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Nitrogen ebullition in a Colorado plains river

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Abstract Rates of ebullition and composition of
bubbles were measured along a nutrient-enriched
segment of the South Platte River below Denver,
Colorado. Ebullition was widespread in the South
Platte up to 81 km downstream from Denver. Ebull-
itive fluxes of 0.44 and 0.29 g N m^{-2} d^{-1} were
recorded at two sites downstream of Denver and
represented 6–16% of the diffusive N$_2$ efflux from this
region. These data indicate that not accounting for
ebullitive N$_2$ losses can, at some locations, lead to a
considerable underestimation of dentrification rates
using the open-channel (gas exchange) method. Gas
bubbles often were >98% N$_2$; methane dominated in a
few organic-rich areas. Rates of ebullition related
significantly to variations in temperature and dis-
solved organic carbon. Ebullition was not observed in
four tributaries of the South Platte River, despite their
moderate to high concentrations of nitrate and
dissolved organic carbon. The data demonstrate that
ebullition can contribute significantly to N$_2$ effluxes in
running waters exhibiting high rates of denitrification.

Introduction

Denitrification, the microbial reduction of nitrate
(NO$_3^-$) primarily to N$_2$ (but also some N$_2$O), is an
important component of the nitrogen cycle in aquatic
ecosystems; it reduces the nitrogen available for
phototrophic uptake or export to downstream eco-
systems. Sediments within and adjacent to river
channels have proven to be active sites of denitrifi-
cation (Clément et al. 2002; Sjodin et al. 1997).

Mean annual rates of denitrification in the South
Platte below Denver, Colorado, can be high (0.5–
1.62 g N m^{-2} d^{-1}; Pribyl et al. 2005; Sjodin et al.
1997). High rates of denitrification have been mea-
sured for some other rivers (Howarth et al. 1996;
Laursen and Seitzinger 2002; Schaller et al. 2004),
but rates of denitrification for the South Platte below
Denver are five or more times higher than denitrifi-
cation rates documented for many other US rivers
(Forshay and Stanley 2005; Kemp and Dodds 2002;
Piña-Ochoa and Álvarez-Cobelas 2006; Seitzinger
1988). Rates for the South Platte River are equivalent

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to 90% nitrate removal over distances of 49–180 km, although these rates are partly offset by the return of nitrate-rich irrigation water downstream of Denver.

McMahon and Dennehy (1999) found the waters of the South Platte to be substantially supersaturated with N_2O (median N_2O-emission rate, 1.49×10^{-3} g N m^{-2} d^{-1}). Although such N_2O emissions are significant from the perspective of atmospheric chemistry because N_2O is a potent greenhouse gas (300 times as potent as CO_2), N_2O fluxes account for only a small proportion (<1%) of the total nitrate conversion in the South Platte and in fresh waters generally (Seitzinger 1988).

Accurate measurements of denitrification are essential both in balancing N budgets for aquatic systems or watersheds and in understanding the effects of anthropogenic N enrichment. The high-precision measurement of N_2 by membrane-inlet mass spectroscopy (MIMS) (Kana et al. 1994, 1998) has led to the recent development of an open-channel (gas exchange) method for measuring denitrification in running waters (Laursen and Seitzinger 2002; McCutchan et al. 2003), which has been successfully applied to the South Platte River near Denver (Pribyl et al. 2005). The open-channel method offers significant advantages over the traditional mass-balance approach based on estimation of mass balance for ammonia and nitrate (Hill 1979), which can suffer from accumulated measurement errors (Cornwell et al. 1999), and also estimates based on the addition of ^{15}N (Böhlke et al. 2004; Steingruber et al. 2001), which are best suited to small waterbodies.

During previous studies of the South Platte (McCutchan et al. 2003; Pribyl et al. 2005), ebullition (bubbling) from the river sediments was observed at various locations. Preliminary gas analysis revealed that the bubbles consisted almost entirely of N_2 (J. McCutchan, unpublished data). This finding is significant, since N_2 bubbling in rivers is undocumented and suggests the presence of an alternative pathway for the flux of N_2 from aquatic systems to the atmosphere. Previous studies of ebullition events have tended to focus on organic-rich reducing environments such as lakes, swamps, peat bogs and paddy fields, for which methane is the predominant emission (Chanton and Whiting 1995; Chareonsilp et al. 2000; Tokida et al. 2005). The formation and release of N_2-rich gas bubbles has been reported for laboratory cores and microcosms used

for studying denitrification (Liikanen et al. 2002). High content of N_2 in gas bubbles released from marsh and marine sediments has been attributed to the molecular diffusion from aerated overlying water (Chanton et al. 1989) or the stripping of N_2 from pore waters by methane ebullition (Chanton and Whiting 1995; Kipphut and Martens 1982; Lamontagne and Valiela 1995), but may be explained by denitrification. Ebullition can be significant in the transport of N_2O from both recently irrigated soils (Clough et al. 2003) and spring-fed rivers (Clough et al. 2005). Nitrogen ebullition caused by rapid denitrification also has been recognized as a significant process in fixed-film reactors, particularly where nitrate concentrations exceed 6 mg l^{-1} (Harremoes et al. 1980). Denitrification-related N_2 ebullition processes in nitrate-enriched running waters have not been studied.

