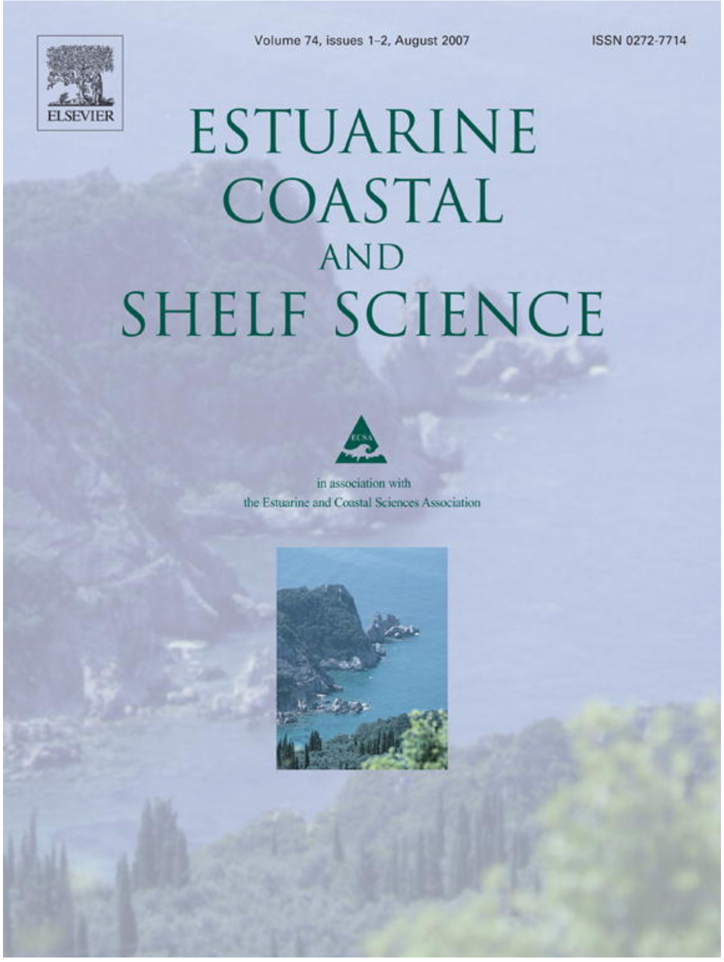

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Nutrient and phytoplankton trends on the western Black Sea shelf in response to cultural eutrophication and climate changes

Oleg A. Yunev [a,*], Jacob Carstensen [b], Snejana Moncheva [c], Aleksey Khaliulin [d], Gunni Ærtebjerg [b], Scott Nixon [e]

[a] *Institute of Biology of the Southern Seas, Animal Physiology, National Academy of the Sciences of Ukraine, Nakhimov Av. 2, Sevastopol 99011, Ukraine*
[b] *National Environmental Research Institute, Roskilde DK-4000, Denmark*
[c] *Institute of Oceanology, Bulgarian Academy of Sciences, Varna 9000, Bulgaria*
[d] *Marine Hydrophysical Institute, National Academy of the Sciences of Ukraine, Sevastopol 99011, Ukraine*
[e] *Graduate School of Oceanography, University of Rhode Island, Narragansett, RI 02882-1197, USA*

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Abstract

Long-term trends (1960s–1990s) in surface winter nutrients and summer oxygen concentration of the euphotic zone, as well as seasonal and interannual variability in surface chlorophyll *a* (chl *a*) and Secchi depth (Z_d) were investigated for different shelf regions (depth <50 m) of the western Black Sea. Increasing phosphate and nitrate levels and changes in the summer oxygen concentration on the shelf before the mid-1980s corresponded well with the increase in riverine nutrient inputs. At the same time, decreasing silicate levels resulted almost equally from enhanced diatom stripping and trapping of silicate in the numerous dams constructed on the Danube River. The associated decrease in the Si:N ratio caused a shift towards more non-siliceous phytoplankton blooms. A decoupling of winter nutrient levels and summer oxygen concentration on the shelf after the mid-1980s suggests that other sources of inputs, such as regenerated nutrients from shelf sediments and/or upwelling, may have increased substantially. Large variations in the regional climate during the 1980s and 1990s could potentially account for increases from either or both of these sources and the resulting high summer primary production despite decreasing winter nutrients. The seasonal pattern in chl *a* within the Ukrainian NW shelf is similar to the open Black Sea, with low chl *a* in summer and high concentrations in cold months. The seasonal chl *a* variations on the Romanian and Bulgarian shelves also show high concentrations in May/June, most likely related to the Danube River maximum discharge during spring. As a result, chl *a* annual means in these two regions are significantly higher than – in the Ukrainian NW shelf.

Keywords: western Black Sea shelf; nutrients; oxygen; chlorophyll *a*; Secchi depth; long-term variability; seasonality; eutrophication trends

1. Introduction

The 20th century was marked by significant changes in land use throughout the world, and the watershed of the Black Sea was no exception (Mee, 1992; Zaitsev, 1992; Leppäkoski and Mihnea, 1996; Mee et al., 2005). One of the prominent anthropogenic changes was the alteration of nitrogen, phosphorus and silicon fluxes to coastal ecosystems (Nixon, 1995; Conley, 2000; Cloern, 2001; Dortch et al., 2001; Turner et al., 2003). Generally, increased N and P inputs to coastal areas stimulate excessive phytoplankton growth, increase algae biomass, and change oxygen concentrations in the surface and bottom waters. At the same time, declines in dissolved silicate (an essential nutrient for diatoms) from eutrophication and dam constructions, as well as the consequent alteration of the N:P:Si ratios to levels not optimal for diatom growth, may stimulate abrupt shifts in the phytoplankton community from diatom dominance to a progressively increasing importance of opportunistic non-siliceous phytoplankton species such as coccolithophores, dinoflagellates, and microflagellates.

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* Corresponding author.
E-mail address: yunev@mail.ru (O.A. Yunev).

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Published data and information for assessing the state of eutrophication in Europe are mainly available from the Baltic Sea, the Wadden Sea, and the North Sea, whereas few data are accessible from other European marine waters, including the Black Sea (Leppäkoski and Mihnea, 1996; European Environment Agency, 2001). The lack of data from the Black Sea is particularly unfortunate because environmental degradation in the Black Sea is probably the most severe among the various basins of the World Ocean, and cultural eutrophication is cited as one of the key anthropogenic pressures (Intergovernmental Oceanographic Commission, 1996). The Black Sea has a drainage area/water basin area ratio of over 5, among the highest of large semi-enclosed water bodies, and there are more than 163 million people living in the drainage basin (Mee, 1992; Leppäkoski and Mihnea, 1996). The combination of a large drainage area and a high population density with the long residence time of water within the system (∼2000 years, Ozsoy, 1999) clearly makes the Black Sea ecosystem very sensitive to land-use practices.

In the 1990s several reviews on ecosystem changes in the Black Sea appeared (e.g., Mee, 1992; Leppäkoski and Mihnea, 1996; Zaitsev and Alexandrov, 1997; Besiktepe et al., 1999). Some of these changes may have been direct or indirect consequences of developing eutrophication. The precipitous reduction of the unique community "Zernov's *Phyllophora* field" in the center of the NW shelf in the 1970s is a typical example of seaweed population degradation caused by eutrophication, because *Phyllophora* is vulnerable to light limitation and hypoxia (Zaitsev, 1992). Other ecosystem changes in the Black Sea concerned with eutrophication include benthic species mass mortality related to hypoxia/anoxia events (Zaitsev and Alexandrov, 1997), replacement of large species of crustacean plankton by smaller species (Zaitsev, 1992), introduction of opportunistic predators such as the snail *Rapana thomasiana* or the ctenophore *Mnemiopsis leidyi* into the Black Sea waters (Shushkina and Vinogradov, 1991; Zaitsev, 1992; Shiganova, 1998; Besiktepe et al., 1999).

