NUTRIENT RETENTION, TOTAL N AND P EXPORT, AND GREENHOUSE GAS EMISSION FROM THE DANUBE DELTA LAKES

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Abstract. The nutrient balance of N and P, the sedimentary production of CH_4 and the diffusive emission rates of CH_4 and CO_2 were analyzed in two lake complexes (Uzlina-Isac and Puiu-Roșu-Roșulet) of the Danube Delta during post-flood conditions in May and at low water level in September 2006. The input of dissolved inorganic N and P to the lake complexes decreased by >53% and 60%, respectively, with increasing distance to the main branches of the Danube. However, by including organic and particulate fractions to the total N and P budget, the input decreased only by ~ 40% and 14%, respectively. Retained nutrients fueled primary production and anaerobic benthic processes such as sulfate reduction and methanogenesis in the sediments particularly in the through-flow lakes receiving inflow from the Danube. Input of CH_4 from the Danube River, from reed beds and benthic release contributed to CH_4 concentrations in surface waters. Next to CH_4, CO_2 was also either transported to these lakes or resulted from aerobic remineralization within the water column and in top sediments. Emission patterns of CO_2 widely overlapped with those of CH_4. The highest greenhouse gas emissions were observed in the lake complex adjacent to the Danube River in May due to strong winds, and they decreased with increasing hydrological distance from the Danube. Overall, this study supports the earlier findings that wetlands are efficiently retaining inorganic nutrients, which become recycled, partially transformed, and exported as organic and particulate N and P. Further, Danube Delta lakes are net sources of atmospheric greenhouse gases due to intense remineralization of organic matter.

Key words: wetland lakes, DIN and SRP retention, TN and TP export, nutritional limitations, methane and carbon dioxide emissions

INTRODUCTION

The Danube Delta is the second largest river delta in Europe (4,455 km^2) after the Volga Delta. It forms a highly productive transition zone between the Danube river system and the Black Sea. The fluvial delta (49%) is strongly influenced by river water from the southern Danube branch, Sfântu Gheorghe. The fluvio-marine delta (51%) is characterized by through-flow and saltwater intrusion from the Black Sea. Hence, the flow direction depends on the height of the water level in the delta relative to the Black Sea, and the water flow is maintained by a sequence of artificial channels. In general, the hydraulic gradient prevents saltwater intrusion into the lakes (Panin 1996).

The Delta itself is the vastest compact zone of reed beds in the world (Oosterberg *et al*., 2000), and effectively filters nutrients, heavy metals and other contaminants from the through flowing water (Friedrich *et al*., 2003). Compared to other deltas in the world, the Danube Delta is 'relatively' unaffected by anthropogenic input (Oosterberg *et al*., 2000). Nevertheless, in the beginning of the last century, and specifically in the last five decades, man-induced changes took place. These encompass channel dredging with the purpose to improve navigation and to let oxygen and nutrient rich water penetrate deeper into the delta to increase fish production. Other changes include the reclamation of about 20% of the delta area as agricultural polders or fishponds, which increased eutrophication. The river water input into the Danube Delta additionally increased from 3% in 1980 up to 10% of the total Danube discharge (Bondar 1996).

Transition towards hypertrophy has affected biodiversity and productivity of most aquatic and wetland systems in the Danube Delta (Cristofor *et al*., 2003). Compared to the early sixties, the loads of inorganic N and P of the Danube River increased five- and three-fold, respectively, and eutrophication became a serious problem not only in the delta lakes but also coastal Black Sea (Almazov 1961, Mee 1992, Cociaşu *et al*,. 1996, Friedrich *et al*., 2002). Even an increased production of greenhouse gases in the Black Sea due to nutritional loading from Danube river water was suggested (Amouroux *et al*., 2002). On the other hand, the self-purification capacity of the delta lakes can preserve the Black Sea ecosystem to a certain degree from nutrient loading and contamination. Therefore, it is essential to better understand nutrient retention versus export in the Danube Delta lakes (DDL).

All DDL sampled in this study (Fig. 1) are eutrophic in respect to N and P concentrations. These lakes show seasonal dynamics with higher N and lower P concentrations in spring than in summer (Oosterberg *et al.,* 2000) and they act as efficient sinks for nutrients during the growing season: Between June and September 1999, the uptake capacity of inorganic nutrient was more than 76% of total input determined from the internal benthic fluxes plus the main external inflows (Friedrich *et al*. 2003). It was further observed that the inorganic N load and nutrient retention rates decrease with increasing hydrological distance from the main rivers of the Danube Delta (Oosterberg *et al*., 2000, Friedrich *et al*., 2003).

