Benthic Nutrient Cycling and Diagenetic Pathways in the North-western Black Sea

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Benthic fluxes of nutrients and metals were measured in the coastal zone of the north-western Black Sea, which is influenced by the Danube and Dniestr rivers. The results from the benthic flux chambers deployed during two EROS 21 cruises in summer 1995 and in spring 1997 yield information on benthic nutrient cycling and diagenetic pathways at the sediment-water interface. This information is discussed in the light of benthic activity as well as pore-water data. The benthic recycling of nutrients varied seasonally due to the availability of oxygen and organic material, and spatially due to river influence. Areas of high benthic fluxes near-shore and of low benthic fluxes offshore on the shelf were distinguished. Nutrients and suspended particulate matter discharged by the Danube is kept nearshore by the coastal current. The oxygen concentrations in the bottom water varied strongly between the two seasons. In summer, the bottom water at the near-shore stations turned anoxic. In spring, the higher oxygen concentrations are related to more intense mixing of the water column due to stormy periods and high river discharge. Highest oxygen concentrations were found on the offshore continental shelf. However, the benthic oxygen consumption rates in spring (13–23 mmol m^{-2} day^{-1}) were as high as in summer. Areas with highest nutrient concentrations in the overlaying bottom water were found at the Danube delta front and Danube prodelta. On the Danube delta front and the Dniestr mouth, ammonia fluxes were lower in spring (1·1–1·7 mmol m^{-2} day^{-1}) than in the summer (2·6–4·4 mmol m^{-2} day^{-1}) due to higher nitrification rates and the lower influx of organic matter. In spring, the concentrations of dissolved iron and manganese in the bottom water were one order of magnitude lower than during the summer. This decrease in flux rates is related to the higher oxygen concentrations in the bottom water in spring. A rough comparison of the river's nutrient load and the benthic recycling over a certain area showed that the near-shore benthic phosphate and silica recycling account for 50% and 35% of the Danube input in summer, respectively. The fluxes of ammonia from benthic recycling and from the Danube discharge were at the same order of magnitude in both seasons. Nitrogen is introduced by the rivers mostly as nitrate. Benthic recycling is the dominant source of ammonia. The Danube input is phosphate deficient. In brief, benthic nutrient recycling is an important factor in sustaining high productivity of the system.

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Introduction

The ocean margins, including estuarine, coastal and shelf systems, comprise only 10% of the surface area of the world's oceans. However, they account for up to 30% of the marine primary production and 90% of the world's fish catch. Today, approximately 60% of the human population lives within coastal areas, a percentage which is still increasing (LOICZ, 1995). Coastal ecosystems represent extremely valuable resources. However, they are degrading at an alarming rate. Principal causes are the increased nutrient input (nitrogen and phosphorous) by large rivers leading to coastal eutrophication. Decreased fluxes of silica and particles due to dam construction change the structure of aquatic ecosystems and accelerate coastal erosion (Billen *et al.*, 1991; Jørgensen & Richardson, 1996; Humborg *et al.*, 1997 Morris & Fan, 1998).

Over the last few decades, increased eutrophication in the Black Sea has been forced by increased delivery of nutrients from land-based sources from the

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Danube, Dniepr and Dniestr rivers. Anoxia during summer and the successive loss of biodiversity indicate that nutrient concentrations and primary production have reached critical levels (Cociasu *et al.*, 1996). In addition, the construction of large dams (Iron Gates I in 1972 and Iron Gates II in 1984) has decreased the transport of sediment and dissolved silica from the Danube River into the Black Sea. As a result, the silicon to nitrogen ratio has changed. This change in the nutrient supply has shifted the composition of phytoplankton from diatom communities (silicious algae) towards nanoplanktonic species for the benefit of dinoflagellates and coccolithophores (Bodeanu, 1992; Humborg *et al.*, 1997;). This has caused severe changes in the structure and functioning of the planktonic food-web, with an explosive development of opportunistic gelatinous organisms (jelly fishes, dinoflagellates) that are of negligible food value (Mee, 1992).

The Danube River represents the largest driving force in the Black Sea system. It contributes 77% of the mean annual discharge into the Black Sea ($265 \, \text{km}^3 \, \text{yr}^{-1}$). At the beginning of the 1960s, Almazov (1961) reported a total annual inorganic nitrogen input from the Danube of $1 \cdot 4 \times 10^5$ t, a phosphate load of $0 \cdot 12 \times 10^5$ t and a silicate discharge of $7 \cdot 9 \times 10^5$ t. Three decades later, monitoring at the Sulina mouth (one of three main branches of the Danube into the Black Sea), revealed that the Danube emits $6–8 \times 10^5 \, \text{t yr}^{-1}$ of total inorganic nitrogen, $0 \cdot 23–0 \cdot 32 \times 10^5 \, \text{t yr}^{-1}$ phosphate and $1 \cdot 5–3 \times 10^5 \, \text{t yr}^{-1}$ silica into the Black Sea (Cociasu *et al.*, 1996). The N and P load of the Danube increased by factors of five and three, respectively, while Si input decreased by a factor of three during these years. Humborg *et al.* (1997) report that the Si/N ratio decreased from 42 in the early 1960s to about 2·8 at present.

In the framework of the EC European River–Ocean Systems (EROS) 2000 and 21 projects ' The interactions between the Danube, Dniestr and Dniepr Rivers and the North-western Black Sea (1994–1998) ', the functioning of the damaged coastal marine ecosystem was investigated. One important aspect was the benthic biogeochemical cycling of nutrients, within the large, shallow shelf area close to the river mouths.

Benthic nutrient regeneration is an important process in regulating the distribution of nutrients in the water column (Devol, 1987; Kristensen, 1988), especially in the coastal marine environment. This supply can support a substantial part of primary production. In the coastal zone, for instance, benthic nitrogen regeneration has been estimated to supply 26–101% of the phytoplankton demand (Kristensen, 1988). Benthic organisms transport particles and fluid during feeding, burrowing, tube construction and irrigation activity and thus influence benthic flux rates significantly (Aller, 1988).

In this paper, we verify the importance of benthic nutrient recycling for the shelf area in the North-western Black Sea. We have used benthic flux chamber experiments to quantify flux rates of nutrients and redox sensitive metals. Combined with porewater data and abundances of the benthic fauna, we evaluated seasonal and spatial differences in the benthic nutrient cycling and diagenetic pathways.

Material and methods

Location

We carried out benthic flux experiments in the coastal zone of the Black Sea influenced by the Danube and Dniestr rivers (Figure 1); within the Danube delta front (BS 95-17, BS 97-2), further south within the prodelta (BS 95-22, BS 97-8) and in front of the Dniestr mouth (BS 95-11, BS 97-13). One station was chosen on the offshore shelf (BS 97-16) and on the shelf edge (BS 95-3, BS 95-26, BS 97-23). The station located in Varna Bay (BS 95-31) was not sampled in 1997 and is discussed in the paper by Friedl *et al.* (1998). Fluxes were measured during two seasons, in summer 1995 and spring 1997. Unfortunately, it was not possible to carry out cruises in autumn and winter due to rough weather conditions during these seasons in the Black Sea.

Flux chamber deployments

The benthic lander contains two stainless steel flux chambers that cover sediment areas of $400 \, \text{cm}^2$ and enclose about 3–6 l of water (Tengberg *et al.*, 1995; Mengis *et al.*, 1996). The device was lowered to the bottom, tethered to a free-floating buoy, and was retrieved after 24 hr. An electronic system triggers up to 15 mechanical functions. The flux chambers were pushed into the sediment and the top lids closed after half an hour. Spring actuated syringes were used to take 10 water samples from each chamber at 2-h intervals. During operation, the samples were stirred continuously at a velocity of about 1 rps, resulting in a corresponding boundary layer thickness of about 1 mm. In one flux chamber, the oxygen concentration and pH were recorded continuously by an O_2 and pH sensor coupled with a Seabird Electronics (SBE 16) sealogger unit. At the end of the experiment, the grab shovels at the bottom of the chambers closed and two box sediment cores of about 30 cm were retrieved.

