

## Losses of inorganic carbon and nitrous oxide from a temperate freshwater wetland in relation to nitrate loading

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**Abstract.** We studied the export of inorganic carbon and nitrous oxide ( $\text{N}_2\text{O}$ ) from a Danish freshwater wetland. The wetland is situated in an agricultural catchment area and is recharged by groundwater enriched with nitrate ( $\text{NO}_3^-$ ) ( $\sim 1000 \mu\text{M}$ ).  $\text{NO}_3^-$  in recharging groundwater was reduced ( $57.5 \text{ mol NO}_3^- \text{ m}^{-2} \text{ yr}^{-1}$ ) within a narrow zone of the wetland. Congruently, the annual efflux of carbon dioxide ( $\text{CO}_2$ ) from the sediment was  $19.1 \text{ mol C m}^{-2}$  when estimated from monthly in situ measurements. In comparison the  $\text{CO}_2$  efflux was  $4.8 \text{ mol C m}^{-2} \text{ yr}^{-1}$  further out in the wetland, where no  $\text{NO}_3^-$  reduction occurred. Annual exports of inorganic carbon in groundwater and surface water was  $78.4 \text{ mol C m}^{-2}$  and  $6.1 \text{ mol C m}^{-2}$  at the two sites, respectively.  $\text{N}_2\text{O}$  efflux from the sediment was detectable on five out of twelve sampling dates and was significantly ( $P < 0.0001$ ) higher in the  $\text{NO}_3^-$  reduction zone ( $0.35\text{--}9.40 \mu\text{mol m}^{-2} \text{ h}^{-1}$ , range of monthly means) than in the zone without  $\text{NO}_3^-$  reduction ( $0.21\text{--}0.41 \mu\text{mol m}^{-2} \text{ h}^{-1}$ ). No loss of dissolved  $\text{N}_2\text{O}$  could be measured. Total annual export of  $\text{N}_2\text{O}$  was not estimated. The reduction of oxygen ( $\text{O}_2$ ) in groundwater was minor throughout the wetland and did not exceed  $0.2 \text{ mol O}_2 \text{ m}^{-2} \text{ yr}^{-1}$ . Sulfate ( $\text{SO}_4^{2-}$ ) was reduced in groundwater ( $2.1 \text{ mol SO}_4^{2-} \text{ m}^{-2} \text{ yr}^{-1}$ ) in the zone without  $\text{NO}_3^-$  reduction. Although the  $\text{NO}_3^-$  in our wetland can be reduced along several pathways our results strongly suggest that  $\text{NO}_3^-$  loading of freshwater wetlands disturb the carbon balance of such areas, resulting in an accelerated loss of inorganic carbon in gaseous and dissolved forms.

## Introduction

Most atmospheric carbon fixed during net primary production is lost from wetlands during decomposition processes (Morris & Lajtha 1986), but the oxygen ( $\text{O}_2$ ) depletion common to wetland sediments (e.g. Nyman & DeLaune 1991; Devito & Dillon 1993), often reduces decomposition rates compared to aerated conditions (Gale & Gilmour 1988). This is because electron acceptors other than  $\text{O}_2$  are less favorable with respect to available energy from a thermodynamic perspective (Korum 1992).

Depending on the redox conditions, carbon losses from wetland sediments to the atmosphere occur as gaseous carbon dioxide ( $\text{CO}_2$ ) or methane ( $\text{CH}_4$ ), either as efflux directly from the sediment surface (Raich & Schlesinger 1992)

or through air spaces of plants (Sorrel & Boon 1994). Sediment physico-chemical conditions exert major control on the  $\text{CO}_2$  efflux, which for example increases in response to greater nutrient availability (Bridgham & Richardson 1992). However, groundwater transport of dissolved and particulate forms also contribute to inorganic carbon losses from sediments (Howes et al. 1985; Pulliam 1993), although the hydrological mediation of inorganic carbon transport in wetlands has received little attention.

Many studies indicate that wetlands have a high potential to reduce natural and anthropogenic inputs of nitrate ( $\text{NO}_3^-$ ) (Brinson et al. 1984; Devito et al. 1989). Nitrous oxide ( $\text{N}_2\text{O}$ ) is produced in most nitrate reduction pathways (Tiedje 1988; Bowden 1987) as well as in biomass burning and fuel combustion. Eichner (1990) recently showed that nitrogen fertilization of soils results in substantial  $\text{N}_2\text{O}$  efflux to the atmosphere, and soil processes may contribute up to 90% of the annual global  $\text{N}_2\text{O}$  emission (Bouwman 1990).  $\text{N}_2\text{O}$  is also soluble in water, and groundwater may act as a vector, transporting  $\text{N}_2\text{O}$  produced in agricultural soils to riparian wetlands. The behaviour of  $\text{N}_2\text{O}$  in groundwater from such ecosystems is almost unknown at present. In a riparian forest the efflux of  $\text{N}_2\text{O}$  was insignificant and showed no correlation to other soil parameters such as the concentration of  $\text{NO}_3^-$  in groundwater (Weller et al. 1994).

We hypothesize that as anthropogenic inputs of  $\text{NO}_3^-$  to wetlands increase, carbon turnover may be intensified and significantly increase the export of dissolved and gaseous inorganic carbon compounds. Also the export of  $\text{N}_2\text{O}$  can be expected to increase. There is concern that increased efflux of such gases to the atmosphere contributes to greenhouse warming and climate change (Denmead 1991).

In this study our aim was to examine the export of inorganic carbon from a temperate freshwater wetland in relation to  $\text{NO}_3^-$  loading. Monthly in situ measurements of  $\text{CO}_2$  and  $\text{N}_2\text{O}$  efflux from the sediments to the atmosphere were made at sites with and without strong nitrate reduction in the groundwater. In groundwater and surface water we also measured concentrations of dissolved inorganic carbon (DIC), dissolved  $\text{N}_2\text{O}$ ,  $\text{O}_2$ ,  $\text{NO}_3^-$ , and sulfate ( $\text{SO}_4^{2-}$ ) to quantify the export or consumption of these chemical constituents.

