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Spatial distribution and recent changes in carbon, nitrogen and phosphorus accumulation in sediments of the Black Sea

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Abstract

Sediment cores from the Black Sea were analyzed along two transects across the basin in West–East and North–South direction and ranging from the oxic and suboxic shelf to the anoxic slopes and abyssal plain. On the North-Western shelf, the average concentrations of total organic carbon (TOC), total nitrogen (TN) and total phosphorus (TP) in recent sediments showed a decrease with increasing distance to the shore. Compared to the shelf, TP concentration was depleted on the slope and towards the central basin whereas TOC and TN concentrations increased towards the deep central basin. Anthropogenic nutrient loads of the last 50 years have left a clear signature in the sedimentary record. On the shelf, TN and TP were about 40% and 10% higher, respectively, than in the period 1850–1950. Anthropogenic impact on deep-sea sediments is within the natural variability for the last 50 years (+5% TN and +8% TP). Our data and a literature survey were the basis for identifying three major sedimentary areas and for estimating the total annual accumulation of 1.3×10^6 t TOC, 1.4×10^5 t TN and 4.7×10^4 t TP. A mass balance based on river inputs, outflow to the Sea of Marmara and the total accumulation rates indicated that 20% of the TN inputs accumulated in the sediments of the Black Sea whereas denitrification eliminated more than 55% of the inputs. In contrast, a single removal process controls the TP budget with the sedimentary accumulation, mainly on the shelf, representing 80% of the total incoming load.

Keywords: Accumulation; Black Sea; Mass balance; Nutrients; Sedimentation; Sediment core; Transect

1. Introduction

Nutrient export from the continents to the coastal zones can trigger eutrophication of marine ecosystems (Cloern, 2001; Smith et al., 2003). Recent analyses of the acceleration of biogeochemical cycles in coastal systems demonstrate the effects of severe nutrient loading. For example, a large zone of oxygen depleted waters in the Gulf of Mexico affects the continental shelf close to the Mississippi Delta (Rabalais et al., 2002). Anoxic

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conditions increase phosphorus release from sediments (Conley et al., 2002) and reduce benthic denitrification (Childs et al., 2002), thus maintaining high nutrient conditions in the system. Reduced oxygen exposure time increases organic carbon preservation in continental margin sediments (Hartnett et al., 1998). As a result, semi-enclosed basins such as the Baltic Sea (Emeis et al., 2000; Karlson et al., 2002), the Adriatic Sea (Degobbis et al., 2000) and the Black Sea (Mee, 1992; Lancelot et al., 2002) with long water residence times and low tidal energies are particularly susceptible to increased anthropogenic nutrient loads (Cloern, 2001). The Black Sea represents a very sensitive system because of its extensive watershed receiving nutrient loads from catchments of three highly polluted rivers: Danube, Dniepr and Dniestr.

Nutrient input into the Black Sea increased dramatically during the last century. A previous study (Zaitsev, 1993) estimated that annual inflow loads of nitrate and phosphate from Danube River into the Black Sea were about 2.5 and 4 times higher in the 1980's than in the 1950's. Similar trends were reported for Dniepr and Dniestr rivers (Zaitsev, 1993). In the recent years, international monitoring programs of the Danube reported a stabilization and reduction of nitrogen and phosphorus fluxes (EPDRB, 1997). Dissolved inorganic nitrogen (DIN) and total phosphorus (TP) loads for the year 2000 were only about 1.9 and 1.1 times higher than in the 1950's (ICPDR, 2004). Because the Black Sea represents a semi-closed basin with a well-known exchange rate through the Bosporus (Polat and Tugrul, 1995), phosphorus inflow minus outflow must be balanced by sediment accumulation under steady state conditions (Fonselius, 1974). A similar mass balance holds for nitrogen if the processes of nitrogen fixation and denitrification are considered at near steady-state conditions. Basin-wide nutrient accumulation rates are necessary to constrain present day nutrient budgets and to reconstruct anthropogenic changes (Conley, 1999; Emeis et al., 2000). However, such an approach faces the difficulties of assessing different redox and sedimentation regimes on shelf, slopes and abyssal plain (Cowie and Hedges, 1992). For instance, measurements with benthic flux chambers on shelf revealed large differences in nutrient release from sediment and indicated that a large fraction of riverine nutrient load

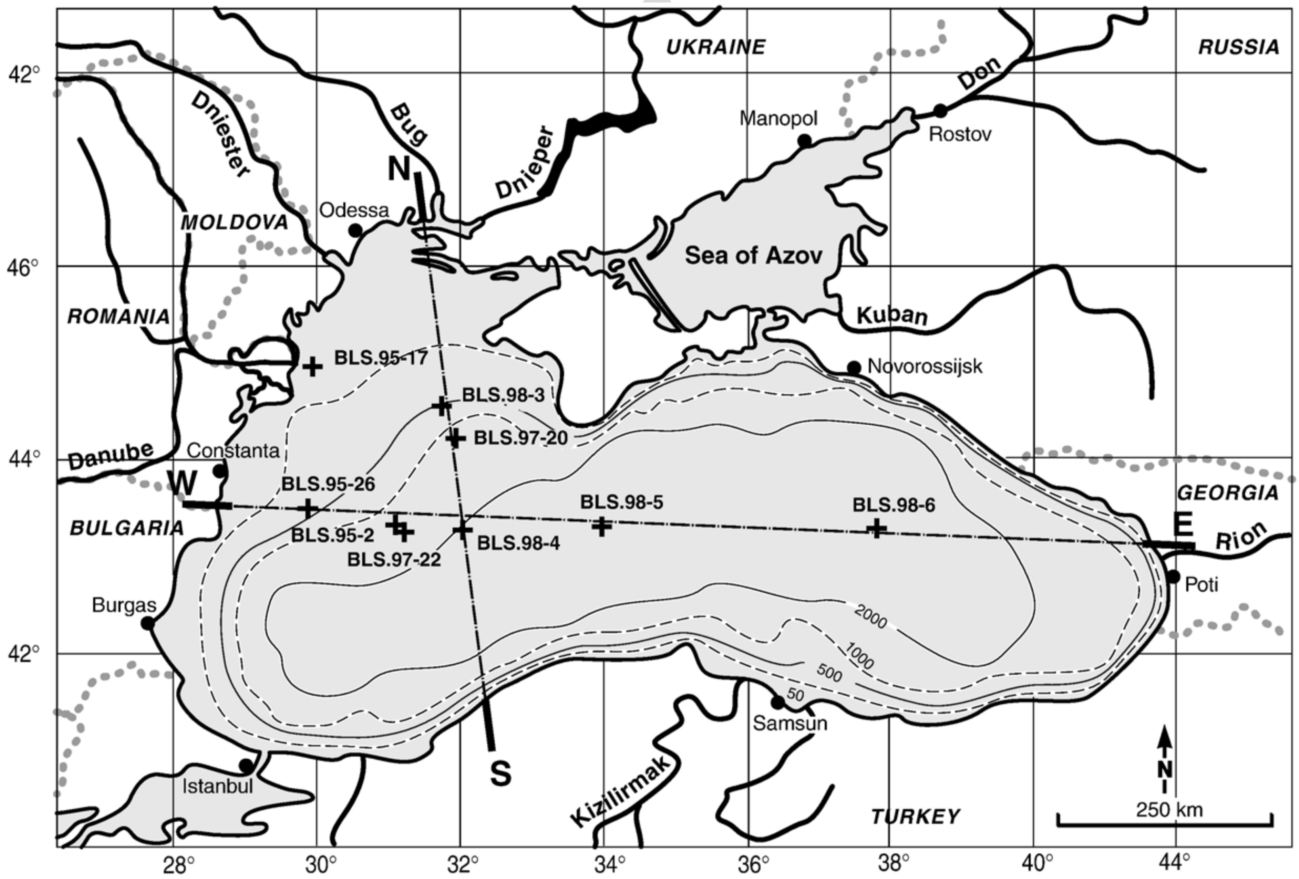

Fig. 1. Map of Black Sea showing the distribution of sediment cores along West–East and North–South transects.

Table 1
Annual river discharge into the Black Sea and the Sea of Azov

	Annual rivers discharge			
	Q[a]		Q[b]	
	[km^3 yr^{-1}]	[%]	[km^3 yr^{-1}]	[%]
Black Sea basin				
Rivers				
1. Rivers of the north-western coastline:	255.4	73.4	255.7	77.6
1.1. Danube	200	57.5	190.7	57.9
1.2. Dnieper	43.5	12.5	52.6	16
1.3. Dniestr	9.1	2.6	9.8	3
1.4. Southern Bug	2.2	0.6	2.6	0.8
1.5. Ingul	0.6	0.2		
2. Rivers of the Crimea	0.3	0.1		
3. Rivers of Russian coastline	6.5	1.9		
4. Rivers of the Caucasus coastline (Rioni, Choroh, Inguri, Kodori and others)	46	13.2	41	12.4
5. Rivers of the Turkish coastline (Ishil-Iirmak, Kuzul-Irmak and others)	38	10.9	29.7	9
4. Rivers of the Bulgarian and Romanian coastline	1.8	0.5	3	0.9
Total	348	100	329.4	100
Azov Sea basin				
Rivers				
1. Don			29.5	68.8
2. Kuban			13.4	31.2
Total			42.9	100

[a] Jaosvili, 2002.
[b] Panin and Jipa, 2002.

was remobilized supporting strong benthic–pelagic coupling (Friedl et al., 1998; Friedrich et al., 2002). So far, little systematic data are available to quantify changes in nutrient accumulations from shelf to pelagic sediments whereas organic carbon accumulation in the Black Sea sediments was intensively debated over the last decade. Arthur and Dean (1998) and Calvert and Karlin (1998) presented overviews of the organic carbon accumulation in the abyssal sediments of the Black Sea during the Holocene. A laminated, organic carbon rich sapropel was described as a result of the onset of water-column anoxia. High carbonate fluxes, a result of the first blooms of the coccolith *Emiliania huxleyii*, diluted the organic carbon concentration in the recent sediments although the organic carbon accumulation rates remained rather constant over the entire Holocene (Arthur and Dean, 1998).