FIGURE 1. Stations of benthic flux chamber deployments on the shelf of the north-western Black Sea during the cruises of August 1995 and May 1997. The general nearshore circulation predicted by the GHER model (Beckers *et al.*, 2002) is indicated by arrows. The arrows also depict the approximate boundaries of the areas with high and low benthic flux.

Analytical determinations

Total iron and manganese concentrations were determined in HNO_3 acidified subsamples by GF-AAS. Alkalinity data were obtained from titration of 5 ml of the sample with 0·01 mM HCl to pH 4·3. The pH and alkalinity measurements were carried out within 4 h of retrieval of the lander. Filtered subsamples from the syringes were analysed on board by standard colorimetric methods (Deutsche Einheitsverfahren, 1995) with a ' PROCON ' autoanalyser for soluble reactive phosphate (ammoniummolybdate method) and nitrate (2,6 dimethylphenole method) on board. Soluble reactive ammonium (Phenylhypochlorite method) and nitrite (diazo method) were determined with a photometer ' MERCK SQ 300 ' on board. Silica was analysed photometrically with molybdenum blue.

Porewater sampling and analytical procedures are described in detail in Wijsmann *et al.* (2002). The description of methane determinations is given in Ivanov *et al.* (2002).

Flux calculations

The concentrations measured in the syringes of the flux chamber were corrected for the replacement of the sampled volume by external bottom waters. Fluxes were calculated by fitting a linear regression to the changes in concentration versus time. Based on the concentration measurements of each compound, fluxes are calculated according to:

$$F = h\frac{d(C)}{dt} \tag{1}$$

where h is the height (m) of the enclosed water column in the flux chamber and $d(C)/dt$ (mmol m^{-3} day^{-1}) represents the accumulation rate of a compound in the benthic chamber. In the 1997 investigation, all measured data were included in the linear regression analysis (Table 1). The fluxes of the 1995 investigation were taken from Friedl *et al.* (1998).

Benthic fauna and bacteria

Subsamples for meiobenthos studies were collected from the two box grabs of the lander with a sampling area of 20 × 20 cm. The subsamples were stained with congo red, stored in plastic boxes and preserved in buffered formaldehyde (4%). In the laboratory, the

TABLE 1. Benthic fluxes (F) of O_2, nutrients and metals in mmol m^{-2} day^{-1} and start concentrations (C_o in mM) of chamber A and B in spring 1997 and summer 1995

Location		O_2	NH_4^+ A	NH_4^+ B	NO_2^- A	NO_2^- B	NO_3^- A	NO_3^- B	HPO_4^- A	HPO_4^- B	$Si(OH)_4$ A	$Si(OH)_4$ B	Fe^{2+} A	Fe^{2+} B	Mn^{2+} A	Mn^{2+} B
Danube delta front																
BS 97-2 45°12.17'N 29°50.79'E	F	−22·6	0·44	1·46	0·02	0·01	−0·04	−0·12	0·15	0·00	1·93	1·76	0·26	0·43	0·20	0·41
	R²	0·81	0·05	0·51	0·76	0·55	0·07	0·32	0·70		0·89	0·97	0·87	0·87	0·95	0·92
	S	3·8	0·71	0·51	0·003	0·003	0·05	0·06	0·03		0·24	0·24	0·04	0·06	0·02	0·04
	C_o	0·166	0·0068	0·0019	0·00035	0·00033	0·0054	0·0056	0·0018	0·0019	0·0121	0·0104	0·0005	0·0005	0·00017	0·00018
BS 95-17	F	−25·90	2·64	2·91					0·03	0·04	5·22	6·31		0·53		0·43
	R²	0·85	0·96	0·99					0·85	0·91	0·85	0·89		0·99		0·98
	S	3·1	0·22	0·06					0·01	0·005	0·78	0·78		0·02		0·02
	C_o	0·13	0·0035	0·003					0·00039	0·00024	0·036	0·035		0·0083		0·0002
Danube prodelta																
BS97-8 44°35.04'N 29°11.32'E	F	−13·36	1·68	1·18	−0·02	0·03	−0·18	−0·17	−0·14	0·10	2·64	2·69	0·00	0·17	0·27	0·27
	R²	0·96	0·85	0·98	0·88	0·87	0·92	0·83	0·22	0·59	0·97	0·96		0·16	0·94	0·98
	S	0·99	0·23	0·06	0·002	0·004	0·02	0·03	0·09	0·03	0·16	0·2		0·12	0·02	0·01
	C_o	0·095	0·0033	0·0034	0·00072	0·00074	0·0066	0·0069	0·0033	0·0024	0·0205	0·0212	0·0016	0·0008	0·00041	0·00036
BS 95-22	F	0·00	0·11	0·14					0·03	0·01	0·32	0·93	0·51	0·38	0·18	0·12
	R²		0·83	0·61					0·76	0·92	0·11	0·74	0·67	0·78	0·84	0·75
	S		0·02	0·04					0·007	0·001	0·35	0·21	0·14	0·08	0·03	0·03
	C_o	0·00	0·0005	0·0006					<dl	0·00013	0·039	0·04	0·004	0·0035	0·0057	0·0058
Dniestr mouth																
BS97-13 46°02.93'N 30°29.36'E	F	−19·61	1·08	1·24	0·05	0·07	0·13	0·16	0·00	−0·04	2·51	3·22	0·60	0·47	0·48	0·54
	R²	0·99	0·91	0·94	0·88	0·98	0·96	0·98		0·33	0·98	0·92	0·87	0·88	0·91	0·95
	S	0·43	0·1	0·11	0·006	0·004	0·01	0·01		0·02	0·13	0·34	0·07	0·06	0·05	0·05
	C_o	0·147	0·0013	0·0014	0·00016	0·0001	0·0007	0·0007	0·0023	0·0023	0·0151	0·0124	0·0007	0·001	0·00038	0·0004
BS 95-11	F	0·00	4·45	2·88					0·60	0·33	6·05	6·38	1·59	2·10	2·32	1·87
	R²		0·99	0·99					0·99	0·99	0·98	0·91	0·86	0·68	0·89	0·8
	S		0·15	0·08					0·01	0·01	0·29	0·61	0·22	0·49	0·27	0·32
	C_o	0·00	0·006	0·0056					0·0005	0·00044	0·043	0·048	0·01	0·0012	0·0063	0·005
Continental shelf																
BS 97-16 45°09.73'N 31°02.96'E	F	−16·00	0·16	−0·28	−0·04	−0·04	0·23	0·30	0·00	0·00	0·26	0·35	0·00	0·00	0·08	0·11
	R²	1·00	0·53	0·34	0·98	0·97	0·99	0·99			0·19	0·21			0·61	0·86
	S	0·35	0·05	0·14	0·002	0·004	0·01	0·01			0·19	0·24			0·02	0·02
	C_o	0·19	0·0002	0·0006	0·00029	0·0003	0·0006	0·0005	0·004	0·004	0·0049	0·0042	0·0001	0·0001	0·0002	0·00009
Shelf edge																
BS 97-23 43°41.88'N 30°03.52'E	F	0·00	0·13	0·09	0·01	0·01	−0·13	−0·18	−0·03	0·00	−0·77	0·14	0·63	0·22	0·06	0·06
	R²		0·89	0·92	0·61	0·60	0·96	0·98	0·19		0·18	0·29	0·98	0·65	0·80	0·89
	S		0·02	0·01	0·004	0·004	0·01	0·01	0·02		0·78	0·08	0·04	0·05	0·01	0·01
	C_o		0·0001	<dl	0·0007	0·0008	0·0023	0·0026	0·0055	0·0056	0·0363	0·0345	0·0002	0·004	0·00042	0·00043
BS 95-26	F	−5·70	0·14	0·03					0·02	0·07	0·73	1·17	18·69	13·98	1·47	0·83
	R²	0·96	0·89	0·12					0·86	0·98	0·61	0·79	0·99	0·96	0·99	0·99
	S	0·64	0·002	0·03					0·009	0·005	0·21	0·21	2·1	1·24	0·01	0·05
	C_o	0·021	0	0·0001					0·00043	0·00027	0·04	0·038	0·0005	0·0007	0·0001	0·0002
BS 95-3 44°00.38'N 30°29.09'E	F	0·00	0·00	0·00					0·00	0·00	0·00	1·31	0·00	0·52	0·01	0·04
	R²											0·62		0·98	0·30	0·77
	S											0·28		0·02	0·01	0·01
	C_o		0	0					0·00046	0·00037	0·039	0·035	0·00068	0·0004	0·00025	0·00019
Bay of Varna																
BS 95-13 43°15.95'N 28°07.76'E	F	233·30	0·30	0·08					0·06	0·08	2·31	6·66	0·00	0·83	0·09	0·24
	R²	0·92	0·86	0·24					0·94	0·85	2·80	0·97		0·83	0·60	0·97
	S	2·5	0·07	0·05					0·005	0·01	0·4	0·42		0·17	0·03	0·02
	C_o	0·093	0	0					0·00079	0·00062	0·012	0·015	0·001	0·0002	0·0002	0·0004

