780 'COMParative ANalysis of eutrophicatION: Black Sea and Baltic Sea (COMPANION)', and partly by the CESUM-BS Project. We thank our friends and colleagues Gunni Ærtebjerg, National Environmental Research Institute (Denmark), and Aleksander Toompuu, Institute of Marine Systems, Tallinn Technical University (Estonia), for valuable comments to the manuscript and fruitful discussions and 3 anonymous reviewers for constructive criticisms. This manuscript benefited greatly from the scientific and editorial advices of Scott Nixon, to whom we thank for continuous guidance and moral support.

LITERATURE CITED

Allen JR, Slinn DJ, Shammon TM, HartnollRG, Hawkins SJ (1998) Evidence for eutrophication of the Irish Sea over four decades. Limnol Oceanogr 43:1970–1974

Besiktepe ST, Unluata U, Bologa AS (eds) (1999) NATO TU-Black Sea Project: environmental degradation of the Black Sea: challenges and remedies. Kluwer Academic Publishers, Dordrecht

Bezborodov AA, Eremeev VN (1993) The Black Sea: the oxic/anoxic interface. Marine Hydrophysical Institute, Sevastopol (in Russian)

Bodeanu N (1993) Microalgal blooms in the Romanian area of the Black Sea and contemporary eutrophication conditions. In: Smayda TJ, Shimizu Y (eds) Toxic phytoplankton blooms in the sea. Elsevier, Amsterdam, p 203–209

Bodeanu N, Moncheva S, Ruta G, Popa L (1998) Long-term evolution of the algal blooms in Romanian and Bulgarian Black Sea waters. Cercet Mar 31:37–55

Cloern JE (2001) Our evolving conceptual model of the coastal eutrophication problem. Mar Ecol Prog Ser 210:223–253

Cociasu A, Dorogan L, Humborg C, Popa L (1996) Long-term ecological changes in Romanian coastal waters of the Black Sea. Mar Pollut Bull 32:32–38

Codispoti LA, Friederich GE, Murray JW, Sakamoto CM (1991) Chemical variability in the Black Sea: implications of continuous vertical profiles that penetrated the oxic/anoxic interface. Deep-Sea Res Part A 38:691–710

Conley DJ, Schelske CL, Stoermer EF (1993) Modification of the biogeochemical cycle of silica with eutrophication. Mar Ecol Prog Ser 101:179–192

Dortch Q, Rabalais NN, Turner RE, Qureshi NA (2001) Impacts of changing Si/N rations and phytoplankton species composition. In: Rabalais NN, Turner RE (eds) Coastal hypoxia: consequences for living resources and ecosystems. Coastal and estuarine studies. American Geophysi-

