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Greenhouse gas fluxes from the eutrophic Temmesjoki River and its Estuary in the Liminganlahti Bay (the Baltic Sea)

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Abstract We studied concentrations of carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O) in the eutrophic Temmesjoki River and Estuary in the Liminganlahti Bay in 2003–2004 and evaluated the atmospheric fluxes of the gases based on measured concentrations, wind speeds and water current velocities. The Temmesjoki River was a source of CO_2, CH_4 and N_2O to the atmosphere, whereas the Liminganlahti Bay was a minor source of CH_4 and a minor source or a sink of CO_2 and N_2O. The results show that the fluxes of greenhouse gases in river ecosystems are highly related to the land use in its catchment areas. The most upstream river site, surrounded by forests and drained peatlands, released significant amounts of CO_2 and CH_4, with average fluxes of 5,400 mg CO_2–C m^{-2} d^{-1} and 66 mg CH_4–C m^{-2} d^{-1}, and concentrations of 210 µM and 345 nM, respectively, but N_2O concentrations, at an average of 17 nM, were close to the atmospheric equilibrium concentration. The downstream river sites surrounded by agricultural soils released significant amounts of N_2O (with an average emission of 650 µg N_2O–N m^{-2} d^{-1} and concentration of 22 nM), whereas the CO_2 and CH_4 concentrations were low compared to the upstream site (55 µM and 350 nM). In boreal regions, rivers are partly ice-covered in wintertime (approximately 5 months). A large part of the gases, i.e. 58% of CO_2, 55% of CH_4 and 36% of N_2O emissions, were found to be released during wintertime from unfrozen parts of the river.

Keywords Carbon dioxide · Estuary · Greenhouse gas · Methane · Nitrous oxide · River

Abbreviations

DIC	Dissolved inorganic carbon
ECD	Electron capture detector
FID	Flame ionization detector
GC	Gas chromatograph
GWP	Global warming potential
k_{600}	Gas transfer velocity normalized to a Schmidt number of 600
pCO_2	Partial pressure of CO_2 in water
TIC	Total inorganic carbon
TOC	Total organic carbon
tot-N	Total nitrogen
tot-P	Total phosphorus

Introduction

Traditionally, rivers have been seen as links between terrestrial and marine ecosystems, as they receive, transport and process nutrients and organic matter

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(Raymond and Bauer 2001; Wetzel 2001). They also act as important conduits for gas exchange between terrestrial ecosystems and the atmosphere (Kling et al. 1991; Cole and Caraco 2001a; Hope et al. 2001; Richey et al. 2002; Mayorga et al. 2005; Cole et al. 2007). Surface runoff and groundwater that rivers receive contain high amounts of greenhouse gases, namely CO_2, CH_4 and N_2O, originally produced in terrestrial ecosystems (Jones and Mulholland 1998a, b; Hasegawa et al. 2000; Hope et al. 2001). Gases emitted from rivers can also be produced in rivers in situ when the nutrients and organic matter that rivers receive are transformed by microbial processes to gaseous products (Raymond and Bauer 2001). Hence, most of the gases emitted from rivers are of terrestrial origin, being derived from either gases leached from terrestrial ecosystems or gases produced in rivers from the organic matter derived from catchments (de Angelis and Lilley 1987; Jones and Mulholland 1998a; Reay et al. 2003; Mayorga et al. 2005). By processing the nutrients and organic matter to gases, river ecosystems can remove part of the C and N load of marine ecosystems, but at the same time they increase the atmospheric load of greenhouse gases. However, a part of the nutrients, organic matter and greenhouse gases that rivers receive ends up in estuaries, which are considered to be important sources of greenhouse gases in marine ecosystems (Bange et al. 1994, 1996; Frankignoulle et al. 1998; Seitzinger and Kroeze 1998; Borges 2005).

Estuaries and near-shore coastal areas are known to be significant sources of marine CO_2 (Borges 2005; Borges et al. 2006), CH_4 (Bange et al. 1994; Upstill-Goddard et al. 2000) and N_2O (Seitzinger and Kroeze 1998; Seitzinger et al. 2000). Estuaries and coastal areas are estimated to contribute up to 35–60% of total marine N_2O emissions (Bange et al. 1996; Seitzinger et al. 2000), and up to 75% of total marine CH_4 emissions (Bange et al. 1994). Estuaries are generally sources of CO_2, while marginal seas are net sinks for atmospheric CO_2 (Borges 2005). Recent reviews concerning CH_4 and CO_2 emissions from estuaries have pointed out that minimal data are available for high latitudes (Upstill-Goddard et al. 2000; Borges 2005). Global estimations of N_2O emissions between rivers and estuaries are based on nitrogen input from watersheds to aquatic ecosystems (Seitzinger and Kroeze 1998; Seitzinger et al. 2000) but few field measurements have been made.

Greenhouse gas content in and emissions from rivers reflect the properties of the surrounding catchments, such as topography, soil type and texture, and land use and other anthropogenic activities (Jones and Mulholland 1998a; Reay et al. 2003). High amounts and fluxes of CO_2 and CH_4 have been found in small streams and rivers surrounded by peatlands and forests (Lilley et al. 1996; Jones and Mulholland 1998a; Neal et al. 1998; Hope et al. 2001; Dawson et al. 2002), whereas high fluxes of N_2O have been measured from rivers receiving N containing wastewaters or surrounded by N fertilized agricultural soils (McMahon and Dennehy 1999). The CO_2 concentrations and fluxes in terrestrial and aquatic ecosystems depend on photosynthesis and degradation of organic matter. Methane is produced during anaerobic carbon degradation, and high CH_4 concentrations and fluxes have been found in aquatic ecosystems and water saturated terrestrial ecosystems with anaerobic conditions (Cicerone and Oremland 1988). In aerobic conditions a fraction of the CH_4 is consumed by aerobic methane oxidation (Hanson and Hanson 1996). Nitrous oxide is produced as an intermediate of denitrification (Knowles 1981), a by-product of nitrification (Firestone and Davidson 1989) and by dissimilatory reduction of NO_3^- to NH_4^+ (Smith and Zimmerman 1981). The presence of N_2O in terrestrial and aquatic ecosystems is therefore related to the availability of inorganic nitrogen.

We studied both temporal and spatial variations in greenhouse gas dynamics in the Temmesjoki River and Estuary in the Liminganlahti Bay, in the Bothnian Bay of the northern Baltic Sea. We show how gas dynamics vary along the river as land use in the catchments changes. Additionally, our data reveal a seasonal pattern of gas dynamics along the river continuum and the impact of wintertime on aquatic gas concentrations and fluxes in boreal regions.

Materials and methods

Study sites

The dynamics of CO_2, CH_4 and N_2O emissions were measured along the course of the Temmesjoki River and Estuary and in the Liminganlahti Bay (64°52′N, 25°21′E, Finland), which is located in the north of the Gulf of Bothnia, Finland (Fig. 1). The Temmesjoki

River is a eutrophic river having a catchment mostly occupied by forests (52%), peatlands (20%) and agricultural soils (17%). Before entering the bay, the Temmesjoki River receives waters from the Tyrnävänjoki River and the Ängeslevänjoki River. The Temmesjoki Estuary is a freshwater estuary, since the Liminganlahti Bay has a salinity of <1‰, and the salinity of the northern parts of the Bothnian Bay is <2‰ (Kronholm et al. 2005). On average, 40% of the water in the Liminganlahti Bay has a riverine origin and most of it comes from the Temmesjoki River. The surface area of the Liminganlahti Bay is 109 km^2 and its mean depth is 2.6 m. The sea level and water movements in the bay vary irregularly depending mostly on wind and atmospheric pressure, tidal variations being negligible. With south and west winds, water flows from the sea up the Temmesjoki River. During the measurement period, the prevailing wind direction in the Liminganlahti Bay was 115° (in 2003 May–August) and 150° (in 2004 May–October) (Finnish Meteorological Institute, Oulu Airport).

Characteristics of the study sites and sampling strategy

There were five intensive study sites (sites 1–5, from upriver to downriver) in the Temmesjoki River (Fig. 1). For sites 1 and 2, forests and peatlands affected by forestry and peatland ditching dominated in the catchments (Table 1). Agricultural activity was substantial after site 2, and coverage of agricultural soils increased towards the estuary (site 5) (Table 1). In surface waters of the Temmesjoki River and Estuary in 2003–2004, at a depth of 10 cm, we measured the concentrations of gases, nutrients (NH_4^+–N, $NO_2^- + NO_3^- - N$, total N i.e. tot-N, total organic C. i.e., TOC, total inorganic C, i.e., TIC, tot-P, SO_4^{2-}) and O_2 as well as pH and temperature. At sites 1–5, measurements were done four times in 2003 (once in May, July, August and October) and eight times between April and August 2004 (1–3 times a month) (Table 2). Water currents and depths were measured (sites 1–4) five times during summer 2004.

Three sites were studied in Liminganlahti Bay (sites 6–8). Site 6 was located near the mouth of the Vanha Liminganjoki River, site 7 near the mouth of the Lumijoki River, and site 8 in the middle of the bay (Fig. 1). In the Liminganlahti Bay, measurements were done four times in 2004, twice in June and twice in July (Table 2).