In this paper we report mass accumulation rates of organic and inorganic carbon, nitrogen and phosphorus from 10 sediment cores covering different sedimentation regimes in the Black Sea from the continental shelf to the abyssal plain. The dataset is supplemented with a literature survey of published sedimentation rates and sedimentary carbon, nitrogen and phosphorus concentrations on the Black Sea. This study aims at evaluating the effects of sedimentation rate and redox conditions on carbon, nitrogen and phosphorus accumulation by comparing the sediment regime on the shelf, slope and abyssal plains. We then, address the question how these different accumulation zones reacted to increasing anthropogenic nutrient inputs over the last years. Finally, the sediment dataset is used together with published inflow and outflow estimates in order to constrain the elimination pathways for TN and TP in the world's largest anoxic basin.

2. Study site and methods

2.1. The Black Sea basin

The Black Sea is an elliptical basin extending over 1200 km in the East–West direction with a surface area of 413,000 km^2, a volume of 547,000 km^3 and a maximum depth of 2212 m (Zaitsev and Mamaev, 1997). The drainage basin of the Black Sea measures about 2×10^6 km^2 and includes six riparian countries (Turkey, Bulgaria, Romania, Ukraine, Russia and Georgia) and 16 other countries in eastern and central Europe. Large European rivers are draining this area: Danube, Dniepr, Dniestr, Southern Bug, Don and Kuban (Fig. 1). Partitioning of the average annual river discharge into the Black Sea of about 380 km^3 yr^{-1} is shown in Table 1. The Danube River is the main tributary of the Black Sea and contributes more than 55% of the total freshwater input.

The rather simple morphometry of the Black Sea basin has the consequence that the main functional depositional areas lay within clear depth intervals. Therefore, the seafloor can be divided into five zones: (1) the over 200-km wide and less than 100-m deep continental shelf in the northwestern part of the Black

Table 2
Bathymetry of the Black Sea basin (GEBCO, 2003)

Sedimentary area	Depth [m]	Sections area	
		[km^2]	[%]
Shelf	0–100	131,800	31.9
Shelf break	100–200	13,700	3.3
Upper slope	200–1000	34,800	8.4
Lower slope	1000–1800	62,200	15.1
Abyssal plain	1800–2212	170,500	41.3
Total		413,000	100

Sea; (2) the shelf break with a depth down to 200 m; (3) the steep continental upper slopes (200–1000 m); (4) the much gentler lower slope (1000–1800 m); (5) and finally the large deep-sea basin with water depths near 2000 m. Summaries of bathymetric and morphometric data are shown in Table 2. The large northwestern shelf can be further divided into an inner and an outer shelf (Panin and Jipa, 2002). The continental shelf is generally characterised by oxic water column conditions. The shelf break is situated near oxycline and is influenced by suboxic conditions, whereas the upper slope, lower slope and deep-sea basin are exposed to anoxic waters.

2.2. Coring sites

A set of sediment cores was collected during three cruises on the Black Sea in 1995, 1997 and 1998. Sediment cores were collected using either a 50 × 50 cm single-spade box corer (1995 and 1997) or a gravity corer using 7.5-cm diameter tubes (1998). Sub-cores from box corer were taken by inserting 7.5-cm diameter tubes. The length of cores varied between 20 and 80 cm. The cores laid on two transects (W–E and N–S) reaching from the oxic conditions on the northwestern shelf to the oxycline at the slope and to the permanent anoxic deep basin (Fig. 1). The W–E and N–S transects include six and three cores, respectively (Fig. 2), with the core at the deepest position (BLS.98-4) being part of the W–E transect as well. Representing riverine deposits, a core in front of the Danube mouth (BLS.95-17) completes the W–E transect (Fig. 1).

2.3. Sediment core analysis

The cores were transported from the Black Sea to the laboratory in upright position and stored in a cool room at 4 °C. Cores were cut it into halves for photographic documentation and description, and sub-sampled with a thin metal disc parallel to laminae every 0.5 cm for the first 10 cm and in 1 cm intervals below 10 cm according to sediment characteristics. Wet sub-samples were freeze-dried for three days and water content was measured for porosity determination.

For measurements of *total organic carbon* (TOC) and *total nitrogen* (TN), 50–60 mg of freeze dried and finely powdered sediment were suspended in 20 ml 0.5 M HCl and sonicated for 4 min to remove inorganic carbon. A 10 ml aliquot was filtered on pre-combusted Whatman glass fiber filters. Another aliquot was used for phosphorus determination. TOC and TN analyses were performed using a CNS-Analyzer following the standard procedure described in DEV (1996). Analytical error of measurements was 5% for TOC and 4% for TN.

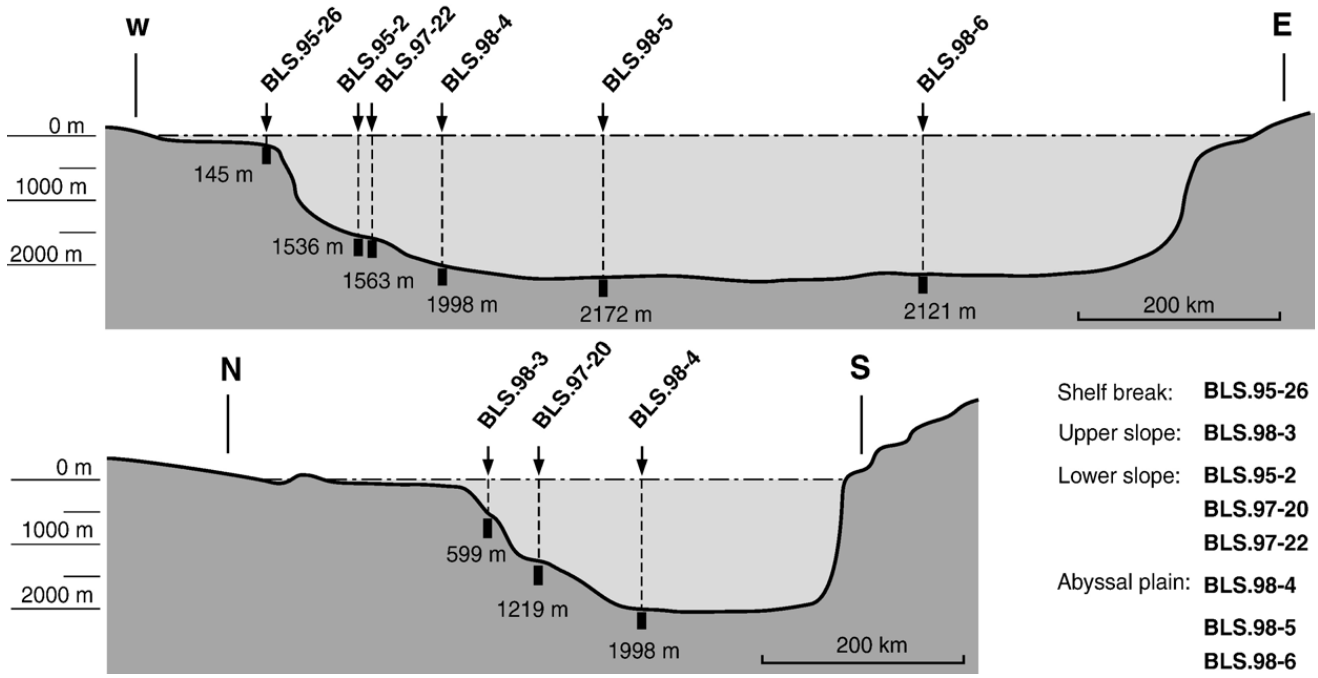

Fig. 2. "Ideal" profile along West–East and North–South transects through the Black Sea suggesting the bottom morphology and sediment cores distribution.