Fluxes from 1997 cruise are derived from linear regression on the basis of all measured data. Only regressions with R²>0·3 are considered. Negative fluxes indicate consumption. R² is the correlation coefficient of the regression, S is the standard deviation of the flux. 1995 data from Friedl *et al.* (1998). <dl indicates below detection limit.

samples were washed on three mesh sieves (1-mm, 0·250-mm and 0·125-mm). The material was sorted under a binocular. The organisms found in samples were identified to either the species or in the case of Foraminifera, Ostracoda and Mollusca to the genus level. Biometric measurements were conducted for specimens larger than 1 mm. Faunal density and biomass were calculated for 1 m^2. Biomasses represent the wet preserved weight (including shells). The biomass of Black Sea invertebrates was calculated by using standard mean weight for meiobenthic taxa and the direct weighting of macrobenthic taxa. Data on abundances of benthic animals and wet wt. biomass in the flux chambers (Table 2) were used to estimate the role of bioturbation on the benthic flux rates and to calculate ventilation rates of selected Polychaeta species. A detailed description of the faunal composition and the ecologic importance of the benthic organisms is given in Gomoiu (1996).

For bacteria analysis, 1–5 ml of water was filtered through Millipore black polycarbonate membrane filters (pore size: 0·2 µm), fixed with 0·5 ml of 70% ethanol, and dried. The number of bacteria cells were determined with epifluorescence microscopy after fluorescence staining with fluorescamin (Poglazova & Mitskevich, 1984).

Results

Sediment description

On the Danube delta front, the sediment consists of fine mud, threaded with burrows of molluscs and tubes of polychaeta. Old tubes were filled with oxygenated mud. The seafloor of the Danube prodelta is covered with soapy mud containing bioturbating organisms. Old tubes were filled with yellowish oxygenated mud. In front of the Dniestr mouth, the sediment consisted of sandy mud with polychaeta and abandoned filled tubes. The sediment on the offshore continental shelf is composed of shells, devoid of matrices. Deeper strata consisted of mud with shells and a living specimen of Mollusca. At the shelf edge, the sediment is composed of non-cohesive mud containing *Modiolius* and *Dreissena* shells. A more detailed description of abiotic sediment characteristics is given in Wijsman *et al.* (1999).

Flux chamber data

Bottom water concentrations and fluxes of oxygen, ammonia, nitrite, nitrate, phosphate, silicate, iron and manganese are listed in Table 1. We found seasonal and spatial variations in oxygen concentrations in the enclosed chamber water (Table 1, Figure 2). In summer, the bottom water at the near-shore stations was hypoxic or anoxic. In spring, anoxic conditions were not found near-shore. However, the oxygen consumptions in summer and spring was similar (13–26 mmol m^{-2} day^{-1}, Table 1). Comparable oxygen fluxes in the sediment (average 21 mmol O$_2$ m^{-2} day^{-1}) are reported for the same area by Wijsman *et al.* (1999). Higher oxygen concentrations in spring may be related to more intense mixing of the water column due to the stormy periods and higher river water discharge in spring. The offshore continental shelf, which is shallower than 60 m, was the area with the highest oxygen concentrations at the sediment–water interface. At the shelf edge, similar to the deep central basin, in the water below approximately 80-m depth, permanently anoxic conditions prevail.

The change in the concentration of nitrogen compounds with time in the flux chambers is shown for deployment in front of the Dniestr mouth (Figure 3). Ammonia concentrations in the bottom water and benthic fluxes were higher in summer (0·006 mM, 3–4·5 mmol m^{-2} day^{-1}, Table 1, Figures 4 and 5) than in spring (0·001 mM, 1–1·2 mmol m^{-2} day^{-1}) in the area directly influenced by the Dniestr. On the offshore continental shelf and the shelf edge, in both seasons, very low ammonia concentrations (<0·001 mM) and fluxes (Table 1, Figure 5) were observed.

Since no nitrate was measured during the summer cruise, no seasonal comparison is possible. Nitrate concentrations in the bottom waters in spring varied from 0·0007 mM on the continental shelf and Dniestr mouth up to 0·007 mM in the Danube-influenced area. Net denitrification was observed in the vicinity of the Danube, whereas nitrification outcompeted denitrification near the Dniestr and on the shelf.

Phosphate concentrations in the bottom water of all stations were more than one order of magnitude higher in spring (0·002–0·006 mM) than in summer (<0·0001 mM). The benthic flux rates were also higher, except for the Dniestr mouth area and the offshore shelf area where no phosphate flux could be detected in spring.

The silica concentrations in spring (0·01–0·03 mM) were lower than in summer (0·04 mM) at most stations. Lowest concentrations were observed on the continental shelf (0·004 mM). Silica dissolution rates of up to 6·4 mmol m^{-2} day^{-1} were higher in summer, with lowest fluxes on the offshore shelf (0·8–1·2 mmol m^{-2} day^{-1}).

The evolution of iron, manganese and phosphate concentrations with time during the flux experiment

TABLE 2. Benthic fauna from flux chamber samples, summarized in taxons

	Danube delta front BS 97-2						BS 97-8 Danube prodelta						BS 97-16 continental shelf					
	Density (ind. m^{-2})		Biomass (g m^{-2})		% Biomass		Density (ind. m^{-2})		Biomass (g m^{-2})		% Biomass		Density (ind. m^{-2})		Biomass (g m^{-2})		% Biomass	
	Box A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B
Foraminifera	24 500	24 500	1·1	1·1	2·9	0·5	17 750	17 750	0·8	0·8	0·4	2·2	12 000	12 000	0·5	0·5	0·4	0·6
Worms	4886	7180	17·8	7·5	46·2	3·7	16 048	22 050	23·1	35·8	11·8	97·8	2352	2083	31·0	15·2	23·2	17·3
(Polychaeta)	3668	4141	17·3	7·2	45·0	3·5	5660	5956	23·1	35·8	11·8	97·7	1397	1201	31·0	15·2	23·2	17·2
Mollusca	24	73	19·6	198·5	50·9	95·8	123	25	171·5		87·8	0·0	49	49	98·0	68·8	73·2	78·2
Crustaceans		661		0·1		0·1							4509	4093	4·3	3·4	3·2	3·9
Total zoobenthos	29 410	32 414	38·5	207·2			33 921	39 825	195·4	36·6			18 910	18 225	133·9	88·0		