## **Materials and methods**

### *Study area*

The study area is a riparian freshwater wetland at the Voldby Stream, Denmark ( $56^\circ 14' \text{ N}$ ,  $9^\circ 49' \text{ E}$ ), situated in an agricultural catchment area. The vegetation

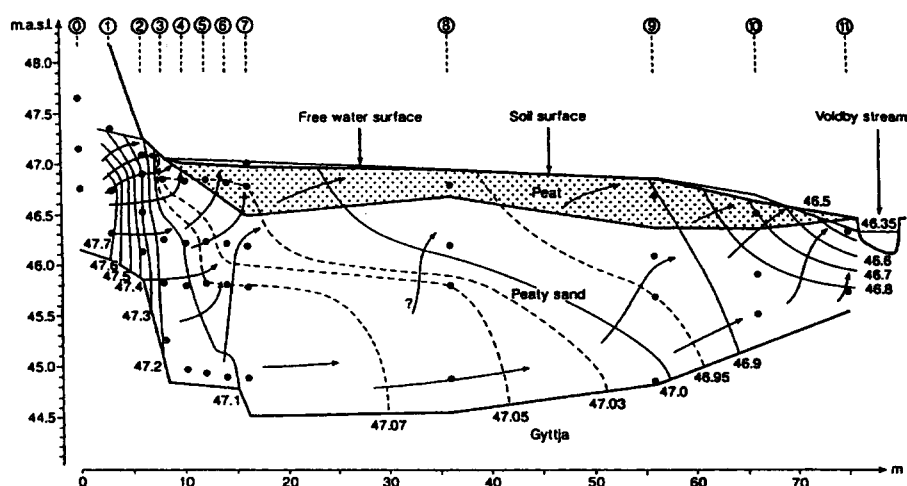


Figure 1. Cross section of the wetland showing the geological sediment profile and equipotential curves of hydraulic potentials (solid and stippled lines; meter water column), measured in piezometers ( $\odot$ , nests 0–11). Positions are in metres above sea level (m.a.s.l.). Arrows in bold indicate groundwater flow pattern (Redrawn from Dahl [1995]).

is characterized by scattered stands of alder and willow and a diverse herb layer (e.g. *Carex paniculata*, *Epilobium palustre*, *Glyceria maxima*, *Phalaris arundinacea*, *Scirpus sylvaticus*, *Typha latifolia*). The sediment profile is composed of an upper layer of fibric peat to a depth of ~50 cm. This is followed by peaty sand to a depth of ~200 cm which is succeeded by impermeable gyttja (Figure 1). The sediment composition has been described in detail elsewhere (Dahl 1995, Paludan 1995).

The wetland is fed by groundwater discharging from the surrounding agricultural land. Nearly all of the 0.314 ha wetland area is permanently inundated with shallow water, resulting in a surface sheet flow towards the stream.

The study of inorganic carbon and nitrogen fluxes was made at two sites within the wetland (Figure 2). Site LN was placed between piezometer nest 3 and 4 where the sediment was waterlogged but rarely inundated. Site LF was placed at piezometer nest 8. Shallow water to a depth of 5–10 cm permanently inundated this site.

### Hydrology

A transect of piezometers was established from the hillslope to the stream (Figure 2) along the apparent groundwater flowline. The piezometers (bottom 10 cm with screen) were installed in 3 to 4 depths from 15 cm to approximately 205 cm depth (Figure 1). Hydraulic potentials were measured monthly in

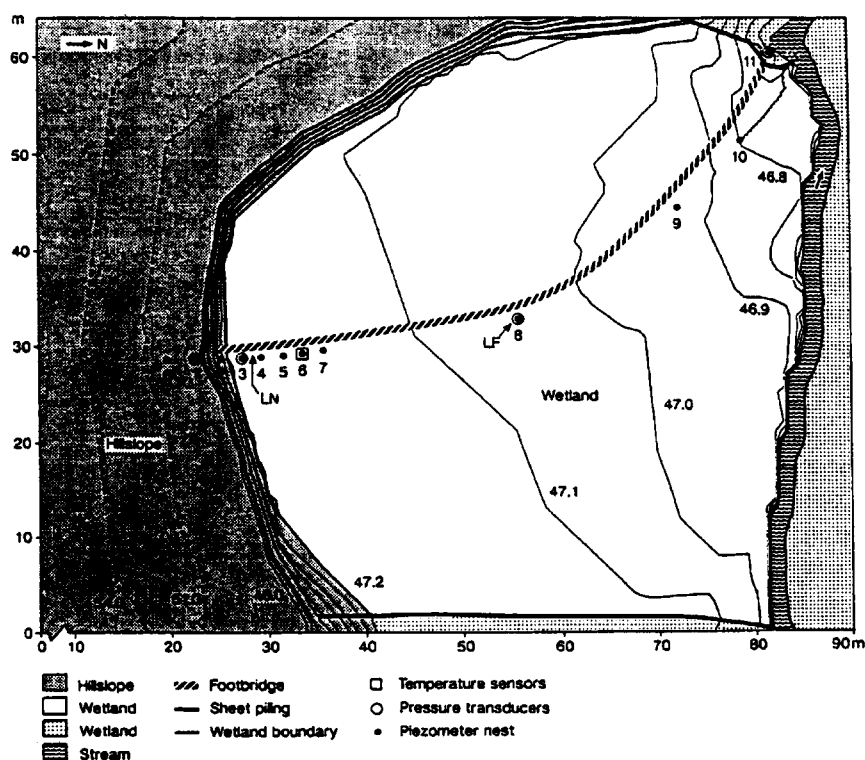


Figure 2. Topographic map showing the study area. Numbers (0–11) indicate piezometer nests. As indicated by arrows study site LN was situated between piezometer nest 3 and 4 and study site LF at piezometer nest 8. Contour lines indicate level above sea (metres) (Redrawn from Dahl [1995]).

the period from July 1993 to June 1994 (except for January and February because of ice). The groundwater flow at the two study sites was calculated by Darcy's law (Freeze & Cherry 1979) using an aquifer depth of 60 cm (15 to 75 cm depth). From the equipotential curves of hydraulic potentials (Figure 1), the direction of groundwater flow at site LN was determined to be between piezometer 3–75 [first number refers to piezometer nest and last number to depth (in cm)] and 4–15. The horizontal distance between these piezometers are 2 m and the groundwater flow is characterized by upwelling which connects the different sediment layers hydrologically. Also, at site LF the fibric peat and the sandy peat layers were hydrologically connected due to upwelling groundwater. However, at this site the dominant flow direction was between piezometer 7–15 and 8–15 and between piezometer 7–75 and 8–75, and these flow directions were used when calculating the groundwater flow. The horizontal distance between these piezometer nests is 20 m. The

hydraulic conductivity in the sediment profiles was determined by bromide addition and recollection (Dahl 1995), and was  $1 \times 10^{-5} \text{ m sec}^{-1}$  between piezometer 3–75 and 4–15 as well as in the peaty sand between piezometer 7–75 and 8–75. In the peat between piezometer 7–15 and 8–15 the value has been estimated to be  $4 \times 10^{-6} \text{ m sec}^{-1}$  (Dahl 1995). The vertical distribution of different hydrological conductivities was accounted for in the calculation of flow rates between piezometer nest 7 and 8.

Based on fortnightly flow determinations throughout 1993 the surface runoff to the stream was on average  $3000 \text{ l h}^{-1}$  (range  $1700$  to  $4600 \text{ l h}^{-1}$ ) for the entire wetland (Dahl 1995). However, surface transport of water is only of significance at site LF.

### *Gas sampling*

Measurements of  $\text{CO}_2$  and  $\text{N}_2\text{O}$  fluxes from the sediment to the atmosphere were made monthly (July 1993 to June 1994) at the two sites. To measure gas flux, PVC chambers (25 cm long by 10.0 cm inner diameter, with the one end capped) ( $n = 5$  per site) were placed into specially designed chamber holders within  $1 \text{ m}^{-2}$  of the sediment, resulting in 10 cm of the chamber being above ground. A chamber holder consisted of a double walled PVC tube (16 cm long by 8.5 cm in inner and 11.0 cm in outer diameter) placed permanently in the sediment between the vegetation and with the top edge on a level with the sediment surface. Between sampling events numerous slits in both the inner and outer wall allowed exchange of water and nutrients between the sediment contained in the holder and the exterior.

