DELTA LAKES AS NUTRIENT SINKS - A PROCESS STUDY IN THE DANUBE DELTA

JANA FRIEDRICH[1]*, CHRISTIAN DINKEL[1], ERWIN GRIEDER[1], SILVIU RĂDAN[2], SANDRA STEINGRUBER[1] & BERNHARD WEHRLI[1]

[1]EAWAG-ETH Zürich, Limnological Research Center, CH-6047 Kastanienbaum, Switzerland
*Present address: GeoForschungsZentrum, Telegrafenberg PB 5.1, D-14473 Potsdam, Germany (janaf@gfz-potsdam.de)
[2] National Institute of Marine Geology and Geo-ecology – GeoEcoMar, 23-25 Dimitrie Onciul Street, RO-70318 Bucharest, Romania

Abstract. Results of a joint project of EAWAG and GEOECOMAR on the nutrient retention capacity of Lakes Uzlina, Matita and Rosu within the Danube Delta are reported in this paper. Two expeditions were organized, first in June and the second in September 1999. Special emphasis was placed on processes of nutrient cycling at the sediment-water interface. It has been carried out water analyses, benthic flux chamber experiments, denitrification experiments, porewater analyses, measurements of O_2-profiles in the sediment and sediment sampling to identify and quantify the pathways of nutrients in these lakes. Methane production and the distribution of methanogenic and sulfate reducing microorganisms in the sediment has been analyzed. The dataset contains very important information on the self-cleaning capacity of the delta lakes.

Key words: nutrients, methane, sulfur, iron, benthic recycling, self-cleaning capacity, lakes, Danube Delta

1. BACKGROUND AND GOALS OF THE PROJECT

Before entering the Black Sea, the Danube forms a wide branching delta. The Danube Delta is the second largest river delta in Europe. A mosaic of shallow lakes and channels, fringed by reed, lies between the main branches. During high water level most of the delta plain is flooded. The Danube Delta, with its small channels, lakes and wetlands, represents a natural filter for various contaminants and nutrients transported in solution or adsorbed onto suspended matter. However, the capacity of the delta system to retain these compounds has been diminished due to agricultural activities effected near the Danube river and inside the delta. Furthermore, the hydrology within the Delta was modified as a result of engineering works such as drainage programs, dike building, impoundments and channel dredging. Before 1980, about 3% of the total Danube discharge was flowing through the Delta, the rest being distributed within the three main branches. The water input into the Delta increased up to 10% after the channels Crisan-Caraorman, Mile 36 and the six Sf. Gheorghe meander cuts were built (Bondar, 1996). Gâstescu *et al.* (1999) estimate the average water residence time in the Delta as 2.2 month at present. With increasing water flow through the Delta, the input of nutrients increased as well, due to higher load and concentrations. Hence, the capacity to retain these nutrients decreased. Although levels of dissolved nitrogen and phosphorus in lakes of the Delta are lower than those in the main channels (Buijse *et al.*, 1997), nutrient concentrations in the lakes increased over the last decades, as well. A survey of the trophic state of selected Danube Delta lakes carried out by Romanian Danube Delta Institute and Dutch Institute for Inland Water Management and Waste Water Treatment revealed that the Lakes Uzlina, Matita and Rosu are mesotrophic to eutrophic (Oosterberg *et al.*, 1997).

To our knowledge, no nutrient budgets for Danube Delta lacustrine ecosystems are available. Therefore, we focused our research on the nutrient retention of Delta lakes. Specific questions we address are:

1. What is the nutrient input into the Delta lakes with respect to the distance from the main Danube distributaries?
2. What is the amount of benthic nutrient cycling?
3. How important is the temporal and permanent nutrient retention in the lakes?

The nutrient retention capacity of the Lakes Uzlina, Matita, Rosu and Rosulet during high water level in June and low water level in September 1999 was analyzed, with special emphasis on nutrient cycling at the sediment-water interface. We carried out water analyses, benthic flux chamber experiments, denitrification experiments of ^{15}N-labeled sediment cores, porewater analyses with dialysis porewater samplers, measurements of O_2-profiles in the sediment with microelectrodes, and sediment sampling, in order to identify and quantify the pathways of nutrient cycling in these lakes. The methane production and the distribution of methanogenic and sulfate reducing microorganisms in the sediment was analyzed. The present paper makes known results of this investigation on the water column chemistry, selected benthic fluxes and porewater fluxes, and give a nutrient budget for Lake Uzlina. At the moment, we cannot answer yet the question of the permanent nutrient retention. This will be stated later elsewhere (Friedrich *et al.*, in prep.).

2. METHODS

2.1. Study sites

We focused our research on Lakes Uzlina, Matita and Rosu/Rosulet. Lake Uzlina is situated within the fluvial delta plain (Gorgova-Uzlina depression), very close to the southern Danube branch Sf. Gheorghe and is the head of a through-flow chain (Fig. 1).