In addition to sites 1–8, there was one site in the Temmesjoki River (site A), which was located about 1 Km upstream from site 5 (Fig. 1, black square). At site A, similar measurements to those for sites 1–5 were done during all seasons (once or twice a month

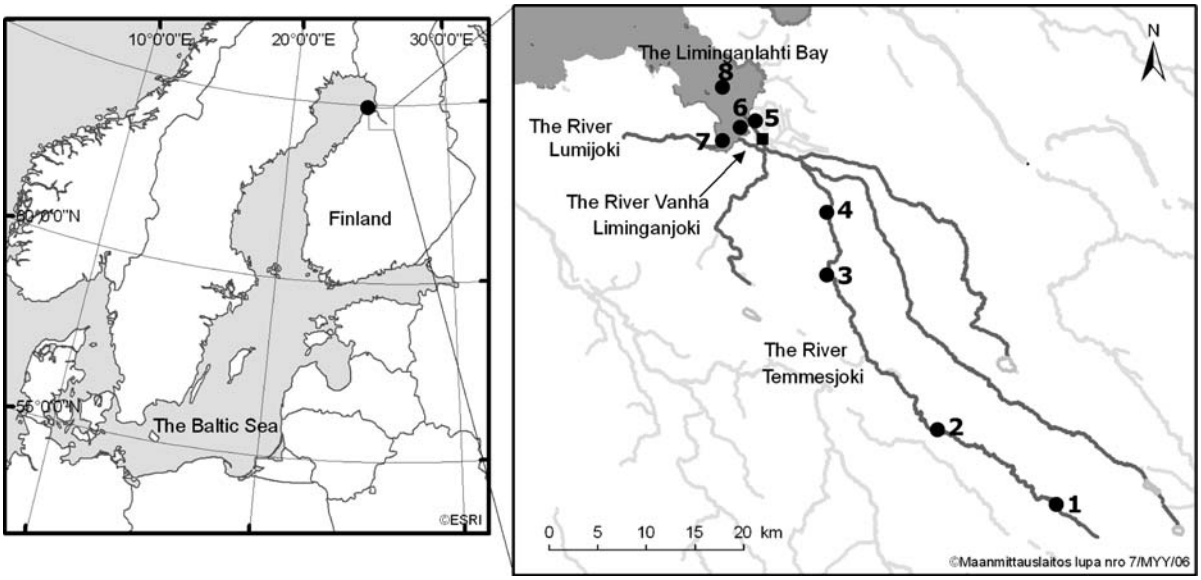

Fig. 1 The study sites in the River Temmesjoki (1–5) and in the Liminganlahti Bay (6–8). Black circles represent the study sites 1–8. Black square represents the study site A

Table 1 Characteristics of catchment area and river channel

Site	Catchment					River channel		
	Area (km^2)	Land use (%)				Width (m)	Length (m)[a]	Flow (m^3 s^{-1})[b]
		Wetland	Forest	Agriculture	Other			
1	43	52	46	0	2	3	6,256	0.4
2	105	41	53	0	6	7.5	30,554	0.99
3	261	24	61	6	9	8	48,410	2.5
4	311	21	62	7	10	6	56,528	2.9
5	1,180	20	52	17	11	41	71,500	11

[a] Length of river channel from the starting point of the river to the study site

[b] Averages of the modeled flow in 2003–2004

Table 2 Sampling strategy at the various sites

	River (site A)	River (sites 1–5)	Bay (site 6–8)
Fluxes with floating chamber	–	–	4 (2004, summer)
Concentrations of gases	21 (2003–2004)[b]	12 (2003–2004)[c]	4 (2004, summer)
Water quality[a]	21 (2003–2004)[b]	12 (2003–2004)[c]	4 (2004, summer)
Water current and depth	–	5 (2004, summer)	–

Number of measurements and time of measurements in parenthesis

[a] Water quality: NH_4–N, NO_2–N, tot-N, TOC, TIC, tot-P, SO_4^{2-}, O_2 conc., pH, temperature

[b] All seasons: once or twice a month from May 2003 to November 2004

[c] In May, July, August and October of 2003, eight times in 2004 between April and August

between May 2003 and November 2004) (Table 2). Water currents and depths were not determined at site A.

Measurements

The concentrations of CH_4 and N_2O, and dissolved inorganic carbon (DIC, the sum of CO_2, HCO_3^-, and CO_3^-), in water were determined by the headspace equilibration technique (McAuliffe 1971). In 2003, water samples from sites 1–5 were taken and stored in glass bottles (V, 120 ml), which were closed with rubber septa without headspace. Samples were preserved with sulfuric acid (2 ml 20% H_2SO_4). Acid was injected into the bottles through the septa using two needles. The first needle was used to inject acid and the second one allowed outflow of excess fluid. Within 4 days, water samples of 30 ml were drawn into polypropylene syringes (Terumo Europe, Leuven, Belgium) from the storage bottles for gas analysis. In 2004, water samples (30 ml) from sites 1–8 were drawn directly into the syringes with the help of a 10–15 cm long piece of PVC-tube in water. From study site A, water samples were drawn into syringes from a Limnos water sampler (Limnos Oy, Turku, Finland). The 30 ml water samples in the syringes were preserved with sulfuric acid (1 ml 20% H_2SO_4) in the field and were analyzed within 2 days. In the laboratory, the acidified water in the syringe was equilibrated with added N_2 gas (30 ml) and the headspace gas concentrations were analyzed with GC.

The concentrations of dissolved CH_4, DIC, and N_2O in the water samples were calculated from the headspace gas concentrations according to Henry's law using the values from Lide and Fredrikse (1995). Preservation of the water samples with sulfuric acid dropped the water pH to <4. At a pH below four, all inorganic carbon in water (CO_3^{2-}, HCO_3^- and CO_2) is present as CO_2, thus the measured CO_2 concentration from an acidified sample represents the DIC of the water. The proportion of CO_2 in the water samples was calculated from the DIC using the pH and temperature of the water determined in the field and the equations and constants published by Buttler (1982).

At the bay sites (sites 6–8), the fluxes of gases (CH_4, CO_2 and N_2O) across the water–air interface were measured with floating static chambers (Huttunen et al. 2002). Dark chambers (area 60 × 60 cm^2, height 25 cm) made from aluminum were equipped with pontoons. The floating depth of the chambers was adjusted to 3–4 cm by placing weights as necessary on the tops of the chambers. Measurements were done from the boat and the chambers were allowed to float freely. Pressures in the chambers were allowed to equilibrate with atmospheric pressure by means of a 2 m long PVC-tube with an inner diameter of 2 mm. Headspace gas samples of 50 ml were taken into polypropylene syringes (Terumo Europe, Leuven, Belgium) equipped with three way stopcocks (Codan Steritex, Hoejvangen, Denmark) five times during the 30 min incubation period. Gas samples were analyzed with gas chromatography (GC). The samples were analyzed either directly from the syringes within 24 h or were injected into evacuated vials (12 ml, Labco Exetainer®, Labco Co., UK) to be analyzed within 2 weeks. The gas fluxes (mg CO_2–C m^{-2} d^{-1}, mg CH_4–C m^{-2} d^{-1}, and µg N_2O–N m^{-2} d^{-1}) were calculated by taking into account the change in gas concentration with time in the chamber and the surface area of the chamber. Fluxes were accepted when the coefficient of determination of the linear regression of gas partial pressure versus time was higher than 0.9. However, if gas fluxes were negligible, non-linear ($r^2 < 0.9$) measurements were also taken into account and the criteria that coefficients of determination have to be >0.9 was not used. In these cases, the fluxes were obtained from the slope of the linear regression plotting gas concentration against time, regardless of the value of the coefficient of determination.

Gas analyses were performed with two different gas chromatograph systems. The air samples and the water headspace samples stored in syringes were analyzed with GC (Hewlett Packard 5890 Series II, Hewlett Packard, Palo Alto, California) equipped with a flame ionization detector (FID) for CH_4, a thermal conductivity detector for CO_2 and CH_4 (>1,000 ppm CH_4), and an electron capture detector (ECD) for N_2O (see Nykänen et al. 1995 for details). The gas samples stored in glass vials were analyzed with a GC (Agilent 6890N, Agilent Technologies Deutschland GmbH, Waldbronn, Germany) equipped with a peristaltic pump (Minipuls 3, Gilson Inc., Middleton, USA) and an autosampler (Gilson autosampler 222XL, Gilson Inc., Middleton, USA). The Agilent GC had two columns (HaysepQ 80/100″ × 0.9 m and HaysepQ 80/100″ × 2.7 m), FID and ECD. The temperature of the oven was 60°C and the carrier gas was N_2 (flow = 35 ml min^{-1}). The sensitivity of the ECD was improved by flushing it with a 5% CH_4/95% Ar gas mixture (flow = 0.4 ml min^{-1}). The calibration of the GCs was done with the following standards: 1.98 ppm CH_4, 396 ppm CO_2, and 389 ppb N_2O (Linde Gas, Germany).

At sites 1–8, water samples for nutrient analysis were taken directly into plastic bottles, whereas from site A water samples were taken into bottles with the Limnos water sampler (Limnos Oy, Turku, Finland). Water was allowed to overflow from the bottles prior to sample collection. At sites 1–8, pH and O_2 concentrations were measured with electrodes (Microprocessor pH meter pH 320, WTW, Germany with Hamilton pH electrode, Switzerland; Dissolved Oxygen Meter Oxi 330 with Dissolved Oxygen Probe CellOx 325, WTW, Germany) and temperature was measured with the thermometer built into the O_2 meter or with a separate thermometer (Fluke 51 K/J Thermometer, Fluke Corporation, WA, USA). The pH electrode was calibrated with pH 7.00 (model STP 7) and pH 4.01 (model STP 4) buffers (WTW, Weilheim, Germany). At site A, water temperature was measured from a mercury thermometer installed in the water sampler, and water O_2 concentrations and pH were determined for the water samples in the laboratory (within a few hours of sampling) according to SFS-EN 25813 (SFS Standardization 1993) and SFS-3021 (SFS Standardization 1979) standards, respectively.