Retention of nutrients, their transformation into phytoplankton and plant biomass, and subsequent decomposition in sediments may lead to release of greenhouse gases from DDL. Next to carbon dioxide (CO_2), methane (CH_4) represents an important greenhouse gas in global climate (Cicerone and Oremland 1988), contributing about 15% of the anthropogenic greenhouse effect (Amouroux *et al.,* 2002). Regarding natural sources, methane is mainly (~83%) emitted by wetlands (IPCC 2007). Emission rates are highly variable over space and time, e.g., local emissions from most types of natural wetlands can vary by a few orders of magnitude over a few meters (IPCC 2001). The Danube Delta has been identified as an important source of greenhouse gases to the Black Sea shelf and to the atmosphere (Rădan *et al*., 2000; Amouroux et al. 2002). Although wetlands act as a source of CH_4, most also act as a CO_2 sink due to photosynthesis and sequestration of organic matter in wetland soils or sediments. The balance between net CO_2-assimilation and CH_4-emission determines if a wetland can be regarded as a net sink or a net source of greenhouse gases (Brix *et al*., 2001).

In this study, dissolved inorganic N and P (DIN and SRP) and total N and P (TN and TP) concentrations along throughflow lake systems were determined to better resolve nutrient transport, recycling and nutritional limitations for biomass formation. In addition, benthic releases of methane were

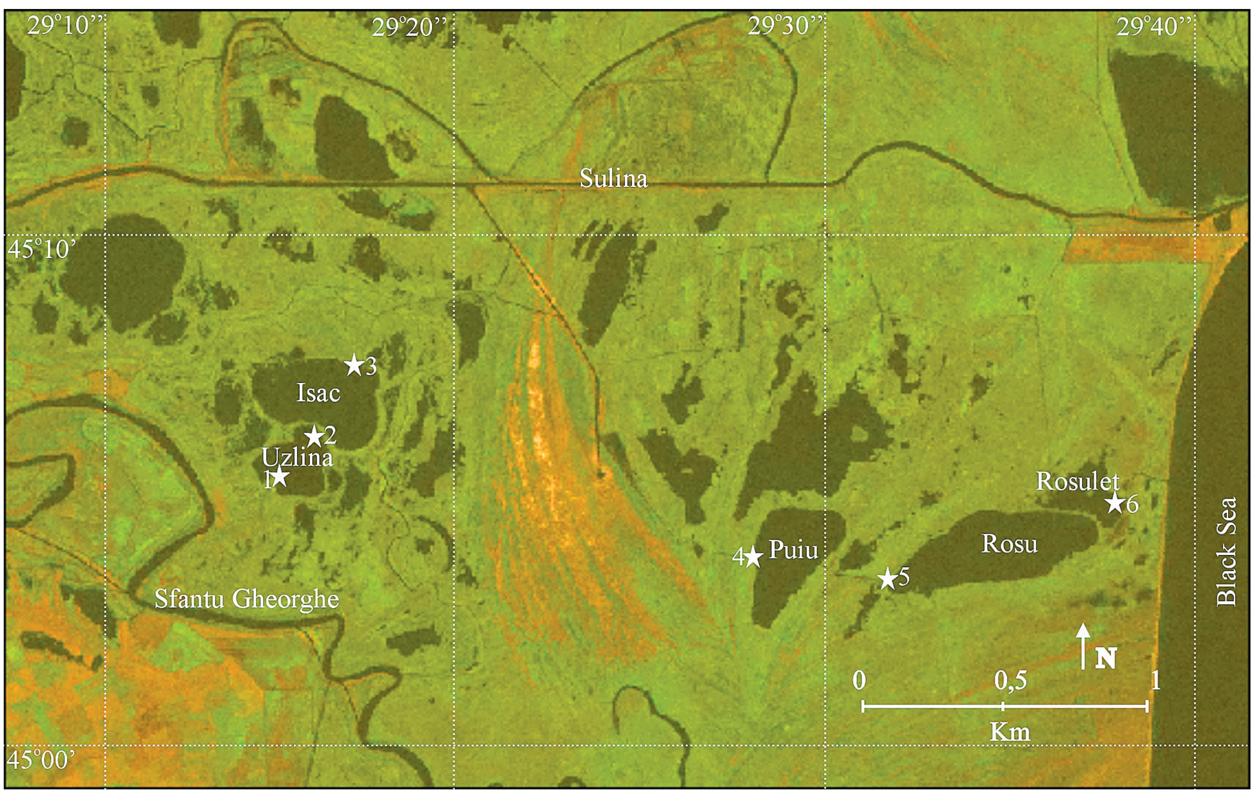

Fig. 1 Selected Danube Delta lakes showing the main sampling stations. White stars indicate the sampling stations: (1) Uzlina-in, (2) Uzlina-out, (3) Isac-out, (4) Puiu-in, (5) Rosu-in, and (6) Rosulet-out. Sulina and Sfantu Gheorghe represent the main branches of the Danube River in the delta influencing the studied lakes

measured to follow up on the remineralization of organic biomass in lake sediments. Determining the flux of CO_2 and CH_4 to the atmosphere finally allowed linking nutrient dynamics and greenhouse gas emissions from large wetland lakes.