The effects of eutrophication and altered nutrient ratios on phytoplankton have also been documented for the Black Sea. Average phytoplankton biomass in the NW shelf area was 670 mg wet weight m^{-3} in the 1950s, increasing to 1030 mg m^{-3} in the 1960s, 18,690 mg m^{-3} in 1970s, and 30,000 mg m^{-3} in the 1980s (Zaitsev, 1993). The average density of *Skeletonema costatum* in Romanian waters in 1962–1965 was about 2 million cells/l, increasing to 97 million cells/l in the 1970s (Mihnea, 1985). Intensive and frequent harmful algal blooms have been recorded in the Romanian and Bulgarian sectors of the western Black Sea shelf (Bodeanu, 1993; Bodeanu et al., 1998; Petranu et al., 1999; Moncheva et al., 2001). In Bulgarian waters the average proportion of diatom biomass decreased from 86% before the 1970s to 42% during 1971–1990 (Moncheva and Krastev, 1997).

Despite a wide spectrum of eutrophication manifestations, there are few regular long-term data sets in the Black Sea (an important exception is the phytoplankton study of Bodeanu and colleagues, who monitored the Romanian shelf area for almost 40 years, e.g., Bodeanu et al., 1998, 2002). Moreover, even in the case of the long-term phytoplankton observations, the results are generally presented as multiannual averages of biomass or cell numbers. Such averaging is unfortunate because it obscures potentially important nonlinear responses to nutrient enrichment as shown by data analysis (Zaitsev, 1992) and by model studies (Kemp et al., 2001; Mee et al., 2005). Such non-linear behavior suggests that the ecosystem may decline through a series of resilient steady states, characterized by thresholds for the collapse of each steady state. Besides, the ecosystem may demonstrate hysteresis or even irreversibility, and lowering nutrient loading by nutrient management does not automatically imply that the system will definitely return to earlier levels of organization (Mee et al., 2005). Long-term and detailed data sets, including a large variety of ecosystem variables, are required to critically assess such mechanisms.

Together with measurements of phytoplankton species abundance, composition, and biomass, chlorophyll *a* (chl *a*), Secchi depth (Z_d), nutrient and oxygen concentrations are important measures of ecosystem status. Fortunately, the four latter properties are also easily measured and widely available (e.g., European Environment Agency, 2001; Wasmund et al., 2001; HELCOM, 2002; Yunev et al., 2005; Andersen et al., 2006). Since 1961 numerous measurements of chl *a* have been made in the Black Sea, primarily to study seasonal and interannual variability in different regions of the deep, open part of the sea (e.g., see references in Yunev et al., 2002). Patterns of long-term changes in chl *a*, vertical distribution of chemical properties (Konovalov et al., 1999; Konovalov and Murray, 2001; Yunev et al., 2002, 2005), and in Z_d (Mankovsky et al., 1996; Vladimirov et al., 1999; Yunev et al., 2005) have also been published for the open Black Sea. In contrast to the situation for the deep, open waters, detailed seasonal, interannual, and long-term studies on chl *a* and Z_d variability in the Black Sea shelf regions (<200 m) have not previously been available.

Long-term chemical investigations on the Black Sea shelf have mainly been carried out in the Romanian sector at individual stations in winter or on the whole Romanian shelf area in summer (Cociasu et al., 1996, 1997). As discussed in these studies, the winter sampling stations were located either in Danube Branches (like Sulina station), or slightly south of the Navodari industrial complex (Constanta station). As a result, these measurements largely reflect variations in the Danube River nutrient loads or local effects from industrial wastewater discharges (Constanta station). It should also be noted that investigations of summer nutrients within the Romanian shelf did not include measurements during the late 1970s, that phosphate and silicate data are missing for the late 1980s, and that no nitrate data are available before the beginning of the 1980s (Cociasu et al., 1997).

Actually, the gaps in detailed seasonal and long-term hydrochemical, biological, and bio-optical data for the Black Sea shelf area are consequences of national constraints to marine monitoring and the lack of consistent International Co-operative Marine Science Programs prior to the relatively recent political changes in Eastern Europe (Unluata et al., 1993). This contrasts markedly with the Baltic Sea, where eutrophication was recognized as a major environmental threat resulting in establishment of the Baltic Marine Environment Protection Commission (Helsinki Commission, HELCOM) in 1974. This led to data collection under the Baltic Monitoring Program (BMP) and trends assessment (e.g., Schulz et al., 1992; HELCOM, 2002).

With the initiation of international, regional, multi-disciplinary databases created within the framework of the NATO TU Black Sea and MEDAR/MEDATLAS II Projects at the end of the 1990s and beginning of the 2000s (Ivanov et al., 1998; Maillard et al., 2002), long-term studies of various eutrophication aspects for the Black Sea became possible. These databases include principal physical, chemical, biological and bio-optical variables from almost all Black Sea riparian countries. The data are generally on a basin-wide scale and cover the period of most dramatic change for the Black Sea ecosystem, starting from the ‘little impact’ state in the 1960s (e.g., see references in Yunev et al., 2002, 2005). The NATO TU-BS database and data from several national marine institute databases have already been used to study temporal trends in the variability of chl *a*, depth-integrated primary production, Z_d and chemical characteristics in the open regions of the Black Sea (Konovalov et al., 1999; Vladimirov et al., 1999; Konovalov and Murray, 2001; Yunev et al., 2002, 2005).

In this paper we report long-term changes of nutrients, oxygen, phytoplankton and bio-optical variables in different Black Sea shelf regions starting from the 1960s. Our aim was to investigate a potential link between changing anthropogenic nutrient inputs and ecological changes on the Black Sea shelf, but the results lead us to speculate on the influence of climatic change in this region as well.

2. Materials and methods

We investigated surface (0 m) nutrients (phosphate, nitrate and silicate, μM), oxygen (mg l^{-1}) in the surface and below the thermocline, surface chl *a* (mg m^{-3}) and Z_d (m) of the inner western shelf regions (depth <50 m) of the Black Sea (Fig. 1). The study area is the widest shelf region of the Black Sea, extending from Crimea in Ukraine across Romania and along the Bulgarian shelf down to the northwestern coast of Turkey. Besides, the area is subjected to a high anthropogenic load, mainly through 4 large rivers: the Danube, the Dnepr, the Dnestr, and the Southern Bug, with a mean annual discharge of about 210, 50, 10 and 3 $km^3\ yr^{-1}$, respectively (Zaitsev et al., 2006). It should be noted that only the Danube River collects discharges from huge industrial and agricultural areas of 9 European countries (Mee, 1992). The density in the subsurface waters of the western shelf is largely determined by salinity except during warm months (approx May–September), when temperature effects predominate (Ozsoy and Unluata, 1997). Within this region, the halocline and thermocline generally coincide at a typical depth of ~10–20 m during summer (Aubrey et al., 1996).

This study is based on nutrient data from 1960 to 1995, oxygen data from 1960 to 1998, and chl *a* and Z_d data mainly from 1980 to 1995, pooled from 2 databases: NATO-TU-BS DB and MEDAR/MEDATLAS II Projects (MED/MAT DB) (Ivanov et al., 1998; Maillard et al., 2002). We added supplementary data from 3 institutes in Ukraine and Bulgaria (Institute of Biology of the Southern Seas and Marine Hydrophysical Institute, National Academy of the Sciences of Ukraine, Sevastopol, as well as Institute of Oceanology, Bulgarian Academy of Sciences, Varna) to expand the temporal range of data and increase the frequency of observations. For the Romanian shelf we also used published chl *a* data from 1963 and 1976 (Skolka, 1968; Bologa, 1977).

The high spatial variability of phytoplankton characteristics in the shelf area compared to the open Black Sea (e.g., according to *in situ* and satellite chl *a* data, Kopelevich et al., 2002; Yunev et al., 2002) may confound our understanding of temporal variations in chl *a* and, most likely, other eutrophication variables as well. In order to deal with this variability, we divided the western and northwestern interior shelf into 3 sub-regions, based on bathymetry, surface currents, chl *a* maps constructed from satellite data, as well as field data on anthropogenic impacts on the shelf areas (Fig. 1A) (US Global Ocean Flux Study Office, 1989; Zaitsev, 1993; Sur et al., 1994; Cociasu et al., 1996; Ozsoy and Unluata, 1997). The regional subdivision is described in detail by Yunev et al. (2002).