Water samples for nutrient analysis were frozen within 24 h of sampling and stored at −20°C prior to analysis. Ammonium was analyzed photometrically according to Fawcett and Scott (1960) (sites 1–8) or following the SFS 3032 standard (SFS Standardization 1976; site A). Combined NO_2^- + NO_3^- was analyzed with an ion chromatograph (DIONEX 2010i equipped with DIONEX Ion Pac® AS4A-SC 4 mm column, Dionex Corp., USA; sites 1–8) or according to the SFS-EN ISO 13395 standard (SFS Standardization 1997b; site A). The concentration of SO_4^{2-} was analyzed with an ion chromatograph (see above; sites 1–8) or according to the SFS-EN ISO 10304 standard (SFS Standardization 1995; site A). Total organic and inorganic C (TOC and TIC) were analyzed according to the SFS-EN 1484 standard (SFS Standardization 1997a), total P was analyzed according to the SFS 3026 standard (SFS Standardization 1986) and total N according to the SFS-EN ISO 11905-1 standard (SFS Standardization 1998).

Data processing

The degree of saturation of gases in water was calculated by comparing the measured gas concentrations in the water samples to that in equilibrium with the atmosphere. For atmospheric gas concentrations we used an annual average of measured ambient air gas concentrations for the sites. Ambient air concentrations were measured at the intensive sites (1–5) during sampling. For the bay sites and site A annual averages from site 5 were used.

Gas transfer velocities (k_{600} cm h^{-1}) for the river sites were calculated according to Borges et al. (2004), assuming that the effects of water current velocity and wind speed are additive.

$$k_{600} = k_{600current} + k_{600wind} \tag{1}$$

The effect of water current velocity was calculated with the following parameterization, originally presented by O'Connor and Dobbins (1958), and normalized to a Schmidt number of 600 by Borges et al. (2004).

$$k_{600current} = 1.719w \times 0.5h - 0.5 \tag{2}$$

where w is the water flow (cm s^{-1}) and h is the water depth (m). For the dates when the flow and depth were not measured, they were approximated from the closest measurements. The effect of wind speed was calculated according to Borges et al. (2004) (Eq. 3) and according to Kremer et al. (2003a, b) (Eq. 4)

$$k_{600wind} = 1.98 + 0.18 \times u_{10} \tag{3}$$

$$k_{600wind} = 1 + 2.58 \times u_{10} \tag{4}$$

where u_{10} is the wind speed (m s^{-1}) at 10 m height. The average of the two parameterizations was used for $k_{600\mathrm{wind}}$ in Eq. 1. Gas transfer velocities for different gases (k_{gas}, cm h^{-1}) at each site were calculated with the following equation:

$$k_{gas} = k_{600}\left(\frac{Sc_{gas}}{600}\right)^{x} \tag{5}$$

where Sc$_{\mathrm{gas}}$ is the ratio of the kinematic viscosity of water and the diffusion coefficient. Schmidt numbers for the gases were calculated according to the values published by Wanninkhof (1992). The value used for exponent x was chosen to be −0.5, which has been used for rivers and estuaries having turbulent conditions but moderate wind speeds (Jähne et al. 1987). Fluxes were calculated using the calculated k_{gas} values and excess gas concentrations (calculated from measured concentrations) with the equation:

$$F = k_{gas} \times (C_w - C_a) \tag{6}$$

Wind speeds and directions were provided by the Finnish Meteorological Institute measured from the Oulu Airport (every 10 min), which is located next to the Liminganlahti Bay, 8 km north of the Temmesjoki Estuary.

For the bay sites, gas k_{600} values were also calculated from the gas concentrations measured in the water and the fluxes measured in the floating chambers. When the fluxes and concentrations of gases and Schmidt numbers are known, k_{gas} can be determined according to Eq. 6, and k_{600} according to Eq. 5.

Statistical analyses were made using the SPSS statistical package (SPSS Inc., USA). The significance of the linear correlations was analyzed by two-tailed Pearson tests. Correlation analysis was made (Pearson correlation coefficients, two-tailed significances) for gas fluxes, saturations and water quality parameters. Variation in gas fluxes and saturations between the sites was tested with One-Way ANOVA using Tukey's-b as a post hoc test.

Results and discussion

Gas transfer velocities at the Temmesjoki river and Liminganlahti bay

Gas transfer velocities (k_{600} cm h^{-1}) calculated for the three gases at various sites are presented in Table 3. At the river sites the gas transfer velocities varied from 12.5 to 15.8 cm h^{-1}. At the narrow and shallow upstream sites (1–2) the water current velocity had a greater impact on k_{600} than the wind

Table 3 K_{600} values calculated with wind speed (sites 1–8) and water current (sites 1–4), averages and standard errors of mean presented in parenthesis, and K_{600} values calculated from fluxes measured with floating chambers for CO_2, CH_4 and N_2O and the average K_{600} of the three gases (sites 6–8)

Site	K_{600} (cm h^{-1})		
	$K_{600\text{current}}$	$K_{600\text{wind}}$	$K_{600\text{current + wind}}$
Calculated with water current and wind speed			
River			
1	10.0 (0.2)	5.8 (0.6)	15.8 (0.7)
2	11.5 (1.4)	4.0 (1.0)	15.5 (1.2)
3	7.1 (0.4)	7.5 (0.3)	14.6 (0.5)
4	5.6 (0.3)	7.7 (0.6)	12.5 (1.4)
5	ND	ND	ND
Bay			
6	–	7.7 (0.9)	7.7 (0.9)
7	–	7.6 (0.9)	7.6 (0.9)
8	–	7.2 (0.3)	7.2 (0.3)

	CO_2	CH_4	N_2O	Average
Calculated from the fluxes measured with floating chambers				
6	3.8	15.1 (2.9)	3.3 (2.0)	8.6 (2.5)
7	20.4 (5.1)	50.6 (28.6)	11.1 (5.1)	30.7 (13.4)
8	–	27.1 (9.3)	4.6	22.6 (8.5)

speed. The effect of wind speed increased at the downstream sites (3–4). This result is in agreement with prior studies that showed higher k_{600} values in shallow, fast running, turbulent streams than in slowly flowing streams and estuaries (O'Connor and Dobbins 1958; Raymond and Cole 2001).

At the bay, k_{600} values were also determined from the measured gas concentrations and fluxes measured with floating chambers. k_{600} values determined from chamber measurements were significantly higher than those calculated according to wind speeds and gas concentrations (Table 3). They were also higher than the values measured from similar ecosystems with low or moderate wind speeds (Raymond and Cole 2001; Borges et al. 2004; Abril and Borges 2005). It is well known from recent literature that chamber measurements could lead to artificially high *k*-values and thereby to overestimation of fluxes (Borges et al. 2004; Matthews et al. (2003). The wind speed was always below 6 m s^{-1} during measurements. At such low wind speeds it is likely that the currents and bottom stress of the shallow bay have an effect on gas transfer velocity. Turbulence and water flow in the Liminganlahti Bay can be heterogeneous and may vary from day to day. The bay is shallow and, depending on the direction of the wind, water flows from the bay towards the river or vice versa. Therefore, the gas transfer velocities calculated using wind speeds might be underestimations, especially as they fall into the lower end of values measured from other estuaries (Raymond and Cole 2001; Borges et al. 2004; Abril and Borges 2005).

Temporal variation in gas dynamics in Temmesjoki River—the importance of winter

The results from site A showed that the supersaturations of CO_2 and CH_4 in river water were highest in winter (Fig. 2; Table 4). There are three possible explanations for high carbon gas supersaturations during winter. (i) There is no surface runoff in wintertime in boreal regions since the soil is frozen. Thus, the water entering the Temmesjoki River in winter is mainly groundwater filtrated through anoxic soil layers, causing river water to be rich in carbon gases produced in terrestrial ecosystems. (ii) Parts of the rivers are frozen during winter. Prior studies from lake ecosystems have shown that as ice forms, a physical barrier to gas transfer between the water and atmosphere forms, and then high concentrations of CO_2 and CH_4 can accumulate in the water beneath the ice (Striegel and Michmerhuizen 1998; Semiletov 1999; Kortelainen et al. 2000). (iii) In winter, photosynthesis is suppressed in the cold and dark water, and therefore CO_2 is not being consumed (Semiletov 1999; Dawson et al. 2001). Snow cover above the ice also reduces penetration of light, further diminishing photosynthesis. Those parts of rivers remaining unfrozen in winter due to high turbulence can easily exhaust dissolved gases accumulated in the river water in ice-covered areas. Previous studies have shown various seasonal patterns in river water CO_2 and CH_4 concentrations. The Hudson River, which has only a short ice-cover period, shows higher CO_2 concentrations in summer (Raymond et al. 1997). Results from rivers without any ice-cover periods are heterogeneous; some rivers exhibit the highest concentrations of CO_2 in autumn and winter when photosynthesis is reduced (Dawson et al. 2001), some show the highest CO_2 concentrations in summer when discharge is low and DOC concentrations are high (Raymond et al. 2000) and some lack a clear