MATERIALS AND METHODS

Study sites

Water samples were taken from five through-flow lakes (Table 1) located in the Romanian part of the Danube Delta (Fig. 1). The Lakes Uzlina and Isac (lake complex I) belong to the fluvial delta formed by the Gorgova-Uzlina lake complex (Oosterberg *et al*., 2000), and are strongly influenced by Danube river water. The other three Ls. Puiu, Roşu, and Roşuleţ (lake complex II) are situated further from the Danube branches and belong to the fluvio-marine delta. Based on aquatic vegetation and turbidity, Ls. Uzlina, Roşu, and Roşuleţ qualify as turbid systems, whereas L. Isac behaves as an intermediate between clear and turbid and lacks floating vegetation and large loads of suspended solids (Coops *et al.,* 1999). These lakes receive their water by artificial channels and by the Danube branches Sfântu Gheorghe and Sulina. Lake Roşu is separated only by partially submerged sand bars, reed, and floating reed islands (*Phragmites sp*. plaurs) from Lake Roşuleţ and represents the largest lake in the Danube Delta.

The water level of the Danube and the associated delta rises to highest levels between April and June, and then decreases to lowest levels in September and October (Panin 1996, Constantinescu and Menting 2000). In late fall and winter, when the water level in the Danube Delta is low, water inundating reed areas flows back into the lakes and severe easterly winds might additionally push Black Sea water into the Puiu-Roşu-Roşuleţ complex. The hydraulic residence times during the sampling campaigns varied between 10 and 29 days (Table 1). In May 2006, we encountered post-flooding conditions with extremely high water flow compared to September, when hydrological conditions resembled values as those reported by the Constantinescu and Menting (2000). For example, the mean water level of the Danube River entering Lake Uzlina was 3.7 m in May and 2.3 in September 2006, which can be related to the hydrological mean water level of the Danube River before entering the delta at Tulcea (3.3 m in May and 1.7 m in September).

Sampling and analyses

For nutrient and methane analyses, from each lake either close to the in- or outflow, water column and sediment porewater samples were collected in May and September 2006 (Fig. 1). Water samples were retrieved using a Niskin bottle from three depths (~0.5 m depth, ~1.5 - 3 m depth, and ~0.5 m above sediment). For methane concentration measurements, samples were transferred bubble-free into 25 mL crimp-seal bottles, poisoned with particulate Cu-(I)-Cl (saturated solution), sealed gas-tight, and stored up-side down for further lab analysis at Eawag (Switzerland). For analyses of inorganic N and P concentrations, samples (200 mL) were collected in acid-rinsed HDPE bottles, and stored at 4°C in the dark.

Aliquots (~100 mL) of water column samples were used unfiltered for analyses of total N and total P. Remaining aliquots (~100 mL) were filtered (0.45 µm pore size, cellulose nitrate, Nucleopore) and used for analyses of total dissolved N, nitrate, nitrite, ammonium, total dissolved P, and soluble reactive P (SRP). For N and P analyses, unfiltered and filtered water samples were digested with a peroxodisulfate solution

Table 1 Hydrological data of sampling sites in Ls. Uzlina, Isac, Puiu, Roşu, and Roşuleţ during post-flood conditions in May and low flow in September 2006. Hydrological data are based on the circulation model SOBEK of the Danube Delta (Bondar unpubl. data, Constantinescu and Menting 2000).

Parameters	Uzlina	Isac	Puiu	Roşu	Roşuleţ	Uzlina	Isac	Puiu	Roşu	Roşuleţ
Open water surface area (km^2)	4.83	10.2	8.25	13.65	3.71	4.83	10.2	8.25	13.65	3.71
Reed surface area (km^2)	9.73	15.4	21.08	26.03	14.02	9.73	15.4	21.08	26.03	14.02
Sampling locations	**in- and outflow**	**outflow**	**inflow**	**inflow**	**outflow**	**in- and outflow**	**outflow**	**inflow**	**inflow**	**outflow**
Sampling time (month)	May	May	May	May	May	Sept.	Sept.	Sept.	Sept.	Sept.
Lake volume (n×10^6 m^3)	17.9	40.8	32.2	66.9	15.6	11.1	27.5	28.1	51.9	11.5
Depth at sampling site (m)	3 and 3	4.2	2.8	6.4	4.3	2 and 2	3	3.4	5.8	2
Average depth (m)	3.7	4	3.9	4.9	4.2	2.3	2.7	3.4	3.8	3.1
Average through-flow (m^3 s^{-1})	19	39	22	34	18	13	21	15	21	12
Hydraulic residence time (d)	11	12	17	23	10	10	15	22	29	11

for 1 hour at 120°C to completely oxidize organic N and P to NO_3^- and SRP. In digested and non-digested samples, nitrate, nitrite, and ammonium concentrations were determined colorimetrically by using a Technicon autosampler (DEV 1996). The analytical error of the method was ~5%. Concentrations of DIN, SRP, TN and TP are reported as mean ± one standard deviation (n = 3).

Porewater samples were collected at 1 cm intervals from the top sediment to ~0.5 m depth using dialysis porewater samplers or 'peepers' (Hesslein 1976, Urban *et al*., 1997). Equilibration happens through diffusion of solutes across the dialysis membrane into the cells. The peepers consisted of a plexiglas plate (50×15×1.5 cm) containing about 480 milled cells. Before sampling, all cells were filled with ultrapure and oxygen-free water (Nanopure), and a filter membrane (0.2 µm pore size, Truffyn, Gelman) was mounted on both sides and fixed with plexiglas sheets of the same geometry at the basic plate. At the sampling sites, peepers were manually positioned by a diver in the top sediment. Peepers were recovered four days later and the porewater was extracted with medical syringes from the cells. For CH_4 concentration analysis, 3 ml porewater were transferred to a 25 ml crimp-seal vial, poisoned with Cu-(I)-Cl, sealed gas-tight, and stored for further analyses. For SO_4^{2-} analyses, 5 ml porewater were stored in a clean PP-tube (Greiner) at 4°C in the dark. Sulphate concentrations were measured at Eawag.