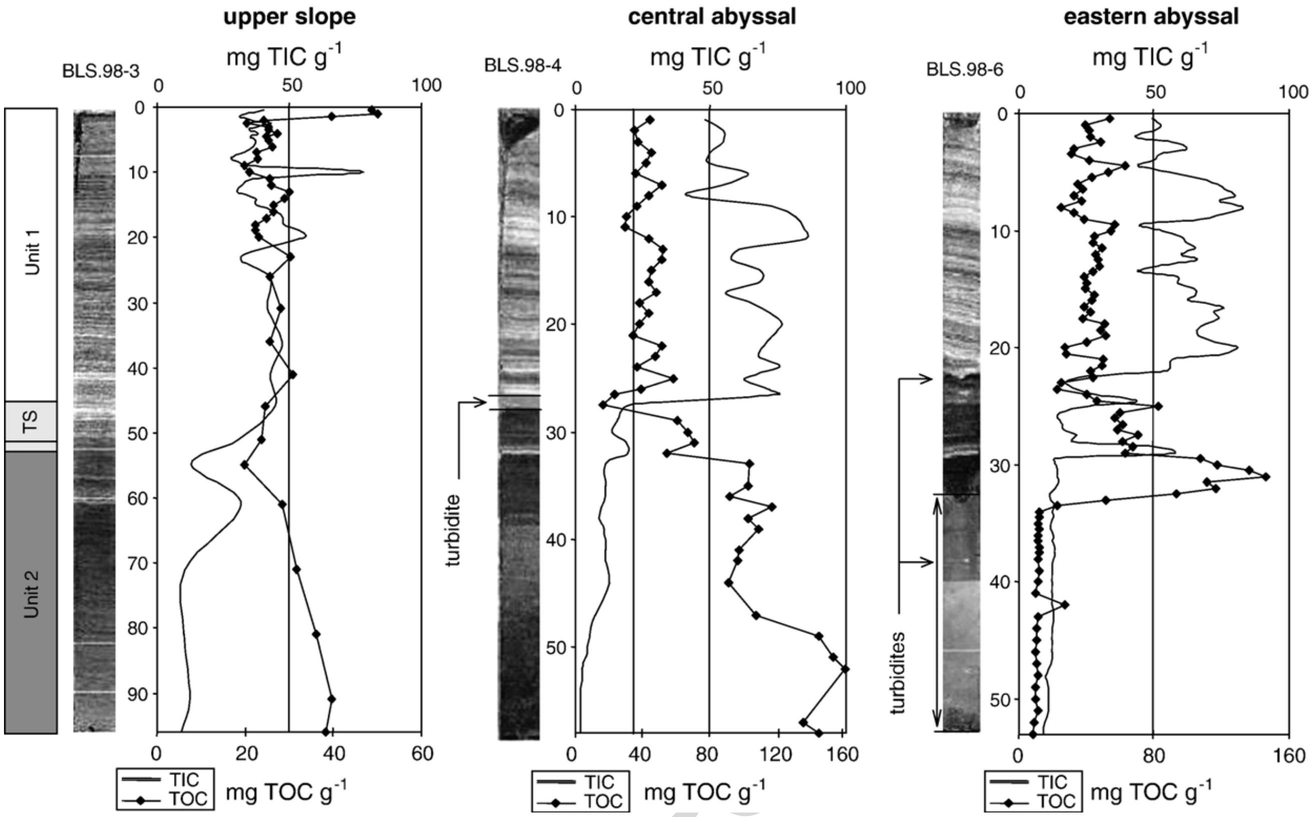

Fig. 3. Photograph of three sediment cores together with the plot of total organic carbon (TOC) and total inorganic carbon (TIC) versus depth with the stratigraphic units division according to Hay et al. (1991), Ross et al. (1970), Ross and Degens (1974).

Total inorganic carbon (TIC) was determined using a Coulometrics Inc. CO_2 coulometer with the acidification method (DEV, 1996), which provided an absolute determination of carbon dioxide concentration evolved in acidification process. For samples containing more than 5% carbonate the precision was 1.2% and for lower concentrations, the error of measurements increased to 3.5%.

For measuring *total phosphorus* (TP) an unfiltered 10-ml sediment suspension was digested with a 5% potassium peroxidesulphate solution in an autoclave at 120 °C for 3 h (DEV, 1996). Total phosphorus was then analysed as orthophosphate with the ammoniummolybdate method on a Procon autoanalyzer. The precision of measurements was 2.5%.

For *sediment chronology*, freeze-dried samples from four cores (BLS.95-2, BLS.95-3, BLS.98-5 and BLS.98-6) were gamma counted for ^{210}Pb according to the method of Goldberg (1963) and Krishnaswami et al. (1971) and for ^{137}Cs (Pennington et al., 1973) using a well germanium detector with an analytical error of 3%. Sedimentation rates (SR in cm yr^{-1}) were corrected for compaction according to Appleby and Oldfield (1978) and Robbins (1978) with a maximum error of 5%.

Four of the sediment cores were analyzed for element concentrations of *Fe*, *Ca* and *Ti* using X-ray fluorescence (XRF) core scanner (Jansen et al., 1998; Röehl and Abrams, 2000). This system of nondestructive analysis was applied on a split-core surface at a resolution of 1 cm (BLS.97-20, BLS.97-22 and BLS.98.3) and 0.6 cm (core BLS.98-4). A calibration was performed in order to obtain concentration data of the quantified elements with an analytical error of 5%.

3. Results

3.1. Sediment core characteristics

The uppermost 1 m of the Black Sea sediments consists of three distinct stratigraphic units (Ross et al., 1970) reflecting the hydrographic evolution in the basin during the Holocene and Upper Pleistocene. Three sediment cores — one from the slopes (BLS.98-3, N-S transect) and two from the abyssal plain (BLS.98-4 and BLS.98-6, W–E transect) are compared in Fig. 3. The separation between Unit 1 and Unit 2 by the Transition Sapropel (Ross et al., 1970) can be clearly distinguished. Unfortunately the cores were too short to locate the

Table 3
Average (wt.%) total organic carbon (TOC), total inorganic carbon (TIC), total nitrogen (TN), total phosphorus (TP), calcium (Ca), titanium (Ti), and the percentage $CaCO_3$ calculated from TIC and Ca concentration signed with (a) and (b), respectively along the W–E and N–S transects for Unit 1 and Unit 2 sediments

Core	Coordinates	Depth [m]	Unit	TOC [mg g^{-1}]	TIC [mg g^{-1}]	TN [mg g^{-1}]	TP [mg g^{-1}]	Ca [mg g^{-1}]	Ti [mg g^{-1}]	$CaCO_3$ [a] [%]	$CaCO_3$ [b] [%]	C:N Molar	C:P Molar	P:Ti Molar
Transect W–E														
BLS.95-17	45°12.23′ N 29°50.82′ E	26	Bioturbat	26±1.3	11.4±0.4	3.6±0.14	0.95±0.02		3.8±0.19	9.5		8	71	0.4
BLS.95-26	43°41.84′ N 30°03.47′ E	145	Bioturbat	10.8±0.5	55.7±1.9	0.7±0.03	0.68±0.02			46.4		18	41	
BLS.95-2	43°17.13′ N 31°02.19′ E	1536	Unit 1	41.5±2.1	64.3±2.3	3.3±0.13	0.80±0.02			53.5		15	134	
BLS.97-22	43°16.65′ N	1563	Unit 1	44.0±2.2	62.1±2.2	3.6±0.14	0.75±0.02	158±7.9	0.6±0.03	51.7	40	14	151	1.9
	31°02.69′ E		Unit 2	91.2±4.6	11.3±0.4	7.7±0.31	0.85±0.02	25±1.3	1.3±0.07	9.4	6	14	277	1
BLS.98-4	43°20.23′ N	1998	Unit 1	42.6±2.1	69.4±2.4	3.8±0.15	0.52±0.01	166±8.3	0.5±0.03	54.6	45	13	211	1.6
	32°09.54′ E		Unit 2	117.7±6	7.4±0.3	9.6±0.38	0.89±0.02	24±1.2	1.1±0.06	6.3	4	14	314	1.3
BLS.98-5	43°16.04′ N 33°59.83′ E	2172	Unit 1	41.9±2.1	55.3±1.9	4.1±0.16	0.51±0.01			46.1		12	213	
BLS.98-6	43°01.35′ N	2121	Unit 1	42.7±2.1	62.5±2.2	4.1±0.16	0.49±0.01			52.1		12	226	
	37°34.36′ E		Unit 2	110.2±5.5	13.4±0.5	9.4±0.37	0.60±0.02			11.1		14	474	
Transect N–S														
BLS.98-3	44°40.19′ N	599	Unit 1	27.2±1.5	40.1±1.4	2.4±0.10	0.82±0.02	114±5.7	1.8±0.09	33.4	30	13	86	0.7
	31°46.82′ E		Unit 2	36.4±1.8	10.5±0.4	3.2±0.13	0.90±0.02	32±1.6	2.8±0.14	8.8	8	13	104	0.5
BLS.97-20	44°08.14′ N	1219	Unit 1	34.6±1.7	49.1±1.7	2.8±0.11	0.53±0.01	112±5.6	1.4±0.04	40.9	32	14	169	0.6
	31°59.50′ E		Unit 2	70.6±3.5	10.2±0.4	5.6±0.22	0.52±0.01	25±1.3	2.1±0.11	8.5	8	15	350	0.4
BLS.98-4	43°20.23′ N	1998	Unit 1	42.6±2.1	64.9±2.3	3.8±0.15	0.52±0.01	166±8.6	0.5±0.03	54.6	45	13	211	1.7
	32°09.54′ E		Unit 2	117.7±6	7.4±0.3	9.6±0.38	0.89±0.02	23±1.2	1.1±0.06	6.3	4	14	341	1.3

[a] Calculated from TIC concentrations.
[b] Calculated from Ca concentrations.