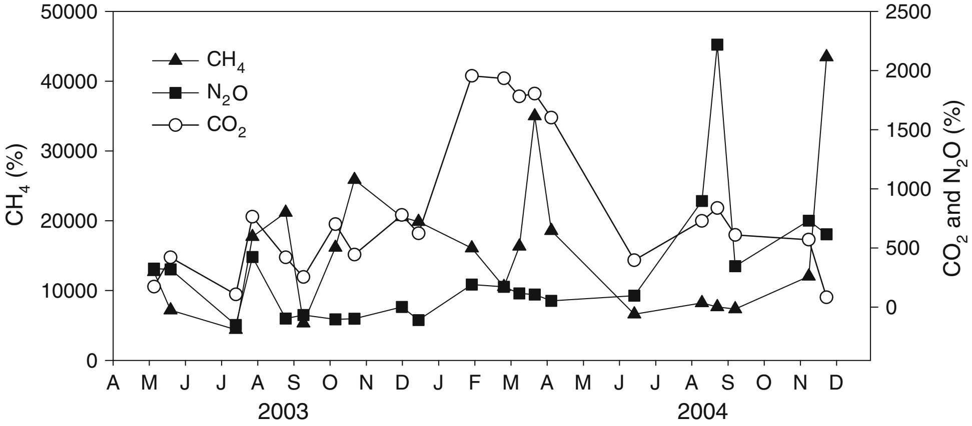

Fig. 2 Saturations of CO_2, CH_4, and N_2O in the river water at the site A in 2003 and 2004

seasonal pattern for CO_2 or CH_4 concentrations (Dawson et al. 2004). CH_4 concentrations in various Pacific Northwest rivers did not show any consistent seasonal trends (Lilley et al. 1996). The accumulation of CO_2 and CH_4 has been well documented in ice-covered lakes (Striegel and Michmerhuizen 1998; Semiletov 1999; Kortelainen et al. 2000), but to the best of our knowledge, this is the first time this phenomenon has been described for rivers.

In contrast to CH_4 and CO_2, the supersaturations of N_2O did not peak in the winter but were highest in spring and late summer (Table 4). N_2O can accumulate in waters beneath ice-cover, but not of such quantities as CH_4 and CO_2 (Kortelainen et al. 2000). The N_2O concentration seems to be more related to the amount of flooding and leaching of N and N_2O from the catchments. N_2O supersaturations measured from site A correlated positively with $NO_2^- + NO_3^- - N$ ($r = 0.845$, $P < 0.001$), tot-N ($r = 0.784$, $P < 0.001$), and TOC ($r = 0.708$, $P < 0.001$). Rivers in boreal zones receive high amounts of water and nutrients as snow in their catchments melts. Another peak in runoff occurs in late summer and autumn after rainstorms (Hyvärinen 1994; Kortelainen et al. 1997). Especially if catchments contain agricultural areas, runoff water in spring can contain high concentrations of nitrogen, phosphorus and organic matter as floodwater flushes bare agricultural soils. In addition to nutrients, a river may receive some N_2O dissolved in runoff waters from agricultural soils. Agricultural soils are known to have high concentrations of N_2O in spring during thawing periods (Syväsalo et al. 2004). Other studies have also shown the highest N_2O concentrations in river water in spring and late summer/autumn (Robinson et al. 1998; Cole and Caraco 2001b).

We evaluated gas fluxes from site A, according to the gas transfer velocities (*k*-values) determined for site 4. The calculated average annual gas fluxes from site A were 22,800 mg CO_2–C m^{-2} d^{-1}, 19 mg CH_4–C m^{-2} d^{-1}, and 2 mg N_2O–N m^{-2} d^{-1} (Table 4). Annual emissions from the site would then be 8,300 g CO_2–C m^{-2}, 7.0 g CH_4–C m^{-2}, and 0.8 g N_2O–N m^{-2}. We also calculated the average fluxes for different seasons (Table 4). If winter is assumed to last from the beginning of November to the end of March, winter emissions from the site would be 4,800 g CO_2–C m^{-2}, 3.8 g CH_4–C m^{-2}, and 0.3 g N_2O–N m^{-2}, representing 58, 55 and 36% of the annual emissions, respectively.

Due to high wintertime supersaturations, average supersaturations and evaluated fluxes for the river sites 1–5 do not represent yearly averages (see next chapter). Those sites were only measured during a period from early spring to autumn. The results from site A showed that the average gas concentrations measured year round (including winter) were 30% higher for CO_2, 59% higher for CH_4 and 11% higher for N_2O when compared to the averages calculated for the measurement period of sites 1–5 (Table 6).

The Temmesjoki River—land use in the catchment determines river water quality and gas dynamics

All the river sites were sources of CO_2 (70–14,300 mg CO_2–C m^{-2} d^{-1}) (Figs. 3a, 4a) and CH_4

(3.2–120 mg CH_4–C m^{-2} d^{-1}) (Figs. 3b, 4b) to the atmosphere throughout the measurement period. At sites 1–4, water was generally supersaturated with N_2O, whereas the estuary site (5) showed both under and supersaturations (Fig. 3c; Table 6). N_2O fluxes varied from −460 to 2,900 µg N_2O m^{-2} d^{-1} (Fig. 3c). CH_4 and CO_2 fluxes were similar to those found earlier for temperate and boreal rivers, 260–24,900 mg CO_2–C m^{-2} d^{-1} and 0.3–340 mg CH_4 m^{-2} d^{-1} (de Angelis and Lilley 1987; Lilley et al. 1996; Jones and Mulholland 1998a, b; Neal et al. 1998; Hope et al. 2001). Rivers, even in a pristine state, are generally known to be sources of CO_2 and CH_4 to the atmosphere (de Angelis and Lilley 1987). However, draining of peatlands, as in the catchment around site 1, likely elevates the concentrations of CO_2 and CH_4 in river waters. Supersaturations of N_2O in the Temmesjoki River were generally within the range of previously published values for rivers (McMahon and Dennehy 1999; Reay et al. 2003; Cole and Caraco 2001b), but lower than those measured from highly N loaded rivers (McMahon and Dennehy 1999; Reay et al. 2003). Low N_2O concentrations have been measured from rivers in pristine regions (Reay et al. 2003).

The river water gas concentrations strongly reflected the land use in the catchments. The carbon gas fluxes and supersaturations were highest from the sites surrounded by drained peatlands and forests, whereas the N_2O fluxes were related to the presence of agriculture in the catchment. The highest fluxes and supersaturations of both CO_2 (average of 5,400 mg CO_2–C m^{-2} d^{-1}, 1,036%; $P < 0.001$) (Fig. 4a; Table 6) and CH_4 (65 mg CH_4–C m^{-2} d^{-1}, 94,980%; $P \leq 0.001$) (Fig. 4b; Table 6) occurred at the most upstream site (site 1). There the Temmesjoki River received most of the water from the drained peatlands, resulting in low pH, low concentrations of O_2 and $NO_2^- + NO_3^- - N$ and a high concentration of inorganic carbon (TIC) (Table 5), and the river water probably received a lot of dissolved CO_2 and CH_4 from peatland-derived ground waters. The content of organic C, which remained at the same level at various river sites, was not the determining factor for C gas emissions. Other studies have stated that in small streams and rivers, most of the CO_2 and CH_4 emitted originate from terrestrial ecosystems (de Angelis and Lilley 1987; Jones and Mulholland 1998a; Mayorga et al. 2005).

Table 4 Gas saturations in surface water and calculated average gas fluxes at the site A in winter ($n = 22$), spring ($N = 6$), summer ($N = 15$) and autumn ($N = 8$), averages and standard errors of mean in parenthesis

	Average saturation (%)					Calculated average flux[a]				
	All seasons	Winter[b]	Spring[b]	Summer[b]	Autumn[b]	All seasons	Winter[b]	Spring[b]	Summer[b]	Autumn[b]
CO_2	890 (89)	1,220 (160)	730 (310)	560 (69)	520 (70)	22,800 (2,200)	31,900 (3,580)	21,900 (7,340)	15,600 (2,540)	11,900 (2,450)
CH_4	15,440 (1,420)	21,160 (2,450)	12,810 (2,460)	10,270 (1,620)	11,360 (3,040)	19 (1.7)	25 (0.3)	15 (0.3)	14 (2.0)	14 (3.4)
N_2O	264 (27)	234 (21)	231 (24)	366 (84)	178 (29)	2.2 (0.4)	1.8 (0.3)	1.7 (0.3)	3.5 (1.2)	1.0 (0.4)

[a] mg C m^{-2} d^{-1} for CO_2 and CH_4, mg N m^{-2} d^{-1} for N_2O

[b] Winter is from November to March, spring is from April to May, summer is from June to August and autumn is from September to October

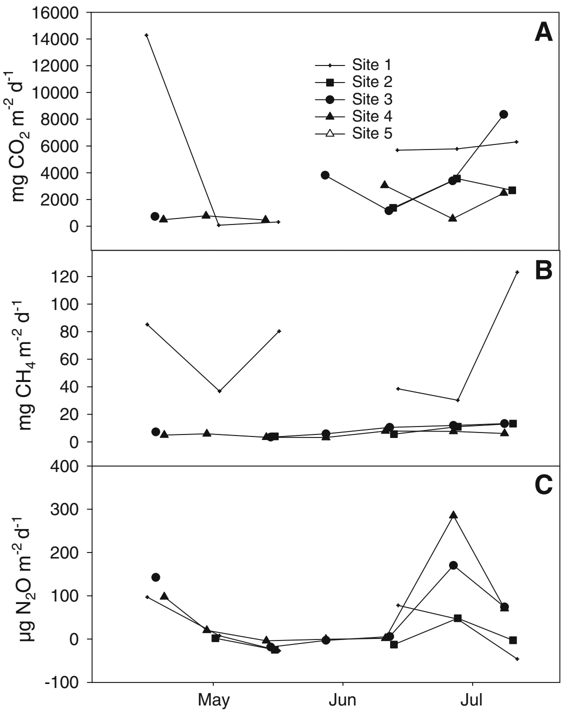

Fig. 3 (**a**) CO_2, (**b**) CH_4, and (**c**) N_2O fluxes calculated from measured gas concentration data and from gas transfer velocities in the Temmesjoki River (sites 1–5) in 2004, daily averages and standard errors of the means