Concentrations of CO_2 and CH_4 in lake surface water were assessed using a continuous-flow high-resolution technique. Water was continuously collected *in situ* from a depth of 1 m and pumped (150 L h^{-1}) through a system of three consecutively aligned polypropylene fiber filters (<2 mm pore size) to screen large particles from the samples. The equilibrium between water and air was reached using a water/air equilibrator. Simultaneous recording of GPS coordinates allowed for concentration measurements at high spatial resolution.

Gas measurements were performed using an INNOVA Bruel & Kjaer 1312 multi-gas monitor based on photo-acoustic infrared detection method. The gas sample is pumped from the equilibrator headspace into the detection cell. The infrared light is emitted by a pulsating source, passes a narrow-band optical filter, and is selectively absorbed by the gas trapped. The gas temperature increases and decreases in response to the pulsating light transmitter. This causes an equivalent increase and decrease of the gas pressure in the closed cell. Two ultra-sensitive microphones located in the cell walls are measuring the pressure wave, which is directly proportional to the gas concentration. Carbon dioxide and methane concentrations are measured in parallel by using different optical filters. The detection limits are 3 ppmv for CO_2, and 0.1 ppmv for CH_4. Data are provided at 2 minute intervals. Parameters that influence gas exchange across the water-air interface, such as wind speed, water temperature and air temperature were also measured aboard ship. Wind speed was measured at about 12 m height.

Flux calculations

Benthic fluxes (µmol m^{-2} h^{-1}) of methane and sulphate across the water-sediment interface were calculated along linear concentrations changes with sediment depth using Fick's first law of diffusion. As molecular diffusion coefficients (m^2 s^{-1}) we used 1.57×10^{-9} for methane and 9.4×10^{-10} for sulphate (after Furrer and Wehrli 1996). The gas fluxes across the water-air interface were calculated from the transfer velocity using the relations of Crusius and Wanninkhof (2003) and the Schmidt numbers of the gases (Jahne *et al*., 1987).

RESULTS AND DISCUSSION

Distribution and retention of dissolved inorganic N and P in through-flow lakes

At Uzlina-in, concentrations of DIN and SRP were among the highest measured along the through-flow in the DDL (Fig. 2), and resembled values from Danube river water (112 µM DIN and 2.7 µM TP) measured at the outflow of the Iron Gate I Dam (Schreiber *et al*., 2003). Hence, water flowing into lake complex I was derived almost directly from the Danube River, which is also corroborated by other studies (Constantinescu and Menting 2000, Garnier *et al*. 2002, Friedrich et al. 2003). At Uzlina-in, concentrations of 84±6 µM DIN and 0.9±0.2 µM SRP were measured in May, and 75±3 µM DIN and 2.9±0.3 µM SRP in September (Fig. 2). Seasonal differences were only observable through loading of Uzlina-in with river-derived P in September, which was previously also observed by Oosterberg *et al*. (2000). In fall, SRP concentrations were by a factor of three higher than in spring. Extreme flooding in April and May 2006 may have resulted in a dilution of riverine concentrations, although it is assumed that P transport in streams does not significantly change during increased hydrological flow (Zessner *et al*., 2005).

Leaving Lake Isac, the water flows through a series of channels and reed beds until it is diverted into the Puiu-Roşu-Roşuleţ lake complex II (Fig. 1). At the inlet (Puiu-in), the values of DIN changed from 28±1 to 5±2 µM and those of SRP from 0.9±0.02 to 0.4±0.01 between May and September 2006 (Fig. 2). Furthermore, in May, concentrations were higher at Puiu-in relative to the outflow of lake complex I. This surplus may result from nutrient input by the Crişan channel and from remineralization of organic materials, particularly in the flooded reed beds. However, these processes seem to become insignificant during low hydrological flow in September (Table 1), when nutrient concentrations were very similar at Isac-out and Puiu-in. Minor decreases in oxygen concentrations during channel transport in September indicate reduced remineralization, while substantial changes in O_2 in May suggest higher mineralization rates (data not shown). This observation is further corroborated by less benthic consumption of sulphate and less release of methane at Isac-out, and Puiu-in in fall than in spring.

