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Temporal variation of surface chlorophyll *a* in the Romanian near-shore waters

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Abstract

Chlorophyll *a* (Chl *a*) dynamics in the near-shore waters of the NW Black Sea was investigated between 2002 and 2010 in the Mamaia Bay (north of Constanta, Romania) in relation to some physical-chemical parameters. Chl *a* ranged from values below detection limit (0.17 $\mu g \cdot l^{-1}$) to 76.13 $\mu g \cdot l^{-1}$, and showed large temporal variability (CV = 142.3%), strongly related to the Danube's discharges, meteorological conditions, and anthropogenic pressures.

Seasonally, Chl *a* showed a winter/early spring maximum, sometimes followed by a stronger one in April/early May, closely linked to the Danube's higher discharges in spring. After significantly lower concentrations in late spring/early summer, Chl *a* exhibited its strongest maximum in summer (July–August), followed by another one in autumn (late September–October).

Interannual variation of Chl *a* seems to be controlled by the hydrometeorological conditions in summer. Thus, the highest annual Chl *a* means were observed in 2006 (8.56 ± 8.35 $\mu g \cdot l^{-1}$) and 2010 (9.20 ± 11.72 $\mu g \cdot l^{-1}$), when, also, the summer Chl *a* concentrations were maximal due to the large riverine discharges. The lowest annual Chl *a* mean was observed in 2004 (4.57 ± 9.81 $\mu g \cdot l^{-1}$), closely linked to minimal summer Chl *a* resulted from a strong P limitation during summertime.

Keywords: Chlorophyll *a*, shallow coastal waters, NW Black Sea, the Danube's discharges.

Introduction

Over the last few decades, the Romanian near-shore waters have experienced significant changes caused by important modifications of the nutrient regime of the Danube's catchment area, seriously altering phytoplankton structure, both qualitatively and quantitatively (Lancelot *et al*., 2002; BSC, 2008).

Phytoplankton community in the Romanian coastal waters has been subject to numerous studies during the last 50 years (Skolka, 1960; Bodeanu, 1987–1988, 1993; Bodeanu & Roban, 1989; Mihnea, 1997; Bodeanu *et al*., 2004). One of the most discussed areas was the Mamaia Bay, located north of Constanta, where the anthropogenic impact related to urbanization, intensive recreational, and port activities (Bodeanu, 1993), as well as the marked influence of the Danube's discharges which have led to enhancement of primary productivity.

Despite the numerous studies on inter- and intra-annual variations of both quantitative and qualitative composition of the phytoplankton community in the Romanian coastal waters, chlorophyll *a* (Chl *a*), the main indicator of phytoplankton biomass and primary productivity level, has been rather sporadically discussed (Skolka, 1968; Bologa, 1977, 1978; Bologa *et al*., 1980, 1985; Mihnea, 1988, 1997; Velikova *et al*., 2005; Vasiliu *et al*., 2010). Relatively rare during 1960–1970, the chlorophyll measurements have been intensified since the mid-1980s, once it was included in the list of biological parameters monitored within the Romanian Monitoring Program (Mihnea, 1988, 1997), and later in the list of indicators of eutrophication within the Water Framework Directive and Marine Strategy Directive.

Apart from *in situ* measurements, since the late 1970s, Chl *a* datasets have been obtained from satellite images provided by CZCS (1978–1986), SeaWiFS (1997–2010), Aqua-MODIS and MERIS (both from 2002 to the present). In the open Black Sea, satellite observations have provided accurate Chl *a* data (Blondeau *et al*., 2004), successfully used for reliable spatial and temporal patterns of distribution of primary productivity (Nezlin *et al*., 1997; Kopelevich *et al*., 2002; Yunev *et al*., 2002; Cokacar *et al*., 2004**)**. On the contrary, in the coastal waters, remotely sensed Chl *a* is a less accurate indicator of actual chlorophyll concentrations than in the open sea due to increased turbidity and atmospheric effects. Hence, in the Romanian shelf waters, despite important information on the potential relationships with climate forcing and nutrient enrichment, satellite-derived Chl *a* seems to be significantly overestimated due to the large optical complexity of this ecosystem (Oguz & Edinger, 2006). The latter implies the necessity for regular *in situ* monitoring of Chl *a* to gain a better understanding of the Black Sea coastal ecosystem's functioning under the conditions of highly variable environmental factors.

The main aim of this work is to investigate chlorophyll *a* variability, both interannual and seasonal, in the Romanian near-shore waters, and to identify the main factors controlling its dynamics.

Materials and Methods

Investigations were conducted in the Mamaia Bay, north of Constanta (Fig. 1), from January 2002 to December 2010 within the Romanian Monitoring Program framework carried out by the National Institute for Marine Research and Development "Grigore Antipa", Constanta (NIMRD). The sampling station Cazino-Mamaia (bottom depth of 1.5 m) was chosen for the analysis of surface chlorophyll temporal variability, as this site is one of the long-term research stations in the NW Black Sea. It is considered representative for the Romanian coastal waters dynamics because it has been subjected to pronounced influence of both the Danube's discharges and anthropogenic pressures.

Water samples for physical-chemical, chlorophyll, and phytoplankton analysis were collected weekly from the surface layer. Temperature was measured using a reversible thermometer. Salinity was measured by the titration method of Mohr-Knudsen (Grasshoff *et al.*, 1999), immediately after collection of samples. Nutrient samples were stored frozen at –20 ºC until their subsequent analysis in the laboratory. PO_4-P, SiO_4-Si, NO_3-N and NH_4-N were determined according to standard methods for seawater analysis (Grasshoff *et al.*, 1999).

For Chl *a* measurements, variable volumes (0.5–2 l) of seawater were filtered through Whatman glass-fiber filters GF/F (nominal pore size 0.7 µm), immediately after sampling. The filters were preserved frozen (–20 ºC) until subsequent analysis, which was performed within a month. Pigments were extracted with 90% acetone and measured by spectrophotometry, concentrations being calculated by using the SCORE-UNESCO equations (UNESCO, 1966).

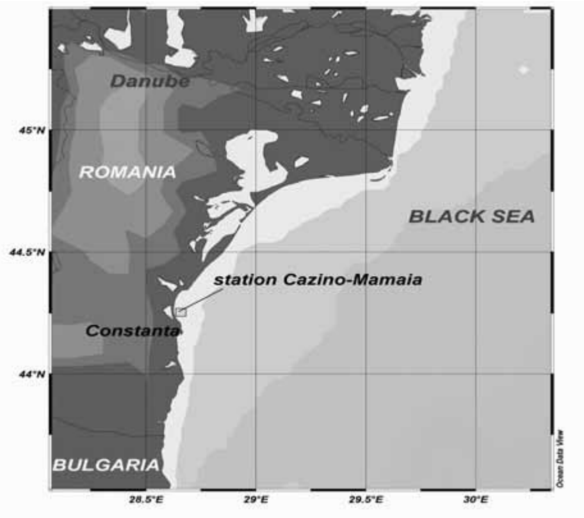

Fig. 1: Location of the sampling station Cazino-Mamaia.

Phytoplankton samples were preserved with 4% formaldehyde seawater buffered solution. Qualitative and quantitative phytoplankton determinations were performed by employing prior sedimentation method (Morozova-Vodianiskaya, 1954) to concentrate the samples. After 20 days, the samples were decanted down to 15–20 cm^3. The taxonomic identification of species and counting of cells in a 0.1 ml fraction of each sample was carried out under ZEISS inverted microscopes, using a 40^x objective lens for nanoplankton (less than 15–20 µm) and 10^x or 20^x for larger cells. The cell biovolume was calculated using relevant morphometric measurements of phytoplankton cells and approximation by corresponding geometric shapes after EDLER (1979).

Meteorological data (air temperature, wind direction, and speed) were kindly provided by ANM (National Meteorological Administration). It is important to note that the authors treated March as the winter month and September as the summer month.

Monthly and seasonally averaged data were visualized by the Ocean Data View 4 software (Schlitzer, 2006) and STATISTICA 8 software, respectively. The nonparametric Kruskal-Wallis (K-W) test was employed to test the differences between years and seasons for a given variable, because of the non-normal distribution of most of the variables considered. The K-W test is a nonparametric equivalent to one-way ANOVA by ranks, testing the null hypothesis that three or more groups all come from the same distribution. The Mann-Whitney significance test was applied to analyze the differences between every pair of groups. In order to investigate the factors influencing the temporal variability of Chl *a*, the relationships between physical-chemical and biological variables were tested after log transformation of all variables that did not comply with the assumption of normality. All statistical analyses were carried out to the significance level of $\alpha = 0.05$.

Results

Temporal variability of surface Chl *a* in the Romanian near-shore waters was examined in relation to sea surface temperature (SST), salinity (SSS), inorganic nutrients and total phytoplankton biomass, and numerical abundance (Tot. B and Tot. A, respectively). The ranges, means, standard deviations, and medians of physical-chemical, chlorophyll *a* and phytoplankton data for the period 2002–2010 are presented in Table 1.

Table 1. Summary descriptive statistics for physical-chemical variables, Chl a, phytoplankton numerical abundance, and biomass during the period 2002–2010.