Before sampling, the incubation chambers were gently placed into the holders and a rubber septum placed on top of each chamber for gas sampling. When necessary, chambers were shaded against solar radiation to prevent high temperatures inside the chambers. The in situ measurements were always initiated at 9 am. From July 1993 to September 1993 the incubation period was 2 1/2 hour and samples were collected at 30 min intervals. For practical purposes the incubation period was shortened to 1 1/4 hour at the remaining sampling events. Thus, from October 1993 to June 1994 gas samples were collected at 15 min intervals. Within the incubation period a linear accumulation of gasses occurred in the chambers (Figure 3). Within each time interval one sample of 5 ml gas was withdrawn from each incubation chamber using a glass syringe. After drawing the gas sample the syringe piston was filled with liquid paraffin and closed with a rubber cap to prevent contamination with atmospheric air. To prevent a vacuum build up in the incubation chamber and a consequent risk of contamination with atmospheric air, 5 ml of atmospheric air was injected into the chamber after each gas sample withdrawal. The calculated gas fluxes were later corrected for this dilution.

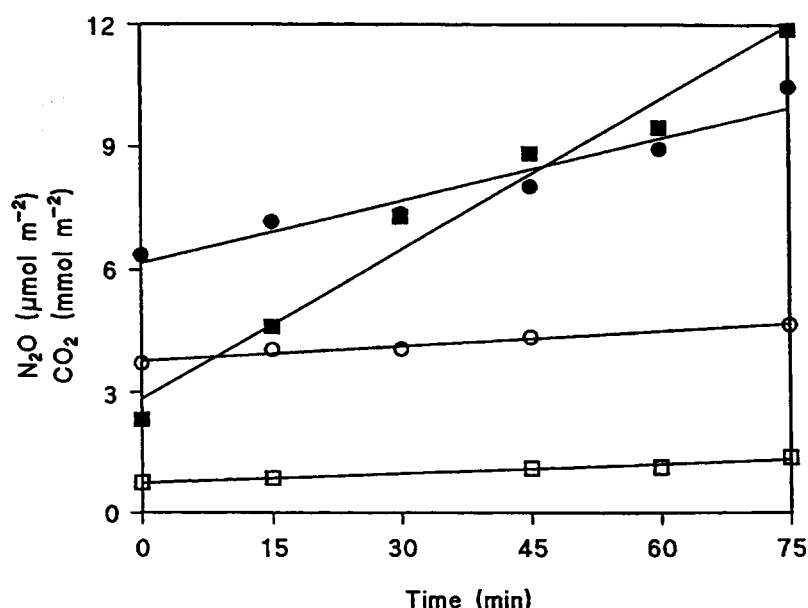


Figure 3. Amounts of CO<sub>2</sub> (May 1994) and N<sub>2</sub>O (March 1994) (per square metre) in an incubation chamber as a function of incubation time. CO<sub>2</sub>: ● (LN), ○ (LF). N<sub>2</sub>O: ■ (LN), □ (LF). Slope of lines represents gaseous efflux rates.

### Groundwater and surface water sampling

Concentrations of DIC, dissolved N<sub>2</sub>O, NO<sub>3</sub><sup>-</sup>, sulfate (SO<sub>4</sub><sup>-</sup>) and oxygen (O<sub>2</sub>) were measured monthly (period as above) in groundwater and surface water. Water was sampled from piezometer 3-75, 4-15, 7-15, 7-75, 8-15, and 8-75. In addition, surface water (denoted 7-0 and 8-0, respectively) was sampled at piezometer nest 7 and 8. To ensure sampling of fresh groundwater the piezometers were emptied 24 hr before a sampling event. Samples were obtained from piezometers by a peristaltic pump and a 0.6 cm (inner diameter) Tygon tube with the opening constantly placed at the screened depth in each piezometer. Groundwater was continuously pumped and first sampled when water temperature reached a constant level. Surface water was sampled by use of a 100 ml syringe.

Water samples for determination of DIC and dissolved N<sub>2</sub>O were collected into 12 ml Exetainers (Labco) and preserved with 0.3 ml 80 % ZnCl<sub>2</sub>. One week of storage at 5 °C did not change the concentration of N<sub>2</sub>O and DIC in preserved samples and all samples were analyzed within this period. In unpreserved samples with high NO<sub>3</sub><sup>-</sup> concentrations the N<sub>2</sub>O concentration increased up to 7 times within the same period. For measurement of DIC and dissolved N<sub>2</sub>O in the water samples 8.0 ml of the water was replaced with

headspace He(g) (Risgaard-Petersen & Rysgaard 1995).  $\text{H}_2\text{SO}_4$  (2N) was then added (0.3 ml) in order to dissociate the inorganic carbon into carbon dioxide. Then the exetainer was shaken for 1 min to equilibrate the  $\text{CO}_2$  between water and headspace gas.

Additionally, water was sampled in exetainers ( $\text{O}_2$  determination) and polyethylene bottles ( $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  determination).

### *Chemical determinations*

Gas samples and equilibrated headspace gas in water samples (exetainers) were analyzed for  $\text{N}_2\text{O}$  and  $\text{CO}_2$  on a gas chromatograph (Schimadzu GC-14A) equipped with a Thermal Conductivity Detector and an Electron Capture Detector (Heysep D). Gas samples were analyzed within 24 hours after collection. The gas composition in glass syringes remained unchanged for at least 48 hours. The rate of gas flux is expressed in moles of gas  $\text{m}^{-2} \text{h}^{-1}$  and was calculated for each chamber using linear regression analysis (Figure 3).

With respect to the water samples, correction for dissolved  $\text{N}_2\text{O}$  and  $\text{CO}_2$  in the water was calculated by use of Bunsen solubility coefficients of 0.5616 and 0.9118, respectively (Weiss 1974; Weiss & Price 1980).

Dissolved  $\text{O}_2$  was determined by Winkler titration (Fenchel & Hemmingsen 1974).  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  were determined by ion chromatography (Schimadzu HIC-6A) equipped with an IC-A1S column. Prior to analysis, the water was filtered through a  $0.2 \mu\text{m}$  membrane filter.

### *Total alkalinity and $\text{CO}_2$ partial pressure*

In November 1993 additional water (4–15, 8–0, and 8–15) was sampled to determine pH and conductivity ( $25^\circ\text{C}$ ). Total alkalinity (TA) was determined by Gran titration (Stumm & Morgan 1981) with 0.100 M HCl on 50 ml unfiltered sample ( $n = 2$ ). In the pH range below 8.3, it is reasonable to equate TA with the carbonate alkalinity (CA), which will be almost entirely bicarbonate. The difference between DIC and CA under these assumptions almost equals the concentration of free  $\text{CO}_2$  in the water ( $[\text{CO}_2(\text{aq})]$  moles  $\text{l}^{-1}$ ), and the partial pressure of  $\text{CO}_2$  ( $p\text{CO}_2$  kPa) was calculated by Henry's law:  $p\text{CO}_2 = [\text{CO}_2(\text{aq})] \cdot K_H^{-1}$ , where  $K_H$  (moles  $\text{l}^{-1} \text{kPa}^{-1}$ ) is the solubility constant for  $\text{CO}_2$  (Stumm & Morgan 1981).