Generally, two phenomena in the western part of the Black Sea determine the spatial-temporal heterogeneity of the biological and chemical components in the surface layer: (1) the Danube River outflow; and (2) a basin scale, cyclonically meandering, boundary current (‘Rim Current’: Oguz et al., 1993), which is confined by a series of anticyclonic eddies along its periphery (Eremeev et al., 1992; Oguz et al., 1993). As a result, significant quantities of freshwater containing nutrients discharged by the Danube River are transported southwards (i.e. downstream) along the coast. CZCS (coastal zone color scanner) data from 1978 to 1986, for example, have shown a gradual but significant decrease in chl *a* concentration from the Romanian shelf towards both the south and north (Kopelevich et al., 2002). Thus, Region 2 (the Romanian shelf) is strongly influenced and Region 3 (the Bulgarian shelf), to a lesser degree, by Danube River discharges, whereas Region 1 (the Ukrainian shelf) is predominantly influenced by the Dnepr, the Dnestr and the Southern Bug rivers (Fig. 1A).

It has been shown that the summer phytoplankton production in many European seas depends on the amount of inorganic nutrients accumulated during winter (European Environment Agency, 2001; Wasmund et al., 2001). For this reason, we pooled surface nutrients for the cold months (January–March) to study long-term trends. In contrast, temporal trends in oxygen levels were analyzed for the warm months (May–September) for the layers above and below the thermocline (i.e. near-surface water and at about 20 m depth or just off the bottom at stations with depths <20 m). We assumed that interannual variations of oxygen concentration in the surface layer during a particular season and region with moderate changes of the temperature and salinity were dependent mainly on the phytoplankton photosynthetic activity, which again was associated with the winter nutrient stocks in the surface layer. The decline in oxygen concentration below the thermocline was assumed to be related mainly to increased oxygen consumption from the degradation of sinking particulate organic matter from primary production

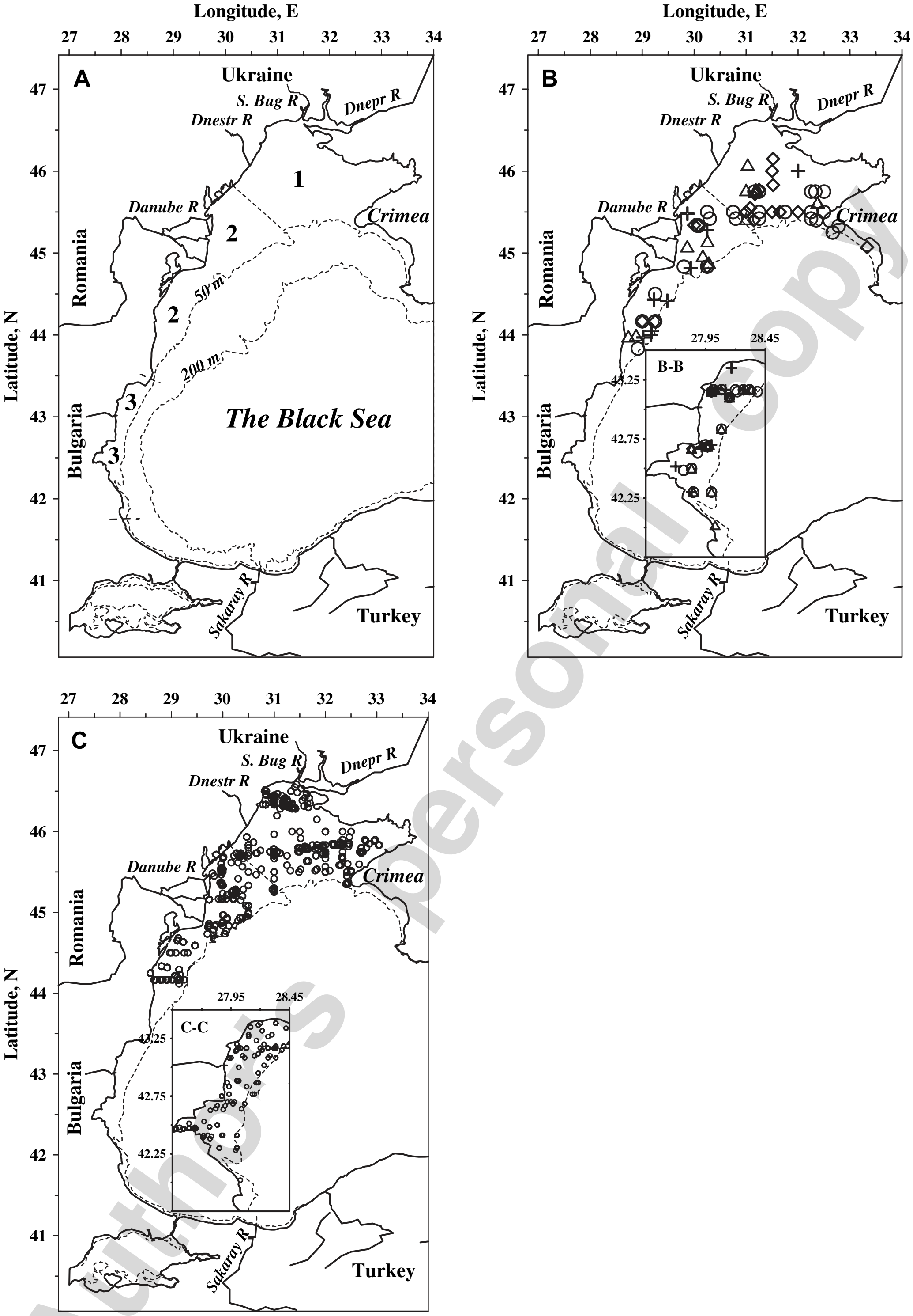

Fig. 1. Sub-regions of the inner shelf (depth <50 m) in the western part of the Black Sea (A) and examples of stations location where biological and chemical measurements were sampled during different monthly and interannual periods: chl *a* measurements in March–May (△), December–February (+), June–August (○), September–November (◇) during 1987–1992 correspondingly in Regions 1, 2 (B) and Region 3 (B-B); phosphate in Regions 1, 2 (C) and silicate in Region 3 (C-C) in January–March during 1960–1995.

(Elmgren, 1989; Konovalov et al., 1997). Thus, the interannual variability of oxygen concentration in the two layers might be a good indicator of the phytoplankton primary production changes.

Chl *a* was measured by 2 methods (spectrophotometry and fluorometry) as discussed in detail by Yunev et al. (2002). Comparison between the 2 methods allowed us to pool chl *a* data and use data without any method-specific correction in accordance with the results of Yunev et al. (2002, 2005). Nutrient and oxygen analytical techniques, and determination of Z_d, as well as the criteria for the integration of data sampled by different Black Sea riparian countries were given in the reports of the TU-BS DB chemical and bio-optical expert groups (Ivanov et al., 1998).

Because there were many missing chl *a* and Z_d data for almost all individual years and all regions, we assessed their seasonal patterns based on data sets compiled for different quasi-stationary interannual periods. We defined these periods (to some extent conditionally) according to the results reported for long-term changes of different phytoplankton and biogeochemical characteristics in the Black Sea (Cociasu et al., 1996; Zaitsev and Alexandrov, 1997; Petranu et al., 1999; Konovalov and Murray, 2001; Yunev et al., 2002). Unfortunately, even with this treatment the compilation of data on the spatial-temporal distributions of chl *a* in the shelf area of the western part of the basin contains large discrepancies, for example, with regard to sampling intensity and coverage for the different months (Fig. 1B,B-B). Moreover, in two regions (Regions 1 and 3) chl *a* data were missing for 2 periods: pre-eutrophication (before 1971) and early phase of the eutrophication (1971−1976). But, the number of chl *a* observations, for example, for 1980−1986 and 1987−1992 were approximately similar (105 and 125, respectively) and almost evenly distributed between regions. However, this compares with 9 observations for the pre-eutrophication period from just one region (Region 2). The inconsistencies were similar for Z_d data (410 observations). On the other hand, the spatial coverage of chemical data was more homogeneous (e.g., Fig. 1C,C-C) and both nutrient and oxygen data were sufficient to analyze the long-term variability on an annual basis.