Parameter	No. samples	Min.	Max.	Mean	St. dev.	Median
SST, ºC	438	-0.80	29.30	13.30	7.55	13.30
SSS, psu	438	6.36	19.42	14.60	2.35	15.10
PO_4-P, µM	438	0.01	3.40	0.42	0.41	0.31
SiO_4-Si, µM	438	0.50	62.60	13.51	9.41	11.00
NO_3-N, µM	438	0.95	45.86	8.65	6.67	6.82
NH_4-N, µM	438	0.18	64.30	6.88	5.24	5.81
Chl *a*, $\mu g \cdot l^{-1}$	438	0.17	76.13	6.59	9.38	3.78
Tot. B, $g \cdot m^{-3}$	438	0.002	219.4	3.55	16.22	0.44
Tot. A, $10^6 \cdot cells \cdot l^{-1}$	438	0.006	50.22	1.38	3.81	0.32

Sea surface temperature (SST) and salinity (SSS)

SST showed no significant statistical differences between the studied years (K-W, $p = 0.581$). Over the investigated period, SST showed minima in January–February, while maxima were observed in July–August (Fig. 5). The highest SSTs were observed in the summer of 2010 (25.26 ± 3.18 ºC; Fig. 2), closely linked to high air temperatures recorded during July–August (25.66 ± 2.43 ºC). The lowest summer SSTs were measured in 2003 and 2004 (20.96 ± 3.71 ºC and 20.04 ± 3.54 ºC, respectively; Fig. 2), when pronounced upwelling events occurred in the June–July period (prevailing southerly and southeasterly winds) (Mihailov *et al.*, 2012). In the cold season, the highest SSTs (6.83 ± 1.64 ºC) were measured in the warm winter of 2007 (air temperature of 5.33 ± 3.42 ºC), while the lowest (1.56 ± 1.64 ºC) were in the coldest winter of 2003 (air temperature of 0.48 ± 4.16 ºC) (Fig. 2).

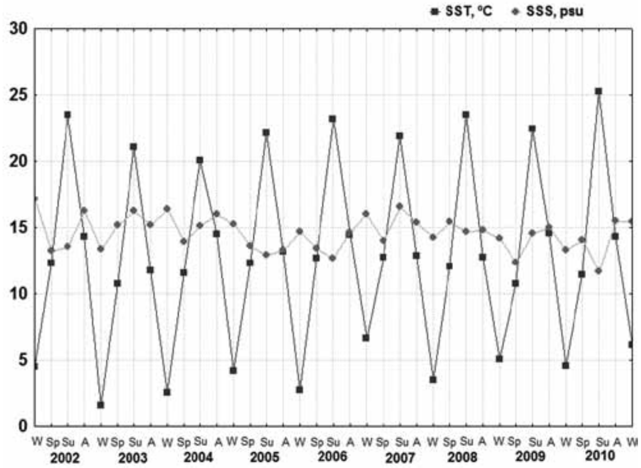

Fig. 2: Interannual variability of SST and SSS in the Romanian near-shore waters, in 2002-2010 (W-winter, Sp-spring, Su-summer, A-autumn).

SSS exhibited large temporal variability closely linked to the Danube's flow fluctuation and meteorological conditions. The K-W tests applied for variable SSS revealed statistically significant differences both between years ($p < 0.0001$) and seasons ($p = 0.0001$). The Mann-Whitney tests showed significantly lower SSSs in 2005, 2006, 2008, 2009, and 2010 compared with 2003, 2004, and 2007 (Table 2), while in terms of seasonal variation, lower SSSs were measured in spring and summer (Table 3). The lowest seasonal SSSs were observed in the summers of 2005 (12.95 ± 2.64 psu), 2006 (12.79 ± 3.75 psu) and 2010 (11.64 ± 2.14 psu, minimum for the studied period), and spring of 2009 (12.20 ± 2.4 psu) (Fig. 2).

Nutrients

Nutrient regime was characterized by a large variability (Table 1) mainly due to the Danube's discharge fluctuations, water masses circulation, benthic nutrient recycling, and anthropogenic pressures. The K-W tests applied for the variables phosphate ($p < 0.0001$), silicate ($p = 0.01$), nitrate ($p < 0.0001$), and ammonia ($p < 0.0001$) revealed statistically significant differences between years. Phosphate, silicate, and ammonia were recorded in significantly higher concentrations in 2010 compared with most of the other investigated years, while nitrate showed higher concentrations in 2005 and 2008. It is worth pointing out significantly lower concentrations of phosphate and ammonia in 2004, and nitrate in 2009 and 2010 (Table 2).

In terms of seasonal variation, statistically significant differences were found for all nutrients analyzed (K-W, $p < 0.0001$, for PO_4-P; K-W, $p < 0.0001$ for SiO_4-Si; K-W, $p < 0.0001$ for NO_3-N; K-W, $p = 0.001$ for NH_4-N). Thus, phosphate recorded significantly higher concentrations in winter and autumn, silicate in winter, nitrate in spring, and ammonia in autumn (Table 3).

Table 2. Mann-Whitney significance tests between years in terms of Chl a, Tot. A, SSS and nutrients.

		2002	2003	2004	2005	2006	2007	2008	2009	2010
2002	**Chl *a***			*0.014*						
	Tot. A									
	SSS									
	PO_4-P									
	SiO_4-Si								*0.036*	*0.009*
	NO_3-N				*0.0003*	*0.028*		*<0.0001*		*0.004*
	NH_4-N			*0.016*						*0.001*
2003	**Chl *a***			*0.046*		*0.017*				
	Tot. A									
	SSS				*0.001*	*0.008*		*0.031*		*0.006*
	PO_4-P			*0.014*						
	SiO_4-Si								*0.001*	*0.009*
	NO_3-N				*<0.0001*	*0.002*		*<0.0001*		*0.037*
	NH_4-N			*0.001*						*0.006*
2004	**Chl *a***	<	<			*<0.0001*			*0.007*	*0.002*
	Tot. A					*0.017*				
	SSS				*0.0004*	*0.006*		*0.018*	*0.0004*	*0.005*
	PO_4-P		<		*0.001*	*0.006*		*0.002*	*0.0005*	*<0.0001*
	SiO_4-Si									*0.01*
	NO_3-N				*0.011*			*0.0004*	*0.01*	*0.0002*
	NH_4-N	<	<		*<0.0001*	*0.001*	*0.004*	*0.02*	*0.048*	*<0.0001*
2005	**Chl *a***									
	Tot. A									
	SSS		<	<		*0.006*	*0.0005*			
	PO_4-P			>		*0.002*	*0.012*			
	SiO_4-Si									
	NO_3-N	>	>	>			*0.006*		*0.0004*	*<0.0001*
	NH_4-N			>					*0.012*	
2006	**Chl *a***		>	>			*0.02*	*0.0004*	*0.015*	
	Tot. A			>				*0.03*	*0.005*	*0.048*
	SSS		<	<	>		*0.007*			
	PO_4-P			>	>		*0.024*			*0.007*
	SiO_4-Si							*0.014*	*0.032*	*0.001*
	NO_3-N	>	>					*0.029*	*0.002*	*<0.0001*
	NH_4-N			>						*0.026*
2007	**Chl *a***					<				
	Tot. A									
	SSS				>	>		*0.035*	*0.001*	*0.007*
	PO_4-P				<	<		*0.014*	*0.003*	*<0.0001*
	SiO_4-Si									*0.013*
	NO_3-N				<			*0.0002*	*0.014*	*0.0002*
	NH_4-N			>						*0.019*
2008	**Chl *a***					<				*0.028*
	Tot. A					<				
	SSS		<	<			<			
	PO_4-P			>			>			*0.018*
	SiO_4-Si					>				
	NO_3-N	>	>	>		>	>		*<0.0001*	*<0.0001*
	NH_4-N			>						*0.001*
2009	**Chl *a***			>		<				
	Tot. A					<				
	SSS			<			<			
	PO_4-P			>			>			
	SiO_4-Si	>	<			>				
	NO_3-N			<	<	<	<	<		
	NH_4-N			>	<					*<0.0001*
2010	**Chl *a***			>				>		
	Tot. A					<				
	SSS		<	<			<			
	PO_4-P			>		>	>	>		
	SiO_4-Si	>	>	>		>	>			
	NO_3-N	<	<	<	<	<	<	<		
	NH_4-N	>	>	>		>	>	>	>	

Upper right values represent the level of significance (*p*); the absence of *p* values shows not significant differences between years
Lower left symbols compare years in the first column with years in the first row.

Table 3. Mann-Whitney significance tests between seasons in terms of Chl a, Tot. A, Tot. B, SSS and nutrients.

		Winter	Spring	Summer	Autumn
Winter	**Chl *a***	■		***<0.0001***	
	Tot. A	■		***0.0004***	
	Tot. B	■	***0.015***	***<0.0001***	
	SSS	■	***0.007***	***0.016***	
	PO$_4$-P	■	***<0.0001***	***0.0004***	
	SiO$_4$-Si	■	***0.001***	***<0.0001***	***<0.0001***
	NO$_3$-N	■	***0.008***	***0.001***	***<0.0001***
	NH$_4$-N	■			***0.0003***
Spring	**Chl *a***		■	***<0.0001***	
	Tot. A		■		
	Tot. B	>	■	***0.043***	
	SSS	<	■		***0.0003***
	PO$_4$-P	<	■		***<0.0001***
	SiO$_4$-Si	<	■	***<0.0001***	
	NO$_3$-N	>	■	***<0.0001***	***<0.0001***
	NH$_4$-N		■		***0.0001***
Summer	**Chl *a***	>	>	■	***0.003***
	Tot. A	>		■	***0.015***
	Tot. B	>	>	■	***0.005***
	SSS	<		■	***0.001***
	PO$_4$-P	<		■	***<0.0001***
	SiO$_4$-Si	<	<	■	***<0.0001***
	NO$_3$-N	<	<	■	***0.014***
	NH$_4$-N			■	***0.024***
Autumn	**Chl *a***			<	■
	Tot. A			<	■
	Tot. B			<	■
	SSS		>	>	■
	PO$_4$-P		>	>	■
	SiO$_4$-Si	<		>	■
	NO$_3$-N	<	<	<	■
	NH$_4$-N	>	>	>	■

Upper right values represent the level of significance (*p*); the absence of *p* values showed not significant differences between seasons
Lower left symbols compare seasons in the first column with seasons in the first row.