	Dniestr mouth BS 97-13						BS 95-11 Dniestr mouth						BS 97-23 shelf edge					
	Density (ind. m^{-2})		Biomass (g m^{-2})		% Biomass		Density (ind. m^{-2})		Biomass (g m^{-2})		% Biomass		Density (ind. m^{-2})		Biomass (g m^{-2})		% Biomass	
	Box A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B
Foraminifera	21 750	21 750	1·0	1·1	4·5	10·0	41 876	41 876	1·9	1·9	84·4	62·2	8500		0·4		99·6	
Worms	15 168	11 370	20·4	8·4	93·9	85·5	686	1102	0·2	1·0	9·5	33·3	860		0·0		0·4	
(Polychaeta)	6176	5539	20·4	8·4	93·8	85·5	220·5	294	0·1	0·9	5·9	30·5						
Mollusca			0·3	0·4	1·6	4·2												
Crustaceans	2863	2912					2088	2088	0·1	0·1	6·1	4·5						
Total zoobenthos	39 781	36 032	21·7	9·8			44 650	45 066	2·2	3·0			9360		0·4			
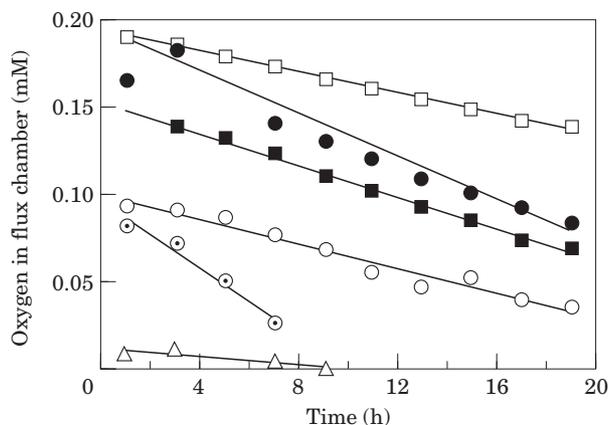
FIGURE 2. Time evolution of oxygen concentrations in the flux chamber in spring and summer. Regression lines are plotted for each investigated area. Summer 1995: (⊙) Danube delta front; (△) shelf edge. Spring 1997: (□) Continental shelf; (●) Danube delta front; (■) Dniestr mouth; (○) Danube prodelta.
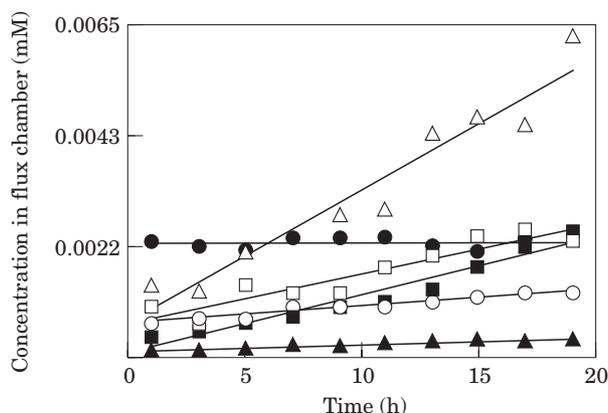
FIGURE 3. Time evolution of the concentration of ammonia (△); nitrite (▲); nitrate (○); phosphate (●); iron (□) and manganese (■) in the flux chamber during the deployment in front of the Dniestr mouth in spring (station BS 97-13 on Figure 1). Regression lines are plotted for each nutrient and metal.

at station BS 97-13, Dniestr mouth, is shown in Figure 3. Iron concentrations in the near bottom water differed between summer and spring. In general, the benthic flux rates of iron were lower in spring. Concentration and fluxes of manganese were comparable during both seasons. However, under anoxic conditions at the shelf edge, the manganese flux was one order of magnitude higher in summer compared to the spring.

Hydrogen sulfide was not detectable at any station. The changes in sulfate concentration were too low to be measured with sufficient accuracy. Hence, it is not possible to quantify sulfate reduction rates with our flux-chamber method.

Porewater profiles

Porewater profiles of ammonia and phosphate are shown for the stations on the Danube delta front, Dniestr mouth and the offshore continental shelf in Figure 6. Only a brief description of the porewater distribution will be given here. Porewater concentrations of ammonia were lowest at the sediment surface and increased with depth. The porewater concentration was several orders of magnitude higher than the concentration in the bottom waters. Phosphate concentrations in the uppermost sediment layer are comparable to those in the bottom waters. In the uppermost centimetres of the sediment, which are affected by bioturbation and the precipitation of Fe-oxides, the concentration fluctuates. The phosphate concentration rapidly increases with depth values, approaching up to 0·11 mM. On the continental shelf, phosphate in the porewater is low and remains constant with depth.

Discussion

Benthic fluxes determined with flux chambers reflect the combined effect of mineralization and dissolution reactions at the sediment surface, transport of solutes by molecular diffusion and transport accelerated by benthic organisms. Unfortunately, it turned out that a direct comparison of diffusive fluxes from porewater profiles with flux chamber data was not possible due to the limited overlap in the stations analysed using both methods.

First, we discuss the diagenetic pathways gained from benthic fluxes and the additional information on benthic fauna, bacteria and porewater data at the different stations. Then, we determined a flux balance of the near-shore and offshore shelf region by comparing the benthic nutrient recycling with the Danube River nutrient input and the water column inventory of the Black Sea.

High and low benthic flux areas

Based on benthic fluxes, we can divide the coastal zone into different areas (Figure 1). Within 20 km from the coast, the sediments are characterized by high benthic fluxes (Figure 5). The offshore region, including the outer continental shelf and the shelf edge, is an area with low benthic exchange rates.

Within the high flux area nearshore, we found subareas with different diagenetic pathways induced by different sedimentation characteristics. Subarea I (Figure 1), in front of the large Danube and Dniestr rivers, is characterized by the direct influence of the
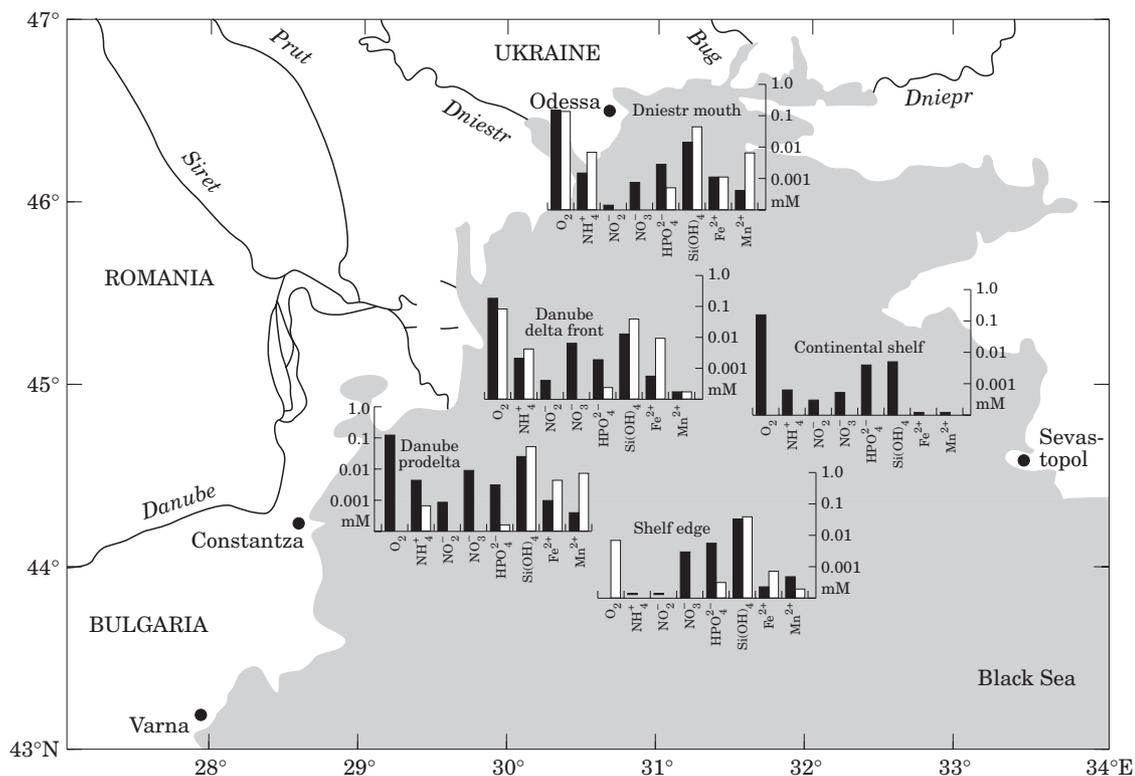
FIGURE 4. Bottom water concentrations of oxygen, nutrients and metals. Black and white columns represent spring (1997) and summer (1995) values respectively, all plotted on a logarithmic scale.