Open-channel estimates of denitrification have been based on the assumption that fluxes of N_2 associated with denitrification are entirely diffusive. Thus, the method may underestimate denitrification rates if ebullitive N_2 fluxes are substantial. Here we address the significance of ebullition in the transport of N_2 from the South Platte River and investigate factors controlling ebullition.

Methods

For this study, 26 sites along a 250-km reach of the South Platte River below Denver and four of its tributaries (St. Vrain Creek, Big Thompson River, Cache La Poudre River, Boulder Creek) were surveyed for ebullition, dissolved and bubble gas concentrations, and concentrations of inorganic nutrients on various dates between May and September 2006 (Fig. 1). Bubble gas compositions and dissolved N_2:Ar ratios were studied in more detail at four locations (sites A–D) on the South Platte River (April–September 2006, $n = 14$), and rates of ebullition were quantified at the two upstream sites, A and B, where denitrification rates were highest (May–November 2006, $n = 15$).

Site description

The South Platte River downstream from Denver was the main focus of this study. The four intensively

sampled sites (A–D) are situated at distances of 5, 24, 44 and 52 km downstream from the point of discharge for Denver's largest wastewater treatment plant, which serves 1.3 million people (Table 1 and Fig. 1). Ebullition from the riverbed has been observed previously within this reach (Pribyl et al. 2005; T. Higgins, unpublished data). The river has a strong seasonal peak in discharge associated with snowmelt and has brief spates caused by summer thunderstorms affecting tributary waters (Fig. 2a).

Fig. 1 Locations of the intensive study sites (A–D) and survey sites ($n = 22$) on the South Platte River and four of its tributaries
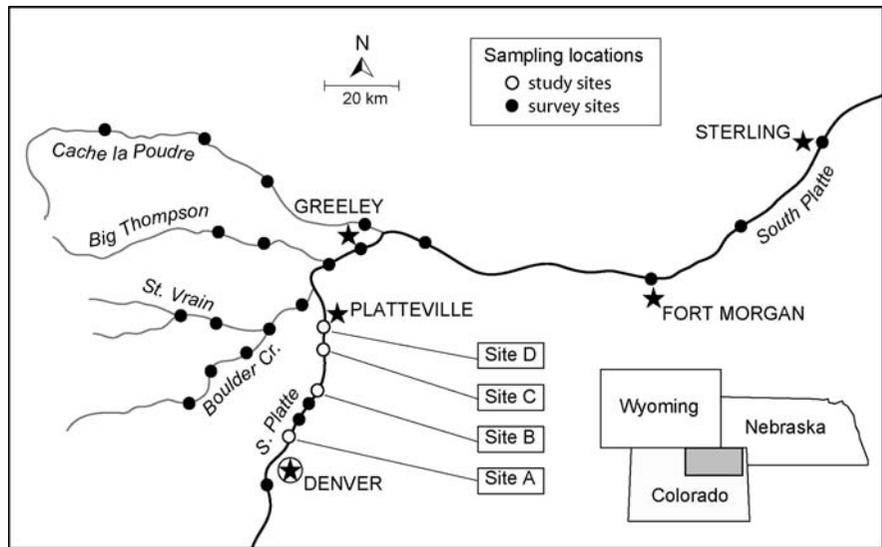
Table 1 Observations of ebullition, dissolved nutrient concentrations, dissolved (channel) N_2:Ar ratios, gaseous (bubble) N_2:Ar ratios and bubble gas composition for the South Platte River and four of its tributaries (April–September 2006)