Chlorophyll a, total phytoplankton numerical abundance and biomass (Tot. A and Tot. B, respectively)

Surface Chl *a* showed large temporal variability (CV = 142.3%), ranging from values below detection limit (0.17 $\mu g{\cdot}l^{-1}$) to 76.13 $\mu g{\cdot}l^{-1}$ during the studied period (Table 1). The K-W test applied for variable Chl *a* revealed statistically significant differences between years (p = 0.001). Further, the Mann-Whitney tests showed significantly higher Chl *a* in 2006 when compared with the rest of the investigated years (except 2002 and 2010), while lower concentrations were observed in 2004 (Table 2). Also, higher concentrations were observed in 2010 compared with 2004 and 2008 (Table 2). Total phytoplankton biomass did not exhibit notable interannual variability (K-W, p = 0.573), while significantly higher total abundances were observed in 2006, except 2002 and 2007 (Table 2).

Regarding the seasonal dynamics of Chl *a*, the K-W test revealed considerable differences between seasons (p <0.0001). Thus, significantly higher concentrations were recorded in summer, while no notable differences were found between the other seasons (Table 3). Both total abundance and total biomass showed significant differences between seasons (K-W, p = 0.042 and p = 0.003, respectively); likewise with chlorophyll, significantly higher values of Tot.A and Tot.B were measured during summer (Table 3). Statistically, the positive correlations between Chl *a* and total abundance and biomass (r = 0.502, p <0.0001, n = 438 and r = 0.416, p <0.0001, n = 438,

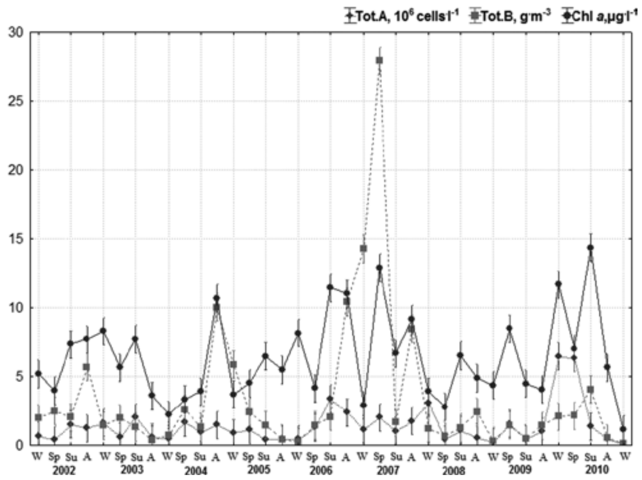

Fig. 3: Interannual variability of Chl *a*, Tot.A and Tot.B in the Romanian near-shore waters, in 2002–2010 (W-winter, Sp-spring, Su-summer, A-autumn).

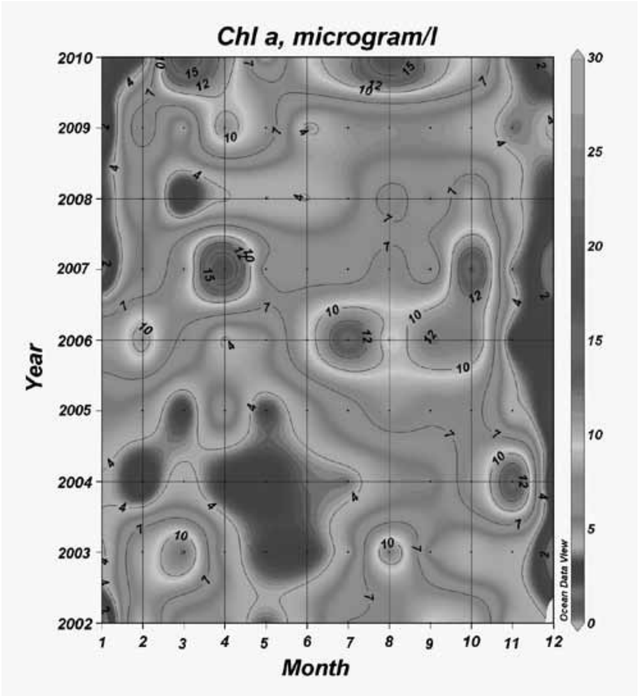

Fig. 4: Temporal variation of Chl *a* (monthly averaged) in the Romanian near-shore waters, in 2002–2010.

respectively) suggested quite similar annual cycles.

In terms of qualitative approach, the phytoplankton community was generally dominated by diatoms, except in 2003 (cyanobacteria and small flagellates accounted for about 80% as abundance) and 2007 (dinoflagellates accounted for more than 85% as biomass). Diatoms' domination was stronger in high-flow years of the Danube; in 2005, 2006, and 2010, diatoms accounted for more than 65%, both in abundance and biomass. Moreover, diatoms accounted for about half the number of species exceeding 10^{6} cells$\cdot l^{-1}$ during the study period (Table 4).

Seasonal cycle of Chl *a* showed a first maximum in winter/early spring (February–March), but this maximum was relatively moderate, except for 2003 (12.41 ± 5.04 $\mu g\cdot l^{-1}$), 2006 (9.80 ± 3.64 $\mu g\cdot l^{-1}$) and 2010 (15.10 ± 20.30 $\mu g\cdot l^{-1}$) (Fig. 4). The winter Chl *a* maximum corresponded to diatoms' blooms (diatoms accounted for more than 60% of total abundance), except 2002 (flagellates *Euglena gracilis* reached abundance of $2.28\cdot10^{6}$ cells$\cdot l^{-1}$ and biomass of 4.56 $g\cdot m^{-3}$, and corresponded to Chl *a* of 6.92 ± 6.99 $\mu g\cdot l^{-1}$) and 2007 (no winter bloom was observed). The highest level of Chl *a* in March 2010 (Fig. 4) corresponded to a strong diatoms bloom (blooming species *Skeletonema costatum* recorded abundances within $2.34\cdot10^{6}$–$49.4\cdot10^{6}$ cells$\cdot l^{-1}$; Table 4), while long-lived winter blooms observed in 2003 and 2006 were associated with successive developments of diatoms and non-diatoms freshwater species. Thus, in 2003, the atypical cyanobacteria bloom observed in February *(Microcystis aeruginosa*, abundance of about $3\cdot10^{6}$ cells$\cdot l^{-1}$; Bodeanu *et al.*, 2004) was succeeded by a weaker diatoms bloom which extended until late March (assemblage dominated by *S. costatum*, maximum abundance of $1.6\cdot10^{6}$ cells$\cdot l^{-1}$ and *Detonula confervacea*, biomasses within 1.86–2.27 $g\cdot m^{-3}$). In 2006, the moderate diatoms bloom (*S. costatum*, abundances within $2\cdot10^{6}$–$4.27\cdot10^{6}$ cells$\cdot l^{-1}$), which lasted from late February until mid-March, was followed in late March by high abundances and biomasses formed by the chlorophytes *Micractinium pussillum* ($5.95\cdot10^{6}$ cells$\cdot l^{-1}$ and 3.57 $g\cdot m^{-3}$, respectively) and diatoms *Thalassiosira nordenskioeldii* ($0.83\cdot10^{6}$ cells$\cdot l^{-1}$ and 8.02 $g\cdot m^{-3}$, respectively). The lowest winter Chl *a* concentrations were measured in 2004 (3.25 ± 5.26 $\mu g\cdot l^{-1}$) and 2008 (3.69 ± 4.96 $\mu g\cdot l^{-1}$) (Figs. 3 and 4), when short-lived (order of days), but relatively strong, diatoms blooms were observed (abundances of $6.82\cdot10^{6}$–$10.77\cdot10^{6}$ cells$\cdot l^{-1}$ in mid March 2004, and $11.88\cdot10^{6}$–$15.18\cdot10^{6}$ cells$\cdot l^{-1}$ in early February 2008, respectively).

Sometimes, the winter Chl *a* maximum was followed by another one in spring (April–May) (Fig. 4). Relatively strong spring blooms were noted in the years characterized by higher river discharges in the spring, and favorable northerly and northeasterly winds, hence, lower salinity in the studied area. The low salinity measured in the springs of 2005 (13.61 ± 3.26 psu), 2007 (13.84 ± 1.79 psu) and 2009 (12.20 ± 2.4 psu) can be associated with higher spring Chl *a* observed in those years (Figs. 2 and 3). Except for 2007, the spring Chl *a* maxima corresponded to relatively intense diatoms blooms (dominant species *S. costatum* in 2005 and *Pseudo-nitzschia delicatissima* in 2009, respectively). In 2005 and 2009, the spring Chl *a* maxima (8.59 ± 9.16 $\mu g\cdot l^{-1}$ and 13.02 ± 21.07 $\mu g\cdot l^{-1}$, respectively, both in April) were stronger than the winter ones (4.36 ± 4.68 $\mu g\cdot l^{-1}$ and 5.44 ± 4.68 $\mu g\cdot l^{-1}$, respectively, both in February) (Fig. 4). The strongest spring maximum of Chl *a* (26.09 ± 33.78 $\mu g\cdot l^{-1}$) was observed in April 2007 and corresponded to very high

Table 4. List of species exceeding 106 cells.l–1 and their annual maximum abundances (10^6 cells.l–1).