rivers. The river inputs maintain high nutrient concentrations. The particulate organic matter is composed of terrestrial matter and river plankton. Most of this material is trapped inside the river plume due to a northward coastal current that ends in an anticyclonic gyre (M. L. Gregoire & J. M. Beckers, pers. comm. 1998). According to Wijsman *et al.* (1999), the organic matter has relatively low C/N ratios, typical for algal-based detritus. Subarea II of the high flux area is located south of the Danube plume. Part of the Danube water is moving southward and provides high nutrient concentrations that support high primary productivity. The organic matter reaching the seafloor is more labile since it mainly consists of fresh marine organic matter. This is supported by a slight decrease in C/N ratios of the deposited organic matter towards the south (Wijsman *et al.*, 1999).

High flux area I. The benthic remineralization near the Dniestr mouth in spring is dominated by the decomposition of diatoms, yielding a high silica flux. High correlations of the benthic release of ammonia with that of silica ($R^2 = 0.9$), nitrate ($R^2 = 0.9$) and nitrate ($R^2 = 0.9$) point to ammonification of organic nitrogen from diatoms, followed by nitrification. At this station, phosphate seems to be taken up from the

sediment since the porewater concentrations were lower than those of the bottom waters.

Bacterial biomass at the sediment surface reached up to $32\ \mu g\ C\ cm^{-3}$ (19×10^{18} cells cm^{-3}). The benthic invertebrate fauna was dominated by surface-deposit feeding nereid polychaetes with up to 77% of the total biomass (Table 2).

In summer, under anoxic conditions, the biomass of the benthic invertebrates was reduced to 3 g m^{-2} and was dominated by Foraminifera (95%). Unfortunately, to date, the role of Foraminifera for the benthic secondary production has not yet been quantified (Giere, 1993). Anoxic conditions in summer allowed for some observations on the relative importance of anaerobic diagenetic transformations. Methane production was only of minor importance since $0.47\ \mu mol\ CH_4\ m^{-2}\ day^{-1}$ were produced in the uppermost 1 cm of the sediment (Ivanov *et al.*, 2002). The contribution of iron and manganese oxides to anaerobic remineralization is of minor importance. Since no sulfate depletion was detected within the overall error of the flux chamber method (<15%), we estimate an upper boundary for the net sulfate reduction rate in the order of 4 mmol organic carbon m^{-2} day^{-1}. Lein *et al.* (1997) reported H$_2$S production of about 2 mmol m^{-2} day^{-1}, which corresponds to a
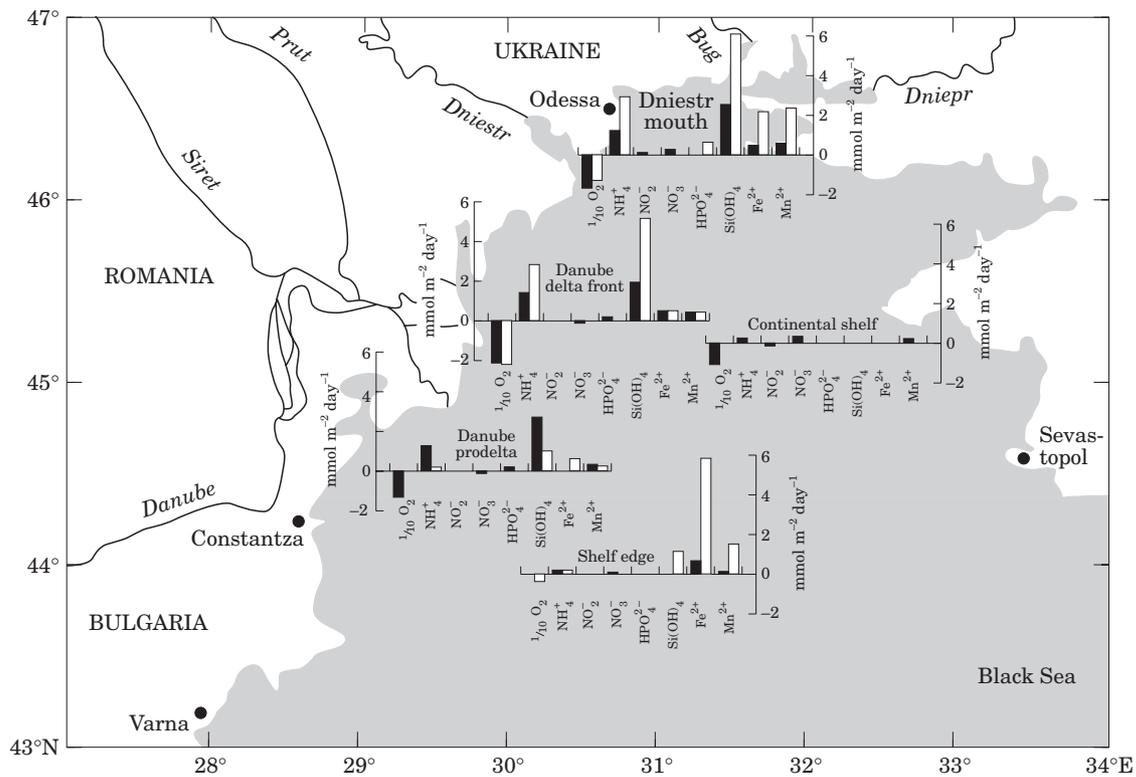
FIGURE 5. Benthic fluxes of oxygen, nutrients and metals. Black and white columns show spring (1997) and summer (1995) values respectively. Oxygen flux to be multiplied by 10.

consumption of about 4 mmol organic carbon m^{-2} day^{-1}.

The Danube delta front area is directly influenced by the Danube plume. There is strong evidence of the riverine origin of most material sedimenting in the area close to the Danube delta, such as the spatial patterns of sediment quality and benthic communities (Gomoiu, 1997), biodegradability of organic matter (Wijsman et al., 1999) and the $\delta^{13}C$ isotopic signature (Galimov, 1997). In spring, the organic matter at the sediment surface is probably less bioavailable, since we found the lowest bacterial biomass (24µg C cm^{-3}) at this station. Cauwet (pers. comm., 1998) observed that the organic matter in the water column is low in nitrogen content. The benthic release of ammonia does not correlate with phosphate, silicate, nitrate and nitrite. This indicates that only weak remineralization of fresh particulate organic matter occurs. In addition, the molar ratio for Si/N/P fluxes is 13:9:1, suggesting that siliceous plankton is a minor source of recycled nutrients. The porewater profile (Figure 6) indicates that part of the ammonia flux originates from diagenetic processes in the top 10 cm of the sediment.