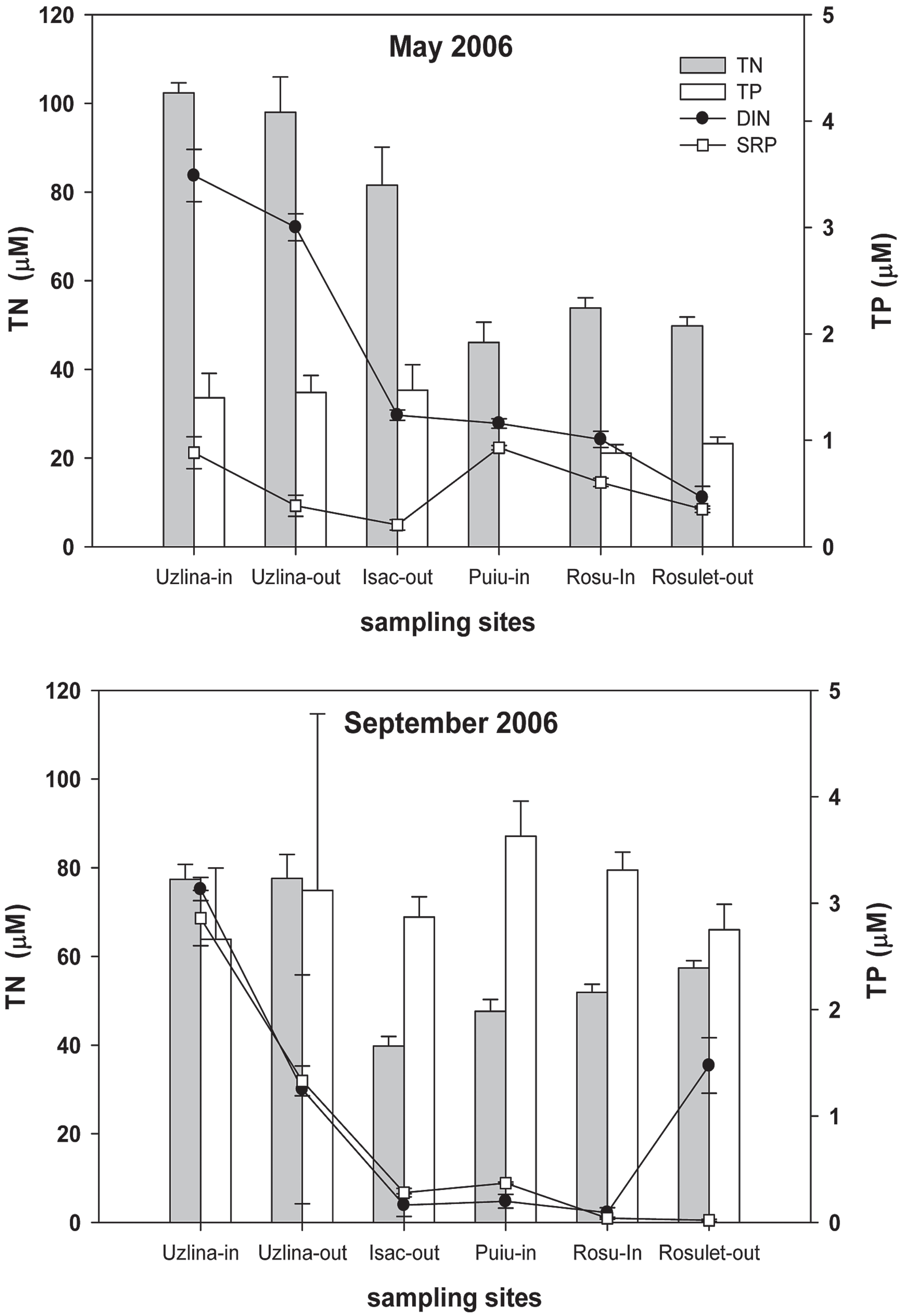

Fig. 2 Concentrations of DIN, SRP, TN, and TP are shown along through-flow (6 sampling sites) in the Danube Delta lakes (Fig. 1) in May (upper panel) and September 2006 (lower panel)

Within both lake complexes a strong reduction in concentrations of inorganic N and P supplied by the Danube River could be observed. In lake complex I (between Uzlina-in and Isac-out), the amount of DIN decreased by 65%, in May and by 95%, in September, and the amount of SRP by 77% and 90%, respectively (Fig. 2). Similarly, along through-flow in lake complex II (from Puiu-in to Roşuleţ-out), concentrations of DIN decreased by 60% in May, and concentrations of SRP by 62% in May and 93% in September (Fig. 2). Interestingly, in September DIN concentrations first decreased in Lakes Puiu and Roşu, however, then strongly increased again, by 87% in Lake Roşuleţ, probably due to high benthic nitrification (Friedrich *et al*., 2003) or remineralization of organic N compounds. On average, along the whole through-flow, DIN reduction equalled 87% in May and 53% in September (including DIN release in Lake Roşuleţ), and SRP reduction was 60% and 99%, respectively. Overall, retention of DIN and SRP in both lake complexes confirmed that wetlands act as an efficient trap for inorganic N and P species (*e.g*., Arrigoni *et al*., 2008), and that retention decreases with hydrological distance from the main Danube River branches (Friedrich *et al*., 2003). In contrast to this earlier investigation nutrient uptake was higher in spring than in fall, except for Lake Roşuleţ. We may explain this trend by chlorophyll$_a$ concentrations that were observed to be lower in June than in September, particularly in Ls. Isac, Puiu, Roşu and Roşuleţ (Oosterberg and Bogdan 2000). We presume that biomass of phytoplankton, algae, and macrophytes was higher in fall than in spring, and N and P demand increased during that phase. Due to reduced hydrological flow by factors of 1 to 2 (Table 1), high consumption may result in intense removal of DIN and SRP from the water column. Therefore, we suspect that the flooding situation in May might have drastically increased transport processes relative to rates of biological uptake.