	2002	2003	2004	2005	2006	2007	2008	2009	2010
BACILLARIOPHYTA									
Cerataulina pelagica (Cleve) Hende, 1937	**3.06 (IX)**		**9.96 (X)**		**7.88 (X)**	**6.23 (X)**	**1.96 (X)**	**2.1 (V)**	**5.4 (VI)**
Chaetoceros curvisetus P.T. Cleve, 1889			**1.99 (VI)**		**1.37 (VI)**				
Chaetoceros rigidus Ostenfeld	**1.27 (VII)**								
Chaetoceros similis f. *solitarius* Proshkina-Lavrenko							**1.28 (II)**		
Chaetoceros socialis H.S. Lauder, 1864	**3.6 (VIII)**		**1.56 (VII)**	**3.73 (VI)**	**2.21 (VI)**			**1.2 (XII)**	**3.77 (X)**
Cyclotella caspia Grunow, 1878					**4.95 (VI)**				**1.48 (VI)**
Detonula confervacea (Cleve) Gran, 1900		**1.08 (III)**	**4.06 (III)**						
Leptocylindrus danicus Cleve, 1889							**1.02 (IX)**		
Navicula sp.									**1.11 (VI)**
Pseudo-nitzschia delicatissima (P.T. Cleve, 1897) Heiden, 1928			**1.88 (VIII)**	**1.06 (VI)**			**1.26 (V)**	**8.69 (V)**	**1.03 (VII)**
Nitzschia pungens var. *atlantica* Cleve				**1.16 (I)**					
Pseudo-nitzschia seriata (P.T. Cleve, 1883) H. Pergallo in H&M Pergallo, 1900				**1.85 (X)**					
Nitzschia tenuirostris Mer.			**1.62 (VIII)**		**15.54 (VII)**		**2.5 (VIII)**		**2.07 (VII)**
Skeletonema costatum (Greville) Cleve, 1873	**3.3 (VII)**	**1.62 (III)**	**6.22 (III)**	**3.56 (III)**	**15.0 (IV)**		**15.18 (II)**		**49.44 (III)**
Thalassionema nitzschioides (Grunow) Mereschkowsky,1902				**1.36 (VIII)**					**5.89 (VII)**
CHLOROPHYTA									
Carteria sp.		**1.56 (VI)**			**1.13 (VI)**				**1.63 (VI)**
Micractinium pusillum, Fresenium, 1858					**5.95 (III)**				
CHRYSOPHYTA									
Apedinella radians (Lohmann) Campbell, 1973				**2.1 (IV)**					
Emiliania huxleyi (Lohmann) Hay&Mohler, 1967			**1.08 (VIII)**						
CRYPTOPHYTA									
Cryptomonas sp.									**1.76 (VI)**
CYANOBACTERIA									
Aphanizomenon flos-aquae (Linnaeus) Ralfs ex Bornet&Flahault, 1888		**3.92 (XII)**	**1.2 (IX)**	**2.7 (XI)**					
Gloeocapsopsis crepidinum (Thuret) Geitler ex Komárek, 1993							**1.14 (V)**		
Microcystis aeruginosa (Kützing) Kützing , 1846	**12.8 (X)**	**3.0 (II)**			**1.5 (IX)**		**1.05 (XI)**		
Microcystis orae Kosinskaja, 1948	**300 (IX)**								
Microcystis pulverea (Wood) Forti in De Toni, 1907 *sensu auct.*									**2.46 (VIII)**
Oscillatoria sp.			**2.5 (III)**			**3.0 (X)**			
EUGLENOPHYTA									
Euglena gracilis G. A. Klebs, 1883	**2.28 (II)**								
Eutreptia lanowii Steuer, 1904	**1.64 (IV)**		**1.13 (IX)**			**7.45 (VI)**	**1.36 (VI)**	**4.32 (X)**	
DINOFLAGELLATA									
Akashivo sanguinea K. Hirasaka G. Hansen&Ø. Moestrup, 2000				**2.48 (I)**					
Gymnodinium cf. *aureolum* (Hulburt, 1957) G. Hansen, 2000						**10.66 (IV)**			
Heterocapsa triquetra (Ehrenberg, 1840) Stein, 1883						**1.64 (IV)**	**2.13 (IV)**		
Prorocentrum minimum (Pavillard, 1916) Schiller, 1931						**1.32 (V)**			
Dinoflagellates (vegetative stages)			**8.8 (XI)**						

Month in which species abundance reached annual maximum is given in brackets

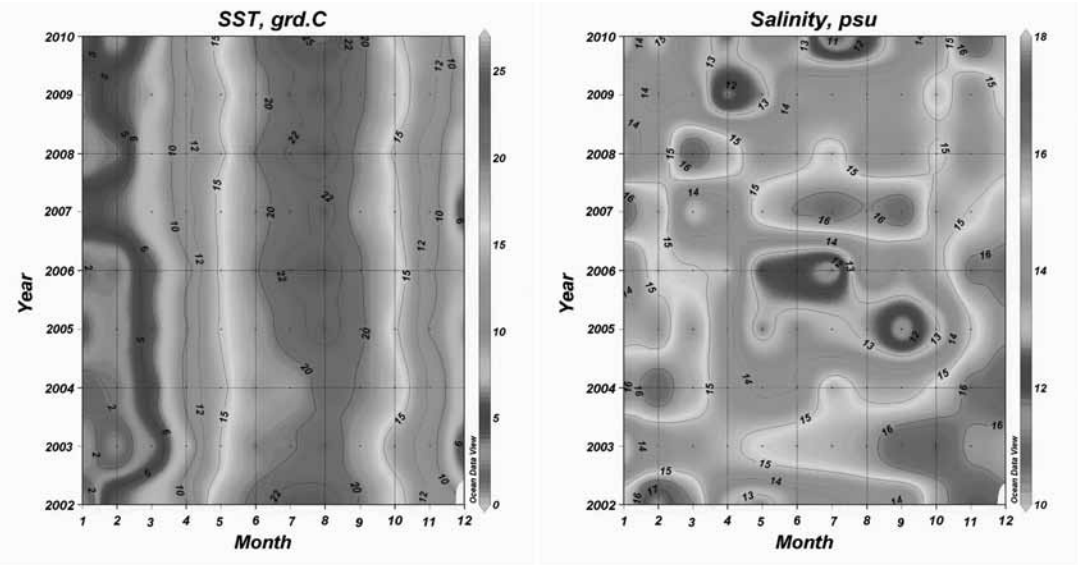

Fig. 5: Temporal variation of SST and SSS (monthly averaged) in the Romanian near-shore waters, in 2002–2010.

abundances ($6.65\cdot10^6$–$11.95\cdot10^6$ cells·l^{-1}) and biomasses (maximal for the whole studied period, 218.05 g·m^{-3}) formed by dinoflagellates (*Gymnodinium* cf. *aureolum* was the dominant species; Table 4). Prior to the onset of this bloom, Chl *a* was recorded in very low concentrations (3.81 ± 3.55 µg·l^{-1}), most likely in connection with lower winter discharges of the Danube, but also with high SSTs measured during the winter (6.83 ± 1.64 ºC; Fig. 2), which weakens the mixing processes (Nezlin & Dyakonov, 1998). Also, high SSTs were measured during the winter of 2009 (5.03 ± 1.91 ºC; Fig. 2), when the winter Chl *a* maximum was moderate (4.75 ± 4.06 µg·l^{-1}; Fig. 3), but the large discharges of the Danube in April (monthly flow of 28.5 km^3 according to FP6 SESAME, 2010) and prevailing northerly winds favored the onset of a stronger diatoms bloom in late April, which extended until mid-May. The high monthly mean of Chl *a* observed in April 2010 (12.49 ± 16.5 µg·l^{-1}) was due to very high concentrations measured in the first half of the month (within 7.50–37.00 µg·l^{-1}), corresponding to the strong and long-lived diatoms bloom starting from early March.

The quantitative parameters of phytoplankton showed a pronounced decrease in late spring/mid-summer, closely linked to lower nutrient stock in the surface layer, and increased grazing pressure (Chu *et al*., 2005). Chl *a* concentrations rarely exceeded 5.0 µg·l^{-1} during the May–June period; only in the early summers of 2006 and 2010, when the higher runoff from the Danube and favorable wind regime (suggested by low salinity in the area; Fig. 5) favored increased levels of Chl *a* (8.83 ± 6.62 µg·l^{-1} and 10.2 ± 6.98 µg·l^{-1}, respectively; Fig. 4), corresponding to strong diatoms blooms (assemblages dominated by *Cyclotella caspia*, abundance of $4.95\cdot10^6$ cells·l^{-1} in June 2006, and *Cerataulina pelagica*, abundance of $5.54\cdot10^6$ cells·l^{-1} in June 2010; Table 4).