In spring, the benthic biomass was dominated by molluscs (Mya arenaria) and surface-deposit feeding polychaetes (Hediste diversicolor, Neanthes spp., Nereis spp.). These polychaetes rework the sediment by burrowing tubes. Furthermore, they influence sediment stratification by transporting organic matter into their tubes due to ventilatory activity and feeding. Ventilatory activity is the quantitatively most important mechanism for the import of nutrients into deeper strata of the sediment. Hylleberg and Henriksen (1980) estimated that bioturbation by the polychaete Nereis virens increases the oxic sediment volume due to bioturbation by 30–50%. The rapid temporal change between ammonia and nitrate production and consumption in the flux chamber at this station is probably due to the periodic ventilation by polychaetes. This suggests that nitrification, and subsequently denitrification, occurs within polychaete tubes at this location.

Figure 7 shows a rough estimate of diagenetic processes due to oxygen consumption in summer at the Danube delta front site. The estimated values were derived on the basis of the diagenetic reactions in Table 3, assuming organic matter at the Redfield ratio (C/N/P=106:16:1). In summer, the decomposition of this organic matter consumes all oxygen. After its depletion, the remainder of the organic matter is successively degraded by denitrification, manganese
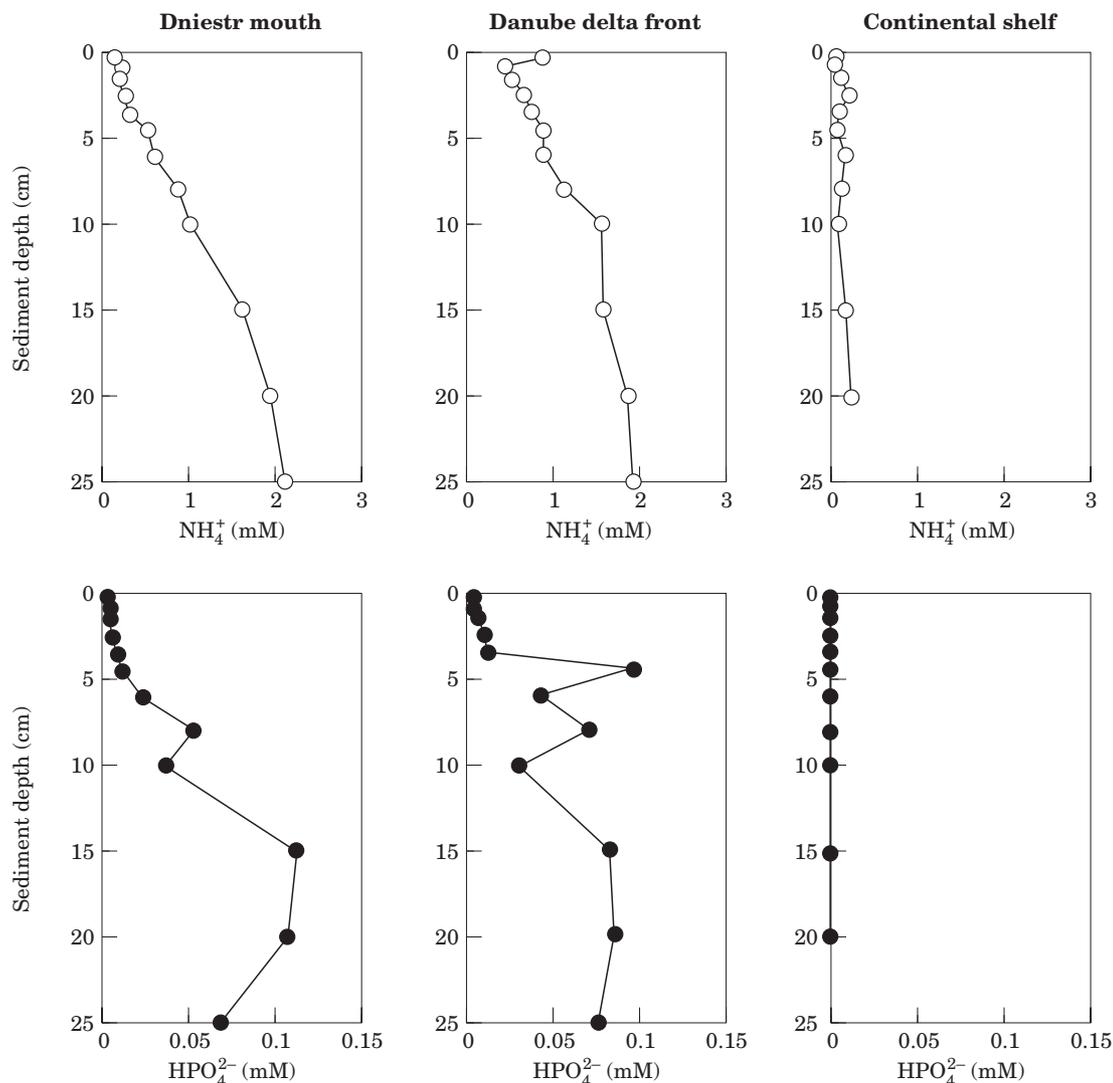
FIGURE 6. Porewater profiles of ammonia and phosphate at station BS 97-13 (Dniestr mouth), BS 97-2 (Danube delta front) and BS 97-16 (Continental shelf).

reduction, iron reduction, sulfate reduction and methane production (Aller, 1982). From the oxygen consumption measured of 26 mmol m^{-2} day^{-1} in the flux chamber (Figure 7), we calculated that 20 mmol C$_{org}$ m^{-2} day^{-1} can be remineralized. Oxic remineralization produces 3 mmol NO$_3^-$ m^{-2} day^{-1}. If no loss to the water column occurs, this amount of nitrate could be used during denitrification for the destruction of up to 3·75 mmol C$_{org}$ m^{-2} day^{-1}. Iron and manganese reduction decomposes about 0·3 mmol or organic carbon m^{-2} day^{-1}. In total, about 24 mmol C$_{org}$ m^{-2} day^{-1} were decomposed and 3·5 NH$_4^+$ m^{-2} day^{-1} were produced, which were partly oxidized to nitrate. If we include the organic matter decomposition by sulfate reduction, an additional 10 mmol C$_{org}$ were decomposed by the

production of 5·3 mmol H$_2$S m^{-2} day^{-1} (Lein *et al.*, 1997). Organic matter decomposition by methane formation can be neglected. The methane flux from the sediment to the water column amounts to only 0·005 mmol m^{-2} day^{-1}. In brief, the intense mineralization at this site is mainly caused by oxic respiration and denitrification (24 mmol C$_{org}$ m^{-2} day^{-1}), whereas sulfate reduction plays an important role in the anaerobic zone of the sediment (10 mmol C$_{org}$ m^{-2} day^{-1}).