cal Union, Washington, DC, p 37–48
Dugdale RC, Goering JJ (1967) Uptake of new and regenerated forms of nitrogen in primary productivity. Limnol Oceanogr 12:196–206
EEA (2001) Eutrophication in Europe's coastal waters. EEA Topic Rep 7/2001:1–87
Falkowski PG, Wilson C (1992) Phytoplankton productivity in the North Pacific Ocean since 1900 and implications for adsorption of anthropogenic CO_2. Nature 358:741–743
Filipov DM (1968) Circulation and structure of the Black Sea. Nauka, Moscow (in Russian)
Genin A, Lazar B, Brenner S (1995) Vertical mixing and coral death in the Red Sea following the eruption of Mount Pinatubo. Nature 377:507–510
Georgieva LV (1993) Species composition and the dynamics of phytocen. In: Kovalev AV, Finenko ZZ (eds) Plankton of the Black Sea. Naukova Dumka, Kiev, p 33–55 (in Russian)
GESAMP (2001) A sea of troubles. GESAMP Rep Stud 70: 1–35
Gray JS (1992) Eutrophication in the sea. In: Colombo G, Ferrari I, Ceccherelli VU, Rossi R (eds) Marine eutrophication and population dynamics. Proc 25th Eur Mar Biol Symp. Olsen & Olsen, Fredensborg, p 3–15
Halpert MS, Ropelewski CF, Karl TR, Angell JK, Stowe LL, Heim RRJ, Miller AJ, Rodenhuis DR (1993) 1992 brings return to moderate global temperature. EOS Trans Am Geophys Un 74:436–439
Humborg C, Ittekkot V, Cociasu A, von Bodungen B (1997) Effect of Danube River dam on Black Sea biogeochemistry and ecosystem structure. Nature 386:385–388
Ivanov L, Besiktepe S, Ozsoy E (1997) Physical oceanographic variability in the Black Sea pycnocline. In: Ozsoy E, Mikaelyan A (eds) Sensitivity to change: Black Sea, Baltic Sea and North Sea. Kluwer Academic Publishers, Dordrecht, p 265–274
Ivanov LI, Konovalov S, Melnikov V, Mikaelyan A and 24 others (1998) Physical, chemical and biological data sets of the TU Black Sea data base: description and evaluation. In: Ivanov L, Oguz T (eds) NATO TU-Black Sea Project: ecosystem modeling as a management tool for the Black Sea, Vol 1. Kluwer Academic Publishers, Dordrecht, p 11–38
Jonge VN de, Boynton W, D'Elia CF, Elmgren R, Welsh BL (1994) Responses to developments in eutrophication in four different North Atlantic estuarine systems. In: Dyer KR, Orth RJ (eds) Changes in fluxes to estuaries: implications from science to management. Olsen & Olsen, Fredensborg, p 79–196
Jørgensen BB, Richardson K (eds) (1996) Eutrophication in coastal marine ecosystems. Coastal and Estuarine Studies 52. American Geophysical Union, Washington, DC
Kideys AE (2002) Fall and rise of the Black Sea ecosystem. Science 297:1482–1484
Kideys AE, Kovalev AV, Shulman G, Gordina A, Bingel F (2000) A review of zooplankton investigations of the Black Sea over the last decade. J Mar Syst 24:355–371
Kiørboe T (1996) Material flux in the water column. In: Jørgensen BB, Richardson K (eds) Eutrophication in coastal marine ecosystems. Coastal and estuarine studies 52. American Geophysical Union, Washington, DC, p 67–94
Konovalov S, Romanov A, Salihoglu I, Basturk O, Tugrul S, Gokmen S (1994) Intercalibration of CoMSBlack-93a chemical data; unification of methods for dissolved oxygen sulfide analyses and sampling strategies CoMSBlack-94a cruise. Report of Institute of Marine Sciences, Erdemli
Konovalov SK, Murray JW (2001) Variations in the chemistry of the Black Sea on a time scale of decades (1960–1995). J Mar Syst 31:217–243
Konovalov SK, Tugrul S, Basturk O, Salihoglu I (1997) Spatial isopycnal analysis of the main pycnocline chemistry of the Black Sea: seasonal and interannual variations. In: Ozsoy E, Mikaelyan A (eds) Sensitivity to change: Black Sea, Baltic Sea and North Sea. Kluwer Academic Publishers, Dordrecht, p 197–210
Konovalov SK, Eremeev VN, Suvorov AM, Khaliulin AK, Godin EA (1999a) Climatic and anthropogenic variations in the sulfide distribution in the Black Sea. Aquatic Geochem 5:13–27
Konovalov SK, Ivanov LI, Murray JW, Eremeeva LV (1999b) Eutrophication: a plausible cause for changes in hydrochemical structure of the Black Sea anoxic layer. In: Besiktepe ST, Unluata U, Bologa AS (eds) NATO TU-Black Sea Project: environmental degradation of the Black Sea: challenges and remedies. Kluwer Academic Publishers, Dordrecht, p 61–74
Konovalov SK, Ivanov LI, Samodurov AS (2000) Oxygen, nitrogen and sulfide fluxes in the Black Sea. Medit Mar Sci 1/2:41–59
Kushnir VM, Yunev OA, Finenko ZZ (1999) Influence of vertical synoptic currents on chlorophyll 'a' distribution in the Black Sea. Okeanologiya 39:202–211 (in Russian)
Lewis MR, Cullen JJ, Platt T (1983) Phytoplankton and thermal structure in the upper oceans: consequences of nonuniformity in chlorophyll profile. J Geophys Res 88:2565–2570
Luther GW III, Church TM, Powell D (1991) Sulfur speciation and sulfide oxidation in the water column of the Black Sea. Deep-Sea Res 38(Suppl 2A):S1121–S1137
Mamayev OI, Arkhipkin VS, Touzhilkin VS (1994) T-S analysis of the Black Sea waters. Okeanologiya 34:178–192 (in Russian)
Mankovsky VI, Vladimirov VL, Afonin EI, Mishonov AV, Solovev MV, Anninsky BE, Georgieva LV, Yunev OA (1996) Long-term variability of the Black Sea water transparency and reasons for its strong decrease in the late 1980s and early 1990s. Marine Hydrophysical Institute and Institute of Biology of the Southern Seas, Sevastopol (in Russian)
Mee L (1992) The Black Sea in crisis: call for concerned international action. Ambio 21:278–286
Møller JS (1996) Water masses, stratification and circulation. In: Jørgensen BB, Richardson K (eds) Eutrophication in coastal marine ecosystems. Coastal and Estuarine Studies 52. American Geophysical Union, Washington, DC, p 51–66
Moncheva S, Gotsis-Skretas O, Pagou K, Krastev A (2001) Phytoplankton blooms in the Black Sea and Mediterranean coastal ecosystem subjected to anthropogenic eutrophication: similarities and differences. Estuar Coast Shelf Sci 53:281–295
Morel A, Berton JF (1989) Surface pigments, algal biomass profiles, and potential production of the euphotic layer: relationships reinvestigated in view of remote-sensing applications. Limnol Oceanogr 34:1545–1562
Murray JW, Codispoti LA, Frederich GE (1995) Oxidation-reduction environments: the suboxic zone in the Black Sea. In: Huang CP, O'Melia CR, Morgan JJ (eds) Aquatic chemistry: interfacial and interspecial processes. ACS Adv Chem Ser 244:157–176
Nielsen SL, Sand-Jensen K, Borum J, Geertz-Hansen O (2002) Phytoplankton, nutrients, and transparency in Danish coastal waters. Estuaries 25:930–937
Niermann U, Kideys AE, Kovalev AV, Melnikov V, Belokopytov V (1999) Fluctuations of pelagic species of the open Black Sea during 1980–1995 and possible teleconnections. In: Besiktepe ST, Unluata U, Bologa AS (eds) NATO