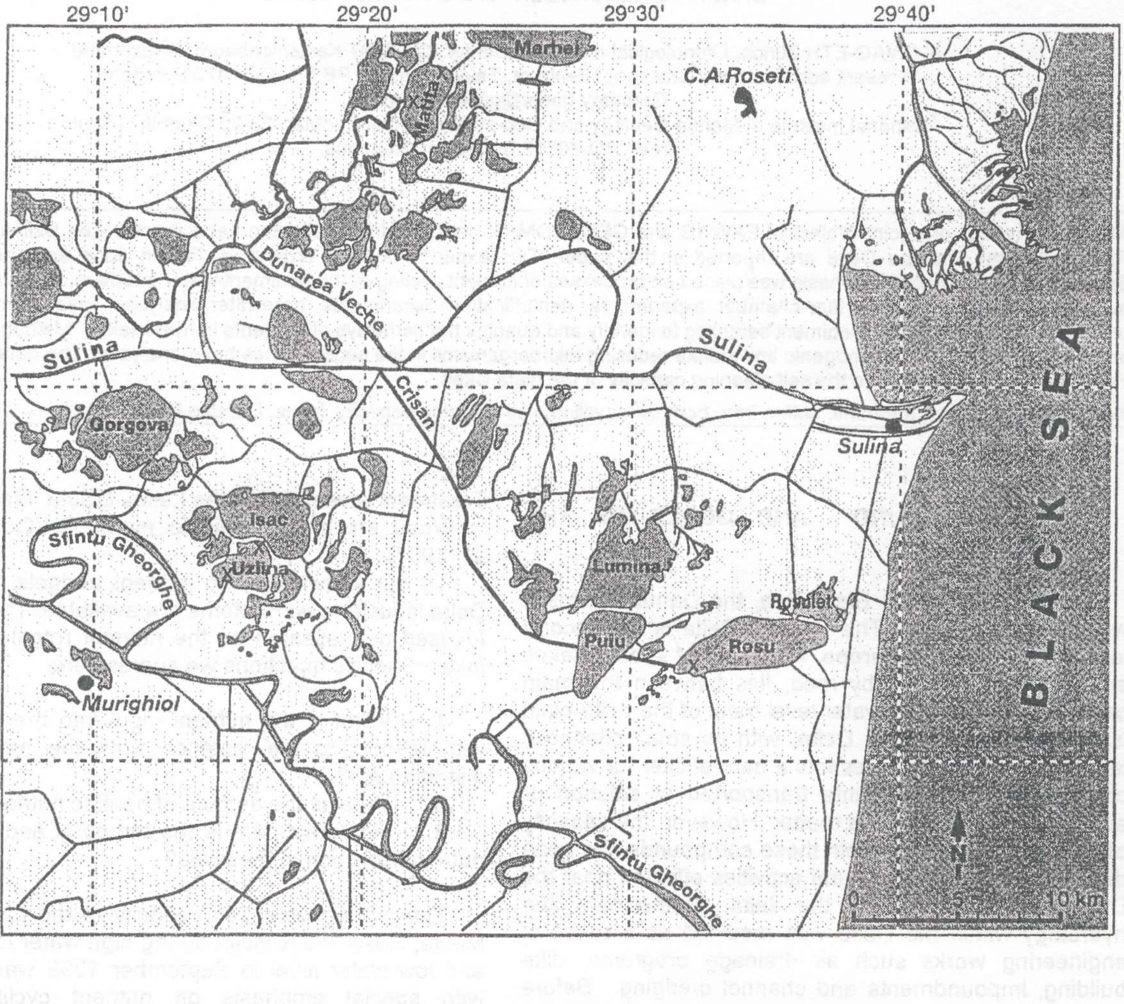

Fig. 1 Research area with Lakes Uzlina, Matita and Rosu/Rosulet location (the position of the stations near the inflow and outflow of each lake is indicated by a cross).

This lake is strongly influenced by Danube inputs from the Sf. Gheorghe branch.

Lake Matita is also situated within the fluvial delta plain (Matita-Merhei deression), but it is not directly influenced by one of the Danube distributaries. The water flowing into the lake already passed through a system of unaltered meandering channels rich in aquatic vegetation and small lakes fringed by reed.

The lakes studied in the marine delta plain are represented by Lakes Rosu and Rosulet, within the Lumina-Rosu depression (Panin, 1996). Lakes Rosu and Rosulet are connected, and are situated in close vicinity of the Black Sea. However, the hydraulic gradient prevents saltwater input into these lakes.

2.2. Field work

The field work was achieved ship-based, with the laboratory-houseboat *"Halmyris"* of GeoEcoMar and the tugboat *"Poarta Albă"*. Two stations were sampled within each lake (Fig. 1). One station was located near the inflow of the lake, the other near the outflow. In addition, water samples have been taken from the inflow channel.

At each station we followed the same sampling procedure according to Table 1.

Water sampling. Water samples were taken with a Niskin bottle at three depths (surface, middle depth, near bottom).

Benthic flux chamber experiments. Fluxes of oxygen, nutrients, sulfur compounds, methane and redox sensitive metals across the sediment-water interface were measured with benthic flux chambers. Design and function of the device is described in detail in Mengis *et al.* (1997a) and Tengberg *et al.* (1995). The benthic lander contains two stainless steel flux chambers that cover sediment areas of 400 cm^2 and enclose about 3-6 litres. The device was lowered to the bottom, tethered to a free floating buoy, and was retrieved after 21 hours. An electronic system triggers up to 15 mechanical functions. The flux chambers were pushed into the sediment and the top lids closed after 30 minutes. Spring actuated syringes were used to take 10 water samples from each chamber in two hour intervals. During operation the flux chambers 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 to 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.

(6 cm diameter) were sampled by a gravity corer. The sediment surfaces were adjusted to have approximately 9 cm of sediment and 13 cm of overlaying water. The overlaying water was stirred by a magnetic stirer. The cores were placed into an incubation basin containing bottom water of the same station. One core was equipped with an O_2 probe and a second one was used as reference core. ^{15}N as NO_3^- (approximately 10% of the natural NO_3^- concentration) was added to the water in the basin and stirred, and the remaining 4 cores were closed. During the experiments, the cores were stored in the dark at in-situ temperatures (25°C). The sediment overlaying water was sampled every hour until 20% of

Table 1 List of measured parameters near the inflow and outflow of Lakes Uzlina, Matiţa and Roşu/Roşuleţ

Station	**Position**	*Station*	**Position**
Uzlina I *Inflow*	29°15'55 E 45°05'12 N	***Uzlina II*** *Outflow*	29°16'02 E 45°04'12 N
Matiţa I *Inflow*	29°21'56 E 45°17'70 N	***Matiţa II*** *Outflow*	29°22'93 E 45°18'39 N
Roşu I *Inflow*	29°32'61 E 45°02'50 N	***Roşuleţ II*** *Outflow*	29°37'72 E 45°03'83 N

Samples	*Porosity*	O_2 §* O_2 §§*	*pH *Alkalinity	*NH_4^+, NO_3^- Tot. Diss. P $Si(OH)_4$	Fe^{2+} Mn^{2+}	*H_2S SO_4^{2-}	^{15}N ^{14}N NO_3^-	POC PN	^{210}Pb ^{7}Be ^{137}Cs	CH_4
Water (surface, middle, deep)		x§	x	x	x	x		x		x
Flux chamber		x§§	x	x	x	x				x
Pore water (0-30 cm)			x	x	x	x				x
^{15}N incubation							x			
Sediment	x	x§§						x	x	

§ Winkler titration
§§ Seabird 16 probe/ microprobe
* analysis on board

Samples of benthic fauna in the box core samples from the flux chamber were taken by colleagues from GeoEcoMar.

Porewater sampling. Porewater was sampled with dialysis porewater samplers, "peepers" at the inflow and near the outflow of each lake. The peepers have a vertical resolution of 1 cm. After equilibration for 5 days with the sediment pore water, the peepers were recovered and protected with gastight lids to prevent partial reequilibration of the solutes. On every station 2 peepers were deployed in order to obtain sufficient sample volume. The peepers were sampled immediately after retrieving. Measurements of alkalinity, pH, ammonia, nitrate and H_2S were carried out on ship board.

Sediment sampling. Sediment cores of about 30 cm length were taken at each station by a gravity corer. The cores were sliced into 0.5 cm and 2 cm intervals and freeze dried for ^{210}Pb, ^{137}Cs, ^{7}Be dating, particulate organic carbon (POC), particulate nitrogen (PN), particulate phosphorus (PP), bacteria and porositiy analysis.

^{15}N incubation experiments. To quantify denitrification rates, at each station 6 sediment cores

oxygen was consumed. The samples were analyzed for NO_3^- and the $^{15}N/^{14}N$ ratio of N_2 with continuous flow isotope ratio mass spectrometer (Micromass) at EAWAG.

O_2 penetration into the sediment. At every station a sediment core was taken to measure oxygen penetration into the sediment with a microelectrode using a portable micromanipulator connected to a laptop computer.

2.3. Analytical procedures

Total alkalinity was measured in all samples by 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 four hours after sampling and retrieval of the flux chambers and the peepers.

Total iron and manganese concentrations were determined in HNO_3 acidified subsamples by GF-AAS.

Subsamples for CH_4 measurements were filled air-free in NaOH containing gastight vials and passed by headspace analysis on a gaschromatograph.