Subarea II, Danube prodelta. Low C/N ratios of the deposited organic matter (Wijsmann *et al.*, 1999) suggest marine plankton in spring. In this area we found the highest bacterial numbers with a biomass of 73 µg C cm^{-3} (43 × 10^8 cells cm^{-3}) on the sediment

Danube delta front
summer
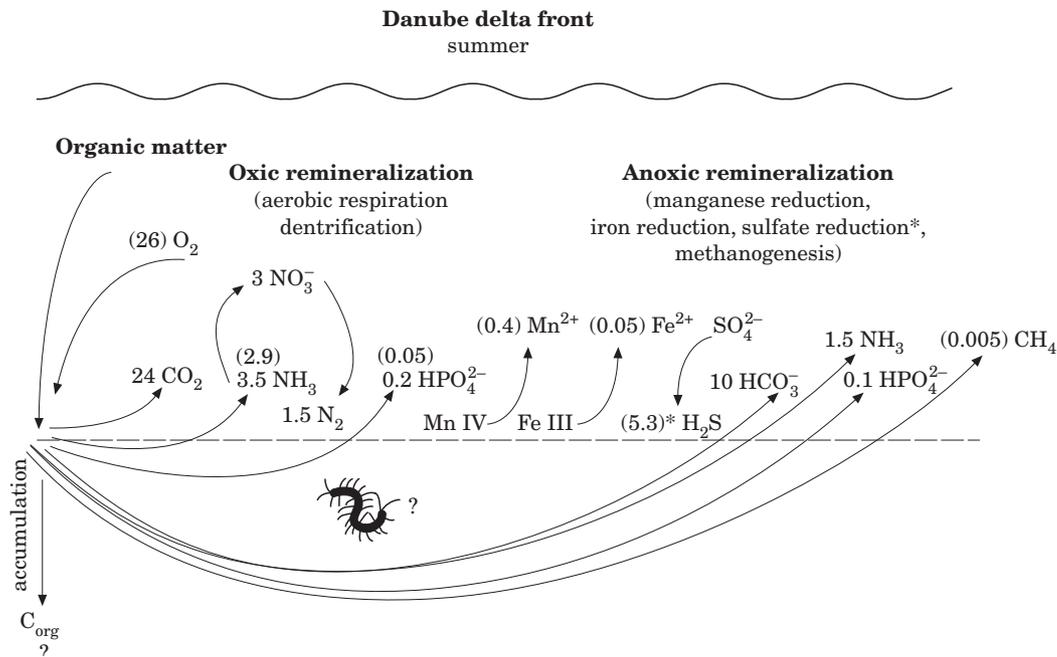
FIGURE 7. Rough estimate of diagenetic processes due to oxygen consumption and flux of reduced components at the Danube delta front in summer. Values were calculated according to reactions in Table 3, assuming Redfield stoichiometry and successive degradation of organic matter. Oxygen flux is corrected for the contribution of denitrification. Values in parentheses represent measured fluxes. Fluxes expressed in mmol m^{-2} day^{-1}. Values with * from Lein et al. (1997).

TABLE 3. Idealized diagenetic reactions (after Aller, 1982)

(1)	Aerobic respiration	$(CH_2O_x(NH_3)_y(H_3PO_4)_z+(x+2y)O_2 \rightarrow xCO_2+yHNO_3+zH_3PO_4+(x+y)H_2O$
	Nitrification	$NH_3+2O_2 \rightarrow HNO_3+H_2O$
(2)	Denitrification	$(CH_2O)_x(NH_3)_y(H_3PO_4)_z+0\cdot8xHNO_3 \rightarrow xCO_2+yNH_3+0\cdot4xN_2+zH_3PO_4+\cdot4H_2O$
(3)	Manganese reduction	$(CH_2O)_x(NH_3)_y(H_3PO_4)+2MnO_2+4H^+ \rightarrow 2xMn^{2+}+xCO_2+yNH_3+zH_3PO_4+3xH_2O$
(4)	Iron reduction	$(CH_2O)_x(NH_3)_y(H_3PO_4)z+2xFe_2O_3+8xH^+ \rightarrow 4xFe^{2+}+xCO_2+yNH_3+zH_3PO_4+5xH_2O$
(5)	Sulfate reduction	$2(CH_2O)_x(NH_3)_y(H_3PO_4)_z+xSO_4^{2-} \rightarrow 2xHCO_3^-+xH_2S+2yNH_3+2zH_3PO_4$
(6)	Methane production	$2(CH_2O)x(NH_3)_y(H_3PO_4)_z \rightarrow xCO_2+xCH_4+2yNH_3+2zH_3PO_4$

Stoichiometries refer to $x=106$, $y=16$ and $z=1$ (Redfield, 1934).

surface. We observed strong correlations between the benthic fluxes of Si and NH_4^+ (0·7). The lack of correlation between P and the metals Fe and Mn suggests that the remineralization of organic matter acts as the main benthic phosphorus source. This assumption is supported by the Si/N/P ratio of 27:12:1 of the benthic flux, which is in the order of the Redfield stoichiometry (Si/N/P=40:16:1). Oxic mineralization and denitrification were shown to be important in spring. By far the most biomass of benthic invertebrates is incorporated in molluscs and polychaetes. However, the presence of molluscs (88% of the biomass in box A, Table 2) does not influence the nutrient fluxes significantly compared to the flux in the absence of molluscs in box B (98% biomass by polychaetes), except ammonia. The ammonia flux was

about 0·5 mmol m^{-2} day^{-1} higher in the presence of molluscs.

The Danube prodelta and the Dniestr mouth in summer are characterized by a rapid sulfate depletion in the porewaters from 12–19 mmol l^{-1} in the upper 0–15 cm to 1·5–5·7 mmol l^{-1} at a depth of 30–40 cm (Lein et al., 1997). Decreasing concentration of sulfate and increasing alkalinity with sediment depth indicate active remineralization by sulfate reducing bacteria. Lein et al. (1997) reported 14 mmol C_{org} m^{-2} day^{-1} being decomposed by sulfate reduction and methane generation. Since no significant change in the sulfate concentration in the flux chamber has been observed, we conclude that reduced compounds are reoxidized in the flux chamber. With oxygen deficiency in summer, sulfate reduction and

probably denitrification are important for organic matter decomposition.

Low flux area

The low flux area on the offshore continental shelf (Figure 1) is not directly influenced by the Danube or the Dniestr. However, a nutrient input from the coastal area has to be taken into account by the cold intermediate layer. This water mass originates in an area of intensive cooling on the shallow north-western shelf region and spreads horizontally through the Black Sea on an isopycnal surface (Tolmazin, 1985). Low nutrient concentrations in the water column, low primary productivity and low flux of organic material to the sediments are characteristic features in this area. Hence, low benthic flux rates are expected. No silica and phosphate fluxes were detectable in the spring. This indicates that very little recent sedimentation of siliceous phytoplankton has occurred. Low ammonification rates of DON are followed by nitrification due to high oxygen in the bottom water. On the continental shelf site, the benthic invertebrates are mostly comprised of molluscs. The high oxygen consumption of 16 mmol m^{-2} day^{-1} cannot be explained by the degradation of organic matter alone. The fluxes in ammonia and nitrate are too low (Table 1). The oxygen consumption must be related to the respiratory activity of the bivalve *Mytilus galloprovincialis*, with a total biomass of 98 g wet wt. m^{-2}.

At the shelf edge, the oxic/anoxic interface is permanently present in the water column at a depth of about 80 m. Under anoxic conditions, benthic denitrification resulting in ammonia generation was observed. Iron and manganese reduction was forced, especially in the summer. However, very low phosphate flux was detected. Organic matter oxidation by sulfate reduction does not seem to be important here since the sulfate reduction rate is very low in the uppermost 4 cm of the sediment (Lein *et al.*, 1997). In this area, the lowest benthic biomass was found (0·4 g m^{-2}, Table 2), contributed exclusively by Foraminifera (99%). Therefore, solutes are transferred across the sediment water interface almost exclusively by molecular diffusion.

Benthic turnover times

Seasonal variations in the flux rates become apparent by comparing the benthic turnover times in spring and summer. For the sake of comparison of different processes, theoretical turnover times were calculated by dividing the nutrient inventory integrated over

TABLE 4. Benthic turnover times (h) in flux chamber

	High flux area		Low flux area	
	August 1995	May 1997	August 1995	May 1997
HPO$_4^{2-}$-P	3–30	48–96	16	720
NO$_3^-$-N		24–168		12–60
NH$_4^+$-N	2–22	5–10	0·2	0·2–7
Si(OH)$_4$-Si	12–96	1	120	96–1056

the whole water column by the corresponding flux estimation.