	Km[a]	n	Ebullition	NO_3^-–N (mg l^{-1})	NH_4^+–N (mg l^{-1})	DOC (mg l^{-1})	Dissolved N_2:Ar	Gaseous N_2:Ar	% N_2	% CH_4
Cache la Poudre		3	None	0.03	0.01	4.2	37.21	n/a	n/a	n/a
Big Thompson		4	None	0.13	0.02	4.6	37.14	n/a	n/a	n/a
St. Vrain		5	None	7.00	0.06	6.7	37.34	n/a	n/a	n/a
Boulder Creek		5	None	0.21	0.01	4.0	37.14	n/a	n/a	n/a
South Platte	−18	3	Some	2.05	0.14	4.7	37.33	79.93	82.6	17.4
Site A	+5	14	Much	4.46	4.43	7.6	38.66	95.28	98.2	1.5
	+10	3	Much	6.04	5.45	9.6	38.37	97.07	98.9	1.6
	+16	3	Much	6.06	3.56	8.2	38.21	97.51	91.2	1.5
Site B	+24	14	Much	7.11	2.06	7.0	37.79	98.86	99.7	1.6
Site C	+44	14	Much	7.12	0.66	6.3	38.18	88.62	98.9	1.7
Site D	+52	14	Much	6.73	0.06	4.4	38.10	87.64	98.6	1.9
	+81	3	Some	4.97	0.06	4.5	37.72	87.55	98.0	2.0
	+104	3	None	6.58	0.10	4.5	37.58	n/a	n/a	n/a
	+171	3	None	4.74	0.19	4.1	37.88	n/a	n/a	n/a
	+211	3	None	4.69	0.04	3.8	37.82	n/a	n/a	n/a
	+247	3	None	2.94	0.05	3.9	37.77	n/a	n/a	n/a

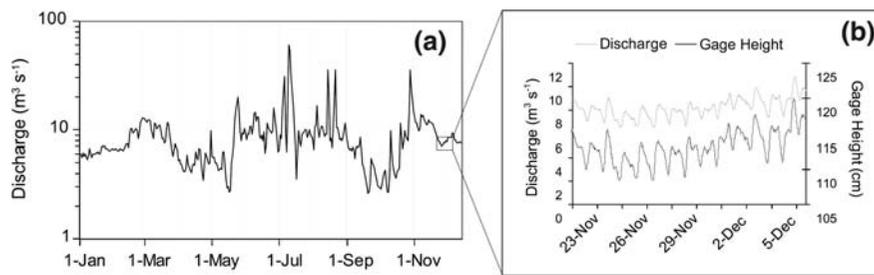[a] Distances (river km) on South Platte River downstream from Denver

Fig. 2 Hydrographs of the South Platte 36 km downstream from Denver for 2006, highlighting (**a**) the seasonal fluctuations in discharge caused by snowmelt and summer storms, and

(**b**) the daily fluctuations resulting from wastewater discharges of Denver (*Source*: USGS)

Discharge exceeding 11 m^3 s^{-1} disturbs much of the riverbed to a depth of 5–10 cm (Cronin et al. 2007). Although spates suppress photosynthesis, they appear to have little effect on rates of respiration or denitrification (Cronin et al. 2007; Pribyl et al. 2005), probably because typical bed movement affects only the surface sediments. The natural flow regime has been substantially altered by impoundments, diversions and wastewater discharges; in addition to altering the annual hydrograph, these changes (particularly wastewater discharge) have resulted in a daily fluctuation of 2–3 m^3 s^{-1} (Fig. 2b). Wastewater discharge typically constitutes approximately 50% of the flow in the 50 km below Denver and up to 90% at low flow just below Denver. The return of nitrate-rich irrigation water as alluvial seepage is also an important element of the South Platte water budget downstream of Denver (Sjodin et al. 1997).

Environmental variables

Concentrations of dissolved nitrate, ammonium and dissolved organic carbon were measured in surface water samples from the 26 survey sites, as well as shallow groundwater samples collected from screened piezometers installed at sites A–D. All water samples for nutrient analyses were filtered through Whatman GF/C filters (effective pore size 1.2 μm). Nitrate was analyzed by ion chromatography (Davi et al. 1993). Ammonium was analyzed by a modified Solarzano method (Grashoff 1976). Dissolved organic carbon was analyzed with a Shimadzu carbon analyzer. Sediments from sites A–D on the South Platte River were dried, sieved and weighed. Particulate organic matter was estimated as the change in mass after combustion at 475°C for 3 h.

Sediment bulk density, water content, and porosity were determined by standard methods (APHA 1998). Measurements of water depth, water temperature, and atmospheric pressure were also routinely made at Sites A–D in order to determine the joint effects of environmental variables on rates of ebullition. Atmospheric pressure was measured with a high-precision pressure transducer (Honeywell, HPB200).

Gas concentrations

Concentrations of dissolved gases at the 26 survey sites were measured with a membrane inlet quadrupole mass spectrometer (MIMS) following McCutchan et al. (2003) and Kana et al. (1994). Samples were collected in 40-ml amber glass vials with 3.2-mm Teflon/silicone septa. Vials were filled with a sampler that flushed the vials 5x with channel water (Kilpatrick et al. 1989). At those study sites where ebullition was observed, gas was collected directly from bubble streams. A small funnel was used to direct bubbles into inverted water-filled sample vials. When filled completely with gas, each vial was sealed with a septum and capped under water. Vials were held on ice until analysis (within 6 h). Concentrations of gas species (N$_2$, Ar and CH$_4$) in the collected bubbles were determined by headspace equilibration using N$_2$-calibrated water, followed by dissolved gas analysis using MIMS. 20 ml of bubble gas was injected through the septum of an inverted vial containing 40 ml of water saturated at 20°C with standard N$_2$ gas; a second, shorter needle allowed an approximately equal amount of the standard to be displaced. The vial was shaken for 1 min, then the liquid fraction was analyzed by MIMS (Kana et al. 1994; McCutchan et al. 2003). For N$_2$ and Ar, mass fragments (m/z)