Filtered aliquots of the water samples, the syringes of the flux chamber and the pore water cells were analyzed on board for dissolved ammonium (phenolhypochlorite method) and dissolved sulfide (dimethyl-p-phenylendiamine method) with a "MERCK SQ 300" photometer. Nitrate and total dissolved phosporus (TDP) were analyzed by standard colorimetric methods (2,6 dimethylphenole and ammoniummolybdate method, respectively) with a "PROCON" autoanalyzer at EAWAG. Silica was analyzed photometrically with molybdenum blue. POC and PN were measured with an C/N analyzer (Elementar, vario el). Sulfate was measured by ion chromatography.

2.4. Data analysis

Benthic fluxes from each chamber were calculated by fitting a linear regression to the changes in concentration versus time, d(C)/dt (mmol $m^{-2}d^{-1}$):

$$J = h\frac{d(C)}{dt} \qquad (1)$$

where h is the height (m) of the enclosed water column in the flux chamber. Fluxes across the sediment-water interface based on porewater profiles were calculated by applying Fick's first law :

$$J = -\phi D_s \frac{dC}{dx} \qquad (2)$$

where J is the flux (mmol $m^{-2}d^{-1}$) and ϕ is the porosity (ml cm^{-3}). The effective diffusion coefficient D_s in the sediments was approximated as

$$D_s = \frac{D}{\phi F} \qquad (3)$$

were D is the molecular diffusion coefficient in seawater 5°C (Furrer & Wehrli, 1996, Li & Gregory, 1974). D was recalculated according to the ambient water temperature. F is the sediment resistivity (Christensen *et al.*, 1987, Berner, 1980) and given by an empirical relationship to ϕ (Manheim, 1970):

$$F = \frac{1}{\phi^m} \qquad (4)$$

For sediments of high porosities (>0.7), m is approximately 3 (Ullman & Aller, 1982).

C:N:P ratios represent the molar ratios of the concentrations of carbon, nitrogen and phosphorus.

3. RESULTS AND DISCUSSION

The complete dataset including calculated fluxes is available from the authors. In this paper we present water column data, benthic nutrient fluxes and give the budget for Lake Uzlina as an example. A more detailed analysis of benthic processes, nutrient budgets and bacteria analysis will be published elsewhere (Friedrich *et al.*, in prep., Zepp *et al.*, in prep.)

3.1. Water column

In June, at high water level, and in September, at low water level, the water of the lakes was oxic. The oxygen content was lowest in the inflow channels and increased from the inflow to the outflow of the lakes, except in Lakes Rosu/Rosulet (Tables 2, 3). In contrast, the nutrient concentrations decreased from inflow towards the outflow of the lakes. The highest nitrate and ammonia concentrations were measured in Lake Uzlina (Table 2, 3), which is strongly influenced by the southern Danube branch, Sf. Gheorghe. The TDP concentrations in this lake were surprisingly low, about 0.2 to 2.8 µM, leading to a high N:P ratio. Therefore, in Uzlina the phosphorus availability sets the upper limit of phytoplankton growth. This lake changed from a dominance of macrophytic vegetation, accompanied by clear water in June, to increasing phytoplankton development in September, leading to turbid greenish water. An obvoius decrease in silica concentrations from inflow to the outflow points to uptake by diatoms. The change from dominance of macrophyte growth in June to phytoplankton development in September might be due to naturally dying back of macrophytic vegetation in autumn, to P release from decomposing macrophytes, and to overfishing of large predator fishes. The C:N ratio of the suspended particulate matter (SPM) increased from 1-4 in June to 22-70 in September. Low C:N ratios are typical for sewage material and C:N ratios >40 are typical of plant detritus, especially from reed (Schlegel 1985).

Lake Matita had almost clear water and less dense macrophyte growth than Lake Uzlina in June. The nitrate and ammonia concentrations were less than 0.5 µM and 1 µM in June, respectively, setting the upper limit of phytoplankton growth. From June to September, the nitrate concentrations increased. The nutrient ratio of Si:N:P in the inflow area of about 48:13:1 (Redfield 1934) did not indicate clear growth limitation for phytoplankton by any single nutrient. This is in great contrast to the situation in June, where N was probably growth limiting. At the lake outflow the situation was different, with phosphate in large excess above nitrogen of about 3:1. The C:N ratio of the SPM was in the range of 4-12. In September, the SPM had a C:N ratio of 11-16. C:N ratios around 7 are typical for phytoplankton and >10 for terrestrial plants.

Lakes Rosu/Rosulet were turbid due to phytoplankton development in June and in September. These lakes were in an intermediate stage between Uzlina and Matita with regard to the nutrient

Table 2 pH, alkalinity, total dissolved phosphorus (TDP), nitrate, ammonia, oxygen, sulfate, iron, manganese, methane, and the molar C:N ratio of particles in the inflow channel and the water column of Lakes Uzlina, Matiţa and Roşu/Roşuleţ in June 1999.

Sample	pH	Alkal. mM	O_2 mM	TDP µM	$N\text{-}NO_3^-$ µM	$N\text{-}NH_4^+$ µM	$Si(OH)_4$ µM	SO_4^{2-} µM	Fe^{2+} µM	Mn^{2+} µM	CH_4 µM	C:N
Uzlina												
*channel 1**		2.91	0.21	0.92	99.52	8.42	76.37	273	12.19	0.62		3
channel 2		2.92	0.21	1.73	91.51	3.78	76.37	265	19.48	0.72		4
inflow 1		2.99	0.37	1.01	97.23	3.07	65.84	280	3.32	0.36	0.45	2
inflow 2		2.99	0.29	1.02	81.22	2.16	64.93	276	3.46	0.33	0.39	2
inflow 3		2.94	0.07	1.11	79.51	5.61	64.01	277	4.26	0.46	0.68	2
outflow 1		1.83	0.25	0.19	20.35	2.90	6.32	286	0.15	0.03	0.44	1
outflow 2		1.93	0.25	0.24	24.35	2.39	6.32	271	0.22	0.03	0.33	2
outflow 3		2.52	0.27	2.86	38.93	6.49	28.75	267	0.98	0.94	7.34	2
Matiţa												
channel 1	7.28	2.95	0.05	3.06	b.d.	1.20	61.26	281	1.07	0.80		6
channel 2	7.35	2.93	0.03	3.03	b.d.	1.26	57.14	282	1.02	0.78	2.47	5
inflow 1	7.4	2.98	0.12	2.43	b.d.	0.48	48.44	292	1.03	0.52	0.69	3
inflow 2	7.36	3.00	0.13	2.76	b.d.	0.37	57.14	292	0.90	0.52	1.21	3
inflow 3	7.21	2.96	0.05	2.86	b.d.	1.75	60.35	289	0.99	0.54	1.15	11
outflow 1	7.71	3.09	0.21	1.79	b.d.	0.45	62.18	287	0.47	0.68	0.04	4
outflow 2	7.73	3.07	0.21	2.09	b.d.	0.03	60.35	286	1.49	0.67	2.00	4
outflow 3	7.78	3.21	0.08	2.03	b.d.	0.22	90.11	260	0.75	1.87	0.25	12
Roşu												
channel 1	7.7		0.18	1.44	1.69	3.64	104.02	287	0.64	0.57	0.78	22
channel 2	7.71		0.16	1.53	2.01	1.85	96.95	284	0.68	0.56	4.65	12
inflow 1	7.63	3.14	0.29	1.53	1.56	2.75	72.21	284	1.05	0.62		15
inflow 2	7.61	3.14	0.29	1.49	2.13	6.60	72.21	285	0.88	0.74	1.04	9
Inflow 3	7.64	3.14	0.19	1.73	2.26	2.76	86.90	283	1.17	0.61	1.91	8
Roşuleţ												
outflow 1	8.2	3.37	0.14	0.29	0.67	b.d.	88.74	280	0.26	0.69		15
outflow 2	8.21	3.36	0.13	0.35	0.61	0.18	71.20	299	0.37	0.95	0.35	12
outflow 3	8.01	3.35	0.09	0.45	1.62	b.d.	115.64	297	0.40	0.86	19.9	12

* 1 surface, 2 mid depth, 3 deep sample
b.d. below detection limit

Table 3. pH, alkalinity, total dissolved phosphorus (TDP), nitrate, ammonia, oxygen, sulfate, iron, manganese, methane, and the molar C:N ratio of particles in the inflow channel and the water column of Lakes Uzlina, Matiţa and Roşu/Roşuleţ in September 1999.