Total N and P transport in the Danube Delta lakes

Inorganic nutrients are efficiently retained in the DDL and converted into biomass or lost due to denitrification in lake sediments (Friedrich *et al*., 2003, Wetzel 2006). This biomass may eventually contribute to the formation of organic N and P in the particulate or dissolved form (Wetzel 1979, Childers *et al*., 2000). Depending on its bioavailability, organic N and P may become either remineralized or transported downstream. In many studies, such as by Friedrich *et al.* (2003), the purification capacity of wetland systems is overestimated because organic N and P have been neglected. In this survey, the amount of TN and TP were measured to include the organic and particulate fraction into the N and P budget. Concentrations of TN and TP at Uzlina-in were 102±3 μM and 1.4±0.2 μM in May, and 77±4 μM and 2.7±0.7 μM in September (Fig. 2). At this site most of TN and TP resided in the inorganic form, whereas with increasing distance from the Danube River increasing proportions of organic as well as particulate N and P were formed and transported in the DDL. It is estimated that up to 50% of TN and 60% of TP resided in organic and/or particulate form. On average (spring and fall), the retention of TN and TP amounted to 40% and 14% along through-flow, respectively. Hence, retention of N and P was far less pronounced in the DDL than if inferred from retention of dissolved inorganic N and P only. The results point to an important role of nutrient incorporation into dissolved and particulate organic matter, affecting the N to P balance of Danube Delta wetlands (Durisch-Kaiser *et al*., unpublished data).

Quantification of nutrient retention in terms of overall transport by the Danube River helps to evaluate its impact on coastal eutrophication in the Black Sea. We assume that approximately 10% of discharge from the River Danube flows through the delta (Friedrich *et al.*, 2003). We further assume that seasonal variability in nutrient uptake is reflected by May and September 2006. Consequently, roughly 4% of TN and 1.4% of TP transported in Danube river water are retained per year in the delta. These numbers are lower than expected from former studies (Friedrich *et al*., 2003), because we take into account the export of organic and particulate N and P fractions. Using an average discharge of 6460 m^3 s^{-1} (ICPDR 2004), this will amount in a reduction of the river's inorganic nutrient load by ~10 kt N y^{-1} and ~0.2 kt P y^{-1}, representative for abstraction of 2.9% N and 0.8% P from the total riverine N and P load per year to the Black Sea (Teodoru *et al*., 2007). Hence, the delta represents an important sink for total N, whereas only a minor sink for total P.

Nutritional limitations

Biomass production demands variable amounts of N and P. Thus, the elemental ratios from TN and TP can be used as indicators for nutrient uptake and also nutritional limitations (Sommer 1990, Guildford and Hecky 2000, Frost *et al*., 2002). From total pools, the TN:TP ratios severely changed from Uzlina-in to Roşuleţ-out. In May, TN:TP ratios were declining from 74 to 34 in lake complex I and then again increased to maximal 61 in complex II. In September, TN:TP ratios were low relative to May, indicating increased N deficiency, but, trends were similar. The TN:TP ratio first decreased in lake complex I (from 31 to 14), but then increased again towards Roşuleţ-out (from 13 to 21). Hence, in May extreme P limitation occurred in complex I, but became less pronounced along transport pathways to the Black Sea. Phosphorous may be regenerated and nutrient limitations altered during transport through channels and reed beds. Carpenter and Lodge (1986), *e.g.*, showed that release of P from aquatic plant detritus mainly occurs via decomposition. On the other hand, in September, when nutrient retention peaked, P limitation was less prominent in complex I, and slightly shifted towards N limitation when passing through complex II. Hence, depending on the strength of nutrient removal, transport through the DDL may even result in a switch of nutritional limitations between the two lake complexes. We suggest different nutrient uptake dynamics in the two lake complexes, due to changes in phytoplankton, algae, and macrophyte biomass and species composition (Ibelings *et al*., 2000). Seasonal differences may also be explained by changes in species composition. It was reported that cyanobacteria start to increase their biomass after June, indicating increasing N limitation in the fall.

Benthic release of greenhouse gases

In the following section, we try to develop a better understanding of the relationship between nutrient retention and organic matter remineralization along through-flow in DDL sediments. Benthic remineralization of riverine and in-lake produced organic biomass not only contributed to greenhouse gas release from the coastal Black Sea (Amouroux *et al*., 2002), but also substantially from both lake complexes (Table 2). Methane release from shallow sediments was high at Uzlina-in compared to the other lakes in complex I in May and September, and compared well to other eu- and hypertrophic lakes (Matthew *et al.,* 2005, Huttunen *et al*., 2006). This was explained by high loads of biomass from primary production boosted by nutrient uptake. Such a particularly intense algal bloom was observed in L. Uzlina in September. In addition, deposition of riverine organic particles may further load sediments of the first delta lake in complex I with organic matter. Export of riverine organic particles tends to increase with stream size and during floods (Meybeck 1981), and the material is widely bioavailable, especially if particles derive from autochthonous sources (Raymond and Bauer 2001, Kaiser *et al*., 2004). In L. Uzlina, particles are most possibly remnants of phytoplankton material and decomposing algae and macrophytes.