As we mentioned above, higher Chl *a* concentrations were measured in summer; most of the times, the seasonal cycle of Chl *a* showed an increasing trend from mid-July, and peaked in August and/or autumn (late September–October) (Fig. 4). Particular situations with low summer Chl *a* were observed in 2004 and 2009 (seasonal averages of 3.88 ± 1.99 µg·l^{-1} and 4.49 ± 2.41 µg·l^{-1}, respectively; Fig. 3). In 2004, an autumn Chl *a* maximum was observed in November (5.12–76.13 µg·l^{-1}), corresponding to intense, but short in duration (order of days) dinoflagellates bloom (abundance and biomass of $8.8\cdot10^6$ cells·l^{-1} and 27.0 g·m^{-3}, respectively), while in 2009, there were no other Chl *a* maxima by the end of the year (Fig. 4). In 2002, there was observed a weak Chl *a* maximum in August (5.26 ± 3.83 µg·l^{-1}), corresponding to diatoms abundances higher than $3.6\cdot10^6$ cells·l^{-1} (blooming species *Chaetoceros socialis*; Table 4). This maximum was followed by a more pronounced one in autumn (10.02 ± 6.10 µg·l^{-1}) resulted from successive strong blooms formed by diatoms (*C. pelagica*, abundance of $3.06\cdot10^6$ cells·l^{-1}; Table 4) and colonial cyanobacteria (*Microcystis orae*, abundance of $300\cdot10^6$ cells·l^{-1} and *M. aeruginosa*, abundance of $12.8\cdot10^6$ cells·l^{-1} according to Bodeanu *et al*., 2004; Table 4). On the contrary, in 2003, the summer maximum of Chl *a* (16.31 ± 21.13 µg·l^{-1} in August), corresponding to high biomasses of dinoflagellates (>2.0 g·m^{-3}), was not followed by another one in autumn (Fig. 4). In 2005, Chl *a* showed relatively moderate peaks in August (8.87 ± 9.62 µg·l^{-1}) and October (7.23 ± 1.20 µg·l^{-1}), while in 2006, Chl *a* showed the highest concentrations in July (20.62 ± 20.54 µg·l^{-1}), corresponding to a strong bloom formed by diatoms *Nitzschia tenuirostris*, abundance of $15.5\cdot10^6$ cells·l^{-1} (Table 4). Favorable hydrological conditions in the summer of 2006 led to relatively high Chl *a* also in August (6.24 ± 3.20 µg·l^{-1}), which corresponded to an abundance of $6.84\cdot10^6$ cells·l^{-1} formed by diatoms *S. costatum*. In autumn, a strong *C.*

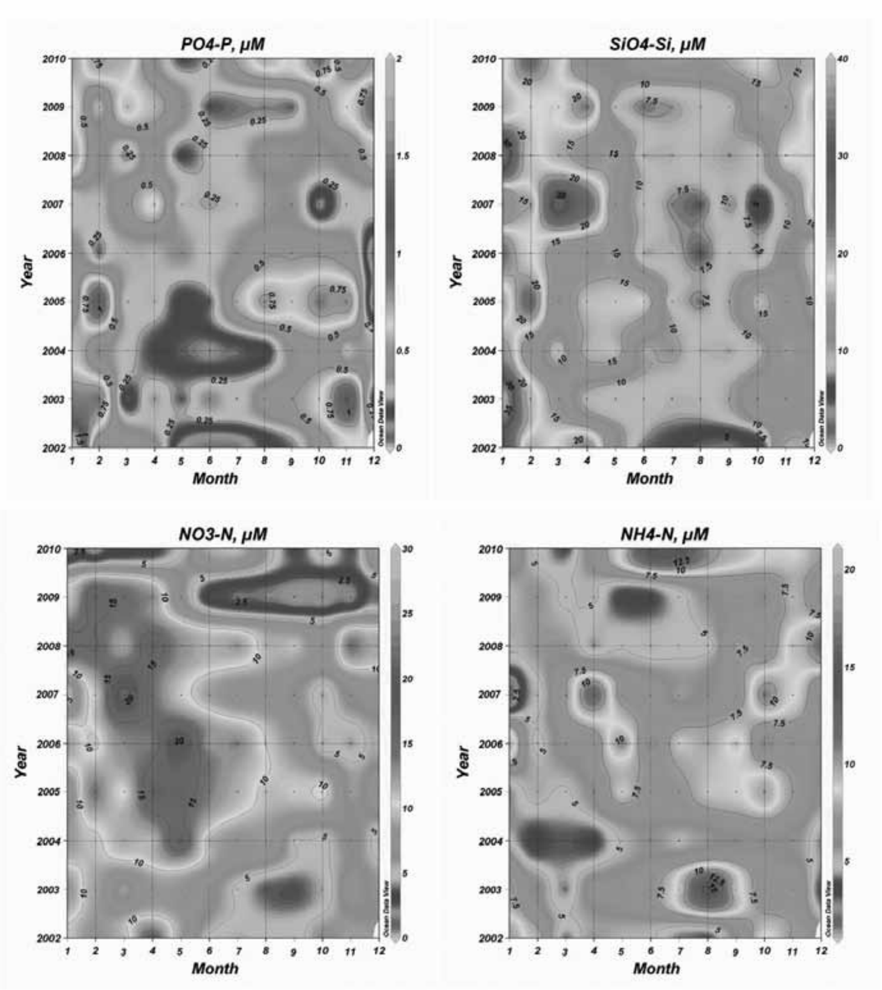

Fig. 6: Temporal variation of nutrients (monthly averaged) in the Romanian near-shore waters, in 2002–2010.

pelagica bloom (abundance of $7.88 \cdot 10^6$ cells$\cdot l^{-1}$; Table 4) was observed from mid-September until late October, and led to a pronounced Chl *a* maximum (16.18 ± 9.23$\mu g \cdot l^{-1}$). In 2007, relatively high Chl *a* in August (8.82 ± 5.94 $\mu g \cdot l^{-1}$) corresponded to dinoflagellates biomasses within 1.01–3.4 $g \cdot m^{-3}$, contrary to August 2008, when summer Chl *a* maximum (8.81 ± 7.80 $\mu g \cdot l^{-1}$) was associated with a relatively weak diatoms development (*Leptocylindrus minimus* and *N. tenuirostris* reached maximum abundance of $3.8 \cdot 10^6$ cells$\cdot l^{-1}$). In both years, stronger autumn Chl *a* maxima formed by large-size diatoms *C. pelagica* (abundance of $6.23 \cdot 10^6$ cells$\cdot l^{-1}$ in 2007, and abundance of $1.96 \cdot 10^6$ cells$\cdot l^{-1}$ and biomass of 12.73 $g \cdot m^{-3}$, respectively, in 2008; Table 4) were observed in October (Fig. 4).

The higher discharges of the Danube recorded in the summer of 2010 (mainly during June–July), along with prevailing northerly winds, led to an increased nutrient stock (Fig. 6), which favored high Chl *a* in July (9.70 ± 4.82 $\mu g \cdot l^{-1}$). This summer Chl *a* maximum corresponded to a strong bloom (assemblages dominated by diatoms *Thalassionema nitszchioides* and *Pseudo-nitszchia delicatissima*, abundance and biomass reached values of $7.67 \cdot 10^6$ cells$\cdot l^{-1}$ and 4.32 $g \cdot m^{-3}$, respectively). In August 2010, the assemblages were dominated by flagellates *Eutreptia lanowii*, cyanobacteria *M. aeruginosa*, *Microcystis pulverea*, but they did not reach large abundances though the level of associated Chl *a* (18.38 ± 14.15 $\mu g \cdot l^{-1}$) was very high. Relatively high Chl *a* concentrations were also measured in the first half of October (4.79–12.06 $\mu g \cdot l^{-1}$), corresponding to a moderate autumn bloom formed by *C. socialis* (abundance ~ $3.8 \cdot 10^6$ cells$\cdot l^{-1}$; Table 4).

Discussion

The large fluctuations of the Danube's discharges, as well as the sharp changes of the local climatic conditions are the main drivers controlling the temporal variability of the phytoplankton parameters (both quantitative and qualitative) in the Romanian coastal waters (Bodeanu, 1993). Significant negative correlation between Chl *a* and salinity ($r = -0.346$, $p < 0.0001$, $n = 438$) indirectly suggests the strong influence of the Danube's discharges on the level of primary production (here expressed as Chl *a*). For instance, the highest Chl *a* concentrations were measured in 2006 and 2010 (annual averages of 8.56 ± 8.35 $\mu g \cdot l^{-1}$ and 9.20 ± 11.72 $\mu g \cdot l^{-1}$, respectively), when the Danube River registered high annual flows (258.7 km^3 and 310.0 km^3, respectively; according to Cociasu *et al.*, 2009; FP6 SESAME, 2010), while the lowest Chl *a* was observed in 2004 (4.57 ± 9.81 $\mu g \cdot l^{-1}$), when the salinity showed the highest annual mean (15.40 ± 1.78 psu) due to lower discharges of the Danube (Cociasu *et al.*, 2009), but also strong upwelling events in the summer (Mihailov *et al.*, 2012). Significant positive correlation between Chl *a* and phosphate (r = 0.132, p = 0.006, n = 438) seems to confirm P limitation in the Romanian coastal waters (Cociasu *et al.*, 1997, 2009; Yunev *et al.*, 2007), especially as the lowest phosphate concentrations in the studied area were recorded in the summer of 2004 (0.24 ± 0.21 μM; Fig. 6), when the chlorophyll level was also minimal (3.88 ± 1.99 $\mu g \cdot l^{-1}$; Fig. 3).