SAMPLE	pH	Alkal. mM	O_2 mM	TDP µM	$N\text{-}NO_3^-$ µM	$N\text{-}NH_4^+$ µM	$Si(OH)_4$ µM	SO_4^{2-} µM	Fe^{2+} µM	Mn^{2+} µM	CH_4 µM	C:N
Uzlina												
*channel 1**	7.86	2.95	0.22	2.12	116.18	0.79	87.72	378	3.84	0.64	0.05	35
channel 2	7.84	2.92	0.21	2.48	116.18	0.89	99.32	375	3.80	0.73	0.23	38
inflow 1	7.67	2.91	0.22	2.48	114.64	2.71	92.63	382	3.75	0.76	0.23	70
inflow 3	7.77	2.94	0.21	2.48	113.11	2.76	89.95	375	3.79	0.77	0.12	43
outflow 1	8.23	2.99	0.36	0.66	38.50	2.14	39.95	376	1.85	0.53	24.15	56
outflow 3	8.27	3.00	0.36	0.70	40.34	1.74	39.95	381	1.67	0.62	2.44	22
Matiţa												
channel 1	7.82	3.31	0.19	1.94	26.15	2.71	97.98	305	2.14	0.61	0.29	74
channel 2	7.95	3.31	0.21	1.94	19.18	1.65	80.57	291	1.69	0.68	0.43	32
inflow 1	7.59	3.31	0.21	1.39	21.87	1.48	88.16	301	2.23	0.73	0.20	11
inflow 2	7.70	3.29	0.21	1.85	22.24	1.60	91.73	296	2.02	0.70	0.27	12
inflow 3	7.74	3.28	0.35	2.01	22.48	1.68	90.84	302	1.94	0.63	0.35	16
outflow 1	8.63	2.68	0.32	0.65	0.56	0.98	20.76	248	1.24	0.90	1.24	11
outflow 2	8.68	2.67	0.32	0.56	0.32	1.11	14.95	244	0.58	0.99	b.d.	11
outflow 3	8.68	2.69	0.35	0.50	0.59	1.04	13.61	247	0.67	0.90	b.d.	11
Roşu												
channel 1	8.62	2.92	0.38	0.43	0.22	0.82	19.86	236	0.96	0.55	b.d.	3
channel 2	8.55	3.00	0.35	0.33	0.15	0.63	18.97	236	1.08	0.58	1.06	5
inflow 1	8.44	3.15	0.35	0.40	0.21	0.77	25.22	237	0.53	0.58	0.26	8
inflow 2	8.36	3.04	0.30	0.34	0.11	0.88	28.79	233	0.50	0.53	b.d.	10
inflow 3	8.36	3.15	0.35	0.42	0.22	0.87	26.56	237	0.80	0.91		10
Roşuleţ												
outflow 1	8.46	3.16	0.33	0.24	<0.01	0.74	14.06	226	4.07	0.46	0.34	12
outflow 2	8.56	3.10	0.33	0.26	<0.01	0.71	14.51	221	0.96	0.44	0.68	12
outflow 3	8.57	3.10	0.32	0.27	0.01	1.06	15.85	214	1.02	0.58	0.45	13

* 1 surface, 2 mid depth, 3 deep sample
b.d. below detection limit

concentrations. The nutrient concentrations decreased from June to September. In September, the nitrate concentration was below the detection limit of 0.01 µM at the outflow of Rosulet. The comparison of our data with the RIZA study (Oosterberg *et al.* 1997) shows that their phosphate values were much lower for Lakes Uzlina, Matita and Rosu/Rosulet. In contrast, they reported higher ammonia concentrations in these lakes. The nitrate concentrations in the lakes are similar in both studies, except for Lake Uzlina in September.

3.2. Benthic fluxes

Due to the high availability of organic material in all three lakes, nitrate and sulfate act as electron acceptors in the absence of oxygen in the sediment, enabling further oxydation of organic matter under anoxic conditions. Fermentative mineralization of organic matter to methane is an important pathway in these shallow lakes, as well. The higher methane fluxes in September (Table 5) are related to increased decomposition of organic matter in the sediment. In June, the highest benthic nutrient release took place at the outflow of Lake Uzlina. The highest benthic P release was observed in this lake (Table 4). Reductive dissolution of iron oxides by iron reducing microorganisms and by H_2S generated by sulfate reducers are probably important processes contributing to the intense phosphate flux. Reduced Fe^{2+} and S^{2-} react to form microcrystalline iron sulfides and/or elemental sulfur, and therefore, the measured H_2S flux remained low. In September no sulfide flux at all was recorded in the flux chamber.

In both seasons, the highest benthic nitrate elimination was observed in Lake Uzlina. In June, Lake Matita showed benthic nitrate elimination that was more than one order of magnitude lower, whereas in September nitrate release was observed (Table 4, 5). In September, in the Lakes Matita and Rosu a rapid change between nitrate consumption and production was observed during the flux chamber experiments. This was probably related to coupled nitrification/denitrification in the upper layer of the sediment.

The results from the ^{15}N-incubation experiments reveal 20-40% of the benthic nitrate loss is subject to denitrification in Uzlina in June and in September. Due to the low nitrate concentrations in Lake Matita it was not possible to measure denitrification rates with sufficient precision. In Lakes Rosu/Rosulet a rapid change between benthic nitrate consumption and production during the flux chamber experiments due to coupled nitrification/denitrification was observed in June. In September denitrification accounts for 20% of the benthic NO_3^- reduction.

Highest benthic ammonia fluxes were detected in Lake Uzlina, and they are twice as high as benthic nitrate elimination. In general, higher benthic fluxes were recorded in September than in June.

3.3. Porewater fluxes

In general, the porewater profiles of nutrients (Fig. 2) and sulfide, iron and methane (not shown here) support the results of benthic fluxes from the flux chamber, although diffusive fluxes calculated from porewater profiles are lower than those measured with benthic chambers. Urban *et al.* (1997) showed that porewater profiles from peepers with a depth resolution of 15 mm do not reflect the rapid processes occuring at the sediment surface. Therefore, porewater profiles are more suited of identifying the depth of solute consumption and release (Friedrich *et al.*, in prep.). The profiles suggest nitrate consumption at the sediment-water interface by denitrification and nitrate ammonification.