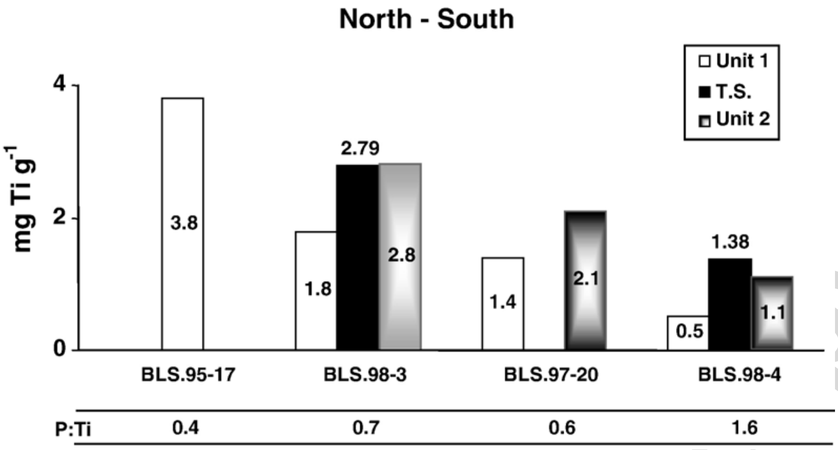

Fig. 4. Ti distribution along N–S transect illustrating the differences in concentration between the units. The general trend is a decrease in concentration from the river influence (BLS.95-17) to deep sea (BLS.98-4). P:Ti molar ratio for the laminated sediment of Unit 1 suggests that the core influenced by the Danube River has the lowest ratio whereas the abyssal core has the highest ratio.

transition to the older Unit 3. Laminated sediment of Unit 1 could be perfectly correlated among both transects although the distance between the cores varied from 150 to 500 km. In the N–S transect, Unit 1 is about 50 cm thick at the northern station (BLS.98-3) and only 30 cm in the central basin (BLS.98-4). This difference

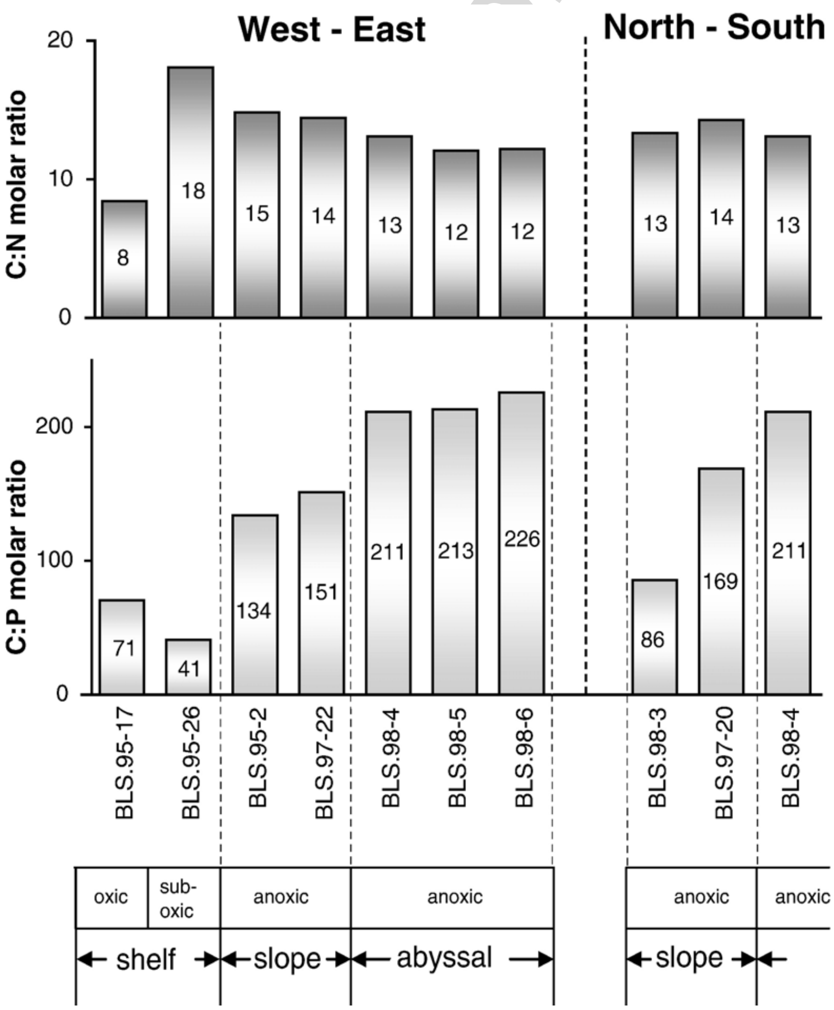

Fig. 5. C:N and C:P molar ratios in recent sediments (Unit 1) of the Black Sea along W–E and N–S transects.

Table 4
Sedimentation (SR) and mass accumulation rates (MAR) of Unit 1 sediments for different areas of the Black Sea

Sedimentary area	Core name	Location	Depth [m]	Coordinates N	Coordinates E	SR [cm yr^{-1}]	MAR [g m^{-2}yr^{-1}]	Methods	Authors
Shelf 0–100 m	A (BLS.95–17)	Danube Delta front	26	45°12′	29°51	1.15	3994	^{137}Cs, ^{210}Pb	(Gulin et al., 2002)
	B	Dniepr Delta front	13	46°33′	31°25′	0.92	3670	^{137}Cs, ^{210}Pb	(Gulin et al., 2002)
	G1 [a]	Coruh River front	70	41°40′	41°33′	0.7	3071	^{137}Cs, ^{210}Pb	(Gulin et al., 2003)
	Average					**0.92**	**3578.3**		
Shelf break 100–200 m	BS4-15BC	SE-shelf	198			0.017	42.2	^{14}C	(Calvert et al., 1991)
	BLS.95-3	*NW shelf*	*134*	*44°00′*	*30°29′*	*0.17*	*425*	*^{137}Cs,^{210}Pb*	*This work*
	Average					**0.094**	**233.6**		
Upper slope 200–1000 m	1470	E slope	906	42°03′	41°18′	0.038	92.3		(Calvert et al., 1987)
	GC01	SW slope	549	41°53′	28°48′	0.033	165		(Arthur and Dean, 1998)
	GC59	SE slope	600			0.028	140		(Arthur and Dean, 1998)
	GC79	S slope	700			0.025	125		(Arthur and Dean, 1998)
	GC71	S slope	411			0.025	150		(Arthur and Dean, 1998)
	AII-1443	E slope	549				47.8		(Calvert and Karlin, 1998)
	D	NW slope	607	44°39′	31°46′	0.22	138	^{137}Cs, ^{210}Pb	(Gulin et al., 2002)
	Average					**0.062**	**122.6**		
Lower slope 1000–1800	GC09	SW slope	1259			0.0105	47		(Arthur and Dean, 1998)
	BLS.95-2	*W slope*	*1535*	*43°17′*	*31°02′*	*0.03*	*72.9*	*^{137}Cs,^{210}Pb*	*This work*
	Average					**0.02**	**59.9**		
Abyssal plain >1800 m	1432	Central	2248	43°01′	34°04′	0.025	62.5		(Calvert et al., 1987)
	BC21	Abyssal W		43°05′	32°02′		85.2		(Hay et al., 1991)
	BC55	Abyssal E	2164	42°45′	37°35′		70.2		(Hay et al., 1991)
	BS4-9BC	Abyssal W	2087	43°00′	33°00′	0.0159	38.7	^{14}C	(Calvert et al., 1991)
	BS4-14BC	Central	2218	43°00′	34°00′	0.0158	35.7	^{14}C	(Calvert et al., 1991)
	BS4-9	Abyssal W	2087	43°00′	33°00′		31.3		(Calvert and Karlin, 1998)
	BS-4-14	Central	2218	43°00′	34°00′		37.7		(Calvert and Karlin, 1998)
	G$_2$ [a]	W abyssal	1971	43°26′	32°08′	0.0394	99.8	^{137}Cs, ^{210}Pb	(Gulin, 2000)
	E	NW abyssal	1983	43°26′	32°09′	0.04	70	^{137}Cs	(Gulin et al., 2002)
	BS4-9	NW abyssal	2094	42°55′	31°22′		58	^{210}Pb	(Crusius and Anderson, 1992)
	BS4-9	NW abyssal	2094	41°51′	30°21′		69	^{210}Pb	(Buesseler and Benitez, 1994)
	BS4-18A	SE abyssal	2150	42°28′	37°36′		50	^{210}Pb	(Crusius and Anderson, 1992)
Abyssal plain >1800 m	ST1	SW abyssal	2100	42°10′	32°35′		36	sed. trap	(Hay et al., 1990)
	ST2	SW abyssal	2100	41°51′	30°21′		12	sed. trap	(Hay et al., 1990)
	BLS.98-5	*Central*	*2172*	*43°16′*	*33°60′*	*0.01*	*32.7*	*^{137}Cs, ^{210}Pb*	*This work*
	BLS.98-6	*E*	*2121*	*43°01′*	*37°34′*	*0.02*	*43.6*	*^{137}Cs,^{210}Pb*	*This work*
	Average					**0.024**	**52**		

For each sedimentary zone an average were estimated (bold values) from literature data and our measurements (italic).
[a] In the absence of the name of the cores in front of the Coruh River and W abyssal sites (Gulin, 2000; Gulin et al., 2003) and we call it G$_1$ and G$_2$.

was expected because of higher terrigenous input from the Danube and the Ukrainian rivers close to the northern station (BLS.98-3). Along the W–E transect, however, Unit 1 showed the same thickness (from 20 to 29 cm).