SigmaPlot for Windows and its supplement ANOVA programs were used for the statistical analysis and data processing. The significance of the difference between means was evaluated with the Student's *t*-test (Zar, 1984) using a significance level of 5% to determine quasi-stationary periods (monthly and interannual), i.e. periods exhibiting relatively stable values of the investigated variables.

3. Results

3.1. Long-term changes of winter nutrients and summer oxygen concentration within the different shelf regions

3.1.1. Phosphate and nitrate in the surface layer

Statistically significant trends in both nutrients using annual means were found from the 1960s within Regions 1 and 2 (no data are available for Region 3) (Fig. 2). Winter phosphate within Region 1 (no nitrate or ammonia data are available) increased from 0.14 ± 0.6 to 0.36 ± 0.2 μM at a rate of ~0.01 μM yr^{-1} (1965−1983) (Fig. 2A). The initial mean values of winter phosphate (before 1970) and nitrate (before 1964) within Region 2 were 0.11 ± 0.04 μM and 1.3 ± 0.1 μM, respectively, followed by a sharp increase (~12-fold) by the mid-1970s: phosphate up to 1.34 ± 0.33 μM in 1973 and nitrate up to 15.8 ± 9.4 μM in 1977 (Fig. 2B,C). It is interesting to note that both the rise and fall periods for nutrients within Region 2 were described well by power functions. After the mid-1980s (phosphate in Region 1), as well as after the end of the 1970s and the mid-1980s (correspondingly phosphate and nitrate in Region 2), changes in the trends of both nutrients were also observed: phosphate within Region 1 stabilized at ~0.21 μM from 1984 to 1995, phosphate and nitrate within Region 2 at 0.3 ± 0.06 and 5.3 ± 1.13 μM, respectively.

3.1.2. Silicate in the surface layer

In contrast to nitrate and phosphate, statistically significant decreases in winter silicate (also using annual means) were found from the 1960s up to the mid-1980s within all shelf regions (Fig. 3). In Region 1, silicate decreased from 26.4 ± 6.5 to 9 ± 2.4 μM at a rate of ~0.74 μM yr^{-1} (1963−1986); in Region 2, from 41.3 ± 7 μM (the mid-1960s) down to 6.0 ± 2 μM (1985−1993) at a rate of ~1.38 μM yr^{-1}; and in Region 3, from 38 ± 5.9 (before the mid-1960s) down to 5.9 ± 1.8 μM (1984−1995) at a rate of ~1.51 μM yr^{-1}. It is worth noting that the rate of silicate decrease in Region 2 was twice as fast as in Region 1 for the same period and it was comparable to that obtained in Region 3.

3.1.3. Oxygen concentration in the surface and below the thermocline

In contrast to nutrients, statistically significant trends in annual means of oxygen concentration were found from the beginning of the 1960s up to the beginning of the 1990s within all shelf regions (Fig. 4). Summer oxygen concentration in the surface increased from ~5 to ~7 mg l^{-1} at a rate of ~0.04 mg l^{-1} yr^{-1} (Fig. 4 left panel), and decreased below the thermocline correspondingly from ~6.5 and ~7.5 mg l^{-1} to ~4 and ~5 mg l^{-1} at rates of ~0.06 and 0.082 mg l^{-1} yr^{-1} within Regions 1, 2 and Region 3 (Fig. 4 right panel). It is worth noting that Region 3 had the largest decrease of summer oxygen concentration below the thermocline. After 1991/1992, there was a pronounced decrease in oxygen concentration in the surface layer and its increasing below the thermocline within all shelf regions.

3.2. Seasonal and long-term changes of the surface chlorophyll a and the Secchi depth

Of the 3 regions examined, the long-term changes of chl *a* were clearly evident only for Region 2 (Fig. 5). The seasonal dynamics of chl *a* within this region were similar prior to-eutrophication and during the early phase of eutrophication, although it should be stressed that each period was represented by data from single years: 1963 and 1976, respectively (Fig. 5A). In both years, a significant increase of chl *a* concentration was observed in the early summer (June) in addition to the high winter and autumn values. This maximum is most likely related to the Danube River maximum discharge during spring (Humborg, 1997). The mean annual chl *a* in Region 2 for 1963 and 1976 were ~0.66 and 1.67 mg m^{-3}, respectively.

The data from the period of the 1980−1995 were, unfortunately, too sparse to investigate the seasonal pattern in detail

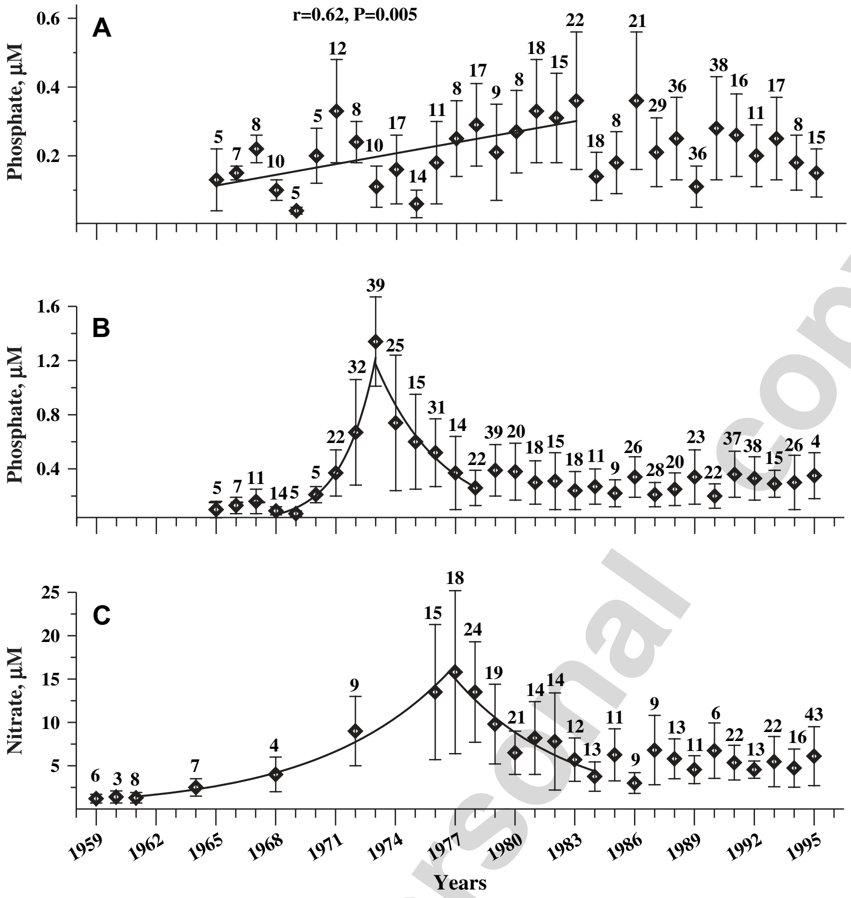

Fig. 2. Long-term changes in winter nutrients within the different shelf regions: (A) phosphate within Region 1; (B) phosphate; and (C) nitrate within Region 2. Each point represents the annual arithmetic mean for the entire interval January–March. Solid lines show the identified trends and standard deviations are marked by error bars with the number of observations used for averaging above.

even for the entire period (Fig. 5B). Nevertheless, a significant increase of chl *a* concentration in May was observed in addition to the high winter and autumn values. It is noteworthy also that the highest chl *a* concentrations during 1980–1992 were measured in May and September (~15.0 and 8.0 mg m^{-3}), following the months of maximum and minimum discharge of the Danube River (April/May and August/September, respectively, Humborg, 1997). Moreover, the chl *a* means in March and May from 1993 to 1995 (average of 1.7 ± 0.9 mg m^{-3}) within the in-Danube shelf were evidently lower than their corresponding means from the previous period 1980–1992 (~5–15 mg m^{-3}) (Fig. 5B). This may suggest a decreasing eutrophication after 1992 within this region, a trend even more apparent in the oxygen concentration throughout all the regions studied (Fig. 4), as discussed below.