Fluxes from porewater across the sediment-water interface (Table 6, 7) indicate highest benthic nutrient turnover in Lake Uzlina at high and low water level. The highest oxygen consumption was measured in Lakes Rosu/Rosulet. The higher oxygen concentrations above the sediment and hence, higher consumption in September is probably related to the photosynthetic activity of benthic algal mats, which developed during lower water level.

Hydrogen sulfide diffusing from the sediment is fixed by Fe^{2+} to build FeS phases. Therefore, the diffusion of hydrogen sulfide and Fe^{2+} remains low. An exception represents the outflow of Rosulet where the Fe^{2+} concentrations are too low to capture hydrogen sulfide from sulfate reduction completely. Highest methane diffusion was observed at high water level in Lake Uzlina and at low water level at the outflow of Lake Rosulet. The peeper for the nutrient profile at the outflow of Lake Rosulet was implanted too deep into the sediment. Therefore, the sediment-water interface was missing.

3.4. Nutrient retention

The nutrient retention of the lakes was estimated with a simple box model. We measured the nutrient input and output of the lake through the main channels, benthic release or uptake of nutrients and loss to the atmosphere in the case of nitrogen. The diffuse water flow through the reed belts of the lakes and groundwater influence was neglected, because these factors were not accessible within the frame of our project. Therefore, with our estimate we rely on water exchange of the lakes through the main channels.

$$\Delta = In - Out + BR - St \qquad (5)$$

In our lake balance (equ. 5), Δ represents the changes in concentration of solutes and water volume of the lake. Δ equals the difference between the inflow of nutrients in the lake *(In)* and the outflow of nutrients *(Out)* plus benthic release *(BR)* minus gas exchange *(G)* and storage *(St)*. The unit of all terms is mmol m^{-2} day^{-1}. Our storage term includes the biological and adsorptive uptake and release of nutrients from and into the water, sedimentation of particulate matter and net sedimentation. With the available measurements we cannot distinguish between these three processes. Due to the high sediment mobility of these shallow river lakes it is difficult to date the sediment cores with radionuclides. Estimates of net sedimentation derived from ^{210}Pb and ^{137}Cs dating are affected with an error as high as the rate itself. We further neglect changes in concentration and volume in the lake box (Δ = 0) and assume a steady-state situation in the lake. This approximation can be justified for our "snapshot"

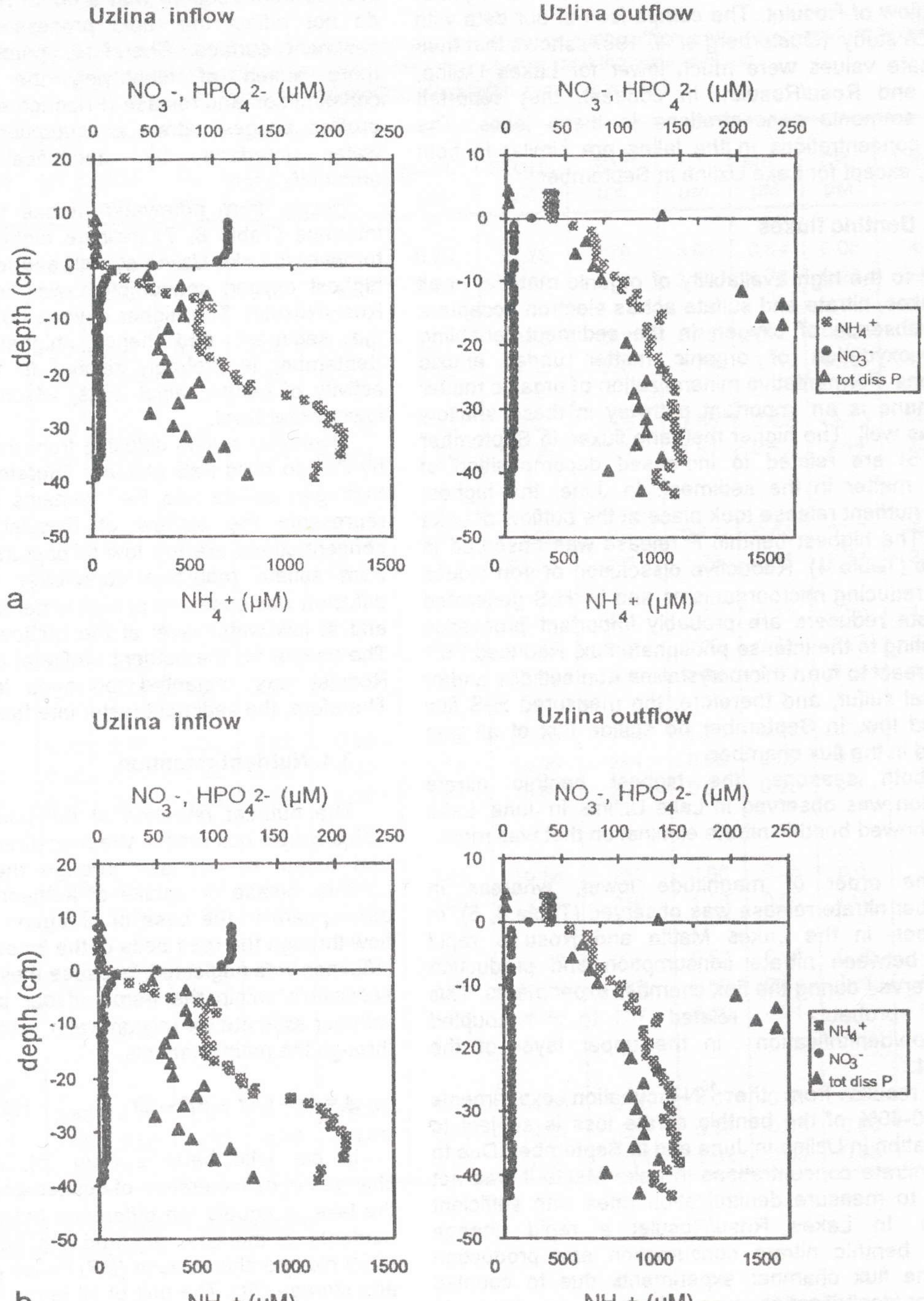

Fig 2. Porewater profiles of nitrate, ammonia and phosphate (in µM) at the inflow and the outflow of Lake Uzlina; (a) – high water level (June 1999); (b) – low water level (September 1999).

Table 4. Benthic fluxes (mmol $m^{-2}d^{-1}$) of O_2, nutrients, sulfate, methane and iron and start concentrations (mM) in chambers A and B, recorded in Lakes Uzlina, Matița and Roşu/Roşuleț in June 1999.