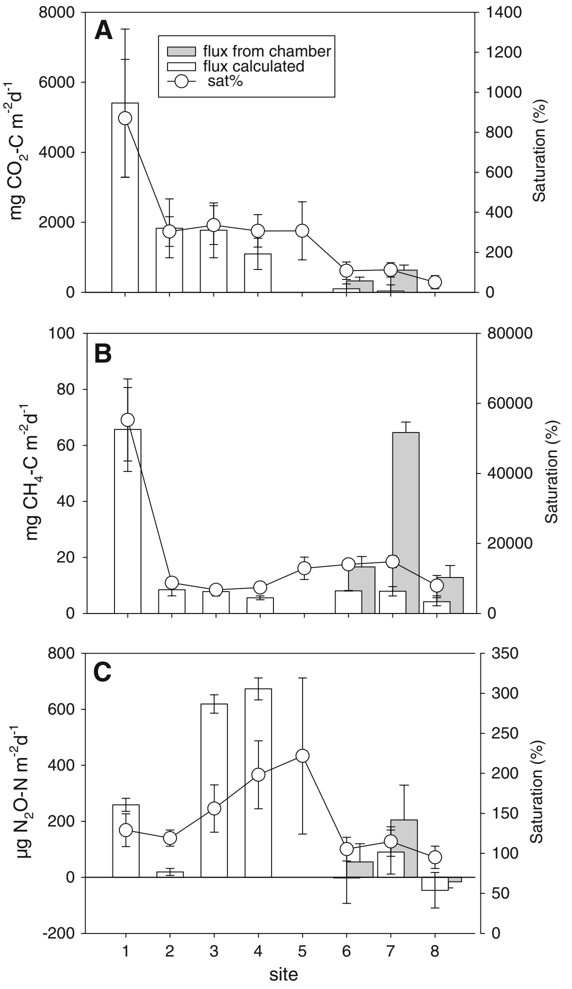

Fig. 4 (**a**) CO_2, (**b**) CH_4, and (**c**) N_2O saturations and fluxes at the river sites (1–5) and the bay sites (6–8). White bars represent the calculated fluxes (in the river and the bay) and gray bars represent the fluxes measured with floating chambers (in the bay). Averages and standard errors of the means are presented for the measurement periods in 2003 (saturations at the river sites) and 2004 (all the parameters)

Our results are consistent with the results of Hope et al. (2004), who found significant CO_2 and CH_4 fluxes from the upstream site of an upland Britain catchment containing drained peatlands. However, the highest concentrations of CO_2 and CH_4 at site 1 (up to 530 µM CO_2 and 15,360 nM CH_4) (Table 6) exceed maximum concentrations found previously (300 µM CO_2 and 2,000 nM CH_4) for temperate and boreal rivers (de Angelis and Lilley 1987; Lilley et al. 1996; Jones and Mulholland 1998a, b; Sansone et al. 1998, 1999; Upstill-Goddard et al. 2000; Hope et al. 2001; Dawson et al. 2002). In contrast to the carbon gases, the saturations and fluxes of N_2O were low at the upstream sites, and started to increase from site 3 (Fig. 4c), where agricultural soils appeared in the catchments and $NO_2^- + NO_3^- - N$ concentrations were orders of magnitude higher than at sites 1–2 (Table 5). In the downstream river sites, the average supersaturation (sites 3–5) was 175% and flux (sites 3–4) was 64 µg N_2O–N m^{-2} d^{-1} (Fig. 4c). The N_2O supersaturations had some positive correlations with the concentrations of $NO_3^- + NO_2^- -$ N ($r = 0.413$, $P = 0.004$) and total N ($r = 0.384$, $P = 0.014$) in river water. Correlations between the N species can be expected because they mostly originate from agricultural soils. Other studies have also found positive, but weak, correlations between N_2O and N species in river water (McMahon and Dennehy 1999; Harrison and Matson 2003; Reay et al. 2003). Reay et al. (2003) reported that N_2O is quickly exhausted from river water, whereas the levels of NO_3^- in river water remained high long after the discharge of agricultural drainage waters.

Table 5 Characteristics of water quality in 2003–2004, averages and standard error of the mean in parentheses

Sites	Carbon (mg C l^{-1})			Nitrogen (µg N l^{-1})			Other variables				
	N	TIC[a]	TOC[b]	NH_4^+	$NO_2^- + NO_3^-$	N-tot	P-tot (µg P l^{-1})	SO_4^{2-} (mg SO_4^{2-} l^{-1})	O_2 (mg O_2 l^{-1})	pH	Water *T* (°C)
1–8	53	2.6 (0.3)	19 (1.2)	61 (5.1)	310 (100)	810 (47)	49 (4)	29 (4.0)	9.7 (0.3)	6.8 (0.1)	13 (0.7)
River	42	2.7 (0.3)	20 (1.5)	58 (5.9)	370 (130)	790 (54)	49 (5.5)	20 (3.2)	9.5 (0.3)	6.5 (0.1)	12 (0.7
1	9	4.1 (1.0)	20 (4.6)	34 (11)	18 (12)	600 (110)	18 (3.0)	10 (9.1)	7.8 (0.7)	6.0 (0.1)	12 (1.4)
2	9	1.6 (0.3)	21 (3.8)	22 (6.6)	67 (30)	610 (100)	29 (4.0)	8 (4.0)	10.6 (0.7)	6.5 (0.2)	11 (1.6)
3	9	2.2 (0.5)	22 (2.7)	52 (6.5)	300 (100)	830 (85)	64 (13)	12 (1.5)	9.5 (0.5)	6.7 (0.2)	12 (1.7)
4	8	2.1 (0.6)	22 (2.5)	71 (7.9)	400 (140)	940 (140)	72 (16)	18 (1.4)	9.4 (0.7)	6.6 (0.1)	11(1.9)
5	7	4.2 (1.2)	16 (1.4)	122 (11)	1,180 (670)	1,050 (110)	69 (7.8)	56 (6.5)	10.3 (0.7)	7.1 (0.3)	14 (2.0)
Bay	12	2.0 (0.1)	15 (1.2)	72 (8.7)	73 (27)	866	51 (5.7)	68 (11)	10.7 (0.6)	7.7 (0.2)	17 (0.8)
6	4	2.0 (0.4)	17 (1.5)	69 (12)	44 (19)	824	46 (4.9)	54 (5.3)	9.6 (1.3)	7.4 (0.2)	17 (1.0)
7	4	2.0 (0.1)	18 (2.0)	94 (19)	170 (49)	1,014	70 (7.9)	52 (9.1)	12.2 (0.5)	7.4 (0.3)	16 (1.2)
8	4	2.0 (0.2)	12 (1.8)	55 (8.6)	1 (1)	761	36 (8.8)	100 (28)	10.1 (0.6)	8.1 (0.3)	17 (1.0)
A	21	8.9 (1.5)	14 (1.5)	280 (39)	300 (40)	1,130 (80)	120 (11)	37 (5.8)	9.0 (0.5)	6.8 (0.1)	11 (1.2)

[a] Total inorganic carbon

[b] Total organic carbon

Thus rapid degassing of the N_2O to the atmosphere is probably the reason for a poor correlation between the dissolved N species and the fluxes or supersaturations of N_2O. It has to be noted that we cannot evaluate here whether the N_2O emitted from river water was leached from catchments or was produced by microbial processes in the river channel itself. Groundwaters and drainage waters from agricultural areas have been reported to contain high amounts of N_2O (Hasegawa et al. 2000, Hiscock et al. 2003). The levels of supersaturation and fluxes of N_2O increased with the presence of agricultural soils and N loads in the catchments, supporting results from earlier studies (McMahon and Dennehy 1999; Reay et al. 2003). However, Cole and Caraco (2001a, b) determined that the Hudson River is not an important source of N_2O at the landscape level. Thus, there are conflicting results regarding N_2O emissions from various rivers.

The gases produced in the catchments were quickly degassed from the river water. For example, the differences in the CO_2 and CH_4 concentrations between sites 1 and 2 were large. Dawson et al. (2004) also reported a sharp decrease in CO_2 and CH_4 concentrations from upstream to downstream in peatland streams. Reay et al. (2003), in turn, reported that most of the dissolved N_2O the river received was degassed from the water within 100 m. For N_2O, we did not find any similar effects, as agricultural soils and thus sources of N_2O were present all along the river course from site 3 to the bay.