The seasonal chl *a* patterns within two other regions (Regions 1 and 3) were obtained only for the entire period of the 1980–1995 (Table 1). Within Region 1, there were two monthly intervals with significantly different chl *a* means: August–March (~1.56 mg m^{-3}) and April–July (0.41 ± 0.21 mg m^{-3}). Contrary to Region 1, chl *a* levels within Region 3 were generally high for all months (> about 1.5 mg m^{-3}) including a pronounced maximum in May/June (3.46 ± 2.2 mg m^{-3}), similar to Region 2. The mean annual chl *a* in Regions 1 and 3 for the whole period was ~1.04 and ~3.1 mg m^{-3}, respectively.

The seasonality of Z_d within all regions was characterized by the availability of 2–3 quasi-stationary monthly intervals which were revealed for the entire period investigated (1980–1995), except for April–May within Region 2 (Table 1). It is interesting to note that the statistically significant increase of Z_d values in April/May of 1993–1995 agrees well with the chl *a* trend (cf. Fig. 5B and Table 1). The average of Z_d for the three seasons in which data were available (spring, summer and autumn) and for the whole period of 1980–1995 within Regions 1 and 3 was ~8.9 and 4.2 m, respectively, and transparencies within Region 2 before 1993 were lower than in Region 1: ~3.8-times for spring and ~1.5-times for summer/autumn.

4. Discussion

Increases in nutrient levels on the western Black Sea shelf were expected given the enhanced nutrient fluxes from land after the 1950s (Mee, 1992 and references therein). Nutrient (phosphate and nitrate + nitrite) measurements in different Danube Branches, viz, at Sulina station, where both loading and concentrations were measured (Cociasu et al., 1997),

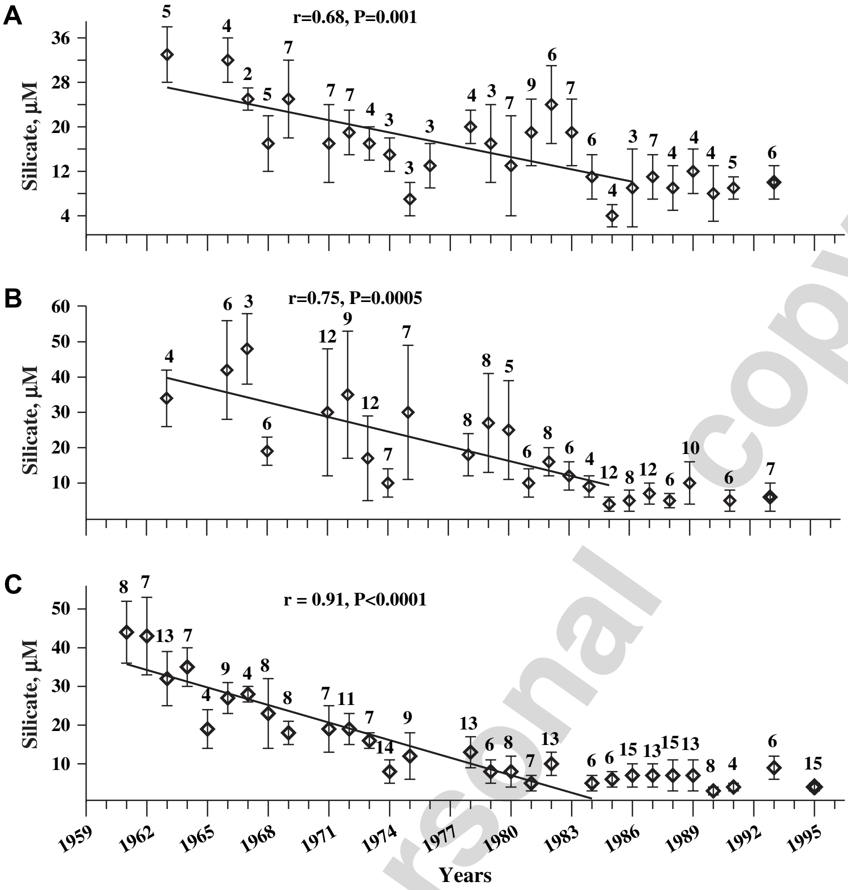

Fig. 3. Long-term changes in winter silicate within the different shelf regions: (A) Region 1; (B) Region 2; and (C) Region 3. Each point represents the annual arithmetic mean for the entire interval January–March. Solid lines show the identified trends and standard deviations are marked by error bars with the number of observations used for averaging above.

and in delta of Chilia Branch, where only concentrations were measured (Zaitsev et al., 2006 and references therein), have shown similar results in terms of loading and concentrations (Fig. 6). They increased from the 1960s (or the beginning of the 1980s) up to approximately the mid-1980s, with relatively constant values to the beginning of the 1990s, and then decreases thereafter. Long-term trends in nutrient inputs from the three other large rivers, i.e. the Dnepr, the Dnestr and the South Bug, were not available because monitoring has been irregular and results are only presented as multiannual averages for different periods (Zaitzev et al., 2006 and references therein). Besides, in contrast to the Danube, these rivers discharge into lagoons which act as biological filters, reducing the concentration and changing the ratio of nutrients (Zaitsev et al., 2006).

Despite the significant long-term changes in the Danube nutrient loading, it has been difficult to convincingly demonstrate any related trends in nutrient and oxygen concentrations within the shelf regions. This is particularly surprising because trends have been documented for the open Black Sea (Konovalov et al., 1999; Konovalov and Murray, 2001; Yunev et al., 2005). This may be because there have been fewer biogeochemical studies of long-term changes in the shelf areas and the shelf studies typically have a limited temporal and spatial extent (Cociasu et al., 1996, 1997). There are also many gaps in the nutrient data during the 1970s and 1980s, the periods of early and intensive eutrophication, and oxygen concentrations were not analyzed at all (Cociasu et al., 1997). Consequently, these studies may not be considered representative of the general hydrochemical trends within the entire NW shelf of the Black Sea.

Trends in summer oxygen concentration up to the beginning of the 1990s (Fig. 4) testify to an overall increasing phytoplankton photosynthetic activity during this period. Initially, the increasing nitrate and phosphate concentrations (Fig. 2) promoted increasing bloom intensity of the characteristic bloom-forming species during 1970s/1980s (Table 2 pattern 2). Diatoms dominated the growing phytoplankton community in this period (Table 2 pattern 1), increasing the stripping of dissolved silicate from the water column through sedimentation (Fig. 3). The reduction in silicate concentration was pronounced when large dams were built in the Danube River in the 1970s/1980s (Humborg et al., 1997) and, especially, after completion of the second Iron Gates barrage in 1983 (Panin and Jipa, 2002). The effect has been termed the 'artificial lake effect' caused by retention of silicate, as well as other nutrients, in the dam reservoir sediments (Mayer and Gloss, 1980; Van Bennekom and Salomons, 1980; Wahby and Bishara, 1980; Humborg et al., 2000). It is worth to note here that