Location		O_2	NH_4^+		NO_3^-		HPO_4^{2-}		SO_4^{2-}		CH_4		Fe^{2+}	
			A	B	A	B	A	B	A	B	A	B	A	B
Uzlina	J	-36.19	5.67	4.99	-2.53	0.72	0.76	0.94	-3.88	-4.7	5.59	-	2.3	1.07
Inflow	± S	3.8	1.1	0.35	0.66	0.71	0.12	0.15	0.89	0.84	1.81		0.17	0.07
	R^2	0.94	0.83	0.96	0.65	0.11	0.83	0.84	0.7	0.8	0.54		0.96	0.97
	C_0	0.136	0.003	0.003	0.051	0.053	0.001	0.002	0.278	0.281	0.004	0.003	0.004	0.003
Outflow	J	-385.4	14.87	7.08	-	-4.93	11.12	1.08	-14.87	-4.05	24.05	5.41	10.15	1.41
	± S	89.1	2.59	0.5		1.03	1	0.37	1.38	0.62	1.88	2.27	0.61	0.2
	R^2	0.9	0.8	0.96	0	0.93	0.94	0.52	0.95	0.84	0.95	0.42	0.97	0.87
	C_0	0.55	0.027	0.012	0.004	0.007	0.019	0.018	0.199	0.201	0.03	0.01	0.013	0.005
Matița	J	-9.39	2.22	3.71	0.33	-0.25	0.14	-	-0.22	-0.22	1.75	2.39	0.14	1.03
Inflow	± S	0.64	0.34	0.44	0.07	0.04	0.02		0.06	0.05	0.66	0.29	0.02	0.07
	R^2	0.96	0.88	0.9	0.75	0.79	0.88	0	0.69	0.69	0.5	0.89	0.85	0.96
	C_0	0.042	<0.001	<0.001	0.001	0.001	0.002	0.003	0.009	0.008	0.001	0.001	0.001	0.001
Outflow	J	-24.11	-	1.35	b.d.	b.d.	0.18	0.14	-4.03	-2.34	1.26	-	-	0.25
	± S	3.8		0.24			0.04	0.07	0.83	0.5	0.61			0.12
	R^2	0.93	0	0.83			0.75	0.72	0.75	0.73	0.35			0.35
	C_0	0.05	0.002	<0.001			0.001	0.002	0.227	0.223	0.001	0.005	0.001	0.001
Roşu	J	-36.43	2.39	3.67	-0.27	-	0.68	0.61	-1.04	-2.83	-	8.36	0.23	0.13
Inflow	± S	18.9	1.18	1.06	0.16		0.14	0.03	0.68	1.0		2.92	0.05	0.04
	R^2	0.79	0.34	0.6	0.26	0	0.74	0.99	0.23	0.5		0.5	0.73	0.6
	C_0	0.038	0.016	<0.001	0.001	0.002	0.003	0.001	0.273	0.273	0.03	0.001	<0.001	<0.001
Roşuleț	J	-45.35	3.72	6.69	3.68*	0.65*	0.5	0.04	-7.49	-2.95	-	-	-	0.04
Outflow	± S	2.01	0.72	1.02	0.2	0.23	0.37	0.02	1.6	0.87				0.02
	R^2	0.97	0.77	0.86	0.61	0.81	0.19	0.47	0.73	0.59				0.4
	C_0	0.171	<0.001	0	0.001	<0.001	0.001	0.001	0.289	0.288	0.004	<0.001	<0.001	<0.001

J benthic fluxes (mmol $m^{-2}d^{-1}$)
(negative values indicate uptake)
S standard deviation of the flux
R^2 correlation coefficient of the regression
(only regressions with R^2>0.5 are considered)

C_0 start concentrations (mM)
* resulting flux of coupled production and consumption
b.d. below detection limit

Table 5. Benthic fluxes (mmol $m^{-2}d^{-1}$) of O_2[§], nutrients, sulfate, methane and iron and start concentrations (mM) in chambers A and B, recorded in Lakes Uzlina, Matiţa and Roşu/Roşuleţ in September 1999.

Location		O_2	NH_4^+		NO_3^-		HPO_4^{2-}		SO_4^{2-}		CH_4		Fe^{2+}	
			A	B	A	B	A	B	A	B	A	B	A	B
Uzlina	J		**6.51**	**12.33**	**-8.6**	**-7.95**	0.07	0.05	**-4.32**	-	**18.61**	**36.59**	-31.7*	**-2.91**
Inflow	± S		0.22	0.49	0.27	0.26	0.03	0.03	1.5		1.57	2.0	13.05	1.38
	R^2		0.99	0.99	0.99	0.99	0.34	0.24	0.5		0.95	0.78	0.6	0.36
	C_0		0.002	0.003	0.110	0.109	0.001	0.001	0.379	0.377	0.010	0.006	0.076	0.024
Outflow	J		**1.62**	**17.21**	**-2.03**	**-7.52**	0.06	**0.76**	2.87	-	-	**3.04**	-	**3.2***
	± S		0.22	2.96	0.32	0.59	0.04	0.8	1.8			0.59		1.31
	R^2		0.89	0.8	0.84	0.95	0.28	0.92	0.24			0.77		0.92
	C_0		<0.001	0.006	0.038	0.043	<0.001	0.001	0.372	0.373	0.009	0.003	0.003	0.002
Matiţa	J	**-49.0**	**10.04**	**6.24**	**0.22***	**1.24***	**0.25**	**0.2**	**-6.71**	**-1.82**	**13.37**	**19.76**	**0.53**	**-0.96**
Inflow	± S	3.4	1.1	0.5	0.39	0.5	0.03	0.04	1.4	0.6	1.4	1.9	0.36	0.19
	R^2	0.96	0.96	0.95	0.82	0.9	0.93	0.78	0.82	0.54	0.94	0.93	0.73	0.56
	C_0	0.2147	0.002	0.001	0.003	0.001	0.001	<0.001	0.271	0.255	0.007	0.011	0.002	0.002
Outflow	J	**-41.1**	-	**-0.9***	**0.06***	**-0.59***	**0.03**	**0.06**	**-4.19**	**-4.23**	**1.0**	**1.12**	**-0.1**	0.04
	± S	2.9		0.04	0.09	0.14	0.01	0.01	0.71	0.71	0.22	0.23	0.02	0.04
	R^2	0.99		0.9	0.77	0.72	0.62	0.82	0.8	0.82	0.77	0.82	0.73	0.15
	C_0	0.2594	0.001	0.001	<0.001	0.001	<0.001	<0.001	0.245	0.236	0.001	0.002	0.001	0.001
Roşu	J		**1.98**	**5.16**	**-0.46***	0.02	-	**0.04**	-	**-2.9**	**3.66**	**7.68**	-0.1	-
Inflow	± S		0.31	0.69	0.02	0.01		0.01		0.61	1.2	1.56	0.04	
	R^2		0.85	0.87	0.91	0.31		0.82		0.74	0.56	0.75	0.43	
	C_0		0.001	0.001	<0.001	<0.001	<0.001	<0.001	0.225	0.224	0.007	0.003	0.002	0.001
Roşuleţ	J		**12.4**	**10.7**	-	-	**0.05**	-	**-8.66**	**-8.27**	**19.76**	**19.0**	-0.59	**-3.11***
Outflow	± S		0.76	0.9			0.01		0.75	1.14	2.21	1.27	0.3	0.97
	R^2		0.97	0.95			0.65		0.94	0.87	0.9	0.97	0.33	0.7
	C_0		0.001	0.001	<0.001	<0.001	<0.001	<0.001	0.212	0.215	0.013	0.013	0.001	0.005

§ oxygen was not measured in Uzlina and Ro□u due to sensor damage

J benthic fluxes (mmol $m^{-2}d^{-1}$) (negative values indicate uptake)

S standard deviation of the flux

R^2 correlation coefficient of the regression (only regressions with R^2>0.5 are considered)

C_0 start concentrations (mM)

* resulting flux of coupled production and consumption

b.d. below detection limit

Table 6 Diffusive fluxes* (mmol m^{-2} day^{-1}) across the sediment surface calculated from porewater profiles in June.