The Romanian coastal waters generally show a winter/early spring diatoms bloom (February–March), closely related to intense mixing processes during the cold season (Bodeanu, 1987–1988; Yunev *et al.*, 2002; Chu *et al.*, 2005; Demidov, 2008). Besides, these processes which provide an internal supply of nutrients in the surface layer, the large fluctuations of the Danube's discharges have a strong influence on the year-to-year variability of the winter/early spring bloom (magnitude, timing, and duration) mainly through the external input of nutrients, and also through the freshwater phytoplankton input (Bodeanu, 1987–1988). Generally, the seasonal cycle of the Danube's discharges exhibits a maximum in April–May, and a minimum in September–October (Humborg, 1997), but in some years, a winter/late winter peak has also been noted. Significant negative correlation between Chl *a* and SSS (r = –0.477, p <0.0001, n = 108) observed in the cold season suggests the influence of the riverine discharges pulses and wind regime on the magnitude and duration of winter/early spring Chl *a* maximum. Winters with larger runoff from the Danube, along with longer periods of prevailing northerly and northeasterly winds, showed strong and long-lived algal blooms in the Romanian shallow coastal waters. Such events were observed in 2003 and 2010, when the long period with dominant northerly and northeasterly winds (from December to March), even with relatively low intensities (less than 3 $m \cdot s^{-1}$ on average), led to strong and long-lived blooms. In 2010, the winter bloom was formed by diatoms *S. costatum*, which accounted for about 98% of total abundance, and corresponded to very high Chl *a* during March–early April (within 7.27–58.47 $\mu g \cdot l^{-1}$). Moreover, this was the strongest winter/early spring Chl *a* maximum along the studied period, and could also be related to the nutrient ratios (N/P = 16.7, Si/N = 2.3 and Si/P = 33.2) close to optimal ratios for diatoms growth (Redfield *et al.*, 1963; Brzenziski, 1985), contrary to the rest of the investigated years (N/P >70.0, Si/N <1.1 and Si/P >50). On the other hand, the large instability of wind regime during the cold season led to relatively sharp shifts of hydrological regime, thus favoring short-lived algal blooms. Such events were recorded in the winters of 2004 and 2008; the onset (mid-March in 2004 and early February in 2008, respectively) and extension (order of days) of these blooms were strongly linked to sharp changes in the salinity regime in the studied area (about 4.0 psu in less than a week). The influence of hydrological regime of the Danube on the winter/early spring Chl *a* peak, through the input of freshwater phytoplankton, was well observed in 2003, when the high winter Chl *a* corresponded to successive blooms formed by freshwater cyanobacteria and diatoms, which lasted from early February to mid-March. A similar situation was observed in 2006, when successive blooms formed by diatoms and freshwater chlorophytes were associated with relatively long period of high levels of Chl *a* (late February–late March).

Stronger winter Chl *a* maximum in high-flow years of the Danube was also reported by Bologa in the late 1970s, starting with the intensification of eutrophication. Relatively high winter Chl *a* (5.74 ± 6.83 $\mu g \cdot l^{-1}$) was measured in 1977 (the Danube's monthly flow in winter exceeded 23 km^3; Cociasu & Popa, 1978), contrary to winters with lower runoff, which showed significantly weaker peaks of winter Chl *a* (< 3.0 $\mu g \cdot l^{-1}$) (Bologa, 1977, 1978; Bologa *et al.*, 1980). Similar to the 2000s, the winter assemblages during the late 1970s were dominated by diatoms, mainly *S. costatum,* which formed strong blooms (Bodeanu, 1987–1988). Winter Chl *a* maxima, corresponding to diatoms blooms (dominant species *S. costatum*), were also observed in the other coastal areas along the Black Sea basin, but the influence of the Danube's discharges generally leads to stronger peaks in the Romanian coastal waters (BSC, 2008; Demidov, 2008; Stelmakh *et al.*, 2009, 2010).

The Danube's increased discharges starting in March–April generally provided favorable conditions for stronger blooms in spring. During the investigated period, the spring bloom was not typical in the Romanian shallow coastal waters; Chl *a* peaks were observed only in years with larger runoff from the Danube during springtime, and generally corresponded to diatoms development (except 2007). This is contrary to the period of intense eutrophication, when dinoflagellates dominated the spring phytoplankton community, and formed stronger blooms every year (Bodeanu, 1987–1988; Mihnea, 1997). Thus, in the late 1970s, the spring Chl *a* maxima observed in April–May (within 3.42–13.09 $\mu g \cdot l^{-1}$) were slightly weaker compared with the studied period (Bologa, 1978; Bologa *et al.*, 1980), while in the 1980s and the 1990s, Chl *a* concentrations were maximal during April–July (Mihnea, 1997), mainly due to abnormal high P input from the Fertilizer Plant Navodari (northern Constanta) since the early 1980s until the mid-1990s (Cociasu *et al.*, 1997; Mihnea, 1997), and decreased grazing pressures as a result of the outburst of *Mnemiopsis* population in the late 1980s (Kovalev & Piontkovski, 1998; Shiganova, 1998). Significant changes in nutrient regime after the mid-1990s resulted from the marked reduction of anthropogenic pressures in the coastal area (Lancelot *et al*., 2002; Cociasu *et al*., 2009) led to lower spring Chl *a*, but a maximum in April–May was also noted, especially in the years with larger spring runoff from the Danube (e.g. in 1997, Chl *a* reached a relatively strong maximum of 10.64 $\mu g \cdot l^{-1}$ in April; Mihnea, unpublished data).

Generally, in the Black Sea shelf ecosystems, the winter-spring Chl *a* maximum is followed by lower surface Chl *a* in April–June, mainly as a result of nutrient depletion, as well as the increased grazing pressure (Chu *et al*., 2005; Demidov, 2008). Spatial-temporal extension of low Chl *a* levels in the Romanian coastal waters is strongly influenced by the Danube's discharges and the wind regime. Thus, shorter periods of low Chl *a* were observed in the years with very large riverine discharges in spring (e.g. in 2006 and 2010, when the monthly flows of the Danube exceeded 30 km^3, according to Cociasu *et al.,* 2009; FP6 SESAME, 2010), while in the years with reduced flows (e.g. in 2003, <18 $km^3 \cdot month^{-1}$; Cociasu *et al*., 2009) and/or dominant southerly winds in spring (e.g. in 2003 and 2004) the periods of low Chl *a* levels were longer. Starting with June–July, Chl *a* showed an increasing trend and peaked in July–August (Fig. 4), generally corresponding to strong diatoms blooms. This summer Chl *a* maximum is quite common for the Black Sea shelf ecosystems (Demidov, 2008); its timing, duration, and magnitude are sensitive to local conditions and exhibit considerable interannual variability (Vedernikov & Demidov, 1993; Sur *et al*., 1996). Significant negative correlation between summer Chl *a* and SSS ($r = -0.290$, $p = 0.005$, $n = 99$) suggests the marked role of the Danube's discharges on the summer primary production in the Romanian coastal waters. On the other hand, the absence of significant correlations between salinity and nutrients in the warm season suggests that the Danube's discharges are not solely responsible for the relatively high nutrient regime in the shallow coastal waters. Upwelling events, quite common in the coastal waters in early summer (Staneva *et al*., 2010; Mihailov *et al*., 2012), benthic nutrients recycling processes, more intense with increasing thermal regime (Friedrich *et al*., 2002), as well as local anthropogenic pressures, provide relatively high nutrient stock, even in conditions of lower discharges of the Danube. However, the strongest summer Chl *a* maxima were recorded in 2006 and 2010; the high discharges of the Danube and prevailing northerly winds favored strong diatoms blooms in mid-July. In both the years, Chl *a* level remained quite high during the warm season; in 2006, a second strong diatoms bloom was observed in August, while in 2010, the high Chl *a* concentrations were most likely due to the interference of phaeopigments resulted from very strong *Noctilluca* blooms observed during summertime (Timofte, 2011), taking into account that the thrichromatic method does not differentiate between chlorophyll and phaeopigments (Aminot & Rey, 2001). No algal blooms were observed in the summer of 2004 (Fig. 4), and this fact can be related to significant lower phosphate levels during July–August (Fig. 6), when many PO_4-P concentrations dropped below detection limit. Except for these situations, the summer Chl *a* maxima were observed in August, and the blooming species changed from year to year closely related to the large variability of environmental conditions. Generally, diatoms dominated the summer assemblages, especially in high-flow years of the Danube (e.g. 2002, 2005, 2006, and 2010), while extensive biomasses of large-size dinoflagellates were observed in summers with lower discharges of the Danube (2003 and 2007). On the contrary, during the intense eutrophication period, the summer assemblages were mainly dominated by dinoflagellates, the diatoms contribution being much less (Bodeanu, 1987–1988; Mihnea, 1997). Prior to the onset of eutrophication, the summer Chl *a* maximum was not observed (Skolka, 1968); it has become a typical feature in the Romanian coastal waters since the mid-1970s (Bologa, 1977, 1978; Bologa *et al*., 1984). While in the late 1970s the summer Chl *a* maximum was relatively weak (Bologa, 1977, 1978), in the 1980s and 1990s, it increased considerably in magnitude (Bologa *et al*., 1984; Mihnea, 1997). Although significantly lower when compared with the previous period, the summer Chl *a* remained high after 2000 (8.60 ± 9.41 $\mu g \cdot l^{-1}$), suggesting high enough nutrient stock for sustaining an increased primary production in the Romanian coastal waters. It is also worth mentioning the onset of summer bloom generally in August, contrary to the intense eutrophication period, in June–July. Similar to the Romanian coastal waters, well pronounced summer peaks of Chl *a* are recorded in the eastern shelf of the Black Sea in line with the larger nutrient supply by mountain rivers during the flood period and local upwelling events (Demidov, 2008), while in the Bulgarian coastal waters there is no clear seasonal pattern, and the timing of intensive growth of phytoplankton varies irregularly (BSC, 2008).