The Liminganlahti Bay—a minor source of gases to the atmosphere

Unlike the Temmesjoki River, the open water area of the Liminganlahti Bay was not a significant source of greenhouse gases. The water in the bay exhibits higher pH values and SO_4^{2-} concentrations and lower TOC and nutrient concentrations than the river water (Table 5). The bay mainly consists of river water, already degassed in the river and the estuary, and is therefore CH_4, CO_2 and N_2O depleted (Fig. 5; Table 6) In the bay, the river water is further diluted by water from the Bothnian Bay and therefore, concentrations and fluxes of gases decrease further. Similar results have been found for other river–estuary systems, where gas supersaturations and fluxes from the water to the atmosphere are lower

Table 6 Concentrations of gases and dissolved inorganic carbon (DIC) and partial pressure of CO_2 (pCO_2) in surface water at the study sites

Sites		*N*	DIC (µM)	CO_2 (µM)	pCO2 (µatm)	CH_4 (nM)	N_2O (nM)
A	Mean (SE)	21	737 (122)	215 (44)	3,520 (370)	632 (98)	36 (5)
	Min–max		52–1,610	16–595	340–8,380	122–1,920	10–95
1–8	Mean (SE)	65	217 (24)	74 (12)	1,400 (164)	870 (265)	18 (1.3)
	Min–max		40–850	0.5–530	10–16,080	62–15,360	7–53
River	Mean (SE)	53	228 (53)	87 (14)	1,710 (220)	984 (322)	19 (1.5)
	Min–max		40–820	4.7–531	150–16,080	87–15,360	6.7–53
1	Mean (SE)	11	342 (87)	210 (51)	4,100 (820)	3,450 (1,350)	17 (3)
	Min–max		57–850	24–531	450–16,080	718–15,360	6.7–39
2	Mean (SE)	12	130 (25)	51 (7)	980 (93)	367 (62)	15 (2)
	Min–max		40–338	10–97	180–2,150	139–869	9.6–29
3	Mean (SE)	11	185 (38)	57 (11)	1,070 (140)	210 (22)	18 (2)
	Min–max		42–451	12–125	240–2,940	87–313	9.8–34
4	Mean (SE)	11	172 (48)	60 (11)	1,100 (140)	308 (63)	23 (4)
	Min–max		49–572	7.3–117	150–2,700	106–825	10–47
5	Mean (SE)	8	354 (100)	50 (13)	1,100 (170)	517 (177)	26 (6)
	Min–max		106–763	4.7–114	110–2,700	239–894	11–53
Bay	Mean (SE)	12	166 (11)	15 (34)	660 (93)	353 (41)	11 (0.7)
	Min–max		91–227	0.45–34	10–2,690	62–588	7.3–15
6	Mean (SE)	4	166 (32)	17 (6)	400 (110)	400 (19)	10 (1)
	Min–max		91–227	4.5–34	100–890	358–452	9.2–13
7	Mean (SE)	4	165 (4)	19 (6)	420 (87)	437 (57)	12 (2)
	Min–max		154–173	2.8–28	64–650	335–588	8.5–15
8	Mean (SE)	4	169 (14)	9 (6)	190 (81)	223 (78)	9.6 (1)
	Min–max		133–193	0.45–27.8	10–620	62–406	7.3–13

in estuaries than in rivers (de Angelis and Lilley 1987; Sansone et al. 1998). However, when comparing gas emissions in estuaries and open seas, estuaries are important marine sources of CH_4 (Bange et al. 1994; Upstill-Goddard et al. 2000; Bange 2006), CO_2 (Borges 2005; Borges et al. 2006) and N_2O (Bange et al. 1996; Seitzinger et al. 2000; Bange 2006).

Saturations and fluxes of CO_2 were smaller at the bay sites than at the river sites ($P < 0.01$) (Fig. 4a; Table 6). The calculated fluxes differ substantially from the fluxes measured with the dark floating chambers. The dark chamber may disturb photosynthesis and uptake of CO_2 from the atmosphere, resulting in higher CO_2 fluxes. CO_2 concentrations in surface water were close to atmospheric equilibrium (Fig. 5a; Table 6). According to the calculated flux (Fig. 5d), the bay sites were either small sinks or sources of CO_2. The fluxes measured with the chambers show that the sites are only minor sources of CO_2 (Fig. 4a). CO_2 saturations correlated negatively with pH ($r = -0.811$, $P = 0.001$) (Table 5). At low pH values, below 6.35, most of the inorganic carbon is present as CO_2; at higher pH values, bicarbonates (HCO_3^-) and carbonates (CO_3^{2-}) dominate (Buttler 1982). In the bay, the mixing of bay and river water results in higher pH and dissociation of CO_2 to bicarbonates (pH of 7.7 in the bay and 6.5 at the river sites), which could also partly explain smaller CO_2 fluxes in the bay than in the river. The CO_2 fluxes in the Liminganlahti Bay are at the lower end of the range of values found previously (from −16 to 9,100 mg CO_2–C m^{-2} d^{-1}) in inner estuaries around the world (Borges 2005; Abril and Borges 2005; Borges et al. 2006). The organic carbon load to Liminganlahti Bay is probably not as high as in other European estuaries, where high levels of anthropogenic labile carbon have been measured (Abril and Iversen 2002). The average CO_2 fluxes measured

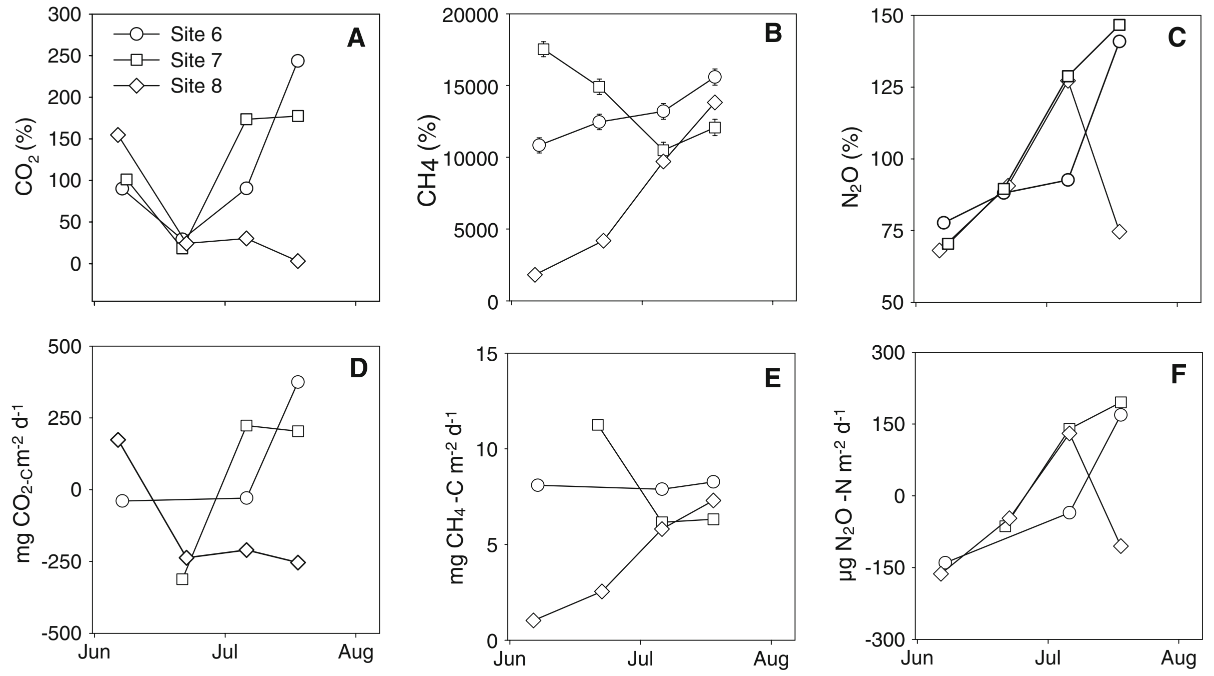

Fig. 5 Saturations of (**a**) CO_2, (**b**) CH_4, and (**c**) N_2O and calculated fluxes (**d**) CO_2, (**e**) CH_4, and (**f**) N_2O at the bay sites (sites 6–8)

from the Liminganlahti, i.e. from the inner estuary, are similar to the average emissions measured from the adjacent northern Bothnian Bay (Algesten et al. 2004). Generally, inner estuaries have shown higher CO_2 emissions than coastal oceans (Borges 2005). The whole northern Bothnian Bay is actually oligohaline rather than brackish water, salinity being <2‰ (Kronholm et al. 2005); thus, most of its water is of riverine origin.

CH_4 fluxes were generally below 40 mg CH_4–C m^{-2} d^{-1} in the bay, but high CH_4 emissions, up to 300 mg CH_4–C m^{-2} d^{-1}, were obtained with chamber measurements at site 7 (Figs. 4b, 5b). Emissions and supersaturations of CH_4 in the Liminganlahti Bay are, on average, within the range previously found for other European estuaries (Upstill-Goddard et al. 2000; Middelburg et al. 2002; Bange 2006). However, the average CH_4 supersaturation of several European estuaries was found to be lower, 3,640% (Bange 2006), than the average CH_4 supersaturation of 11,030% (Fig. 5b) found in Liminganlahti Bay. One reason for this might be the low SO_4^{2-} concentrations in Liminganlahti Bay (Table 5). CH_4 supersaturations correlated negatively with SO_4^{2-} concentrations ($r = -0.795$, $P = 0.002$). Methanogenesis, a thermodynamically less favorable process than sulfate reduction, occurs generally only after the sulfate that is present has been reduced (Capone and Kiene 1988). Sulfate also participates in anaerobic oxidation of CH_4 and therefore reduces CH_4 fluxes (Boetius et al. 2000). Additionally, in the shallow Liminganlahti Bay, a smaller part of the CH_4 is likely to be oxidized than in areas with deeper waters (Abril and Iversen 2002). The volume of water diluting the river water rich in CH_4 is also smaller than the volume of deeper estuaries. A part of the CH_4 in surface waters of the bay may have originated from CH_4 production in anoxic sediments or bottom waters. Although the CH_4 emissions were lower from the open water of the bay than from the river sites, the bay region could be releasing significant amounts of CH_4 from the surrounding wetlands (Heyer and Berger 2000). Average CH_4 emissions from the wetlands of Liminganlahti Bay were found to be 154 mg CH_4–C m^{-2} d^{-1} (Liikanen et al. unpublished data), which is higher than the average emissions of the Temmesjoki River or the open water area of the bay.