TU-Black Sea Project: environmental degradation of the Black Sea: challenges and remedies. Kluwer Academic Publishers, Dordrecht, p 147–173
Nixon SW (1995) Coastal marine eutrophication: a definition, social causes, and future concerns. Ophelia 41:199–219
Oguz T, Besiktepe S (1999) Observations on the Rim Current structure, CIW formation and transport in the Western Black Sea. Deep-Sea Res I 46:1733–1753
Oguz T, Latun VS, Latif MA, Vladimirov VV and 6 others (1993) Circulation in the surface and intermediate layers of the Black Sea. Deep-Sea Res 40:1597–1612
Oguz T, Aubrey DG, Latun VS, Demirov E and 7 others (1994) Mesoscale circulation and thermohaline structure of the Black Sea observed during HydroBlack'91. Deep-Sea Res 41:603–628
Oguz T, Ducklow H, Shushkina EA, Malanotte-Rizzoli P, Tugrul S, Lebedeva LP (1998) Simulation of upper layer biogeochemical structure in the Black Sea. In: Ivanov L, Oguz T (eds) NATO TU-Black Sea Project: ecosystem modeling as a management tool for the Black Sea, Vol 2. Kluwer Academic Publishers, Dordrecht, p 257–300
Ovchinnikov IM, Popov YuI (1987) Formation of a cold intermediate layer in the Black Sea. Okeanologiya 27:739–746 (in Russian)
Ozsoy E, Unluata U (1997) Oceanography of the Black Sea: a review of some recent results. Earth-Sci Rev 42:231–272
Petranu A, Apas M, Bodeanu N, Bologa AS, Dumitrache C, Moldoveanu M, Radu G, Tiganus V (1999) Status and evolution of the Romanian Black Sea coastal ecosystem. In: Besiktepe ST, Unluata U, Bologa AS (eds) NATO TU-Black Sea Project: environmental degradation of the Black Sea: challenges and remedies. Kluwer Academic Publishers, Dordrecht, p 175–195
Platt T, Caverhill C, Sathyendranath S (1991) Basin-scale estimates of ocean primary production by remote sensing: the North Atlantic. J Geophys Res 96:15147–15159
Richardson K (1996) Carbon flow in the water column case study: the southern Kattegat. In: Jørgensen BB, Richardson K (eds) Eutrophication in coastal marine ecosystems. Coastal and Estuarine Studies 52. American Geophysical Union, Washington, DC, p 95–114
Richardson K, Christoffersen A (1991) Seasonal distribution and production of phytoplankton in the southern Kattegat. Mar Ecol Prog Ser 78:217–227
Rousseau V, Leynaert A, Daoud N, Lancelot C (2002) Diatom succession, silification and silicic acid availability in Belgian coastal waters (southern North Sea). Mar Ecol Prog Ser 236:61–73
Sanden P, Hakansson B (1996) Long-term trends in Secchi depth in the Baltic Sea. Limnol Oceanogr 41:346–351
Smetacek V, Bathmann U, Nothing EM, Scharek R (1991) Coastal eutrophication: causes and consequences. In: Mantoura RFC, Martin JM, Wollast R (eds) Ocean margin processes in global change. John Wiley & Sons, New York, p 251–279
Solic M, Krstulovic N, Marasovic I, Baranovic A, Pucher-Petkovic T, Vucetic T (1997) Analysis of time series of planktonic communities in the Adriatic Sea: distinguishing between natural and man-induced changes. Oceanol Acta 20:131–143
Tolmazin D (1985) Changing coastal oceanography of the Black Sea. 1. Northwestern Shelf. Prog Oceanogr 15:217–276
Tugrul S, Basturk O, Saydam C, Yilmaz A (1992) Changes in the hydrochemistry of the Black Sea inferred from water density profiles. Nature 359:137–139
Vedernikov VI, Demidov AB (1997) Vertical distribution of primary production and chlorophyll during different seasons in deep regions of the Black Sea. Oceanology (Moscow) 37:376–384 (English translation)