In summer, the nutrient turnover is, in general, faster than in spring—both in the high and low flux areas (Table 4). The acceleration of turnover times by as much as one order of magnitude in summer must be due to the accumulation of degradable organic matter at the sediment–water interface. In addition, higher temperatures accelerate both microbial processes and the activities of benthic organisms (Rutgers van der Loeff *et al.*, 1984).

Flux balance

In order to assess the role of benthic processes in the overall nutrient cycles in the north-western Black Sea, we try to extrapolate our *in situ* data to the relevant sediment area. To this end, we divided the total shelf surface of 48 000 km^2 into the high flux area within a distance of 20 km from the coast and the low flux area from 20 km to the shelf edge. The high flux area covers 5% (2400 km^2) and the low flux area 95% (45 600 km^2) of the total shelf area. Figure 8 depicts a summary of a water column inventory with nutrient benthic fluxes and the Danube River nutrient input into the shelf of the north-western Black Sea. The benthic fluxes represent an average value from the stations in the high and low flux areas.

In summer, benthic phosphate and silica recycling nearshore account for about 50 and 35% of the average Danube input, respectively. In spring, benthic phosphate and silica fluxes supply only 15 and 20% of the Danube input, respectively. The ammonia input from benthic recycling was on the same order of magnitude in both seasons as the Danube load. During summer, the low flux area offshore is characterized by benthic nutrient recycling in the same order of magnitude as the Danube input.

Dividing the water column inventory of nutrients by the benthic release and average Danube input yields the time theoretically necessary to replace the water column inventory. This gives an estimate of the
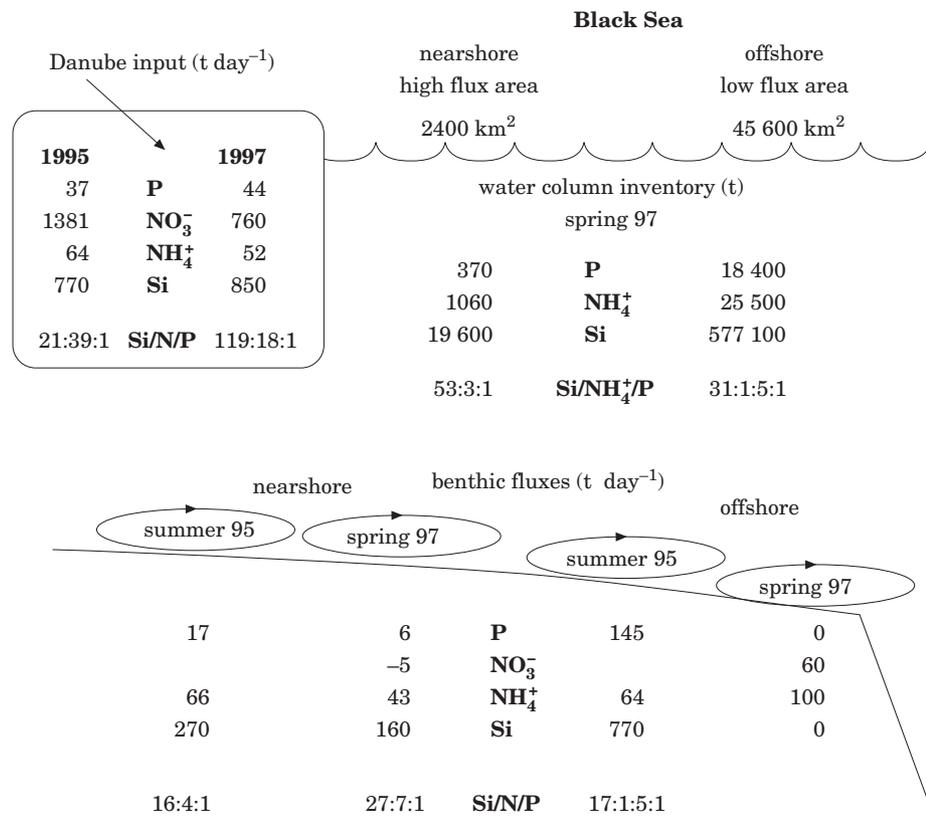
Black Sea

FIGURE 8. Danube inputs of nutrients and benthic nutrient supply (in t day^{-1}) of the shelf area into the north-western Black Sea. Nutrient inventory was calculated from nutrient concentrations in the water column (from Dorogan, 1997, unpubl. data). Nutrient symbols denote HPO_4^{2-}-P, NO_3^--N, NH_4^+-N and $Si(OH)_4$.

importance of the nutrient sources. In spring, nutrients in the water column within the high flux area would be replaced by the benthic supply of ammonia, phosphate and silicate in 25, 62 and 123 days, respectively. The Danube input would replace the water column inventory much faster: ammonia, phosphate and silicate in 20, 8 and 23 days, respectively. In the low flux area during spring, it would take about 255 days to replace the ammonia amount in the water column by benthic supply. However, P and Si release was negligible in spring.

It is evident that, in addition to the influence of the Danube, the benthic processes in the high flux area are highly relevant for the nutrient balance of the Black Sea. However, the benthic nutrient supply in the coastal zone of the Black Sea is still only about half of that determined for Naragansett Bay (Elderfield *et al.*, 1981) and Chesapeake Bay (Callender & Hammond, 1982).

Nutrient ratios

The average N/P ratios of 7:1 in spring and 4:1 in summer ($NH_4^+ - N/P$) of the benthic flux in the high flux area indicate that benthic phosphorous recycling is in excess of nitrogen. The lower N/P ratio in summer shows that denitrification is accelerated after the spring blooms. In 1995, the Danube delivered nitrogen in excess to phosphorous (N/P=39:1), according to the Redfield ratio. In 1997, the N/P ratio of the Danube (19:1) was lower due to a lower nitrogen load and slightly higher phosphorous load. Although the eutrophication of the near-shore shelf of the Black Sea is caused by the nutrient input from the Danube, the benthic release of phosphate might play a role in sustaining the productivity of the system.

Conclusions

The *in situ* flux chamber measurements during two EROS 21 cruises in the north-western Black Sea in summer 1995 and spring 1997 revealed large spatial and seasonal differences in benthic nutrient recycling. Areas of high benthic fluxes nearshore and of low benthic fluxes offshore were found. The high flux area of about 2400 km^2 within 20 km of the coast is

strongly influenced by river input of organic matter and nutrients, which cause high productivity and high sedimentation rates nearshore and, hence, trigger the high benthic fluxes. The anticyclonic circulation nearshore, driven by river influx and wind, keeps water with high nutrient and particle load near-shore. Benthic fluxes are about one order of magnitude higher in this zone than offshore on the shelf. However, due to the large extension of the low flux area ($45\,600$ km^2), both zones provide, on average, similar total benthic fluxes of P, N and Si.

Mass balance calculations of the nitrogen fluxes indicate that denitrification is an important remineralization pathway in the summer, with denitrification rates in the range of a few mmol NO_3^- m^{-2} day^{-1}. During spring, oxic remineralization and denitrification are important for the decomposition of organic matter. Therefore, the Black Sea shelf acts as a strong sink for the riverine nitrate load. As a result, the N/P ratios of benthic fluxes in summer are as low as 4:1 and 1·5:1 in the high and low flux areas, respectively. Since the river input is phosphate deficient, the strong benthic recycling of phosphate is an important factor sustaining high productivity in the coastal zone area of the Black Sea.

Acknowledgements

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