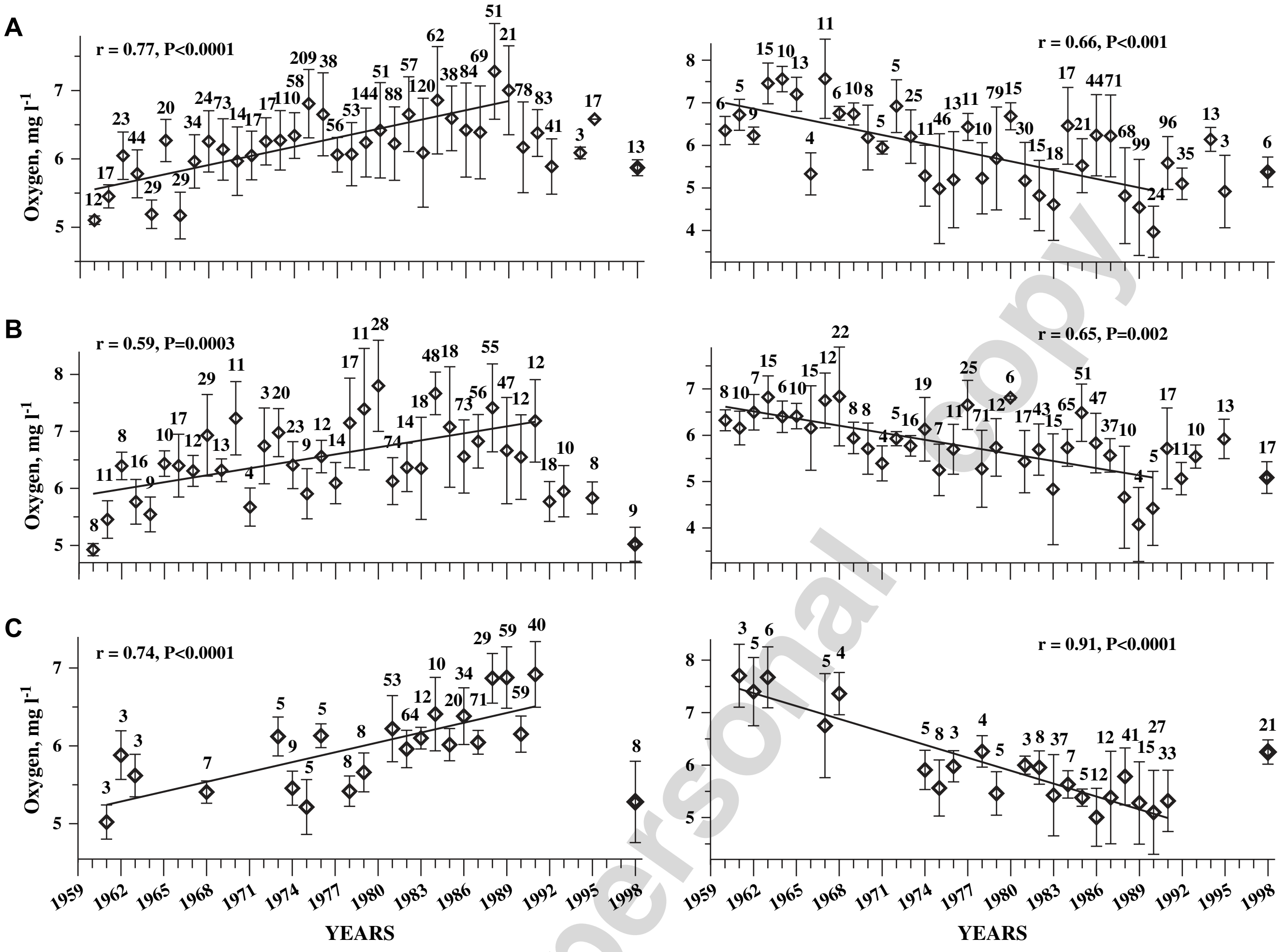

Fig. 4. Long-term changes in summer oxygen concentration in the surface (left panel) and below thermocline (right panel) within the different shelf regions: (A) Region 1; (B) Region 2; and (C) Region 3. Each point represents the annual arithmetic mean for the entire interval May–September. Solid lines show the identified trends and standard deviations are marked by error bars with the number of observations used for averaging above.

the building of the second Iron Gates barrage also induced a large decrease in the sediment discharge: by 50–70% compared to the mean value of the pre-damming sediment flux regime (Panin and Jipa, 2002). Thus, there are two factors for the significant decreases in silicate: (1) Danube River dam constructions trapping silicate in the dam reservoirs; and (2) nutrient enrichment enhancing diatom blooms and stripping silicate from the shelf waters. The fact that the decreases in silicate in Regions 2 and 3 (where the Danube is an important influence) were twice as fast as in Region 1 (where only biological uptake was important) (Fig. 3) suggests that nutrient enrichment and dam construction contributed approximately equally to the silicate trends along the Romanian and Bulgarian shelves.

The stabilization of the winter silicate concentration at ~6–9 μM after 1985 (Fig. 3), resulting in a Si:N ratio close to 1.0, combined with the increase in oxygen concentration in the surface and its decrease below the thermocline in all 3 regions (Fig. 4) may have caused a shift to more non-siliceous phytoplankton species. Generally, diatoms require N and Si in a ratio of about 1:1 (Redfield et al., 1963; Brzezinski, 1985), and in the fresh water competition for resources (N, P and Si) has successfully been used to explain the structure of the phytoplankton community (Tilman et al., 1982). Although the regulating effect of Si on the phytoplankton composition is well-known, the potential effects of silicate changes on primary production and direct proofs of Si-limited diatom growth in marine systems are less investigated (Kristiansen and Hoell, 2002). Therefore, decreasing the Si:N ratio to ~1.0 or less does not necessarily imply a change in the phytoplankton community structure, taking into account that species-specific deviations from the average Redfield ratios are considerable (Ryther and Dunstan, 1971).

However, changes in the nutrient concentrations and the Si:N ratio may have altered phytoplankton cell size and the species composition on the Romanian shelf (Table 2). The diatom/dinoflagellate abundance ratio decreased, the contribution of small-size phytoplankton species ('others') increased from 0.1% up to 41.7%, and the proportion of blooms dominated by *Prorocentrum cordatum* relative to *Skeletonema costatum* increased. In Bulgarian coastal waters similar changes have been observed: the average biomass proportion of diatoms was 86% (versus 14% of dinoflagellates) up to 1970 decreasing to 42% during 1971–1990 (Moncheva and Krastev, 1997).

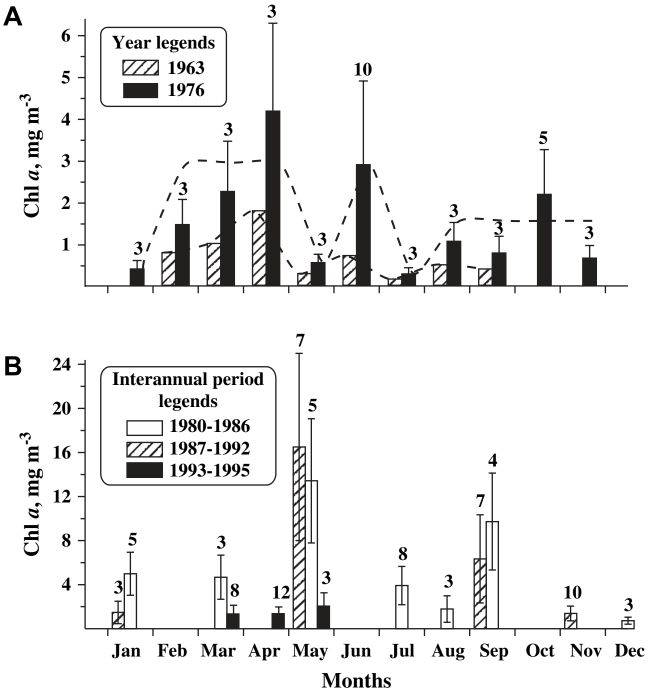

Fig. 5. Seasonal dynamics (dashed lines) of surface chl *a* within Region 2 during different annual (A); and interannual (B) periods. Each bar represents monthly mean for whole annual or interannual periods. Number of observations used for averaging and standard deviation for each month is shown with the bars.