Station	HPO_4^{2-}	NO_3^-	NH_4^+	$Si(OH)_4$	H_2S	SO_4^{2-}	CH_4	Fe^{2+}	O_2
Uzlina I	0.30	-0.03	0.29	0.01	0.001	-0.18	0.82	0.05	-4.39
Uzlina II	0.06	-0.02	1.26	0.80	-	-0.11	-	-	-6.43
Matiţa I	0.04	-0.01	0.62	0.42	-	-0.09	0.04	-0.01	-2.56
Matiţa II	0.02	<-0.01	0.02	0.31	-	-0.17	0.01	-	-3.38
Roşu I	0.02	<-0.01	0.43	0.94	0.006	-0.27	0.51	0.01	-13.93
Roşuleţ II	<0.01	-0.01	0.01	0.05	0.001	-0.02	0.01	<0.01	-1.78

* negative values indicate flux into the sediment

Table 7 Diffusive fluxes* (mmol m^{-2} day^{-1}) across the sediment surface calculated from porewater profiles in September.

Station	HPO_4^{2-}	NO_3^-	NH_4^+	$Si(OH)_4$	H_2S	SO_4^{2-}	CH_4	Fe^{2+}	O_2
Uzlina I	0.05	-0.33	0.49	0.30		-0.35	0.79	0.07	- 9.2
Uzlina II	0.26	-0.15	0.91	1.05	0.004	-0.47	0.99	0.04	- 8.1
Matiţa I	0.02	-0.06	0.91	0.68	0.021	-0.41	0.72	0.03	-16.4
Matiţa II	0.01	0	0.39	0.32	0.001	-0.21	0.23	-	-13.9
Roşu I	0.01	<-0.01	0.97	0.63	0.001	-0.25	0.30	0.01	-19.4
Roşuleţ II					0.868		1.06	<0.01	-14.7

* negative values indicate flux into the sediment

Table 8 Nutrient gross retention (mmol $m^{-2}d^{-1}$) in Lakes Uzlina, Matiţa and Roşu during high water level (June 1999) and low water level (September 1999).

Lake	Throughflow* m^3s^{-1}		Water residence time days		TDP retention mmol m^{-2} d^{-1}		N-NO_3^- retention mmol m^{-2} d^{-1}		N-NH_4^+ retention mmol m^{-2} d^{-1}		$Si(OH)_4$ retention mmol m^{-2} d^{-1}	
	June	*Sept.*	*June*	*Sept.*	*June*	*Sept.*	*June*	*Sept.*	*June*	*Sept.*	*June*	*Sept.*
Uzlina	17	4	11	33	3.42	0.87	21	5.4	8.8	9.3	13.9	9.1
Matiţa	13	3	16	60	0.34	0.3	?	1.3	2.6	5.4	7.6	14.7
Roşu	45	13	15	43	0.89	0.05	2.4	0.1	5.3	7.2	17.9	16.2

* Bondar, pers. com. 2000

measurement lasting only a few days. At steady state, equ. (5) can be rewritten as:

$$In - Out = St + G - BR \qquad (6)$$

We define the term *In-Out* as *net retention*, which will vary according to the hydrologic conditions and the season. A good approximation to *gross retention* is:

$$gross\ retention = St + G \qquad (7)$$

which can be calculated as:

$$gross\ retention = In - Out + BR \qquad (8)$$

Nutrient budgets were calculated using data on water chemistry (Tables 2, 3, 4, 5) and hydrology (Table 8). The nutrient gross retention is given in Table 8. Our nitrogen budget is based on inorganic nitrogen, only. Therefore, a nitrogen budget including the dissolved organic nitrogen fraction might be different. It is likely that a part of the inorganic nitrogen loading leaves the lake in the organic pool. The highest nitrate and phosphate retention was found in Lake Uzlina during high water level. The value of nitrate gross retention in Lake Uzlina in June is very high (21 mmol $m^{-2}d^{-1}$), compared to about 5 mmol $m^{-2}d^{-1}$ in deep, stratified Swiss Lakes (Mengis *et al.* 1997b).

In general, the gross phosphorus and nitrate retention in Lake Uzlina per square meter of lake surface was higher at high water level. In contrast, the ammonia retention was higher during low water level in September.

3.5. Nutrient budget of Lake Uzlina

Now we give a nutrient budget for Lake Uzlina at high water level in June and at low water level in September. The benthic release of phosphorus and ammonia, averaged over the lake surface, exceeded the input from the inflow channel both at high water level in June and at low water level in September. That means, the high nutrient load of the lakes is not only maintained by nutrient rich water from the inflow (external source) but also has an internal source, the benthic release from decomposition of organic material.

At high water level in June, we assume a lake surface of 4.68 km^2, a lake volume of 15.54 million m^3 and a troughflow of about 17 m^3s^{-1} (Bondar pers. com., 2000). Then the gross retention amounts about 91%, 88% and 71% of the daily TDP, NH_4^+ and NO_3^- inputs, respectively (Fig. 3). The gross retention includes uptake in biomass, adsorption and sedimentation processes. The benthic NO_3^- loss (245 kg day^{-1}) accounts for 18% of the total NO_3^- retention in the lake, and about 20-40 % of that nitrogen are lost permanently to the atmosphere by denitrification.

During low water level in September, assuming a lake volume of 10.72 million m^3 and a troughflow of about 4 m^3s^{-1} (Bondar pers. com., 2000), about 95%, 99% and 80% of the daily TDP, NH_4^+ and NO_3^- inputs are retained, respectively (Fig. 3). Denitrification rates were comparable to those in June. However, the biologic uptake of ammonia doesn't match the benthic release of ammonia. As a consequence, the concentration in the lake increases from the inflow to the outflow of the lake. Therefore we suspect that later, in the season when biological activity decreases and less nutrients are taken up, the concentration at the outflow of the lakes increases again. However, we cannot estimate the amount of nutrient release during winter as long as no winter investigations are available.

The net retention reaches a higher percentage at low water level. This is due to longer water residence times