The N_2O concentrations in the bay were close to atmospheric equilibrium values and the bay was alternately either a sink or source for N_2O (Figs. 4c, 5c, 5f). The fluxes and concentrations of N_2O were an order of magnitude lower at the bay than at the river sites (Fig. 5c; Table 6) (for concentrations $P = 0.045$). The N_2O fluxes were highest from site 7, which was located near the mouth of the Lumijoki River (Figs. 4c, 5f). At site 7, the levels of inorganic N species were highest (Table 5). The N content controlled N_2O dynamics, and the N_2O saturations correlated positively with $NO_2^- + NO_3^- - N$ ($r = 0.698$, $P = 0.012$). The N_2O concentrations and fluxes measured are within the range previously reported (Robinson et al. 1998; de Wilde and de Bie 2000; LaMontagne et al. 2003; Bange 2006). The average supersaturation of N_2O (136%) in Liminganlahti Bay is lower than the mean for other European estuaries (465%) (Bange 2006). There are some earlier observations that estuarine waters act occasionally as sinks for N_2O (Robinson et al. 1998). Benthic denitrification is a possible sink for N_2O in the bay (LaMontagne et al. 2003). N_2O emitted from the bay can be of riverine origin or produced in situ from nitrification (Barnes and Owens 1998; de Wilde and de Bie 2000) or denitrification (Robinson et al. 1998). Since the emissions of N_2O from Liminganlahti Bay were small, no significant production of N_2O is likely to be occurring in the bay. The wetlands surrounding Liminganlahti Bay are either small sinks or sources of N_2O, like the open water area of the bay (Liikanen et al. unpublished data).

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References

Abril G, Borges AV (2005) Carbon dioxide and methane emissions from estuaries. In: Tremblay A, Varfalvy L, Roehm C, Garneau M (eds) Greenhouse gas emissions—fluxes and processes: hydroelectric reservoirs and natural environments. Springer, Berlin, pp 187–207

Abril G, Iversen N (2002) Methane dynamics in a shallow non-tidal estuary (Randers Fjord, Denmark). Mar Ecol Prog Ser 230:171–181. doi:10.3354/meps230171

Algesten G, Wikner J, Sobek S, Tranvik LJ, Jansson M (2004) Seasonal variation of CO_2 saturation in the Gulf of Bothnian: indications of marine net heterotrophy. Global Biogeochem Cycles 18:GB4021. doi:10.1029/2004GB002232

Bange HW (2006) Nitrous oxide and methane in European coastal waters. Estuar Coast Shelf Sci 70:361–374. doi:10.1016/j.ecss.2006.05.042

Bange HW, Bartell UH, Rapsomanikis S, Andreae MO (1994) Methane in the Baltic and North Seas and a reassessment of the marine emissions of methane. Global Biogeochem Cycles 8:465–480. doi:10.1029/94GB02181

Bange HW, Rapsomanikis S, Andreae MO (1996) Nitrous oxide in coastal waters. Global Biogeochem Cycles 10:197–207. doi:10.1029/95GB03834

Barnes J, Owens NJP (1998) Denitrification and nitrous oxide concentrations in the Humber estuary, UK, and adjacent coastal zones. Mar Pollut Bull 37:247–260. doi:10.1016/S0025-326X(99)00079-X

Boetius A, Ravenschlag K, Schubert CJ, Rickert D, Widdel F, Gieseke A et al (2000) A marine microbial consortium apparently mediating anaerobic oxidation of methane. Nature 407:623–626. doi:10.1038/35036572

Borges AV (2005) Do we have enough pieces of the jigsaw to integrate CO_2 fluxes in the coastal ocean. Estuaries 28:3–27

Borges AV, Delille B, Schiettecatte L-S, Gazeau F, Abril G, Frankignoulle M (2004) Gas transfer velocities of CO_2 in three European estuaries (Randers Fjord, Scheldt, and Thames). Limnol Oceanogr 49:1630–1641

Borges AV, Schiettecatte L-S, Abril G, Delille B, Gazeau F (2006) Carbon dioxide in European coastal waters. Estuar Coast Shelf Sci 70:375–387. doi:10.1016/j.ecss.2006.05.046

Buttler JN (1982) Carbon dioxide equilibria and their applications. Addison-Wesley Publishing Company Inc., Menlo Park, CA

Capone DG, Kiene RP (1988) Comparison of microbial dynamics in marine and freshwater sediments: contrast in anaerobic carbon metabolism. Limnol Oceanogr 33:725–749

Cicerone RJ, Oremland RS (1988) Biogeochemical aspects of atmospheric methane. Global Biogeochem Cycles 2:299–327. doi:10.1029/GB002i004p00299

Cole JJ, Caraco NF (2001a) Carbon in catchments: connecting terrestrial carbon losses with aquatic metabolism. Mar Freshw Res 52:101–110. doi:10.1071/MF00084

Cole JJ, Caraco NF (2001b) Emissions of nitrous oxide (N_2O) from a tidal, freshwater river, the Hudson River, New York. Environ Sci Technol 35:991–996. doi:10.1021/es0015848

Cole JJ, Prairie YT, Caraco NF, McDowell WH, Tranvik LJ et al (2007) Plumbing the global carbon cycle: integrating inland waters into the terrestrial carbon cycle. Ecosystems (NY Print) 10:172–185. doi:10.1007/s10021-006-9013-8

Dawson JJC, Billett MF, Hope D (2001) Diurnal variations in the carbon chemistry of two acidic peatland streams in north–east Scotland. Freshw Biol 46:1309–1322. doi:10.1046/j.1365-2427.2001.00751.x

Dawson JJC, Billett MF, Neal C, Hill S (2002) A comparison of particulate, dissolved and gaseous carbon in two contrasting upland streams in the UK. J Hydrol (Amst) 257:226–246. doi:10.1016/S0022-1694(01)00545-5

Dawson JJC, Billett MF, Hope D, Palmer SM, Deacon CM (2004) Sources and sinks of aquatic carbon in a peatland stream consortium. Biogeochemistry 70:71–92. doi:10.1023/B:BIOG.0000049337.66150.f1

de Angelis MA, Lilley MD (1987) Methane in surface waters of Oregon estuaries and rivers. Limnol Oceanogr 32:716–722

de Wilde HPJ, de Bie MJM (2000) Nitrous oxide in the Schelde estuary: production by nitrification and emission to the atmosphere. Mar Chem 69:203–216. doi:10.1016/S0304-4203(99)00106-1

Fawcett JK, Scott JE (1960) A rapid and precise method for the determination of urea. J Clin Pathol 13:156–159. doi:10.1136/jcp.13.2.156

Firestone MK, Davidson EA (1989) Microbiological basis of NO and N_2O production and consumption in soil. In: Andreae MO, Schimel DS (eds) Exchange of trace gases between terrestrial ecosystems and the atmosphere. John Wiley & Sons Ltd, Chichester, New York, Brisbane, Toronto, Singapore, pp 7–21

Frankignoulle M, Abril G, Borges A, Bourge I, Canon C, Delille B et al (1998) Carbon dioxide emission from European estuaries. Science 282:434–436. doi:10.1126/science.282.5388.434

Hanson RS, Hanson TE (1996) Methanotrophic bacteria. Microbiol Rev 60:439–471

Harrison J, Matson P (2003) Patterns and controls of nitrous oxide emissions from waters draining a subtropical agricultural valley. Global Biogeochem Cycles 17:1080. doi:10.1029/2002GB001991

Hasegawa K, Hanaki K, Matsuo T, Hidaka S (2000) Nitrous oxide from the agricultural water system contamined with high nitrogen. Chemos Global Change Sci 2:335–345

Heyer J, Berger U (2000) Methane emission from the coastal area in the southern Baltic Sea. Estuar Coast Shelf Sci 51:13–30. doi:10.1006/ecss.2000.0616

Hiscock KM, Bateman AS, Mühlherr IH, Fukada T, Dennis PF (2003) Indirect emissions of nitrous oxide from regional aquifer in the United Kingdom. Environ Sci Technol 37:3507–3512. doi:10.1021/es020216w

Hope D, Palmer SM, Billett MF, Dawson JJ (2001) Carbon dioxide and methane evasion from a temperature peatland stream. Limnol Oceanogr 46:847–857

Hope D, Palmer SM, Billett MF, Dawson JJ (2004) Variations in dissolved CO_2 and CH_4 in a first-order stream and catchment: an investigation of soil-stream linkages. Hydrol Process 18:3255–3275. doi:10.1002/hyp.5657

Huttunen J, Väisänen TS, Hellsten SK, Heikkinen M, Lindqvist OV, Nenonen OS et al (2002) Fluxes of CH_4, CO_2 and N_2O in hydroelectric reservoirs Lokka and Porttipahta in the northern boreal zone in Finland. Global Biogeochem Cycles 16(1):1003. doi:10.1029/2000GB001316