Benthic release of methane decreased along through-flow in lake complex I (Table 2). This may have resulted from less organic matter deposition at the outlet of Ls. Uzlina and Isac as compared to the inlet. Sulphate reduction and methanogenesis were almost equally high in sediments in May, because sulphate influx to top sediments was in the order of methane efflux. In September, methanogenesis clearly dominated anaerobic decomposition in sediments.

Table 2 Benthic fluxes of methane and sulphate calculated from the sediment-water interface in the different lakes in May and September 2006. Positive sediment-water flux indicates efflux, negative values indicate influx. n.d. = not determined.

	CH_4 (µmol m^{-2} h^{-1})		SO_4^{2-} (µmol m^{-2} h^{-1})	
Sampling time	May	September	May	September
Uzlina-in	299	86	-324	-19
Uzlina-out	67	n.d.	-90	n.d.
Isac-out	152	138	-88	-15
Puiu-in	377	99	-188	-80
Roşu-in	291	203	-267	-5
Roşuleţ-out	78	116	-248	-113

Leaving L. Isac, water is diverted through a series of channels and through reed beds until it enters lake complex II at Puiu-in. At this site, benthic release of methane was highest among all lakes in May, but modest in September (Table 2). It is assumed that in May organic matter deposition is also enhanced at the inlet to Lake Puiu, due to organic matter input from the Crişan channel. In addition, benthic P regeneration during channel transport may have diminished P limitation for primary production. In analogy to lake complex I, benthic release of methane also strongly decreased in the Puiu-Roşu system with longitudinal transport of water masses in May. We partially associate this decrease with decreasing availability of nutrients, hence, reduced primary productivity. In September, benthic releases of CH_4 were highest in Lake Roşu, which might be explained by high deposition of algal material from intense blooms that occurred throughout fall in that lake. Comparable to lake complex I, sulphate reduction dominated in May, whereas methanogenesis dominated benthic remineralization in September. Sulphate influx to sediments was high in September in Roşuleţ-out, which might be explained by reversal of flow direction and intrusion of sulphate-richer seawater from the Black Sea during low water level.

Greenhouse gas emissions from Danube Delta lakes

Seasonal monitoring of greenhouse gas fluxes from surface waters of selected lakes showed that CO_2 and CH_4 emissions peaked in lake complex I, particularly in L. Isac in May, due to strong winds (Table 3). Patterns in gas release only partially overlaid with water column concentrations and benthic effluxes of methane (Table 2), suggesting that several factors like lake depths, hydrology, locally different wind-driven mixing, water column temperature and methanotrophic activity might govern diffusive fluxes. Water column concentrations and effluxes measured compare well to literature data collected from eutrophic and hypertrophic lakes (Cole and Caraco 2001, Casper *et al*., 2000). However, note that high standard deviations show high spatial variability of fluxes to the atmosphere (Table 3).

In lake complex I in May, concentrations of CO_2 were highest in L. Uzlina due to massive input of CO_2 from the Danube River, canals, reed beds during flood, and due to remineralization of organic matter within the lake. Generally, river water is known to be supersaturated with CO_2 (Cole and Caraco 2001, Richey *et al*., 2002), particularly downstream of dams (Guerin et al., 2006). Danube water contained approximately 37 µM CO_2 before entering lake complex I (unpublished data). This value is lower than the average concentration of 103 µM found in L. Uzlina in spring, implying that massive remineralization of organic matter in reed beds and lake sediments contribute significant amounts of CO_2 to average concentrations recorded. The average CO_2 efflux from surface water was about 2.3 mmol m^{-2} h^{-1} from this lake in May, and highest diffusive losses occurred at Uzlina-in and Uzlina-out (data not shown). Comparably, about double the amount of CO_2 was released from

Table 3 Surface water concentrations (mean ± standard deviation), and fluxes across the air-water interface (mean ± standard deviation) of CO_2 and CH_4 from the studied lakes. Positive air-water flux indicates emission to the atmosphere. n.d. indicates no data.