In autumn, the increased nutrient stock resulted from the erosion of seasonal thermocline and favorable wind regime, as well as reduced zooplankton grazing pressures, led to relatively strong autumn blooms in the shelf waters (Demidov, 2008). Generally, the autumn Chl *a* maximum was associated with high biomasses of large-size diatoms *C. pelagica*, which in most cases was the dominant species in the autumn assemblages. The diatoms' dominance in autumn was also showed by significant negative correlation between autumn Chl *a* and silicate ($r = -0.223$, $p = 0.047$, $n = 82$), which suggests increased Si consumption by diatoms. Except 2003 and 2009, when no autumn blooms were noted, the lowest autumn Chl *a* maxima were observed in 2005 and 2010 (Fig. 4), closely linked to the absence of *C. pelagica*; diatoms *Pseudo-nitzschia seriata* (in 2005) and *C. socialis* (in 2010) were dominant in the autumn assemblages (Table 4). Similar situations were found in other coastal regions of the Black Sea (e.g. Sevastopol Bay, in the Turkish and Bulgarian coastal waters), where the autumn assemblages have been dominated by large-size diatoms *C. pelagica*, *Pseudosolenia calcar-avis* and a few others, but occasionally, the increased presence of some dinoflagellates species (Stelmakh *et al*., 2009, 2010) was also noted. No pronounced correlation was found between Chl *a* and salinity in autumn, thus suggesting the less important role of the Danube's nutrient discharges on the magnitude of autumn Chl *a* peak, contrary to the winter/early spring and summer peaks. However, strong blooms formed by freshwater cyanobacteria were noted in the autumns of 2002 and 2005, when the Danube's flow was higher (>20 $km^3 \cdot month^{-1}$; Cociasu *et al*., 2009), thus suggesting the riverine influence through freshwater species input. During the intense eutrophication, the autumn Chl *a* peak was observed earlier, in September, and was much weaker than the summer peak (Mihnea, 1997). Contrary to the investigated period, when the large-size diatoms blooms were observed almost yearly, the autumn associations in the period mid-1980s–mid-1990s were dominated by small-size diatoms (*S. costatum*), chryptophytes, chrysophytes and cyanobacteria (Mihnea, 1997); solely in 1985, *C. pelagica* reached abundances higher than $5 \cdot 10^6$ $cells \cdot l^{-1}$; Bodeanu, 1993).

The autumn and winter Chl *a* maxima were comparable during the studied period (8.29 ± 10.87 $\mu g \cdot l^{-1}$ and 7.91 ± 11.87 $\mu g \cdot l^{-1}$, respectively), but both of them were lower than the summer maximum (8.60 ± 9.41 $\mu g \cdot l^{-1}$). These findings suggest the higher contribution of summertime to the annual primary production in the Danube's influence area, contrary to other regions of the basin (except for the eastern shelf and the continental slope), where the winter production significantly exceeds the summer and autumn production (Demidov, 2008). This is consistent with the highest annual means of Chl *a* measured in 2006 and 2010, when the summer Chl *a* concentrations were maximal, but also with the lowest annual mean observed in 2004, when the summer Chl *a* were minimal. However, during the studied period, the differences between the magnitude of summer Chl *a* maximum and the winter and autumn maxima observed in the Romanian shallow coastal waters decreased significantly compared with the 1980s and 1990s (Mihnea, 1997), mainly due to a pronounced decrease of summer Chl *a* (from 11.33 ± 17.39 $\mu g \cdot l^{-1}$ in the 1980s and 21.86 ± 35.98 $\mu g \cdot l^{-1}$ in the 1990s (Mihnea, unpublished data) to 8.60 ± 9.41 $\mu g \cdot l^{-1}$ in the studied period). Consequently, this led to a significant decrease of annual mean of Chl *a* from 11.64 ± 15.61 $\mu g \cdot l^{-1}$ in the 1980s and 15.92 ± 27.72 $\mu g \cdot l^{-1}$ in the 1990s (Mihnea, unpublished data) to 6.59 ± 9.38 $\mu g \cdot l^{-1}$ in the studied period, closely linked to considerably reduced anthropogenic pressures in the area since the late 1990s (Cociasu *et al*., 2009).

Conclusions

In the Romanian shallow coastal waters, surface Chl *a* showed large temporal variability (CV = 142.3%; concentrations within 0.17–76.13 $\mu g \cdot l^{-1}$ during the studied period), mainly controlled by large fluctuations of the Danube's discharges, sharp changes of local climatic factors and anthropogenic pressures.

Seasonal cycle of Chl *a* showed a winter/early spring peak (February–March) in accordance with the normal growth cycle of diatoms, followed by a stronger one in spring (April–May), but only in the springs with large discharges of the Danube. After significantly lower concentrations in late spring/early summer (May–June), Chl *a* exhibited its strongest maximum in summer (July – August), generally corresponding to strong diatoms blooms, followed by another one in autumn (late September–October), mainly associated with large-size diatoms blooms. Some deviations from this cycle were found in 2007, when no winter Chl *a* peak was observed, and especially in 2009, when Chl *a* levels remained low in the warm season, and did not show any peaks from May to the end of the year.

Year-to-year variability of Chl *a* seems to be controlled by the hydrometeorological conditions during summer. Thus, the larger discharges of the Danube, as well as the prevailing northerly winds, led to the highest summer Chl *a* in 2006 and 2010, when, also, the annual Chl *a* means were maximal (8.56 ± 8.35 $\mu g \cdot l^{-1}$ and 9.20 ± 11.72 $\mu g \cdot l^{-1}$, respectively). The lowest annual Chl *a* mean was observed in 2004 (4.57 ± 9.81 $\mu g \cdot l^{-1}$), when, also, the summer Chl *a* concentrations were minimal as a result of lower discharges of the Danube and other local physical processes which led to strong P limitation in the coastal area.

Although significantly lower than in the 1980s and 1990s, Chl *a* level in the Romanian near-shore waters has remained quite high (6.59 ± 9.38 $\mu g \cdot l^{-1}$) after 2000 due to optimal nutrient regime provided through either external (the Danube River, anthropogenic activities) or internal sources (benthic recycling processes).

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References

Aminot, A. & Rey, F., 2001. Chlorophyll *a*: determination by spectroscopic methods. *ICES Techniques in Marine Environmental Sciences,* 30 (1): 1-18.

Blondeau-Patissier, D., Tilstonet, G.H., Martinez-Vicente, V.

& Moore, G.F., 2004. Comparison of bio-physical marine productsfrom SeaWIFS, MODIS and a bio-optical model with in situ measurements from northern European waters. *Journal of Optics A: Pure & Applied Optics*, 6 (9): 875-889.

Bodeanu, N., 1993. Algal blooms in Mamaia Bay (Romanian Black Sea Coast). p. 127-132. In: *Harmful Marine Algae Blooms: Proceedings of the 6th International Conference on Toxic Marine Phytoplankton, October 1993, Nantes, France*. P. Lassus, G. Arzul, E. Denn, P. *et al.* (Eds). Paris, Lavoisier Publ. Inc.

Bodeanu, N., 1987-1988. Structure et dynamique de l'algoflore unicellulaire dans les eaux du littoral roumain de la mer Noir. *Recherches Marines,* 20- 21: 19-250.

Bodeanu, N. & Roban, A., 1989. Les développements massifs du phytoplancton des eaux du littoral roumain de la mer Noir ou cours de l'année 1989. *Recherches Marines,* 22: 127-146.

Bodeanu, N., Andrei, C., Boicenco, L., Popa, L. & Sburlea, A., 2004. A new trend of the phytoplankton structure and dynamics in the Romanian marine waters. *Recherches Marines*, 35: 77- 86.

Bologa, A., 1977. The phytoplanktonic assimilatory pigments along the Romanian coast of the Black Sea during 1976. *Recherches Marines*, 10: 95-107.

Bologa, A., 1978. Monthly dynamics of phytoplanktonic assimilatory pigments in the Romanian coastal waters between Constanta and Agigea during 1977. *Recherches Marines*, 11: 77-83.

Bologa, A.S., Burlakova, Z.P., Tchmyr, V.D. & Kholodov, V.I., 1985. Distribution of chlorophyll *a*, phaeophytin *a* and primary production in the Western Black Sea (May 1982). *Recherches Marines*, 18: 97-115.

Bologa, A.S., Frangopol, P.T., Frangopol, M. & Stanev, I., 1980. Marine phytoplankton photosynthesis in the offshore zone of Constanta (Black Sea) during June-December 1978. *Revue Roumaine de Biologe. Serie de Biologie Vegetale,* 25 (2): 129-133.