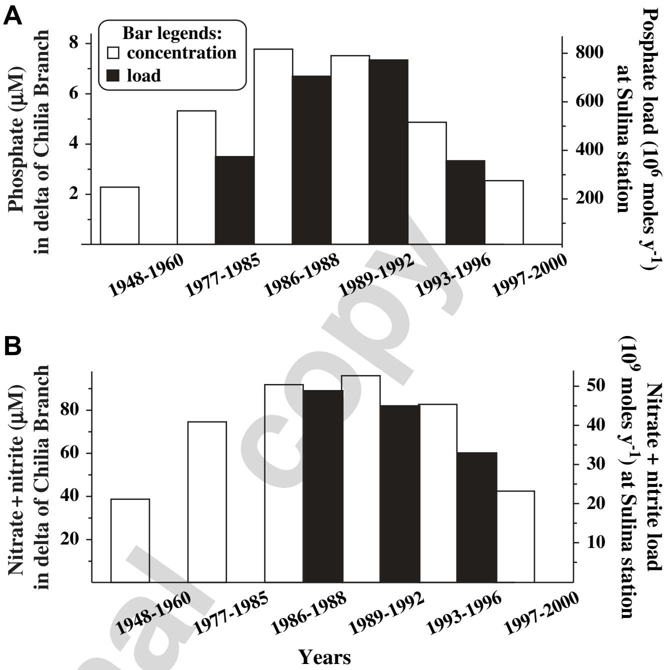

Fig. 6. Multiannual means of the phosphate (A); and nitrate + nitrite (B) concentrations, as well as their load at the different Danube branches: concentrations in delta of Chilia Branch (data from Zaitsev et al., 2006) and load in the Sulina Branch (Sulina station, data from Cociasu et al., 1997).

The pronounced changes of nitrate and phosphate within the Romanian shelf before and after the mid-1970s (Fig. 2B,C) can be attributed to 2 factors: (1) a sharp increase in the nutrient load at various points in the Danube in the second half of the 20th century and especially in the 1970s, as a consequence of the widespread use of phosphate detergents and intensification of agriculture in eastern and central Europe (Mee, 1992); and (2) numerous dam constructions within the upper and middle sections of the Danube which, for example, reduced sediment discharge after, approximately, the mid 1980s greatly (Panin and Jipa, 2002). The removal rate of nutrients in the numerous dam reservoirs was almost certainly significant as well, which could explain the abrupt decrease in nutrient levels in region 2 after the late 1970s (Fig. 2B,C). Indeed, pronounced nutrient trends on the Romanian shelf agree well with long-term changes of phytoplankton biomass in the surface layer off the Romanian coast in the 30-miles zone between Constanta and Portita (Fig. 7).

Table 1
Seasonal patterns of chl *a* and Z_d (mean ± SD for monthly interval) within different inner (<50 m) shelf regions of the western Black Sea during 1980–1995 with number of measurements in parentheses

Region	Monthly interval	Mean ± SD
Chl *a*		
1	January and March	1.53 ± 0.75 (7)
	April–July	0.41 ± 0.21 (32)
	August–November	1.59 ± 0.86 (44)
3	January–February	5.84 ± 3.74 (12)
	March–April	1.72 ± 1.15 (24)
	May–June	3.46 ± 2.20 (38)
	July–August	1.41 ± 0.91 (28)
	September–November	3.62 ± 2.10 (39)
Z_d		
1	January–April	11.7 ± 2.4 (48)
	May–July	9.1 ± 2.0 (30)
	September–November	7.6 ± 2.2 (40)
2	April–May (1980–1992)	2.3 ± 1.5 (6)
	April–May (1993–1995)	4.8 ± 2.1 (26)
	July–October	4.1 ± 1.7 (22)
3	March–May	4.8 ± 2.2 (21)
	June–July	2.6 ± 1.2 (8)
	September–November	5.1 ± 2.3 (28)

While there appears to have been a good correspondence among nutrient, oxygen and phytoplankton trends up to the mid 1980s, these trends were not coordinated in the same manner after 1985. In order to explain this difference, other sources of inorganic nutrients should be considered. In the Black Sea, atmospheric deposition, local coast sources, exchanges between the deep and shelf areas, and sediment releases are the most likely nutrient sources in addition to riverine inputs (Zaitsev et al., 2006). However, atmospheric deposition and local coast sources are considered insignificant for the Black Sea (Zaitsev et al., 2006 and references therein). Nutrient inputs to the shelf from deep regions are not sufficiently investigated (Stanev et al., 2002) despite extensive evidence of strong upwelling in different regions of the western Black Sea (Tolmazin, 1985; Blatov and Ivanov, 1992; Demirov, 1994). At the same time, for example, for the western North Atlantic shelf, Nixon et al. (1996) estimated that nutrient inputs from onwelling exceed land-based inputs by 40–120%.

Table 2
Long-term changes of phytoplankton variables in the Romanian coastal waters. Interannual periods and individual years are shown in parentheses. 'Others' means small-size phytoplankton species, predominantly from the classes *Cryptophyceae*, *Chrysophyceae*, *Cyanophycea* and unidentified microflagellates

Pattern	Magnitude			
1. Contribution (%) of algal groups in phytoplankton density (cells/l)[a]	*(1960–1970)*		*(1971–1980)*	*(1983–1990)*
Diatoms	92.3		84.1	38.3
Dinoflagellates	7.6		11.8	20
Others	0.1		4.1	41.7
2. Maximum densities (10^3cells/l) of 2 main bloom-forming species[a]	*(1960–1970)*		*(1971–1980)*	*(1981–1990)*
Prorocentrum cordatum	50,814		196,920	807,600
Skeletonema costatum	18,080		97,360	141,400
3. Multiannual mean of summer phytoplankton biomass (mg m^{-3})[b]	*(1959–1963)* 495	*(1971–1975)* 719	*(1976–1980)* 2244	*(1983–1990)* 4105
4. Annual and multiannual means of surface chlorophyll *a* (mg m^{-3})[c]	*(1963)* 0.66		*(1976)* 1.67	*(1980–1992)* 9.0

[a] Bodeanu (1993).

[b] Petranu et al. (1999).

[c] This study.

On the other hand, benthic nutrient recycling, under appropriate conditions, may be the same order of magnitude and even higher than riverine load to, e.g., the Black Sea (Zaitsev et al., 2006) or the western North Atlantic continental shelf (Nixon et al., 1996). Unfortunately, as discussed in Mee et al. (2005), remarkably limited information exists regarding the magnitude of the different nutrient fluxes on the Black Sea shelf during different interannual periods, and there are contradictions among existing data sets. Nevertheless, the first *in situ* flux chamber measurements made during two EROS (EC European River-Ocean Systems) cruises in the NW Black Sea in summer 1995 and spring 1997 revealed that benthic phosphate recycling near shore (20 km from the coast) amounted to 50% of the Danube input in summer, and that ammonia fluxes from the sediments were of the same magnitude as the Danube input in both summer and spring (Friedrich et al., 2002).

Moreover, the flux of regenerated nutrients from the sediments depends on the accumulated sedimentation of produced and important organic matter over several years (Nixon, 1981), suggesting that this input has increased over time and may continue to be high for some time after nutrient loads from land have decreased. It is worthy to note that there is a strong linear relationship ($r^2 = 0.94$) between the amount of organic matter produced and/or imported in shallow marine systems and the amount of organic matter consumed on the bottom (Nixon, 1981) and an empirical regression between primary production in the overlying water and sediment oxygen uptake was developed by Seitzinger and Giblin (1996). Thus, internal nutrient sources (benthic regeneration in summer and onwelling from continental slope) are most likely on the same order of magnitude as riverine inputs.

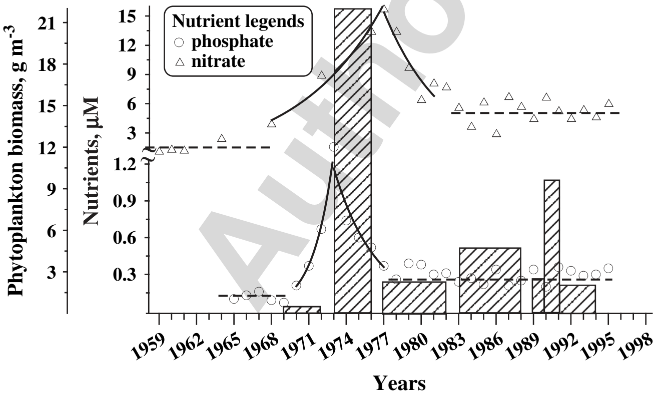

Fig. 7. Long-term changes in multiannual means of phytoplankton biomass (bars) and winter nutrients (symbols) in the surface layer off the Romanian coast (Region 2). Dashed lines show quasi-stationary periods and solid lines show periods of changing nutrient levels. Phytoplankton data were taken from Table 6.15 of Sorokin (2002).