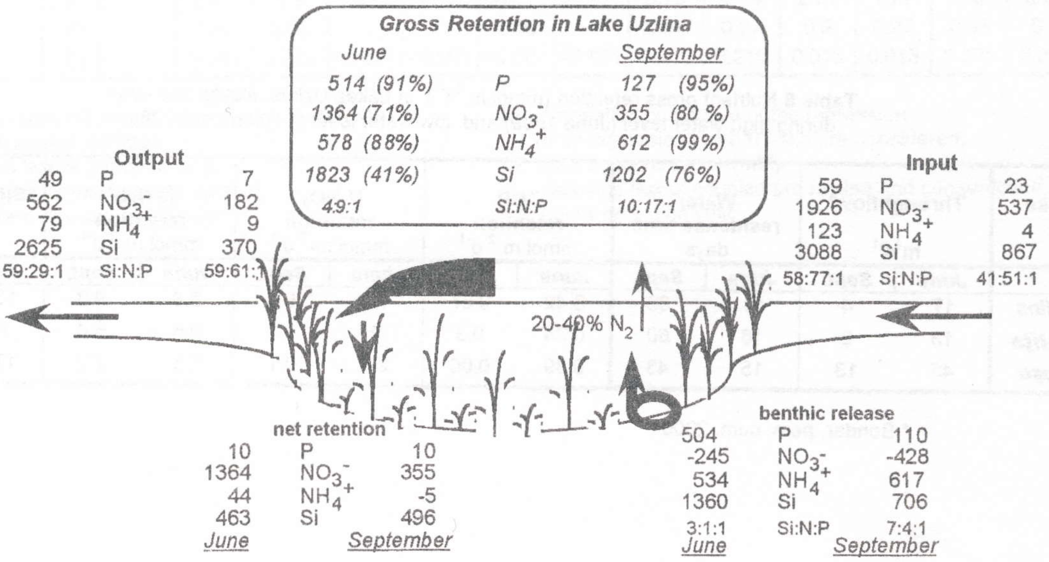

Fig. 3 Nutrient budget for Lake Uzlina at high water level (June 1999) and at low water level (September 1999) (all values are given in kg day^{-1}).

and, therefore, due to more effective nutrient removal processes.

4. CONCLUSIONS

The lakes in the Danube Delta are large sinks for nutrients and, therefore, very important for the self-cleaning capacity of the river system within the Delta. The gross nutrient retention (temporal storage) is more than 80% of the external and internal nutrient input, both in macrophyte and phytoplankton dominated lakes.

The benthic release of nutrients is the important lake-internal source of nutrients within the lakes.

The nutrient input in the lakes decreases with increasing distance from the main Danube branches. Nutrient concentrations at the outflow of the lakes are lower than in the inflow channels.

The question of long term storage of nutrients by sedimentation cannot be answered yet because of the difficulties in determination of sediment accumulation rates due to high sediment mobility.

Winter investigations on benthic nutrient recycling and analysis of organic nitrogen concentrations would help to estimated the long term nutrient removal potential of the lakes.

Acknowledgements. We are grateful to our colleagues from GeoEcoMar in Bucharest and Constanta and to the crew of the tugboat "Poarta Alba" for skillful support during both cruises. Both cruises wouldn't have been possible without the enthusiastic support in Romania by Silviu Rădan, Andrei Ganciu, Dani Grosu, Dan Secrieru, Alina Chiru, Cristian Teodoru, and Cornel Olariu. Constantin Bondar provided data on the hydrology of the Danube Delta. We thank also Nicolae Panin for cooperation. We wish to thank Martin Mengis, Klaus Dombrowski and Antonin Mares for their labwork. This study was supported by the Swiss National Science Foundation, project no. 31-54043.98. J.F. was partly granted by Swiss National Science Foundation.

REFERENCES

BERNER, R.A. ,1980, Early Diagenesis: A Theoretical Approach. Princeton Universitiy Press, Princeton, N.J., 241 p.

BONDAR, C., 1996, Aspects hydrologiques dans "L' étude de cas" du Delta du Danube. GEO-ECO-MARINA, **1**, 67-73, Bucuresti-Constanta.

BUIJSE, A.D., COOPS, H., NĂVODARU, I., DAVID, C., STARAS, M., TUDOR, M., 1997, Eutrophication impacts on submerged vegetation and fishing community in the Danube Delta. RIZA werkdocument 97.169x.

CHRISTENSEN, J.P., MURRAY, J.W., DEVOL, A.H., CODISPOTI, L.A., 1987, Denitrification in continental shelf sediments has major impact on the ocean nitrogen budget. Global biogeochemical sciences, **1**, 2, 97-116.

FRIEDRICH, J., DINKEL, CH., GRIEDER, E., RĂDAN, S., SECRIERU, D., STEINGRUBER, S., WEHRLI, B., (in prep.), Nutrient retention in Danube Delta lakes.

FRIEDRICH, J., DINKEL, CH., ZEPP, K., WEHRLI, B., (in prep.), Benthic decomposition of organic matter in shallow Delta Lakes.

FURRER, G., WEHRLI, B., 1996, Microbial reactions, chemical speciation and multicomponent diffusion in pore waters of an eutrophic lake. Geochimica et Cosmochimica Acta, **60**, 13, 2333-2346.

GÂSTESCU, P., OLTEAN, M., NICHERSU, I., CONSTANTINESCU, A., 1999, Ecosystems of the Romanian Danube Delta. RIZA werkdocument 99.032x.

LI, Y.-H., GREGORY, S., 1974, Diffusion of ions in sea water and in deep-sea sediments. Geochimica et Cosmochimica Acta, **38**, 703-714.

MANHEIM, F.T., 1970, The diffusion of ions in unconsolidated sediments. Earth and Planetary Science Letters, **9**, 307-309.

MENGIS, M., GÄCHTER, R., WEHRLI, B., BERNASCONI, S., 1997a, Nitrogen elimination in two eutrophic lakes. Limnol. Oceanogr., **42**, 1530-1543.

MENGIS, M., GÄCHTER, R., WEHRLI, B., 1997b, Sources and sinks of nitrous oxide (N_2O) in deep lakes. Biogeochemistry, **38**, 281-301.

OOSTERBERG, W., DROST, H.J., DAVID, C., STARAS, M., BOGDAN, L., TÖRÖK, L., 1997, Survey of the trophic state of selected Danube Delta lakes, summer 1996. RIZA werkdocument 97.168x.

PANIN N., 1996, Danube Delta -Genesis, evolution and sedimentology. GEO-ECO-MARINA, **1**, 11-34, Bucuresti-Constanta.

REDFIELD, A.C., 1934, On the proportion of organic derivatives in seawater and their relation to the composition of plankton. James Johnstone Memorial Volume, 176-192, University Press, Liverpool.

SCHLEGEL, H.G., 1985, Allgemeine Mikrobiologie. Georg Thieme Verlag Stuttgart, 417 pp.

TENGBERG, A., DE BOUVEE, F., HALL, P., BERELSON, W., CHADWICK, B., CICCERI, G., CRASSOUS, P., DEVOL, A., EMERSON, S., GAGE, J., GLUD, R., GRAZIOTTIN, F., GUNDERSEN, J., HAMMOND, D., HELDER, W., HINGA, K., HOLBY, O., JAHNKE, R., KHRIPOUNOFF, A., LIEBERMAN, H., NUPPENAU, V., PFANNKUCHE, O., REIMERS, C., ROWE, G., SAHAMI, A., SAYLES, F., SCHURTER, M., SMALLMAN, D., WEHRLI, B., DE WILDE, P., 1995, Benthic chamber and profile landers in oceanography - A review of design, technical solutions and functioning. Progress Oceanography, **35**, 265-294.

ULLMAN, W.J., ALLER, R.C., 1982, Diffusion coefficients in nearshore marine sediments. Limnol. Oceanogr. **27** (3) 552-556.

URBAN N.R., DINKEL, CH., WEHRLI, B., 1997, Solute transfer across the sediment surface of a eutrophic lake: I. Porewater profiles from dialysis samplers. Aquatic Science, **59**, 1-25.

ZEPP K., FRIEDRICH, J., NYUNDU, K., SAHAN, E., WEHRLI, B., (in prep.), Sulfate reducing bacteria and methanogene in sediments of Danube Delta Lakes.