Vinogradov ME, Shushkina EA, Mikaelyan AS, Nezlin NP (1999) Temporal (seasonal and interannual) changes of ecosystem of the open waters of the Black Sea. In: Besiktepe ST, Unluata U, Bologa AS (eds) NATO TU-Black Sea Project: environmental degradation of the Black Sea: challenges and remedies. Kluwer Academic Publishers, Dordrecht, p 109–129
Vladimirov VL, Mankovsky VI, Solovev MV, Mishonov AV, Besiktepe ST (1999) Hydro-optical studies of the Black Sea: history and status. In: Besiktepe ST, Unluata U, Bologa AS (eds) NATO TU-Black Sea Project: environmental degradation of the Black Sea: challenges and remedies. Kluwer Academic Publishers, Dordrecht, p 245–256
Yayla MK, Yilmaz A, Morkoc E (2001) The dynamics of nutrient enrichment and primary production related to the recent changes in the ecosystem of the Black Sea. Aquat Ecosyst Health Manag 4:31–49
Yilmaz A, Yunev O, Vedernikov V, Moncheva S, Bologa AS, Cociasu A, Ediger D (1998) Unusual temporal variations in the spatial distribution of chlorophyll-a in the Black Sea during 1990–1996. In: Ivanov L, Oguz T (eds) NATO TU-Black Sea Project: ecosystem modeling as a management tool for the Black Sea, Vol 1. Kluwer Academic Publishers, Dordrecht, p 105–120
Yunev OA (1994) Typization and parameterization of vertical distribution of chlorophyll in the different regions of the World Ocean. In: Marshall JLe, Jasper JD (eds) Proceedings of the Pacific Ocean Remote Sensing Conference (PORSEC '94), Melbourne, Australia March 1–4, 1994, Vol 2. Bureau of Meteorology Research Center, Melbourne
Yunev OA, Finenko ZZ, Vedernikov VI, Yilmaz A (1999) Vertical chlorophyll distribution in the Eastern Mediterranean and Black Sea: quantitation description, connection between parameters, statistical estimation. In: Balopoulos ETh, Iona A, Sakellariou D (eds) Oceanography of the Eastern Mediterranean and Black Sea. Similarities and differences of two interconnected basins (Athens, Greece, 23–26 Feb 1999). The Institute of Oceanography, Nat Centre for Mar Res, Athens, p 44–45
Yunev OA, Vedernikov VI, Basturk O, Yilmaz A, Kideyes AE, Moncheva S, Konovalov SK (2002) Long-term variations of surface chlorophyll *a* and primary production in the open Black Sea. Mar Ecol Prog Ser 230:11–28
Yunev OA, Suetin V, Suslin V, Moncheva S (2004) Long-term changes in the Black Sea surface chlorophyll *a* according to *in situ* and modern satellite data. In: Dahlin H, Flemming NC, Nittis K, Petersson SE (eds) Building the European capacity in operational oceanography. Proc Third Int Conf EuroGOOS, 3–6 December 2002, Athens, Greece. Elsevier, Amsterdam, p 168–173
Yuneva TV, Svetlichny LS, Yunev OA, Romanova ZA and 5 others (1999a) Nutritional condition of female *Calanus euxinus* from cyclonic and anticyclonic regions of the Black Sea. Mar Ecol Prog Ser 189:195–204
Yuneva TV, Yunev OA, Bingel F, Kideys AE, Shulman GE (1999b) Relationship between lipid content of Black Sea *Calanus euxinus* and dynamic activity of its environment. Rep Acad Sci (Moscow) 369:715–720 (in Russian)
Zaitsev YP (1993) Impacts of eutrophication on the Black Sea fauna. Stud Rev Gen Fish Counc Mediterr (FAO) 64:63–86
Zaitsev YP, Aleksandrov BG (1997) Recent man-made changes in the Black Sea ecosystem. In: Ozsoy E, Mikaelyan A (eds) Sensitivity to change: Black Sea, Baltic Sea and North Sea. Kluwer Academic Publishers, Dordrecht, p 25–32

Editorial responsibility: Otto Kinne (Editor-in-Chief), Oldendorf/Luhe, Germany

Submitted: June 9, 2004; Accepted: January 3, 2005
Proofs received from author(s): May 3, 2005