Hyvärinen V (1994) Hydrological yearbook 1994. The Finnish Environment 176. Finnish Environment Institute, Helsinki

Jähne BK, Münnich O, Bosinger R, Dutzi A, Huber W, Libner P (1987) On parameters influencing air–water gas exchange. J Geophys Res 92:1937–1949. doi:10.1029/JC092iC02p01937

Jones JB, Mulholland PJ (1998a) Influence of drainage basin topography and elevation on carbon dioxide and methane supersaturation of stream water. Biogeochem 40:57–72. doi:10.1023/A:1005914121280

Jones JB, Mulholland PJ (1998b) Methane input and evasion in a hardwood forest stream: effects of subsurface flow from shallow and deep pathways. Limnol Oceanogr 43:1243–1250

Kling GW, Kipphut GW, Miller MC (1991) Arctic lakes and streams as conduits to the atmosphere: implications for tundra carbon budget. Science 251:298–301. doi:10.1126/science.251.4991.298

Knowles R (1981) Denitrification. In: Clark FE, Rosswall T (eds) Terrestrial nitrogen cycles, processes, ecosystem strategies and management impacts, Ecol. bull. 33. Swedish Natural Science Research Council, Stockholm, pp 315–329

Kortelainen P, Saukkonen S, Mattsson T (1997) Leaching of nitrogen from forested catchments in Finland. Global Biogeochem Cycles 11:627–638. doi:10.1029/97GB01961

Kortelainen P, Huttunen JT, Väisänen T, Mattsson T, Karjalainen P, Martikainen PJ (2000) CH_4, CO_2 and N_2O supersaturation in 12 Finnish lakes before and after ice-melt. Verh Int Verein Limnol 27:1410–1414

Kremer JN, Nixon SW, Bugkley B, Roques P (2003a) Technical note: conditions for using the floating chamber method to estimate air–water gas exchange. Estuaries 26:985–990

Kremer JN, Reischauer A, D'Avanzo C (2003b) Estuary specific variation in the air–water gas-exchange coefficient for oxygen. Estuaries 26:829–836

Kronholm M, Albertson J, Laine A (2005) Perämeri Life. Perämeren toimintasuunnitelma. Länstyrelsen i Norrbottens län, raportserie 1/2005

LaMontagne MG, Duran R, Valiela I (2003) Nitrous oxide sources and sinks in coastal aquifer and coupled estuarine receiving waters. Sci Total Environ 309:139–149. doi:10.1016/S0048-9697(02)00614-9

Lide DR, Fredrikse HPR (1995) CRC handbook of chemistry and physics, 76th edn. CRC, Boca Raton, FL

Lilley MD, de Angelis MA, Olson EJ (1996) Methane concentrations and estimated fluxes from Pacific Northwest rivers. Mitt Int Verein Limnol 25:187–196

Matthews CJD, St. Louis VL, Hesslein RH (2003) Comparison of three techniques used to measure diffusive gas exchange from sheltered aquatic surfaces. Environ Sci Technol 37:772–780. doi:10.1021/es0205838

Mayorga E, Aufdenkampe AK, Masiello CA, Krusche AV, Hedges JI, Quay PD et al (2005) Young organic matter as a source of carbon dioxide outgassing from Amazon rivers. Nature 436:538–541. doi:10.1038/nature03880

McAuliffe C (1971) GC determination of solutes by multiple phase equilibration. Chem Technol 1:46–51

McMahon PB, Dennehy KF (1999) N_2O emissions from a nitrogen-enriched river. Environ Sci Technol 33:21–25. doi:10.1021/es980645n

Middelburg JJ, Nieuwenhuize J, Iversen N, Høgh N, de Wilde H, Helder W et al (2002) Methane distribution in European tidal estuaries. Biogeochemistry 59:95–119. doi:10.1023/A:1015515130419

Neal C, House WA, Jarvie HP, Eatherall A (1998) The significance of dissolved carbon dioxide in major lowland rivers entering the North Sea. Sci Total Environ 210/211:187–203. doi:10.1016/S0048-9697(98)00012-6

Nykänen H, Alm J, Lång K, Silvola J, Martikainen PJ (1995) Emissions of CH_4, N_2O and CO_2 from a virgin fen and a fen drained for grassland in Finland. J Biogeogr 22:351–357. doi:10.2307/2845930

O'Connor DJ, Dobbins WE (1958) Mechanism f reaeration in natural streams. Trans Am Soc Civ Eng 123:641–684

Raymond PA, Bauer JE (2001) Use of ^{14}C and ^{13}C natural abundance for evaluating riverine, estuarine, and coastal DOC and POC sources and cycling: a review and synthesis. Org Geochem 32:469–485. doi:10.1016/S0146-6380(00)00190-X

Raymond PA, Cole JJ (2001) Gas exchange in rivers and estuaries: choosing a gas transfer velocity. Estuaries 24:312–317. doi:10.2307/1352954

Raymond PA, Caraco NF, Cole JJ (1997) Carbon dioxide concentration and atmospheric flux in the Hudson River. Estuaries 20:381–390. doi:10.2307/1352351

Raymond PA, Bauer JE, Cole JJ (2000) Atmospheric evasion, dissolved inorganic carbon production, and net heterotrophy in the York River estuary. Limnol Oceanogr 45:1707–1717

Reay DS, Smith KA, Edwards AC (2003) Nitrous oxide emission from agricultural drainage waters. Glob Change Biol 9:195–203. doi:10.1046/j.1365-2486.2003.00584.x

Richey JE, Melack JM, Aufdenkampe AK et al (2002) Outgassing from Amazonian rivers and wetlands as a large tropical source of atmospheric CO_2. Nature 416:617–620. doi:10.1038/416617a

Robinson AD, Nedwell DB, Harrison RM, Ogilvie BG (1998) Hypernutrified estuaries as sources of N_2O emission to the atmosphere: the estuary of the River Colne, Essex, UK. Mar Ecol Prog Ser 164:59–71. doi:10.3354/meps164059

Sansone FJ, Rust TM, Smith SV (1998) Methane distribution and cycling in Tomales Bay, California. Estuaries 21:66–77. doi:10.2307/1352547

Sansone FJ, Holmes ME, Popp BN (1999) Methane stable isotopic ratios and concentrations as indicators of methane dynamics in estuaries. Global Biogeochem Cycles 13:463–474. doi:10.1029/1999GB900012

Seitzinger SP, Kroeze C (1998) Global distribution of nitrous oxide production and N inputs in freshwater and coastal marine ecosystems. Global Biogeochem Cycles 12:93–113. doi:10.1029/97GB03657

Seitzinger SP, Kroeze C, Styles RV (2000) Global distribution of N_2O emissions from aquatic systems: natural emissions and anthropogenic effects. Chemos Global Change Sci 2:267–279

Semiletov IP (1999) Aquatic sources and sinks of CO_2 and CH_4 in the polar regions. J Atmos Sci 56:286–306. doi:10.1175/1520-0469(1999)056<0286:ASASOC>2.0.CO;2

Smith MS, Zimmerman K (1981) Nitrous oxide production by nondenitrifying soil nitrate reducers. Soil Sci Soc Am 45:865–871

Standardization SFS (1976) SFS 3032. Determination of ammonia nitrogen of water. Helsinki, Finland

Standardization SFS (1979) SFS 3021. Determination of pH-value of water. Helsinki, Finland

Standardization SFS (1986) SFS 3026. Determination of total phosphorus in water. Helsinki, Finland

Standardization SFS (1993) SFS-EN 25813. Water quality. Determination of dissolved oxygen. Iodometric method. Helsinki, Finland

Standardization SFS (1995) SFS-EN ISO 10304-1. Water Quality. Determination of dissolved fluoride, chloride, nitrite, orthophosphate, bromide, nitrate and sulfate ions, using liquid chromatography of ions. Part 1: method for water with low contamination. Helsinki, Finland

Standardization SFS (1997a) SFS-EN 1484. Water analysis. Guidelines for the determination of total organic carbon (TOC) and dissolved organic carbon (DOC). Helsinki, Finland

Standardization SFS (1997b) SFS-EN ISO 13395. Water quality. Determination of nitrite nitrogen and nitrate nitrogen and the sum of both by flow analysis (CFA and FIA) and spectrometric detection. Helsinki, Finland

Standardization SFS (1998) SFS-EN ISO 11905-1. Water quality. Determination of nitrogen. Part 1: method using oxidative digestion with peroxodisulfate. Helsinki, Finland

Striegel RG, Michmerhuizen CM (1998) Hydrologic influence on methane and carbon dioxide dynamics at two north-central Minnesota lakes. Limnol Oceanogr 43:1519–1529

Syväsalo E, Regina K, Philatie M, Esala M (2004) Emissions of nitrous oxide from boreal agricultural clay and loamy sand soils. Nutr Cycle Agroecosyst 69:155–165. doi:10.1023/B:FRES.0000029675.24465.fc

Upstill-Goddard RC, Barnes J, Frost T, Punshon S, Owens NJP (2000) Methane in the Southern North Sea: low salinity inputs, estuarine removal, and atmospheric flux. Global Biogeochem Cycles 14:1205–1217. doi:10.1029/1999GB001236

Wanninkhof R (1992) Relationship between wind speed and gas exchange over the ocean. J Geophys Res 97:7373–7382. doi:10.1029/92JC00188

Wetzel RG (2001) Limnology lake and river ecosystems. Academic, Elsevier, San Diego, CA