### *Statistics*

To compare rates of gas fluxes with respect to sampling site and sampling date, we used a two-way analysis of variance. The analyses were made using the GLM procedure of SAS (SAS Institute 1988) on log-transformed data.

## Results

### *Hydrology*

Groundwater flow rates varied little throughout the observation period, but in general the lowest rates occurred in summer and the highest rates in winter. Groundwater was well up at site LN, where flow rates varied between 6.4 and 9.5 l m<sup>-1</sup> h<sup>-1</sup>. At site LF the groundwater flow was much lower (0.03 and 0.04 l m<sup>-1</sup> h<sup>-1</sup>) due to the lower hydraulic conductivity and a smaller gradient in hydraulic potentials (data not shown) as compared to site LN. At site LF the dominant flow of water took place on the sediment surface. This flow was estimated to be 50 l m<sup>-1</sup> h<sup>-1</sup> (runoff 3000 l h<sup>-1</sup>, stream bank length 60 m). This is a maximum estimate since groundwater is discharged (upwelled) to the wetland surface between piezometer nest 8 and the stream (Figure 1).

A March snow melt produced very high water levels in the stream and flooding of the wetland. No groundwater flow could be calculated between piezometer nest 7 and 8 in this situation because of equal hydraulic potentials, though in reality the wetland acted as a river with a flow direction parallel to the direction of the stream flow.

### *CO<sub>2</sub> efflux*

The efflux of CO<sub>2</sub> from the sediment to the atmosphere was significantly ( $P < 0.0001$ ) higher at site LN compared to site LF (Figure 4). At both sites, the CO<sub>2</sub> efflux varied seasonally with lower rates in winter and higher rates in summer and autumn. There was no significant ( $P = 0.07$ ) site and date interaction, meaning that the seasonal pattern in CO<sub>2</sub> efflux was the same at both sites. The minimum rates were 1.05 mmol CO<sub>2</sub> m<sup>-2</sup> h<sup>-1</sup> in March and 0.37 mmol CO<sub>2</sub> m<sup>-2</sup> h<sup>-1</sup> in December at site LN and LF, respectively. At both sites, the maximum rate occurred in October. The values were 4.37 mmol CO<sub>2</sub> m<sup>-2</sup> h<sup>-1</sup> at site LN and 1.45 mmol CO<sub>2</sub> m<sup>-2</sup> h<sup>-1</sup> at site LF.

### *CO<sub>2</sub> efflux related to temperature*

Sediment temperature at both sites was 12.7 to 13.7 °C in August and declined to 0.7 and 2.1 °C in March at site LN and LF, respectively (Figure 4). A significant ( $P < 0.05$ ,  $n = 11$ ) exponential relationship existed between CO<sub>2</sub> efflux (mmol CO<sub>2</sub> m<sup>-2</sup> h<sup>-1</sup>) and sediment temperature,  $T$  (°C):

$$\text{Site LN: } \text{CO}_{2\text{efflux}} = 1.103e^{0.093T} \text{ for } 0.7 \leq T \leq 12.7 \text{ }^{\circ}\text{C}$$

$$\text{Site LF: } \text{CO}_{2\text{efflux}} = 0.539e^{0.076T} \text{ for } 2.1 \leq T \leq 13.7 \text{ }^{\circ}\text{C}$$



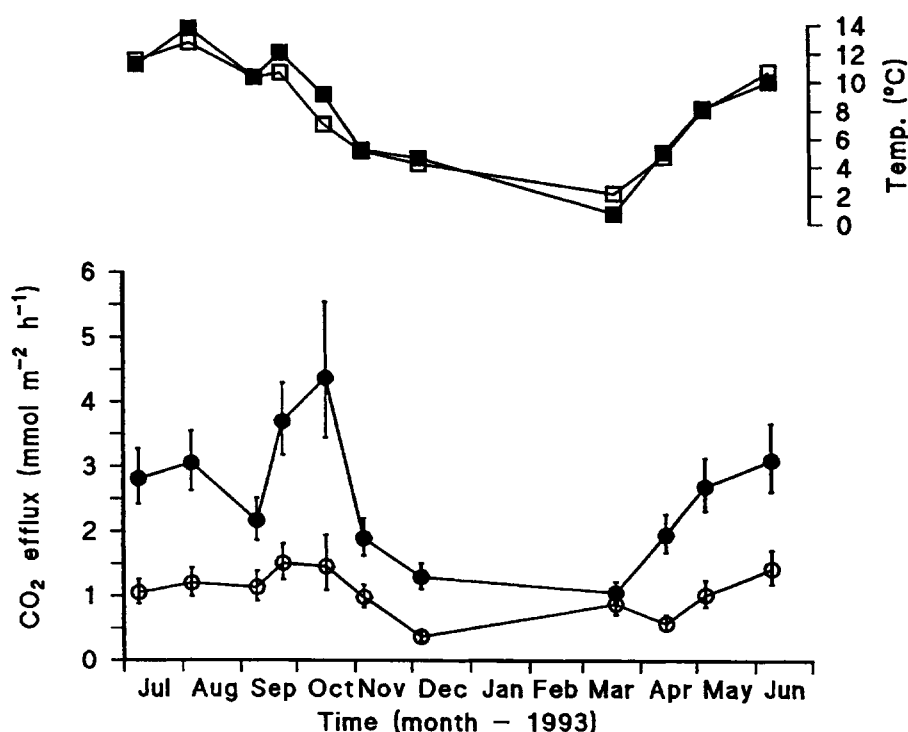


Figure 4. Seasonal efflux of CO<sub>2</sub> from site LN (●) and site LF (○). Error bars indicate  $\pm 1$  standard error ( $n = 4-5$ ,  $n = 2$  in Oct.). The upper panel shows surface sediment temperatures (°C) at site LN (■) and site LF (□).

Based on  $r^2$ , the variation in temperature explained 69% and 39% of the seasonal variation in CO<sub>2</sub> efflux at site LN and LF, respectively.

#### *N<sub>2</sub>O efflux*

Efflux of N<sub>2</sub>O from the sediments was detectable on five sampling dates at site LN and on three sampling dates at site LF (Figure 5). No seasonal trend in N<sub>2</sub>O efflux was evident and the ANOVA test revealed that the efflux was significantly higher ( $P < 0.0001$ ) at site LN compared to site LF. At site LN the efflux varied between  $0.35 \mu\text{mol N}_2\text{O m}^{-2} \text{ h}^{-1}$  in April to  $9.40 \mu\text{mol N}_2\text{O m}^{-2} \text{ h}^{-1}$  in March and at site LF between  $0.21$  to  $0.43 \mu\text{mol N}_2\text{O m}^{-2} \text{ h}^{-1}$ .