The Unit 1 sediment is composed of alternating white and grey–brown to black millimeter-scale laminae interpreted to be the result of annual sediment cycle dominated by diatoms in spring with light layers of *E. huxleyi* in summer and mainly dark lithogenic material during autumn and winter (Hay et al., 1990; Honjo et al., 1987). The normal deep-water Unit 1 deposition is interrupted by sedimentary deposits formed by turbidity currents (turbidites) and reflecting a mass flow from the slope towards the center. Such turbidite sections with different thicknesses are present only in the deep basin cores. Core BLS.98-5, the central basin station and the deepest location, illustrates an extreme case: a 7 cm thick band of laminae overlay a 45 cm homogeneous grey mud turbidite. Closer to shelf, in core BLS.98-4, the normal lamination is developed over the top 28 cm and the turbidite is present only as 1 cm layer (Fig. 3).

For the calculation of the recent accumulation rates of biogenic elements we relied only on average concentrations in the laminated part (Unit 1) of the sediment cores.

Table 5
Average TN and TP concentrations accumulated in sediments of the Black Sea before and after 1950 and calculated increase in concentration over the last 50 years compared to the 100 years deposition prior 1950

Sedimentary area	Core	Period	Concentration		Fold increase	
			TN [mg g^{-1}]	TP [mg g^{-1}]	TN	TP
Shelf break	BLS	1995–1950	1.06±0.04	0.76±0.02	1.4	1.1
	.95-26	1950–1850	0.75±0.03	0.67±0.02		
Upper slope	BLS	1998–1950	3.11±0.12	0.99±0.02	1.6	1.4
	.98-3	1950–1850	1.99±0.08	0.73±0.02		
Lower	BLS	1995–1950	4.41±0.18	0.72±0.02	1.7	1
Slope	.95-2	1950–1850	2.6±0.1	0.71±0.02		
	BLS	1997–1950	4.12±0.16	0.52±0.01	1.5	1
	.97-20	1950–1850	2.83±0.11	0.52±0.01		
	BLS	1997–1950	3.41±0.14	0.88±0.02	1	1
	.97-22	1950–1850	3.31±0.13	0.86±0.02		
Abyssal	BLS	1998–1950	4.1±0.16	0.54±0.01	1	1.1
plain	.98-4	1950–1850	4.1±0.16	0.5±0.01		
	BLS	1998–1950	4.3±0.16	0.55±0.01	1.2	1.1
	.98-5	1950–1850	3.74±0.15	0.5±0.01		
	BLS	1998–1950	4.22±.17	0.51±0.01	1	1.1
	.98-6	1950–1850	4.21±0.17	0.48±0.01		

3.2. Changes in the sediment regime during the last 3000 years

Profiles TIC and TOC concentration are compared in Fig. 3 for one core from the northern slope (BLS.98-3) and two cores from the abyssal plain (BLS.98-4 and BLS.98-6). Average values of total inorganic and organic carbon concentrations over the entire basin are displayed in Table 3. Values obtained from XRF-Ca data were comparable, but systematically lower, probably due to XRF profiler calibration.

Deep basin sediments of Unit 1 is characterized by average concentrations of 65 mg TIC g^{-1} and 43 mg TOC g^{-1}. A drastic change occurs at the transition to Unit 2, where TOC concentration increases by a factor of 3 to about 120 mg g^{-1} and TIC decreases by almost an order of magnitude to 8–13 mg g^{-1}. Caused by carbonate dilution rather than shift in productivity or preservation (Sageman and Lyony, 2004; Lyons and Kashgarian, 2005), the TIC:TOC ratio is therefore an excellent marker for identifying the Unit 1/2 boundary. The 50% smaller TOC concentrations in Unit 2 at the upper slope compared to the abyssal plain are explained by increased terrigenous input and clastic dilution (Lyons and Kashgarian, 2005).

Ti concentration in sediment can be used as a tracer for terrigenous input. Fig. 4 shows a decrease in terrigenous sedimentation from Danube Delta front (BLS.95-17) to slopes and abyssal plain. Along N–S transect, from upper slope to abyssal basin, average Ti concentration in Unit 1 decreases from 1.8 to 1.4 and 0.5 mg Ti g^{-1} (Fig. 4). Assuming that core BLS.95-17 represents an almost pure terrigenous end-member, the comparison of Ti concentrations with the deep basin core (BLS.98-4) implies a terrigenous fraction of around 50 wt.% on slopes and about 15 wt.% on abyssal plain. Unit 1 sediments are therefore a mixture of about 55 wt.% $CaCO_3$, 15 wt.% terrigenous inputs and 10 wt.% organic matter. The unaccounted 20% are probably due to diatoms. This is in good agreement with biogenic silica content of between 15 to 40 wt.% Si (average 35 wt.% Si) measured in the recent sediment (last 50 years) of the coastal Black Sea (Teodoru et al., 2006).

The transition to Unit 2 in Fig. 4 reveals dramatic changes. The Transition Sapropel shows the highest Ti concentrations, reflecting a particularly wet period between about 2700 and 1300 BP (Jones and Gagnon, 1994). Average Ti concentrations in Unit 2 are always about twice as high as in Unit 1, supporting the notion that the sapropel deposition of Unit 2 contains a large terrigenous fraction (Hay et al., 1991). Using again the Ti concentration in core BLS.95-17 as a terrigenous end-member, the allochthonous fractions of Unit 2 are 29 and 35 wt.% in cores BLS.98-4 and BLS.97-20, respectively. $CaCO_3$ contributes less than 10 wt.% but the organic matter fraction may reach 25 wt.%, leaving an unaccounted fraction of 45 wt.% due to diatoms. In the two slope cores of the N–S transect (Fig. 4) terrigenous particles in Unit 2 contribute as much as 73 and 55 wt.%, respectively to the sediment composition.

3.3. Redfield ratios

Note that, all molar ratios refer to Unit 1 only. C:N molar ratios at the shelf in W–E transect show an increase from 8 at the oxic location (core BLS.95-17) to a maximum value of 18 at the suboxic station (BLS.95-26) (Fig. 5). A gradual decrease towards deep sea characterized the slope and abyssal sediments. This decrease in C:N ratios from 18 to 12 reflects both a large deposition of terrigenous organic matter on shelf and slope and the effect of higher organic matter preservation under anoxic conditions.

C:P molar ratios in W–E transect show a progressive decrease at the shelf from a high ratio value of 71 for BLS.95-17 to 41 for the suboxic station (BLS.95-26). The decrease in ratio at oxic shelf indicates preferential loss of carbon in respect to phosphorus due to oxic mineralization of particulate organic matter and more effective P-accumulation in the presence of iron oxides.

A steadily increased C:P ratio was observed for anoxic stations from 134 at slopes to over 225 at the abyssal plain (Fig. 5). This increase in C:P ratio is also mirrored for the anoxic stations of N–S transect indicating a preferential remobilization of P in respect to C under anoxic conditions (Ingall and Van Cappellen, 1990; Ingall et al., 1993).

P:Ti molar ratios for Unit 1 sediment show a general increase towards deep sea (Fig. 4). Ti may serve as a tracer for riverine input and therefore increased P:Ti ratio suggests a shift from allochthonous to biogenic dominated sediments. Average Ti concentration of the material entering the Black Sea with Danube water is 3.8 mg g^{-1} (Panin and Jipa, 2002). Using the average P concentration of core at the Danube mouth (BLS.95-17), P:Ti ratio of the river input can be estimated as 0.4. This value is well above the lithogenic ratio of 0.14 given by Panin and Jipa (2002), and indicates anthropogenic P enrichment. The significantly higher P:Ti ratio of 1.6 at the abyssal station reflects a switch to predominantly biogenic phosphorus sedimentation in the central basin.

3.4. Sediment accumulation rates

Sediment accumulation rates (SR in cm yr^{-1}) measured in the uppermost 10 cm of Unit 1 in four different sediment cores (BLS.95-3, BLS.95-2, BLS.98-5 and BLS.98-6) are listed in Table 4 (italic). For core BLS.95-17 we rely on the results of Gulin et al. (2002). A high sedimentation rate of 1.15 cm yr^{-1} characterized the shelf core (BLS.95-17) close to the Danube mouth (Gulin et al., 2002) where the sediment consists mainly of allochthonous material due to the river input as indicated by high Ti concentration (3.8 mg g^{-1}, Table 3). Sedimentation rate decrease with increasing distance to the shore: 0.17 cm yr^{-1} at the shelf break (BLS.95-3), 0.03 cm yr^{-1} at the lower slope. Lowest sedimentation rates of 0.01 and 0.02 cm yr^{-1} characterize the deep basin. Using an average accumulation rate of 0.015 cm yr^{-1} for abyssal sediment, the Unit 2/Transition Sapropel boundary can be calculated as 1940 yr. B.P. in BLS.98-6 and 2200 yr. B.P. in the core BLS.98-4 whereas Unit 1/ Transition Sapropel base can be traced at 1530 and 1800 yr. B.P. in the core BLS.98-6 and BLS.98-4, respectively.