Parameters	Uzlina	Isac	Puiu	Roşu	Roşuleţ	Uzlina	Isac	Puiu	Roşu	Roşuleţ
Sampling time in 2006 (month)	May	May	May	May	May	Sept.	Sept.	Sept.	Sept.	Sept.
CO_2 concentration (μM)	103 ± 49	49 ± 35	142 ± 77	110 ± 70	63 ± 69	18 ± 10	27 ± 17	n.d.	26 ± 27	n.d.
CH_4 concentration (nM)	714 ± 257	569 ± 370	891 ± 424	534 ± 113	738 ± 575	644 ± 224	613 ± 161	n.d.	538 ± 119	n.d.
CO_2 air-water flux (mmol m^{-2} h^{-1})	2.3 ± 1.3	4.9 ± 4.5	3.4 ± 2.0	2.4 ± 1.8	0.7 ± 1.0	0.2 ± 0.4	1.2 ± 1.7	n.d.	0.1 ± 0.4	n.d.
CH_4 air-water flux (μmol m^{-2} h^{-1})	18 ± 7	80 ± 51	23 ± 11	13 ± 3	11 ± 9	26 ± 9	62 ± 17	n.d.	7 ± 2	n.d.

lake Isac (4.9 mmol m^{-2} h^{-1}), due to strong winds. High input of dissolved CH_4 may also result from the Danube River since rivers downstream of dams not only carry high concentrations of CO_2 but also of CH_4 (Guerin *et al*., 2006). Note that methane concentrations were homogeneously distributed in lake complex I in May. Similar to CO_2, CH_4 efflux was also enhanced by strong winds in L Isac in May. Methane released from benthic decomposition at Uzlina-in further seemed to enforce CH_4 emission at Uzlina-out (data not shown) and in L. Isac (Table 4). This transport of dissolved CH_4 matched well with the current water circulation model within lake complex I (Driga 2004).

In L. Puiu (lake complex II), water column concentrations of CO_2 and CH_4 were strongly impacted by input of water from the Crisan channel in the western part and highest among all lakes investigated in May (Table 3). Nevertheless, only 3.4 mmol m^{-2} h^{-1} of CO_2 and 2.3 μmol m^{-2} h^{-1} of CH_4 were released from this lake in May, with peaks close to the canal entrance (data not shown). Emission of methane can be related to high benthic CH_4 release in May (Table 2). With further longitudinal transport of water masses to Lake Roşu, surface water concentrations of CO_2 decreased, whereas CH_4 stayed fairly constant (Table 3). In comparison, surface emissions of CO_2 and CH_4 decreased along longitudinal transport to minimum values in L. Roşuleţ, a lake in which discharge is most stagnant (Constantinescu and Menting 2000, Table 3).

In September, during hydrological low flow and weak winds, massive algal blooms and macrophyte biomass potentially consumed large proportions of dissolved CO_2 in L. Uzlina and L. Isac, which resulted in reduced emissions compared to May from both lakes (Table 3). Interestingly, surface water methane concentrations were also high during fall although benthic release had ceased compared to May. Compared to CO_2, this is explained by small surface efflux due to weak winds.

Unfortunately, L. Puiu was not studied in fall, due to low water level. It can be expected that during stagnant flow, weak winds, and moderate benthic release of methane in the fall season reduced methane effluxes occurred. In contrast, Lake Roşu is the largest and deepest lake among all, and CO_2 and CH_4 concentrations are increased and comparable to values from lake complex I. They may result from decomposition of intense algal biomass, which was observed there in fall. Weak wind-forcing may explain why emission from this lake is again low (Table 3).

CONCLUSIONS

This study allowed evaluating N and P retention in the Danube Delta lakes *versus* export to the Black Sea and *versus* patterns of greenhouse gas emission. The Danube Delta wetland efficiently traps inorganic nutrients as well as TN, however, to a minor extent only TP. It was estimated that 2.9% of TN and 0.8% of TP from total loads of the Danube River are retained in the delta, and organic and particulate N and P fractions significantly contribute to export of TN (~50%) and TP (~60%) from the delta lakes. Nutrient retention and preferential P mineralization along the flow path between lake complex I and II shifted nutrient ratios from severe P limitation towards slight N deficiency. This trend can be linked to the current understanding of phytoplankton biomass and species distribution in the DDL. At locations of large nutrient and external organic matter input, particularly at Uzlina-in and Puiu-in, an additional massive internal built-up of organic matter sustained intensive benthic remineralization and, hence, high benthic release of methane. In spring 2006, when nutrient availability was diminished along the through-flow, benthic consumption of sulphate and release of methane also decreased. The fall season showed reversed conditions due to stagnant flow, potential saltwater intrusions in L. Roşuleţ, and strong biomass production in Ls. Isac and Roşu/Rosuleţ.

In analogy to nutrients, water column CO_2 and CH_4 derive not only from benthic remineralization but also from input of river or canal water, which, *e.g*., can be clearly observed at Uzlina-in and Puiu-in. Emissions of CO_2 and CH_4 to the atmosphere were only partially coupled to surface water CO_2 and CH_4 concentrations and benthic effluxes of methane, which is explained by different lake depths, hydrology, seasonally different wind strengths, and water column methanotrophic activity. We observed high CO_2 and CH_4 effluxes in the spring time resulting from strong winds, and reduced outgassing in the fall due to stagnant conditions, lower temperature and slow wind speed.

In summary, in this vast wetland greenhouse gas production and emission can be positively correlated to patterns of nutrient input and retention. New and more accurate information on the distribution of dissolved and particulate organic N and P will improve the understanding of nutrient dynamics and export from the DDL. This pilot study shows that improving the spatial resolution of greenhouse gas analyses in such complex wetland-lake environment holds great promise in linking hotspots of emissions with the governing biogeochemical and physical processes.

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