#### *CO<sub>2</sub> partial pressure*

pCO<sub>2</sub> (Table 1) in groundwater was much higher in piezometer 4-15 compared to water in equilibrium with atmospheric air ( $p\text{CO}_2 = 0.033 \text{ kPa}$ ). pCO<sub>2</sub>

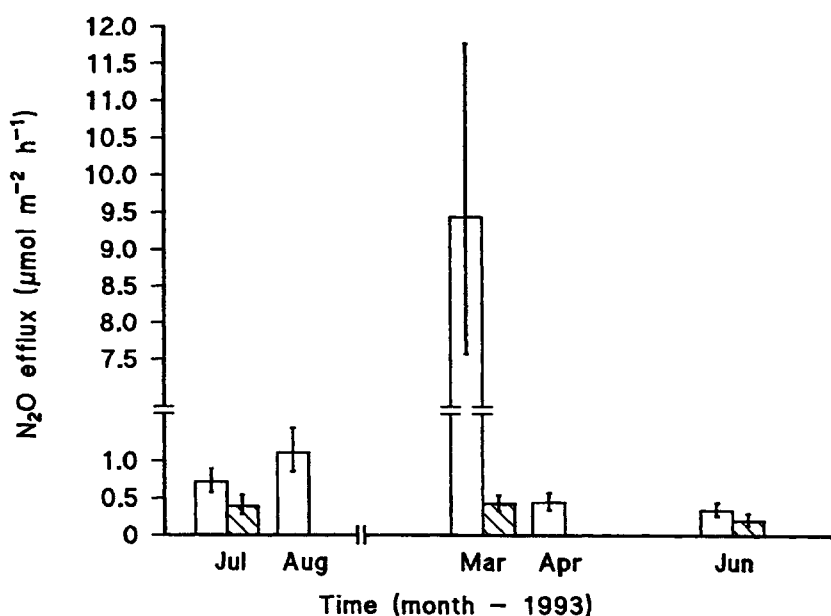


Figure 5. Efflux of N<sub>2</sub>O from the two study sites. Efflux of N<sub>2</sub>O was only detected on five sampling dates as indicated. Open bars are site LN and filled bars are site LF. Error bars indicate  $\pm 1$  standard error ( $n = 4-5$ ).

Table 1. Chemical characteristics of groundwater (15 cm depth) and surface water (0 cm depth) in November 1993. Values of total alkalinity (TA) (meq l<sup>-1</sup>), conductivity ( $\mu\text{S cm}^{-1}$ , 25 °C), pH, and DIC (mmol l<sup>-1</sup>) represent the mean of two determinations. pCO<sub>2</sub> (kPa) was calculated using Henry's Law (see text) with a solubility constant ( $K_H$ ) of 0.646 mmol l<sup>-1</sup> kPa at a water temperature of 5 °C.

Piezometer/surface water	Chemical constituent				
	TA	DIC	Cond.	pH	pCO <sub>2</sub>
4-15	2.22	4.15	324	6.5	2.99
8-15	2.87	3.84	534	6.8	1.50
8-0	2.82	2.97	508	7.3	0.23

was also high in groundwater at site LF but much lower in surface water. Thus, a gas gradient existed from below ground towards the surface.

#### *DIC in groundwater and surface water*

DIC generally accumulated in the groundwater as the groundwater passed through the wetland (Table 2). An increase of 1–2 mM DIC typically occurred between piezometer 3–75 and 4–15. Between piezometer 7 and 8 the increase

*Table 2.* Concentrations of dissolved inorganic carbon (mM) in groundwater and surface water at the study sites. Each value represents the average of two determinations. No data are available from January and February because of ice.

Month	Sampling points							
	3-75	4-15	7-0	7-15	7-75	8-0	8-15	8-75
Jul	2.96	5.52	ND <sup>1</sup>	5.71	4.70	ND	6.96	5.71
Aug	2.69	4.66	3.17	4.84	3.97	4.05	5.47	4.95
Sep	2.54	4.61	3.51	4.45	4.16	3.82	5.60	4.83
Oct	2.62	4.09	3.01	4.11	4.27	3.18	4.47	4.66
Nov	2.50	4.15	2.67	3.80	3.97	2.97	3.84	4.53
Dec	2.79	3.69	1.80	4.00	4.92	1.59	4.33	5.26
Mar	2.65	3.67	1.13	3.70	4.87	1.01	3.17	5.45
Apr	2.52	2.62	2.94	3.94	4.98	3.23	4.56	5.03
May	2.80	3.93	0.61	3.73	4.86	3.91	5.37	4.94
Jun	2.48	3.51	3.48	3.84	4.19	3.98	5.13	4.78

<sup>1</sup> Not Determined.

was less than 1 mM on most dates, although the distance between these piezometers were 10 times the distance between piezometer 3-75 and 4-15. In the summer period at site LF there was a trend towards higher DIC concentrations in the peat as compared to the peaty sand. The lowest concentrations at site LF occurred in surface water and on most dates the concentration was slightly higher at piezometer nest 8 compared to piezometer nest 7.

It should be noted that DIC concentrations in both shallow groundwater and surface water varied seasonally with higher concentrations during the summer.

The seasonal export of DIC is shown in Figure 6. For each date and site the flow of water between the various piezometers was multiplied by the difference in DIC concentration between the same piezometers. Export values on a square metre basis were calculated by including the distance between piezometer nests.

Highest DIC export in groundwater occurred at site LN and ranged from 16 mmol C m<sup>-2</sup> h<sup>-1</sup> during the summer to 7 mmol C m<sup>-2</sup> h<sup>-1</sup> in the winter. An unusually low value (0.9 mmol C m<sup>-2</sup> h<sup>-1</sup>) occurred in April. In contrast, the DIC export in groundwater at site LF was always low and DIC was primarily exported in surface water, with values as high as 2.2 mmol C m<sup>-2</sup> h<sup>-1</sup> in summer. In winter however, the DIC export in surface water was insignificant.

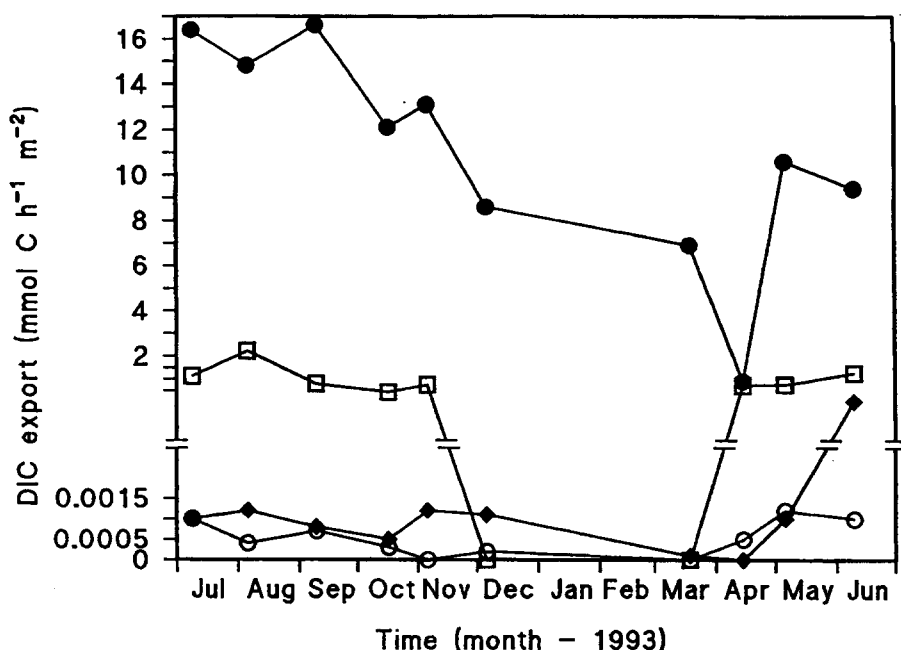


Figure 6. Seasonal export rates of dissolved inorganic carbon (DIC) in groundwater [LN 3-75; 4-15 (●), LF 7-15; 8-15 (○), LF 7-75; 8-75 (◆)] and surface water (LF □) at the two study sites. For calculations: see text.