The mass accumulation rate (MAR, in g m^{-2} yr^{-1}) was calculated as a linear function of sedimentation rate, density of accumulated sediment and porosity. In order to assemble an accurate nutrient budget for the entire Black Sea basin, our database on sedimentation and mass accumulation rates was completed with the available literature data (Table 4). Out of compiled data an average SR and MAR was calculated for each sedimentary zone (bold). MAR decrease gradually from 3580 g cm^{-2} yr^{-1} at the shelf to 230 g cm^{-2} yr^{-1} at the shelf break, 123 at the upper slope and 60 g cm^{-2} yr^{-1} at the lower slope and 52 g cm^{-2} yr^{-1} in the abyssal basin (Table 4).

4. Discussion

In the following section we first discuss the factors affecting C, N and P concentrations, specifically the sediment accumulation rates and the residence time in oxic layer of sediments. By analyzing the average concentrations in the top section of cores we quantify the anthropogenic increase in nutrient accumulation during the past 50 years compared to the century before. Then we use the dataset on accumulation rates to extrapolate the basin wide net C, N and P accumulation. Finally, with a simple mass balance approach we compare the sink terms for the major nutrients with present-day inputs.

4.1. Phosphorus accumulation

Total phosphorus concentration in the sediment decreases along both transects with distance from the shore, indicating the effects of supply as well as redox conditions. Anoxia alone cannot explain the differences in TP concentration in the stations below 200 m as sediments along the N–S transect are constantly exposed to anoxic deep water. Two factors are contributing to decreasing phosphorus concentrations towards the abyssal plain: (1) the calculations based on Ti concentrations indicate a decrease in terrigenous fraction from about 50 wt.% on slopes to only 15 wt.% in abyssal plain due to a gradient in the input of terrigenous particles. This trend implies a lowered capacity of sediments for sorption of phosphate by terrigenous minerals. The iron oxides will not be preserved in the anoxic deep waters whereas soil minerals such as clays may also adsorb phosphorus via ternary complexes with Ca and Mg ions or surface precipitates; (2) satellite maps confirm strong lateral gradients in phytoplankton concentrations (Barale et al., 2002) with high values on the shelf and the coastlines and quite low values in the central gyres. Settling history of the organic matter is therefore different along the coast and offshore: diatoms and coccoliths in productive zones undergo relatively fast settling process with high accumulation rates during algal blooms. For example, bulk sediment accumulation rates at shelf and shelf break are between 4 to 35 times higher than at the open sea. In contrast, the predominant picoplankton in the open sea is recycled intensively

within the water column before settling at the floor where, extensive diffusive losses are expected due to an order of magnitude lower sedimentation rates.

4.2. Influence of redox conditions on organic matter preservation in sediment

Fresh marine organic matter has C:N:P molar ratios of around 106:16:1 (Redfield et al., 1963). Differences in oxygen condition during decomposition of organic matter can explain the difference in C:N and C:P molar ratios between the oxic, suboxic and the anoxic stations. Exposure time to oxic conditions in the sediment strongly influences C, N and P accumulations on shelf (Hartnett et al., 1998). Oxygen concentrations at the sediment/water interface measured at the north-western shelf on a transect toward deep-sea decreased gradually from 284 and 243 µM at a depths of 57 and 72 m, respectively, to 190 µM at the shelf edge (137 m) and zero at the open-sea station (1494 m) (Wijsman et al., 2001). Pore water oxygen profile for the 57 m depth station showed a sharp decrease from almost 300 µM to zero from sediment water interface to below 0.4 cm (Wijsman et al., 2002). A bulk sedimentation rate of around 1 cm yr^{-1} characterizing this area implies that the sediment is actually exposed to oxic conditions for a short period of only 3 months. Moreover, as oxygen concentration of the overlying water decreases with decreasing distance towards oxycline, the oxygen–sediment penetration should decrease, and therefore, the exposure time to oxic conditions should be reduced too.

At the suboxic edge (BLS.95-26) where the river input and the overall sedimentation rates are low, C:N ratio reaches maximum whereas C:P is minimum. Under oxic and suboxic conditions (station BLS.95-17 and BLS.95-26) the burial efficiency for P is much higher than for C and N. In oxic and suboxic zones, P can be retained in sediment by absorption onto Fe hydroxides, whereas C and N are mineralized and released to the overlaying water. Measurements with a benthic flux chamber at suboxic stations showed that high P fluxes from the sediments were accompanied by substantial release of Fe (Friedl et al., 1998). The simultaneous release of Fe and P started when oxygen was depleted within the benthic flux chambers and indicates P bound to Fe hydroxides in these sediments.

The highest C:N ratio of 18 for the suboxic station BLS.95-26 (Fig. 5), indicates a preferential loss of N-rich compounds due to longer residence times of organic matter in the thin oxic layer. At deeper stations C:N ratio is 12, which is close to the Redfield values and indicates better organic matter preservation.

Under anoxic conditions increased C:P ratio with increasing depth and distance from the shore indicates a preferential loss of P during remineralization. Phosphorus regeneration from anoxic sediment in abyssal plain is expected to be high and therefore, the overall burial efficiency for P should be low (Ingall and Van Cappellen, 1990; Ingall et al., 1993; Ingall and Jahnke, 1997). In contrast, C is better preserved under anoxic conditions (Rabouille and Gaillard, 1991; Ingall et al., 1993) and therefore, abyssal sediments should act as a more effective C sinks than the oxic shelf.

4.3. TN and TP accumulation over the last 150 years

To calculate the potential response of sedimentary nutrient accumulation to increased inputs via river system, two periods of the last 150 years are compared (Table 5). The historical development of the Danube nutrient loads over the last 50 years has been reconstructed by ICPDR using the MONERIS mathematical model (ICPDR, 2004). The estimated load of DIN and TP for the year 2000 was about 1.9 and 1.1 times higher than during the 1950's mainly due to increased anthropogenic loads in the catchment. Due to the large fluvial input with variable phosphorus speciation, TP was considered as the appropriate parameter for discussing the P accumulation in the Black Sea sediments. The recent sediment deposited during the last 50 years (1950–1998) shows higher TN and TP concentrations compared to the period 1850–1950, especially on the shelf and slope where the higher sedimentation rates provide a good time resolution. In fact, the recent sediment of the shelf break core (BLS.95-26) show an increase in TN and TP concentration by factors of 1.4 and 1.1, respectively. The same calculation for the upper slope core (BLS.98-3) reveals an increased TN and TP concentration in recent sediment by 1.6 and 1.4 fold, respectively. Overall, the Black Sea sediments responded to increased nutrient loads over the last 50 years by accumulating on shelf and slopes about 40 and 10% more TN and TP, respectively compared to the century prior to 1950. On the other hand, just a marginal increase over the last 150 years is found in abyssal sediment far from the river discharge (Table 5).

4.4. Total nutrient accumulation

Available literature data and our own measurements on the TOC, TIC, TN and TP concentrations for the Black Sea sediment are displayed in Table 6. A weighted average was calculated for each sedimentary zone. The

Table 6
Own measured concentrations (italic) and literature data on organic carbon, calcium carbonate, nitrogen and phosphorus concentrations for Unit 1 sediment of the Black Sea

Sedimentary zone		Core	Location	Depth [m]	TOC [mg g^{-1}]	$CaCO_3$ [%]	TN [mg g^{-1}]	TP [mg g^{-1}]	Authors
Shelf 0–100 m	Inner	4 cores	Danube Delta front	10–25	20.0	12.7	2.7		Reschke et al., 2002
		3 cores	Danube prodelta	25–50	17.0	32.9	2.3		Reschke et al., 2002
		2 cores	Dniestr Delta front	10–25	4.0	37.6	1.0		Reschke et al., 2002
		BLS.95-17	*Danube Delta front*	*26*	*26.0*	*9.5*	*3.6*	*0.95*	*This work*
	Average				**16.5**	**23.4**	**2.3**	**0.95**	
	Outer	10 cores	NW	25–70	17.3	48.9	2.5		Reschke et al., 2002
		6 cores	NW	10–75	18.4				Wijsman et al., 2001
		S	NW	20	14.8		1.9		Garcette-Lepecq et al., 2000
		4 cores	SE+SW	6–80	15.8				Ergin et al., 1996
		BS4-3	SW	85	14.0				Calvert and Karlin, 1991
		St.1	NW	62	25.0		2.4		Weber et al., 2001
		St.2	NW	77	20.0		1.9		Weber et al., 2001
		St.3	NW	100	20.0		1.8		Weber et al., 2001
	Average				**17.5**	**48.9**	**2.3**	–	
Shelf break 100–200		3 cores	WNW	100–150	13.7	59.2	2.2		Reschke et al., 2002
		2 cores	NW	120–135	20.5				Wijsman et al., 2001
		BS-4-15	S	198	22.0				Calvert and Karlin, 1991
		BS4-16C	S	129	13.0				Calvert and Karlin, 1991
		2 cores	SE	100–116	8.2				Ergin et al., 1996
		2 cores	NW	150	52.2	40.5	3.2		Tekiroglu et al., 2001
		St.4	NW	130	20.0		1.7		Weber et al., 2001
		St.5	NW	181	70.0		5.7		Weber et al., 2001
		BLS.95-26	*NW*	*145*	*10.8*	*46.4*	*0.7*	*0.68*	*This work*
	Average				**24.2**	**50.8**	**2.6**	**0.68**	
Upper slope 200–1000		St.6	NW	396	40.0		2.8		Weber et al., 2001
		1450	NW	563		45.0			Brumsack, 1989
		1451	NW	460		52.0			Brumsack, 1989
		1470	E	906	15.7	20.0			Calvert et al., 1987
		3 cores	SW+SE	212–445	20.6				Ergin et al., 1996
		GC01	SW	549	23.2	23.2			Arthur and Dean, 1998
		GC59	SE	600	40.0				Arthur and Dean, 1998
		GC79	S	700	16.0	20.7			Arthur and Dean, 1998
		GC71	S	411	14.2	14.9			Arthur and Dean, 1998
		BLS.98-3	*NW*	*599*	*27.2*	*33.4*	*2.4*	*0.82*	*This work*
	Average				**23.8**	**29.9**	**2.6**	**0.82**	
Lower slope 1000–1800		20/97	NW	1220	29.0	37.9	2.6		Reschke et al., 2002
		22	NW	1494	46.4				Reschke et al., 2002
		2	NW	1526	48.0	42.5	4.4		Reschke et al., 2002
		GC09	SW	1259	44.2	23.2			Arthur and Dean, 1998
		BLS.95-2	*NW*	*1536*	*41.5*	*53.5*	*3.3*	*0.80*	*This work*
		BLS.97-22	*NW*	*1563*	*44.0*	*51.7*	*3.6*	*0.75*	*This work*
		BLS.97-20	*NW*	*1219*	*27.2*	*40.9*	*2.8*	*0.53*	*This work*
	Average				**40.0**	**41.6**	**3.3**	**0.69**	
Abyssal >1800		20/97	NW	1998	40.0	40.8	3.8		Reschke et al., 2002
		1432	Central	2248	21.1	22.0			Calvert et al., 1987
		1445	W	1915		29.0			Brumsack, 1989
		1462	Central	2179		54.0			Brumsack, 1989
		1474	E	2114		40.0			Brumsack, 1989
		6 cores	Central and SE	1945–2218	45.2	51.9	2.8		Tekiroglu et al., 2001
		BS4-14GC	Central	2218	49.9	49.8			Calvert et al., 1996
		1474K	E	2217	50.9	57.3			Calvert et al., 1996