The trends in oxygen concentration after 1985 (Fig. 4) may also be associated with changes in weather conditions, because both benthic fluxes and upwelling depend on physical processes in the shelf area and the open sea (Nixon, 1988; Stanev et al., 2002). Indeed, there is evidence that the 1980s and 1990s within the Black Sea basin were characterized by dramatic variations in the regional climate (Oguz, 2005), which significantly changed the balance in the budgets of nutrients, oxygen, and sulfide, as well as in chl *a* and PP levels in the open Black Sea regions (Konovalov and Murray, 2001; Yunev et al., 2002, 2005). In particular, 1985–1987 and 1991–1993 emerged as very cold periods with mean winter temperatures as low as ~7 °C, interrupted by a relatively warm cycle from 1988 to 1990 with mean winter temperatures of ~8 °C (Belokopytov, 1998). After 1995 the regional physical climate entered a stable warming cycle: sea surface temperature increased at a rate of ~0.2 °C per year until 2002 (Oguz, 2005).

It is also well-known, that low winter temperatures after the mid-1980s increased the intensity of the Rim Current (Ozsoy and Unluata, 1997; Konovalov and Murray, 2001). Thus, taking into account that the shelf water inshore of the Rim Current is confined by a series of eddies (Oguz et al., 1993), we assume that dynamic activity on the shelf increased after the mid-1980s as well. Increasing near-bottom current speeds and mixing on the shelf may have stimulated the rate of metabolism and associated benthic nutrient fluxes (Nixon, 1988) in addition to potentially increasing upwelling, and the upward nutrient flux to shelf waters in summer. Both of these factors would contribute to the increased summer PP rate as suggested by the oxygen trends (Fig. 4). However, this remains a speculation as there are no data on benthic nutrients fluxes for the Black Sea shelf area from before the mid-1990s (Friedrich et al., 2002).

The abrupt change of oxygen concentration after 1990/1991 (Fig. 4), as well as significant decrease of chl *a* and increase of Z_d in some months of 1993–1995 in comparison with the previous period (Fig. 5B and Table 1) could be a result of several factors. First, industrial activities in Eastern Europe declined between 1989 and 1994 and the use of fertilizers and P-containing detergents decreased markedly during the economic recession (Lemarchand and Le Guidec, 1997). However, decreases in the Danube nutrient load were not significant until after 1995 (Ragueneau et al., 2002), and there were no changes in nutrient levels for any of the shelf regions in the first half of the 1990s (Fig. 2). Second, the short warm period from 1988 to 1990 and the gradually warming period after 1995 led, most likely, to a weakening in the Rim Current activity from the beginning of the 1990s and especially after 1995. Unfortunately, 1995 and 1996 were the last years with more or less regular monitoring on the western shelf of the Black Sea (Ivanov et al., 1998).

There are many detailed investigations on algal blooms (changes in their intensity and spreading), as well as phytoplankton abundance, species composition, and size distribution within the Romanian and Bulgarian coastal waters (see references in Bodeanu et al., 1998; Petranu et al., 1999; Moncheva et al., 2001), but no data have been published on the seasonal and long-term changes of chl *a* and Z_d within the entire western shelf. The seasonal variation of chl *a* in Region 1 from 1980 to 1995 (Table 1) agrees well with the pattern for the open Black Sea in 1964–1995 (Yunev et al., 2002), i.e. low chl *a* in the warm months with temperature stratification and high concentrations during the cold autumn and winter months. Moreover, chl *a* levels in May–September and February–March (0.40 and 1.89 mg m^{-3}, for summer and winter–early spring, respectively) in the open sea reported for 1988–1992 (Yunev et al., 2002), agree well with the chl *a* levels at the Ukrainian NW shelf during 1980–1995 (Table 1).

The seasonal dynamics of chl *a* along the Romanian and Bulgarian shelves (Fig. 5 and Table 1), show high concentrations in May/June in addition to the winter–spring, late summer, and autumn maxima, most likely related to the Danube River maximum discharge during spring (Humborg, 1997). As a result, relatively high chl *a* values were observed in these two regions during almost the entire seasonal cycle, which for the period that allowed inter-region comparison (1980–1992) were 3-fold (the Bulgarian shelf) and almost 10-fold (the Romanian shelf) higher than on the Ukrainian NW shelf.

Moreover, data from 1963 and 1977 (Skolka, 1968; Bologa, 1977) highlight the seasonal chl *a* variation within the Romanian shelf during the periods of pre-eutrophication and the early phase of eutrophication (Fig. 5A) and allow us to obtain a rough estimate of the annual chl *a* changes during the different eutrophication phases. Taking into account that mean values during 1980–1992 in Region 2 are ∼2–4-fold larger than those in Region 3 during the same period and months (cf. Fig. 5B and Table 1), and that the mean annual chl *a* for Region 3 is ∼3.1 mg m^{-3}, we estimate that the mean annual chl *a* for Region 2 during 1980–1992 was about 9 mg m^{-3}. Hence, the mean annual chl *a* level within the Romanian shelf increased by ∼2.5 times from the pre-eutrophication period (∼0.66 mg m^{-3}) to the early phase of eutrophication (∼1.67 mg m^{-3}), and again more than 5 times in the period of intensive eutrophication (∼9 mg m^{-3}) in comparison with the previous period. It should be noted that these chl *a* trends agree well with long-term changes in multiannual means of summer phytoplankton biomass in the Romanian coastal waters (Table 2).

Z_d measurements are related to phytoplankton biomass to a great extent (Falkowski and Wilson, 1992; Mankovsky et al., 1996; Sanden and Hakansson, 1996; Vladimirov et al., 1999; Nielsen et al., 2002). In the open waters of the Black Sea, changes in Z_d (before and after 1985) were associated with long-term changes in summer chl *a*: the value in the subsurface maximum and the depth of its location (Yunev et al., 2005), as well as with the variability of surface chl *a* (Yunev unpubl. data). In the present study, the observed seasonal variations of Z_d were not associated with variations in surface chl *a* in most cases and it was not possible to outline any obvious long-term trends in Z_d in any of the shelf regions (Table 1). However, it is well-known that transparency in coastal areas is not only a function of phytoplankton characteristics, but also depends on concentrations of other particulate matter, dissolved humic substances, etc., and these are of particular importance in the river plumes (Wasmund et al., 2001). Indeed, the annual mean Z_d was low in the Romanian shelf (on average 3.2 m for spring, summer and autumn) compared to Region 1 and Region 3 (correspondingly on average to 8.9 and 4.2 m, approximately, for the same monthly intervals). Thus, Z_d appeared related to chl *a* on the spatial scale only.

5. Conclusions

Our analysis of long-term trends in nutrients and oxygen, as well as seasonality of chl *a* and Z_d in three different inner (<50 m) shelf regions of the western Black Sea suggests:

1. Increasing phosphate and nitrate levels before the mid-1980s corresponded well with: (1) the increase in riverine inputs; (2) changes in the summer oxygen concentration both in the surface layer (increase) and below the thermocline (decrease); and (3) multi-annual means of phytoplankton biomass.
2. Decreasing silicate levels before the mid-1980s agreed well with the increase of diatom blooms stripping silicate from the shelf waters, and reduced inputs from the Danube River following construction of numerous dam reservoirs. The associated decrease in Si:N ratio caused a shift towards more non-siliceous phytoplankton blooms.

3. After the mid-1980s nutrient inputs from the sediments and through upwelling may have become increasingly important as a result of decades with eutrophication and changes in the regional climate.
4. A three decade long trend of increasing concentration of dissolved oxygen in the surface water and increasing oxygen deficit of the bottom water during summer was broken after 1991 for reasons that remain unclear. This change may reflect a marked decrease in primary production or a change in the physical stratification of the system.
5. The seasonal chl *a* pattern within the Ukrainian NW shelf was similar to variations in the open Black Sea. The seasonal variations of chl *a* on the Romanian and Bulgarian shelves were closely related to the Danube River maximum discharge during spring with annual means substantially higher than on the Ukrainian NW shelf.

Acknowledgments

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