#### *Dissolved N<sub>2</sub>O in the groundwater and surface water*

Like the efflux of N<sub>2</sub>O the concentration of dissolved N<sub>2</sub>O in groundwater showed marked spatial variability (Table 3). Dissolved N<sub>2</sub>O was consistently detected at piezometer 3-75 but was very irregular at piezometer 4-15. N<sub>2</sub>O was detectable in groundwater at site LF only in December, March, and April. The concentration of dissolved N<sub>2</sub>O in surface water was as high as 0.86  $\mu$ M at piezometer nest 7 but was commonly below detection at piezometer nest 8. Because dissolved N<sub>2</sub>O seemed to be lost to the atmosphere or reduced to N<sub>2</sub>(g) at the study sites, there was no export of N<sub>2</sub>O in groundwater and surface water.

#### *O<sub>2</sub>, NO<sub>3</sub><sup>-</sup>, and SO<sub>4</sub><sup>-</sup> in groundwater and surface water*

The concentration of O<sub>2</sub> decreased between piezometer 3-75 and 4-15 on most sampling dates (Table 4). At site LF the concentration was high in surface water ( $\sim 270$   $\mu$ M), but was zero in groundwater (data not shown).

Site LN was loaded with very high concentrations of NO<sub>3</sub><sup>-</sup> (Table 4). However, tracing the groundwater flowline the concentration decreased almost by

**Table 3.** Concentrations of dissolved  $\text{N}_2\text{O}$  ( $\mu\text{M}$ ) in groundwater and surface water at the study sites. Each value represents the average of two determinations. No data are available from January and February because of ice.

Month	Sampling points							
	3-75	4-15	7-0	7-15	7-75	8-0	8-15	8-75
Jul	0.21	BD <sup>1</sup>	ND <sup>1</sup>	BD	BD	ND	BD	BD
Aug	0.23	BD	0.80	BD	BD	BD	BD	BD
Sep	0.12	BD	BD	BD	BD	BD	BD	BD
Oct	0.42	0.10	BD	BD	BD	BD	BD	BD
Nov	0.19	BD	0.20	BD	BD	BD	BD	BD
Dec	0.22	0.20	0.86	BD	BD	0.31	0.08	BD
Mar	0.24	0.08	0.16	BD	BD	BD	0.18	BD
Apr	0.14	BD	0.66	BD	BD	BD	0.18	BD
May	0.17	0.08	0.11	BD	BD	BD	BD	BD
Jun	0.13	BD	BD	BD	BD	BD	BD	BD

<sup>1</sup> Abbreviations: Below Detection, Not Determined.

**Table 4.** Concentrations of  $\text{O}_2$  ( $\mu\text{M}$ ) and  $\text{NO}_3^-$  ( $\mu\text{M}$ ) in groundwater at site LN. Each value represents the average of two determinations. No data are available from January and February because of ice.

Month	Sampling points			
	3-75	4-15	3-75	4-15
	$\text{O}_2$		$\text{NO}_3^-$	
Jul	2.8	0.0	930	0
Aug	26.8	0.0	1030	10
Sep	8.6	20.5	1000	10
Oct	10.1	7.3	880	20
Nov	6.8	16.8	1070	0
Dec	10.1	4.7	1110	0
Mar	11.3	2.4	1150	20
Apr	6.6	16.2	1040	120
May	24.1	15.4	1020	20
Jun	21.9	15.1	690	30

1000  $\mu\text{M}$  between piezometer 3-75 and 4-15. At site LF the concentration in groundwater and surface water was low ( $< 60 \mu\text{M}$ ) throughout the year (data not shown).

In contrast, the lowest concentrations of  $\text{SO}_4^{--}$  occurred at site LN (Table 5) with no clear trends between piezometer 3-75 and 4-15. At site LF however, the  $\text{SO}_4^{--}$  concentration decreased between piezometer nest 7 and 8. The decrease was as large as 562  $\mu\text{M}$   $\text{SO}_4^{--}$ .

**Table 5.** Concentrations of  $\text{SO}_4^{--}$  ( $\mu\text{M}$ ) in groundwater and surface water at the study sites. Each value represents the average of two determinations. No data are available from January and February because of ice.

Month	Sampling points							
	3-75	4-15	7-0	7-15	7-75	8-0	8-15	8-75
Jul	217	97	447	865	949	242	387	910
Aug	209	64	531	904	947	311	401	910
Sep	197	74	256	961	974	255	456	909
Oct	182	110	416	815	920	471	433	869
Nov	208	118	675	882	918	736	707	848
Dec	205	318	458	939	998	349	695	977
Mar	207	291	182	968	1060	161	406	939
Apr	235	377	754	985	985	571	686	918
May	259	395	867	961	1051	532	675	949
Jun	269	297	815	947	1005	576	659	967

**Table 6.** Annual transport budgets for chemical constituents in the wetland. All units are per  $\text{m}^2$  per yr.

	Study site	
	LN	LF
$\text{CO}_2$ – efflux (mol C)	19.1	8.2
DIC export (groundwater) (mol C)	78.4	0.1
DIC export (surface water) (mol C)	–	6.0
Annual C loss (mol C)	97.5	14.3
$\text{O}_2$ loss (groundwater) (mol $\text{O}_2$ )	0.17	–
$\text{NO}_3^-$ loss (groundwater) (mol $\text{NO}_3^-$ )	57.5	–
$\text{SO}_4^-$ loss (groundwater) (mol $\text{SO}_4^-$ )	–0.15	0.02
$\text{SO}_4^-$ loss (surface water) (mol $\text{SO}_4^-$ )	–	2.1

As for DIC, the temporal transport of  $\text{O}_2$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{--}$  was calculated for site LN, while at site LF only transport of  $\text{SO}_4^{--}$  could be calculated (results not shown).

#### *Annual budgets of DIC, $\text{N}_2\text{O}$ , $\text{O}_2$ , $\text{NO}_3^-$ , and $\text{SO}_4^{--}$*

Assuming no diurnal variation in gas efflux and transport of dissolved components, the number of days between successive measurements was used in the estimate of annual fluxes (Table 6).