(continued on next page)

Table 6 (*continued*)

Sedimentary zone	Core	Location	Depth [m]	TOC [mg g^{-1}]	$CaCO_3$ [%]	TN [mg g^{-1}]	TP [mg g^{-1}]	Authors
	1432	Central	2248				0.62	Calvert, 1990
	1474	E	2114				0.76	Calvert, 1990
	BC21	W		54.1				Hay et al., 1991
	BC55	E		51.0				Hay et al., 1991
	BS4-9BC	W	2087	60.4				Calvert et al., 1991
	BS4-14BC	Central	2218	50.7				Calvert et al., 1991
	BS4-7	SW	1948	48.0				Calvert and Karlin, 1991
	BS4-9	W	2094	62.0				Calvert and Karlin, 1991
	BS-4-14	Central	2218	57.0				Calvert and Karlin, 1991
	BLS.98-4	*Central*	*1998*	*42.6*	*54.6*	*3.8*	*0.52*	*This work*
	BLS.98-5	*Central*	*2172*	*41.9*	*46.1*	*4.1*	*0.51*	*This work*
	BLS.98-6	*E*	*2121*	*42.7*	*52.1*	*4.1*	*0.49*	*This work*
Average				**47.2**	**54.1**	**3.3**	**0.58**	

The bold values represent the weighted average for each sedimentary area.

accumulation C, N and P fluxes were calculated by multiplying the concentrations with the area of the specific zone and the associated mass accumulation rate (Table 7). Accordingly, 1360 kt TOC, 2740 kt TIC, 142 kt TN and 47 kt TP (1 kt = 1000 metric tons) are presently buried annually in the Black Sea sediment. The shelf is the most important sink accumulating 51, 67, 63 and 67% of TOC, TIC, TN and TP, respectively (Fig. 6). The uncertainty induced by one order of magnitude difference between the sedimentation rates of only two sediment cores on the shelf break results in a deviation of only ±5% (within the error of the measurements) and has a minor influence on the total nutrient accumulation.

4.5. Mass balance

In order to estimate the role of the Sea of Azov in the Black Sea nutrient budgets we explore the following scenario: Annual rives nutrient loads to the Sea of Azov for the period 1996–2000 were estimated as 51 kt TN and 7 kt TP (UNDP, 2003; BSEP, 1999). A significant part of the loads is accumulated in the sediment and lost by denitrification, whereas the remaining part is exported to the Black Sea. Due to a lack of data concerning sediment nutrient concentration and accumulation rates we rely on the Black Sea estimates. Extrapolating sedimentary TN and TP accumulation rates of the Black Sea's outer shelf of 0.5 g N m^{-2} yr^{-1} and 0.2 g P m^{-2} yr^{-1} (Table 7) to the surface area of 42,000 km^2, a sink of 21 kt N and 8 kt P yr^{-1}, respectively, was estimated for the sediments of Azov. Moreover, in case of the Black Sea, 67% of the incoming N load is lost by denitrification (Grégoire and Beckers, 2004). Resulting in a denitrification rate of less than 0.2 mmol m^{-2} d^{-1}, this estimate is in a good agreement with data from different coastal areas such as the Coastal North Sea and the Kysing Fjord (Denmark) (Seitzinger, 1988). Similar denitrification rates in the

Table 7
Mass accumulation rates (MAR), average total organic and inorganic carbon, total nitrogen and total phosphorus for Unit 1 sediments and corresponding nutrient fluxes for different sedimentary areas of the Black Sea

Sedimentary area		Area [km^2]	MAR [g m^{-2} yr^{-1}]	Concentration TOC [mg g^{-1}]	Concentration TIC [mg g^{-1}]	Concentration TN [mg g^{-1}]	Concentration TP [mg g^{-1}]	Flux TOC [kt yr^{-1}]	Flux TIC [kt yr^{-1}]	Flux TN [kt yr^{-1}]	Flux TP [kt yr^{-1}]
Shelf	Inner	1300	3578	16.5	28.1	2.3	0.95	77	131	11	4
	Outer	13,0500	234	17.5	48.9	2.3	0.95[a]	534	1493	70	29
Shelf break		13,700	234	24.2	61.0	2.6	0.68	78	196	8	2
Upper shelf		34,800	123	23.8	35.9	2.6	0.82	102	154	11	4
Lower shelf		62,200	60	40.0	49.9	3.3	0.69	149	186	12	3
Abyssal		170,500	52	47.2	64.9	3.3	0.58	418	575	29	5
Total		413,000						1360	2740	142	47

[a] In the absence of the TP concentration for the outer shelf we used the same value as for the inner shelf.

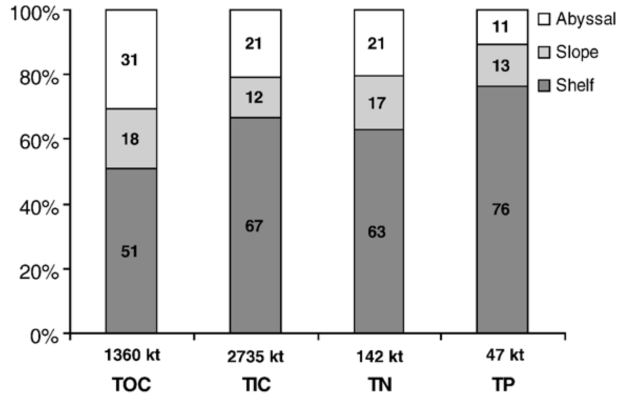

Fig. 6. Accumulation of total organic carbon, total inorganic carbon, total nitrogen and total phosphorus on shelf, slope and abyssal Unit 1 sediment of the Black Sea as percent of total accumulation.

range of 0.16 and 0.3 mmol m^{-2} d^{-1} were measured in the Baltic Sea (Conley et al., 1997) and somewhat higher rates from 0.1 to 1.2 mmol m^{-2} d^{-1} were observed in the Golf of Finland (Gran and Pitkänen, 1999). Applying our estimated rate to the Sea of Azov, about 40 kt N is annually lost by denitrification. The long residence time of around 7.5 years for the Sea of Azov supports the presence of effective denitrification processes. These rough estimates of both N and P removal in the Sea of Azov are comparable to the annually input and therefore, the exported fluxes to the Black Sea should be negligible.