Bologa, A.S., Skolka, H.V. & Frangopol, P.T., 1984. Annual cycle of plankton primary productivity off the Romanian Black Sea coast. *Marine Ecolology Progress Series*, 19: 25-32.

Brzezinski, M.A., 1985. The Si:C:N ratio of marine diatoms: interspecific variability and effect of some environmental variables. *Journal of Phycology*, 21 (3): 347-357.

BSC, 2008. *State of the environment of the Black Sea (2001 - 2006/7)*. T. Oguz (Ed). Publications of the Commission on the Protection of the Black Sea against Pollution (BSC) 2008-3, Istanbul, 448 pp.

Chu, P.C., Ivanov, L.M. & Margolina, T.M., 2005. Seasonal variability of the Black Sea chlorophyll *a* concentration. *Journal of Marine Systems*, 56 (3-4): 243-261.

Cociasu, A. & Popa, L., 1978. Contributions à la connaissance de la dynamique des phosphates et des silicates des eaux marines du littoral roumain de la mer Noir. *Recherches Marines*, 11: 33-51.

Cociasu, A., Diaconu, V., Popa, L., Buga, L., Nae, I. *et al.,* 1997. The nutrient stock of the Romanian shelf of the Black Sea during the last three decades. p. 49-63. In: *Sensitivity to Change: Black Sea, Baltic Sea and North Sea*. Ozsoy, E. & Mikaelyan, A. (Eds). Dordrecht, Kluwer Academic Publishers.

Cociasu, A., Varga, L., Lazar, L. & Vasiliu, D., 2009. Recent data concerning the evolution of the eutrophication level indicators in Romanian seawater. *Journal of Environmental Protection & Ecology*, 10 (3): 701-731.

Cokacar, T., Oguz, T. & Kubilay, N., 2004. Satellite detected early summer coccolithophore blooms and their interannual variability in the Black Sea. *Deep Sea Research Part I: Oceanographic Research Papers,* 51 (8): 1017-1031.

Demidov, A.B., 2008. Seasonal dynamics and estimation of the annual primary production of phytoplankton in the Black Sea. *Oceanology*, 48 (5): 664-678.

Edler, L., 1979. Recommendations on methods for Marine Biological Studies in the Baltic Sea. Phytoplankton and Chlorophyll. *Baltic Marine Biologists Publication. No. 5,* 38 pp.

Friedrich, J., Dinkel, C., Friedl, G, Pimenov, N., Wijsman, J. *et al.,* 2002. Benthic nutrient cycling and diagenetic pathways in the North-Western Black Sea. *Estuarine, Coastal & Shelf Science*, 54 (3): 369-383.

Grasshoff, K., Kremling, K. & Ehrhardt, M., 1999. *Methods of Seawater Analysis*. 3rd Edition. Weinheim, Willey-VCH, 632 pp.

Humborg, C., 1997. Primary productivity regime and nutrient removal in the Danube estuary. *Estuarine, Coastal & Shelf Science*, 45 (5): 579-589.

Kopelevich, O.V., Sheberstov, S.V., Yunev, O., Basturk, O., Finenko, Z.Z. *et al.,* 2002. Surface chlorophyll in the Black Sea over 1978-1986 derived from satellite and in situ data. *Journal of Marine Systems*, 36 (3): 145-160.

Kovalev, A. & Piontkovski, S., 1998. Interannual changes in the biomass of the Black Sea gelatinous zooplankton. *Journal of Zooplankton Research*, 20 (7): 1377-1385.

Lancelot, C., Martin, J-M., Panin, N. & Zaitsev, Y., 2002. The North-Western Black Sea: A pilot site to understand the complex interaction between human activities and coastal environment. *Estuarine, Coastal & Shelf Science*, 54 (3): 279-283.

Mihailov, M.-E., Tomescu-Chivu, M.-I. & Dima, V., 2012. Black Sea water dynamics on the Romanian littoral – case study: the upwelling phenomena. *Romanian Reports in Physics*, 64 (1): 232-245.

Mihnea, P.E., 1988. Chlorophyll *a* in the Romanian Black Sea area. *Rapports de la Commission Intérnationale pour l'Exploration Scientifique de la Mer Méditerranée*, 31: 2-59.

Mihnea, P.E., 1997. Major shifts in the phytoplankton community (1980-1994) in the Romanian Black Sea. *Oceanologica Acta*, 20 (1): 119-129.

Morozova-Vodyaniskaya, N.V., 1954. Phytoplankton of the Black Sea II. *Trudy Sevastopol'skoj Biologicheskoj Stantsii,* 8: 11-99. (in Russian)

Nezlin, N.P., 1997. Seasonal variation of surface pigment distribution in the Black Sea on CZCS data. p. 131-138. In: *Sensitivity to Change: Black Sea, Baltic Sea and North Sea*. E. Ozsoy & Mikaelyan A. (Eds). Dordrecht, Kluwer Academic Publishers.

Nezlin, N.P. & Dyakonov, V.Y., 1998. Seasonal and inter-annual variations of surface chlorophyll concentrations in the Black Sea on CZCS data. p. 137-150. In: *Ecosystem Modeling as a Management Tool for the Black Sea*. L. I. Ivanov & Oguz T. (Eds). Dordrecht, Kluwer Academic Publishers.

Oguz, T. & Ediger, D., 2006. Comparison of in-situ and satellite-derived chlorophyll pigment concentrations and impact of phytoplankton bloom on the suboxic layer structure in the western Black Sea during May-June 2001. *Deep Sea Research Part II: Topical Studies in Oceanography*, 53 (17-19): 1923-1933.

Redfield, A.C., Ketchum, B.H. & Richards, F.A., 1963. The influence of organisms on the composition of seawater. p. 26-77. In: *The Sea, ideas and observations on progress in the study of the seas.* M.N. Hill (Ed). New York, Interscience Publishers.

FP6 SESAME, 2010. Synthesis report on the western Black Sea shelf ecosystem functioning. In: *Southern European Seas: Assessing and Modeling Ecosystem Changes (project no. 036949)*. http://sesame-ip.eu.

Schlitzer, R., 2006. Ocean Data View. http://odv.awi.de.

Shiganova, T., 1998. Invasion of the Black Sea by the ctenophore *Mnemiopsis leidyi* and recent changes in pelagic community structure. *Fisheries Oceanography*, 7 (3/4): 305-310.

Skolka, H., 1960. Espèces phytoplanktonique des eaux roumaines de la mer Noire. *Rapports de la Commission Intérnationale pour l'Exploration Scientifique de la Mer Méditerranée,* 9 (2): 249-268.

Skolka, H., 1968. Les pigments assimilateurs du phytoplankton du littoral roumain de la mer Noire. *Rapports de la Commission Intérnationale pour l'Exploration Scientifique de la Mer Méditerranée,* 19 (3): 395-397.

Staneva, J., Kourafalou, V. & Tsiaras, K., 2010. Seasonal and inter-annual variability of north-western Black Sea ecosystem. *Terrestrial Atmospheric and Oceanic Sciences,* 21 (1): 163-180.

Stelmakh, L.V., Babich, I.I., Tugrul, S., Moncheva, S. & Stefanova, K., 2009. Phytoplankton growth rate and zooplankton grazing in the Western Part of the Black Sea in the Autumn Period. *Oceanology*, 49 (1): 83-92. (in Russian)

Stelmakh, L.V., Senecheva, M.I. & Kuftarkova, E.A., 2010. Long-term variability of the structural and functional characteristics of the phytoplankton in the Sevastopol Bay, *Journal of Environmental Protection & Ecology*, 11 (1): 182-190.

Sur, H.I., Ozsoy, E., Ilyin, T.P. & Unluata, U., 1996. Coastal/deep ocean interactions in the Black Sea and their ecological/environmental impacts. *Journal of Marine Systems*, 7: 293-320.

Timofte, F., 2011. *Contributions to assessing the curent status of zooplankton populations in the Romanian Black Sea waters*. PhD Thesis, University Ovidius, Constanta, Romania, 232 pp. (in Romanian)

UNESCO, 1966. Determinations of photosynthetic pigments in seawater. *Monographs on Oceanographic Methodology, 1*: 11-18.

Vasiliu, D., Gomoiu, M.-T., Boicenco, L., Lazar, L. & Timofte, F., 2010. Chlorophyll *a* distribution in the Romanian Black Sea inner shelf waters in 2009. *Geo-Eco-Marina*, 16: 19-28.

Vedernikov, V.I. & Demidov, A.B., 1993. Primary production and chlorophyll in the deep regions of the Black Sea, *Oceanology*, 33: 193-199.

Velikova, V., Cociasu, A., Popa, L., Boicenco, L. & Petrova, D., 2005. Phytoplankton community and hydro-chemical characteristics of the Black Sea. *Water Science & Technology*, 51 (11): 9-18.

Yunev, O.A., Carstensen, J., Moncheva, S., Khaliulin, A., Aertebjerg, G. & Nixon, S., 2007. Nutrient and phytoplankton trends on the western Black Sea shelf in response to cultural eutrophication and climate change. *Estuarine, Coastal & Shelf Science*, 74 (1-2): 63-76.

Yunev, O.A., Vedernikov, V.I., Basturk, O., Yilmaz, A., Kideys, A.E. *et al.,* 2002. Long-term variations of surface chlorophyll *a* and primary production in the open Black Sea. *Marine Ecology Progress Series*, 230: 11-28.