The annual loss of inorganic carbon in gaseous and dissolved forms was almost 7 times higher at site LN as compared to site LF. At site LN 20% of the export occurred as  $\text{CO}_2$  efflux and 80% as DIC in groundwater. At site LF, these figures were 57% and 0.1%, respectively, and remaining export occurred in surface water (42%). The period from July to October and from May to June accounted for 65–73 % of inorganic carbon export at the two sites.

The annual loss of  $\text{N}_2\text{O}$  could not be estimated, because efflux of  $\text{N}_2\text{O}$  was only detectable on a few sampling dates and because the export of dissolved  $\text{N}_2\text{O}$  was zero.

As groundwater passed through the LN site,  $\text{O}_2$  was consumed resulting in a small annual reduction (Table 6). Also at this site, the steep gradient in  $\text{NO}_3^-$  concentration (Table 4) resulted in a high annual loss of  $\text{NO}_3^-$  from the groundwater (Table 6). At the same time, there was a small annual export of  $\text{SO}_4^{2-}$ . At site LF,  $\text{SO}_4^{2-}$  was primarily lost from surface water, while the loss from groundwater was insignificant.

## Discussion

### *Hydrology*

Precipitation accounts for ~10% of the total water input to the wetland (Dahl 1995). Therefore, the hydrological input to our wetland is dominated by groundwater being discharged from the surrounding agricultural land and the variation in flow at both study sites was correspondingly small throughout the observation period. Thus, exports of dissolved chemical constituents from the wetland are more likely to be determined by processes within the wetland than by variation in groundwater flow. However, extreme rain or heavy snow melt occasionally resulted in flooding of the wetland by stream water for some hours. We were unable to estimate the flow of water from the area during these extreme hydrologic events. Studies in tidal marshes indicate that such situations may cause elevated export of especially particulate organic carbon from the marsh surface (Roman & Daiber 1989).

The importance of below ground dissolved components has rarely been assessed in descriptions of wetland carbon turnover, probably because the measurement of groundwater turnover is difficult. As in this study, Pulliam (1993) used hydraulic potentials in piezometers to quantify groundwater flow in a freshwater swamp, whereas other techniques have been used to assess the effect of porewater turnover on carbon fluxes in for example salt marshes (Howes et al. 1985; Morris & Whiting 1985).

*CO<sub>2</sub> and N<sub>2</sub>O efflux*

At the LN site, the efflux of CO<sub>2</sub> for most sampling dates greatly exceeded the efflux at site LF (Figure 4). A seasonal variation in efflux of CO<sub>2</sub> as observed in this study has also been observed in other wetland studies (Moore 1989; Pulliam 1993). It has often been suggested that sediment temperature is an important factor when explaining the seasonal variability (Morris & Whiting 1985; Bridgham & Richardson 1992), because of its influence on metabolic rates of microorganisms. At our study sites CO<sub>2</sub> efflux rates were positively correlated with sediment temperatures as expressed by a simple exponential model. However, the relationship does not seem to be the same throughout the year as CO<sub>2</sub> efflux rates at equal or lower temperatures were higher in autumn than in summer (Figure 4). Howes et al. (1985) reported a similar hysteresis effect. This suggests, that the availability of substrate for microbial decomposition processes may increase in autumn when dead emergent vegetation is deposited on the sediment surface. As labile organic matter is leached from the dead plant tissue (Webster & Benfield 1986) the substrate quality and quantity may increase in the sediment over a relatively short period of time.

The total efflux of CO<sub>2</sub> from the sediments will be a function of CO<sub>2</sub> evolved during respiration in live roots and rhizomes as well as CO<sub>2</sub> evolved during breakdown of organic matter. Morris & Whiting (1985) and Pulliam (1993) showed that root and rhizome respiration may contribute substantially (~50%) to total sediment CO<sub>2</sub> evolution. However, this factor does not explain the difference in inorganic carbon export between the two study sites, as the vegetation was of almost equal composition and density (pers. observation).

In various wetlands gaseous carbon losses are dominated by either CO<sub>2</sub> or CH<sub>4</sub>, and one factor responsible for this variation is probably the redox conditions (Chanton et al. 1989; Bridgham & Richardson 1992; Gale et al. 1992; Nilsson & Bohlin 1993; Pulliam 1993). At our study sites, efflux of CH<sub>4</sub> was detected only once (August 1993) during the observation period (unpublished results), and the efflux (1.4–1.5 mmol CH<sub>4</sub> m<sup>-2</sup> h<sup>-1</sup>) at that time was only statistically ( $P = 0.05$ ) different from zero at site LN. However, the contribution of methanogenesis to carbon turnover at our study sites could be significant. Thus, the maximum efflux rates of CH<sub>4</sub> from sediments range from 0.2 mmol m<sup>-2</sup> h<sup>-1</sup> in temperate wetlands to 1.2 mmol m<sup>-2</sup> h<sup>-1</sup> in subtropical wetlands as reported by Whiting & Chanton (1993).

The differences between sites with respect to CO<sub>2</sub> efflux and pCO<sub>2</sub> strongly suggest that microbial turnover of sediment organic carbon is significantly higher at site LN than at site LF. The greater availability of NO<sub>3</sub><sup>-</sup> in the sediments at site LN (Table 4) could simply cause an accelerated turnover of



carbon or alternatively favor a different metabolic pathway. Exogenous nitrogen may accelerate decomposition when litter is relatively poor in nitrogen (high C/N ratio). Enrichment of sediments with nitrate has shown to increase the decay rates of wetland macrophyte litter (Jordan et al. 1989; Davis 1991), presumably through increased microbial nitrogen uptake or by production of plant litter enriched with nitrogen (Valiela et al. 1985; Gale et al. 1992). It is unlikely however, that improved substrate quality of the sediment at site LN can account for the observed differences in  $\text{CO}_2$  efflux. No statistically significant differences in the size of organic pools of C, N and P or their ratios (670:44:1) were observed in shallow sediment from the two study sites (Paludan 1995).

Although the efflux of  $\text{N}_2\text{O}$  were larger at site LN as compared to site LF, the efflux rates in general did not exceed  $1 \mu\text{mol m}^{-2} \text{h}^{-1}$  (Figure 5). This is an important result, since soils receiving high loads of nitrogen have been hypothesized to be a major source of  $\text{N}_2\text{O}$  to the atmosphere (Denmead 1991). Our  $\text{N}_2\text{O}$  efflux rates are within the ranges reported from other ecosystems. Thus, in Danish agricultural areas the average efflux rate has been estimated to be  $1.2 \mu\text{mol N}_2\text{O m}^{-2} \text{h}^{-1}$  (Pri  me & Christensen 1991), and in a subtropical tidal salt marsh the efflux rate varied between 0.1 and  $0.2 \mu\text{mol N}_2\text{O m}^{-2} \text{h}^{-1}$  (Smith et al. 1982). Finally, in a Wisconsin wet meadow with almost no external nitrogen input there was an efflux rate of  $1.1 \mu\text{mol N}_2\text{O m}^{-2} \text{h}^{-1}$  (Goodroad & Keeney 1984).