The semi-enclosed basin of the Black Sea facilitates the estimation of element budgets. We therefore focused on TN and TP budget adopting a simple mass balance (Fig. 7) for which the available database was reviewed. The rate at which the nutrient concentration changes

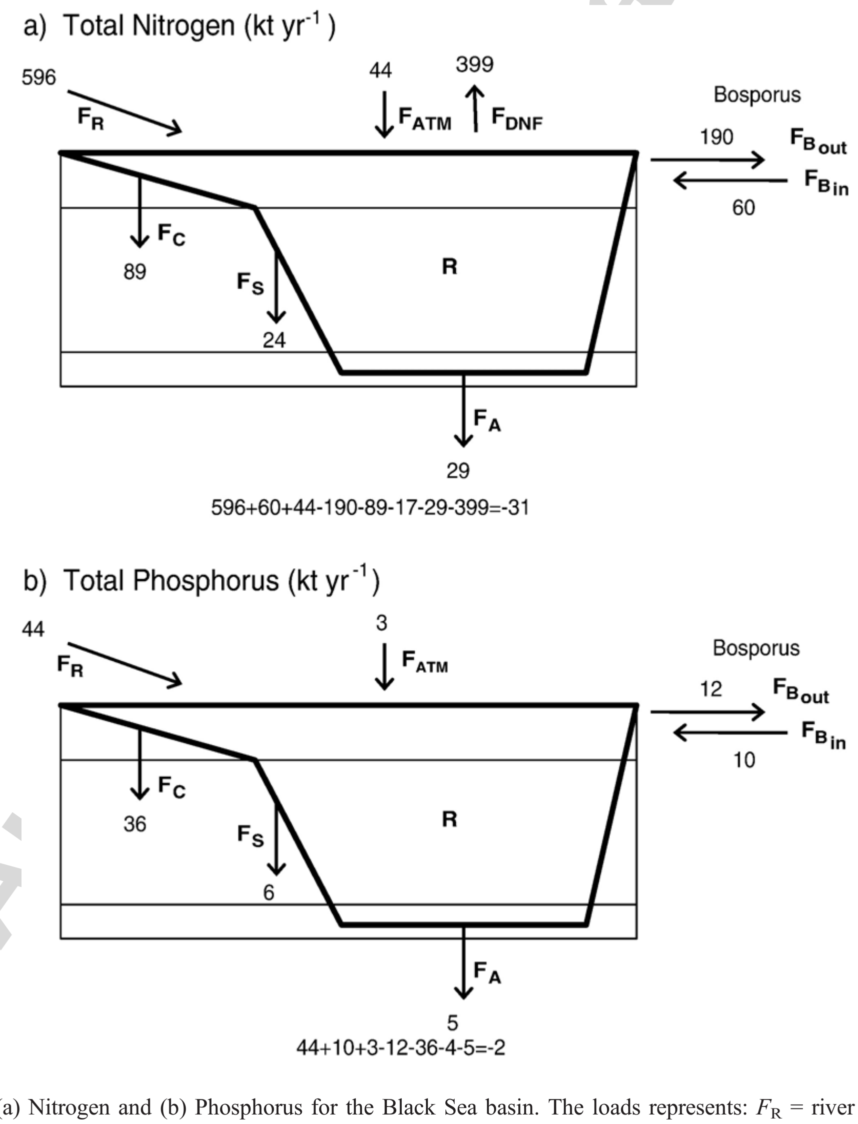

Fig. 7. Mass balance for (a) Nitrogen and (b) Phosphorus for the Black Sea basin. The loads represents: F_R = river input; F_{ATM} = atmospheric deposition; F_B = exchange loads throughout Bosporus; F_{DIN} = denitrification; F_C, F_S and F_A = nutrient accumulation on the recent sediment (Unit 1) of the continental shelf, slope and abyssal basin, respectively.

Table 8
Total nitrogen and phosphorus loads into the Black Sea from UNDP (2003) and BSEP (1999) for the period 1996–2000

	Load	
	[kt TN yr^{-1}]	[kt TP yr^{-1}]
Black Sea		
1. North-western coastline	379.7	30.4
1.1. Danube	345.7	25.4
1.2. Dnieper	11.2	4
1.3. Dniestr	22.8	1
2. Ukraine	42.8	4.6
3. Russia	13.5	1
4. Georgia	1.6	0.4
5. Turkey	38	5.9
6. Bulgaria	75.5	1.1
7. Romania	45.4	0.5
Subtotal	596.5	43.9
Azov Sea		
1. Don	7	3.4
2. Kuban	6.5	0.2
3. Protoka	6.5	0.2
4. Kalmius	8.9	0.8
5. Other rivers	21.9	2
Subtotal	50.8	6.6
Total	647.3	50.5
Load exchange between Black Sea and Marmara Sea		
Influx into the Marmara Sea	190	12
Influx into the Black Sea	60	10

The exchange loads between Marmara and Black Sea were taken from Polat and Tugrul (1995).

with time ($\partial C/\partial t$) in a basin with a known volume (V) must be equal to the sum of inputs (F_{IN}) minus the sum of output (F_{OUT}) and the losses due to sedimentation (F_{SED}):

$$V\frac{\partial C}{\partial t} = \sum F_{IN} - \sum F_{OUT} - \sum F_{SED} \quad (1)$$

For a long time scale (decades and centuries) we can consider the system to approach a quasi-steady state where $\partial C/\partial t \rightarrow 0$.

$$\sum F_{IN} - \sum F_{OUT} - \sum F_{SED} \approx 0 \quad (2)$$

(1) The *input* (F_{IN}) is represented by the sum of rivers/riparian countries loads (F_R), input from Sea of Marmara via Bosporus (F_{Bin}) and atmospheric deposition (F_{ATM}). Basin-wide inflow (F_R) of nutrients via main rivers and other pollutants from land-bases sources (Table 8) was estimated from national reports to the UNDP (2003) and BSEP (1999). Accordingly, the Black Sea receives annually 596 kt TN and 44 kt TP. The input from the Sea of Marmara at Bosporus (F_{Bin}) was estimated as 60 kt TN and 10 kt TP annually (Polat and Tugrul, 1995). The annual atmospheric deposition over the Black Sea (F_{ATM}) was estimated as 44 kt N yr^{-1} (Kubilay et al., 1995) and 3 kt P yr^{-1} (Fonselius, 1974).

(2) The *outflow* (F_{OUT}) is represented by the output to the Sea of Marmara (F_{Bout}). Polat and Tugrul (1995) estimate that annually, the Black Sea exports via Bosporus with the surface currents about 190 kt TN and 12 kt TP to the Sea of Marmara.

(3) Additional sinks include *sedimentation* (F_{SED}) and denitrification (F_{DNF}). The burial of TN and TP in the Black Sea sediments is evaluated separately for continental shelf (F_C), slopes (F_S) and abyssal plain (F_A) (Table 6). The annual accumulation represents 89 kt TN and 36 kt TP for the shelf, 24 kt TN and 6 kt TP for the slopes and 29 kt TN and 5 kt TP for the abyssal sediment. Annually, 67% of the rivers incoming N load is lost via denitrification (F_{DNF}) (Grégoire and Beckers, 2004) which would represent 399 kt N yr^{-1}. Eq. (2) can therefore give as a sum of the following individual fluxes:

$$\sum F_{IN} - \sum F_{OUT} - \sum F_{SED} = F_R + F_{Bin} + F_{ATM} - F_{Bout} - F_C - F_S - F_A - F_{DNF} \approx 0 \quad (3)$$

Inserting the values into Eq. (3), the mass balances become:

$$\text{TN}: \quad 596 + 60 + 44 - 190 - 89 - 24 - 29 - 399 = -31 \quad (4)$$

$$\text{TP}: \quad 44 + 10 + 3 - 12 - 36 - 6 - 5 - 0 = -2 \quad (5)$$

Considering the large area of the Black Sea and the uncertainties in different estimates, the mass balances reveal an excellent agreement between sources and sinks. The imbalance of −31 kt N yr^{-1} and −2 kt P yr^{-1} would imply 3 to 4% higher output estimates compared to the total input. However, the values are well within the expected error of 10% for the present-day inputs. The mass balance (Fig. 7) identified that nutrient accumulation in sediments of Black Sea plays a minor role in N elimination (up to 20%) but it represents a major sink for P, accounting for over 80% of total incoming load. The export to the Sea of Marmara accounts for 20% TP and

25% TN, whereas denitrification, with 57% of the TN input, represents the key process in nitrogen elimination.

5. Conclusions

This study aimed at evaluating the effects of sedimentation rate and redox conditions in the Black Sea on C, N and P accumulation by assessing the sediment regime on the shelf, slope and abyssal plains. Sediment cores from the Black Sea were analyzed along two transects across the basin in West–East and North–South direction and from the oxic shelf to the anoxic slopes and abyssal plain. On the northwestern shelf, the average concentrations TOC, TN and TP in recent sediments showed a decrease with increasing distance to the shore. Compared to the shelf, TP concentration was depleted on the slope and towards the central basin whereas TOC and TN concentrations increased towards the deep central basin.

The analysis of recent sediments revealed higher accumulation rates of N and P on the shelf in response to increased anthropogenic nutrient loads. On average, N and P accumulation was 40 and 10% higher, respectively, during the last 50 years compared to the period of 1850–1950. No significant changes of nutrient deposition were detected for the abyssal plain.

Data from the sediment transects and a literature survey were the basis for identifying three major sedimentary areas in the Black Sea and for estimating the total annual accumulation of 1.3×10^6 t TOC, 1.4×10^5 t TN and 4.7×10^4 t TP in the world's largest anoxic basin. A mass balance based on river inputs, outflow to the Sea of Marmara and the total accumulation rates indicated that 20% of the TN inputs accumulated in the sediments of the Black Sea whereas denitrification eliminated more than 55% of the inputs. These calculations were in good agreement with recent model estimates by Grégoire and Beckers (2004) with a denitrification flux as high as 67% of the total inputs. Total phosphorus accumulated mainly on the shelf and the sedimentation flux represented 80% of the total incoming load. The earlier total estimate by Fonselius (1974) of the P accumulation flux in the Black Sea sediments (6.7 kt/yr) was about an order of magnitude too low. The discrepancy emphasizes the importance of the high accumulation rates on the shelf, which deserve further detailed study.

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