### *DIC and dissolved $\text{N}_2\text{O}$*

As in this study (Table 2) Pulliam (1993) also observed the accumulation of DIC in groundwater as it passed through a wetland. At both study sites the highest DIC concentrations appeared in the warmer part of the year and a similar seasonal pattern was observed by Howes et al. (1985) and Pulliam (1993). DIC may originate from biological processes or from dissolution of sediment carbonates (Stumm & Morgan 1981). As the peat at our study sites was underlain by sand (Figure 1) and peat is low in minerals, biological processes would seem to dominate the production of DIC. This is also supported by the fact, that during the warmer part of the year the highest DIC concentrations were measured in shallow groundwater. This is the water in contact with the metabolically active rhizosphere. The seasonal variation in DIC export (Figure 6) was mainly determined by differences in DIC concentrations between piezometers as the seasonal variation in flow of groundwater and surface water was small. The larger export rate of DIC from site LN compared to site LF is in agreement with the  $\text{CO}_2$  efflux data.

Higher concentrations of dissolved  $\text{N}_2\text{O}$  in the groundwater occurred at site LN compared to site LF (Table 3), but for the study area as a whole

there was no hydrological export of  $\text{N}_2\text{O}$ . The large amounts of  $\text{N}_2\text{O}$  at piezometer 3–75 could originate from the surrounding agricultural area being transported to the wetland by discharging groundwater. In the wetland the  $\text{N}_2\text{O}$  is either transformed to  $\text{N}_2$  or emitted to the atmosphere. The high concentrations of  $\text{N}_2\text{O}$  measured in surface water at piezometer nest 7 most likely originate from nitrogen turnover processes in the surface peat layer which is in contact with the aerob surface water. In soils  $\text{N}_2\text{O}$  is the product of a number of biochemical pathways. Thus, in fertilized soils the nitrification process is important with respect to  $\text{N}_2\text{O}$  production (Aulakh et al. 1984) as is nondenitrifying  $\text{NO}_3^-$  reduction, in which  $\text{NO}_3^-$  is reduced to  $\text{NO}_2^-$ , ammonium ( $\text{NH}_4^+$ ), and possibly also  $\text{N}_2\text{O}$  (Smith & Zimmerman 1981, Sørensen 1978). In a grassland soil however, denitrification was the major process responsible for  $\text{N}_2\text{O}$  production (Ryden 1981).  $\text{N}_2\text{O}$  accumulation should be favoured by the presence of  $\text{O}_2$ , since  $\text{N}_2\text{O}$ -reductases are the most  $\text{O}_2$  sensitive enzymes in the denitrification pathway. Possibly, denitrifying bacteria are favoured in the transient environment at site LN, where some bacteria can utilize both  $\text{O}_2$  and  $\text{NO}_3^-$  as electron acceptors.

#### *Annual exports of inorganic carbon*

The annual efflux of  $\text{CO}_2$  was 2.3 times larger at site LN as compared to site LF (Table 6), and our rates are within the ranges reported for non-tropical wetland sediments (Raich & Schlesinger 1992; Pulliam 1993). In contrast, the annual export of DIC is difficult to compare with other reported values, as they depend on the assessment of the sediment hydrology. In tidal wetlands, losses of DIC have been reported to be 78% (Morris & Whiting 1985) and 38% (Howes et al. 1985) of the  $\text{CO}_2$  efflux, while the DIC loss was insignificant from a swamp (Pulliam 1993).

Reduction of  $\text{NO}_3^-$  was quantitatively a very important biogeochemical process in site LN sediment (Table 6). Different processes that can reduce  $\text{NO}_3^-$  and account for the  $\text{NO}_3^-$  loss is plant uptake, assimilatory and dissimilatory nitrate reduction as well as denitrification (Bowden 1987; Tiedje 1988; Weller et al. 1994).

Yearly averaged plant uptake in freshwater wetlands is approximately  $2.5 \text{ mol N m}^{-2}$  (Bowden 1987) and this would only account for 4% of the nitrate reduction occurring at site LN. Assimilatory nitrate reduction, in which  $\text{NO}_3^-$ -N is incorporated into microbial biomass, is expected to occur when other nitrogen sources (reduced inorganic nitrogen and organic nitrogen) occur in limited amounts (Tiedje et al. 1981). Evidently, nitrate assimilation occur in soil slurries when the  $\text{NH}_4^+$  concentration is lower than  $7 \mu\text{mol kg}^{-1}$  (Rice & Tiedje 1989) and Ambus et al. (1992) concluded that approximately 20% of the nitrate reduction in  $\text{NO}_3^-$  amended soil cores and soil slurries from

a Danish riparian wetland was due to nitrate assimilation. In site LN the groundwater concentration of  $\text{NH}_4^+$  varied between 0.1 and 31  $\mu\text{M}$  throughout 1993 (unpublished results), and it is therefore possible that some of the nitrate reduction occurring at this site could be due to nitrate assimilation. Dissimilatory nitrate reduction to  $\text{NH}_4^+$  is a process which occurs most readily in very reduced environments (Tiedje 1988; Buresh & Patrick 1978). In a slurry study of nitrogen turnover in a Danish riparian wetland, only 12% of added  $\text{NO}_3^-$  was reduced through dissimilatory nitrate reduction to  $\text{NH}_4^+$  (Ambus et al. 1992).

Gaseous nitrogen loss resulting from denitrification is hypothesised to be a major fate of  $\text{NO}_3^-$  retained in riparian wetlands (Haycock & Pinay 1993; Weller et al. 1994) although direct evidence is limited by the lack of accurate field methods for measuring in situ denitrification. However, it is well known from several experimental studies that riparian wetlands have high potential rates of denitrification when measured in anaerobic slurries or soil cores amended with  $\text{NO}_3^-$  and/or glucose (Bryce & Cooper 1990; Ambus & Lawrance 1991; Ambus & Christensen 1993).

In surface water at site LF there was a significant  $\text{SO}_4^{2-}$  loss (Table 6). Probably  $\text{SO}_4^{2-}$  diffuses into the sediment where the availability of  $\text{O}_2$  and  $\text{NO}_3^-$  is low. Thus, in reduced freshwater sediments sulfate reduction seems to be one decomposition pathway contributing to the production of inorganic carbon.

In conclusion, the results of this study show very high losses of inorganic carbon from a riparian waterlogged sediment receiving high loads of anthropogenic nitrate in recharging groundwater. The nitrate was reduced congruently with the high inorganic carbon loss, but several co-occurring nitrate reduction pathways could be responsible for the increased carbon loss. In comparison, the export of inorganic carbon was much lower in a nearby sediment where the environmental impact in the form of nitrate loading was small. The intensive nitrate reduction was accompanied by an increased release of  $\text{N}_2\text{O}$  to the atmosphere, but the rate is within the ranges known from other ecosystems. Although reduction of nitrate in riparian wetlands may improve the environmental quality of downstream aquatic ecosystems, our results demonstrate that a secondary effect of this process is large losses of dissolved and gaseous inorganic carbon compounds from the wetland. This is significant, because  $\text{CO}_2$  is a greenhouse effect gas.

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