used were 28 and 40, respectively. Standards consisting of N_2-saturated water equilibrated at 8°C and 20°C were used to generate standard curves. Gas concentrations in bubbles were back-calculated from measured concentration of N_2 and Ar for the liquid fraction. For determination of CH_4, a cryotrap consisting of dry ice and methanol (−78°C) was used to cryogenically separate CH_4 from the other gases, in place of the liquid N_2 (−170°C) trap normally used for N_2 and Ar analyses. While the most abundant peak in the mass spectrum of methane occurs at m/z 16, it is not practical to use this value for determining methane concentration as the m/z 16 signal is overwhelmed by atomic oxygen derived from fragmentation of CO_2, H_2O and O_2. The next most abundant peak in the methane mass spectrum occurs at m/z 15 corresponding to the CH_3 ionization fragment of methane. There are no substantial interferences at m/z 15, making it the best ion to measure methane concentration. The relationship between CH_3^+ and CH_4 concentrations was determined using methane gas standards, which were treated to the same headspace equilibration and analysis by MIMS as the bubble samples. The nitrous oxide (N_2O) content of bubbles from Sites A and B was measured on 5 December 2006 with a gas chromatograph. Finally, the Ideal Gas Law was used to convert molar concentrations into percentages by volume of N_2, Ar, CH_4 and N_2O.

Ebullition rates

Ebullition rates were quantified at the upstream sites (A and B) with open-bottom cylindrical ($d = 27.5$ cm, $h = 30$ cm) polycarbonate chambers with funnel-shaped tops that collect bubbles. When submerged to 10 cm in the riverbed sediments, each chamber covered 594 cm². Chambers were left uncapped for at least 2 h to minimize the effects of sediment disturbance, then the top was capped with a polyethylene cover which was secured in place with an elastic band. Gas was collected volumetrically over 24–48 h. The chambers were deployed randomly over 1,000 m² at sites A and B on 10 occasions between May and November 2006 ($n = 12$–25 per site). Repeated measurements of ebullition rate were made for individual bubble streams at Sites A and B over the course of the study period with an inverted, submerged graduated cylinder and stopwatch.

Results

Ebullition was observed at six of the twelve sites surveyed on the South Platte River but at none of the sites on its four tributaries (Table 1). Individual bubbles were generally about 0.2–0.4 ml in volume and bubbles ascended rapidly from a precise location at rates of 70–75 bubbles per minute. When bubbling rates were high, bubble tubes formed in the unconsolidated river sediments. Duration of bubble streams varied from 15 s to 200 s and produced 10–285 ml of gas (mean: 54 s, 20 ml).

Upstream of the Denver effluent discharge, ebullition was moderately widespread and bubbles contained a mixture of N_2 (83%) and methane (17%; Table 1). Ebullition was particularly widespread between 5 km and 52 km downstream of Denver; bubbles in this regions were composed almost entirely (98%) of N_2, and dissolved N_2:Ar ratios were high (>38), indicating high rates of denitrification. At 81 km downstream, ebullition and dissolved N_2:Ar ratios were lower, although N_2 remained the dominant component of the bubbles (98%). Ebullition was not observed at the sites farthest downstream (104–247 km), despite the moderately high N_2:Ar ratios of 37.6–37.9 in the sediment porewater in this region. Changes in dissolved N_2:Ar ratios in the South Platte River channel corresponded with variations in temperature, ammonium and dissolved organic carbon, all of which peaked at 5–10 km below Denver and then declined rapidly (Fig. 3a–d), reflecting wastewater discharges from Denver. Concentrations of nitrate increased to 7.12 mg l⁻¹ at 35.5 km from Denver and then declined steadily (Fig. 3e).

At Sites A–D on the South Platte, river-bed sediments consisted mostly of unconsolidated coarse sand and gravel with high porosity (Table 2). The average organic fraction was <0.6% in the upper 10 cm of sediments, although some organic-rich surface deposits were found. Average particle size and porosity tended to decrease downstream, with concurrent slight increases in organic content (Table 2). N_2:Ar ratios for sediment pore water were high at sites A and B, and declined downstream at sites C and D (Fig. 4a). At all four sites, the N_2:Ar ratios of released bubbles were well above that of the ambient atmosphere, particularly so at sites A and B (Fig. 4b). Ammonium concentrations in the shallow
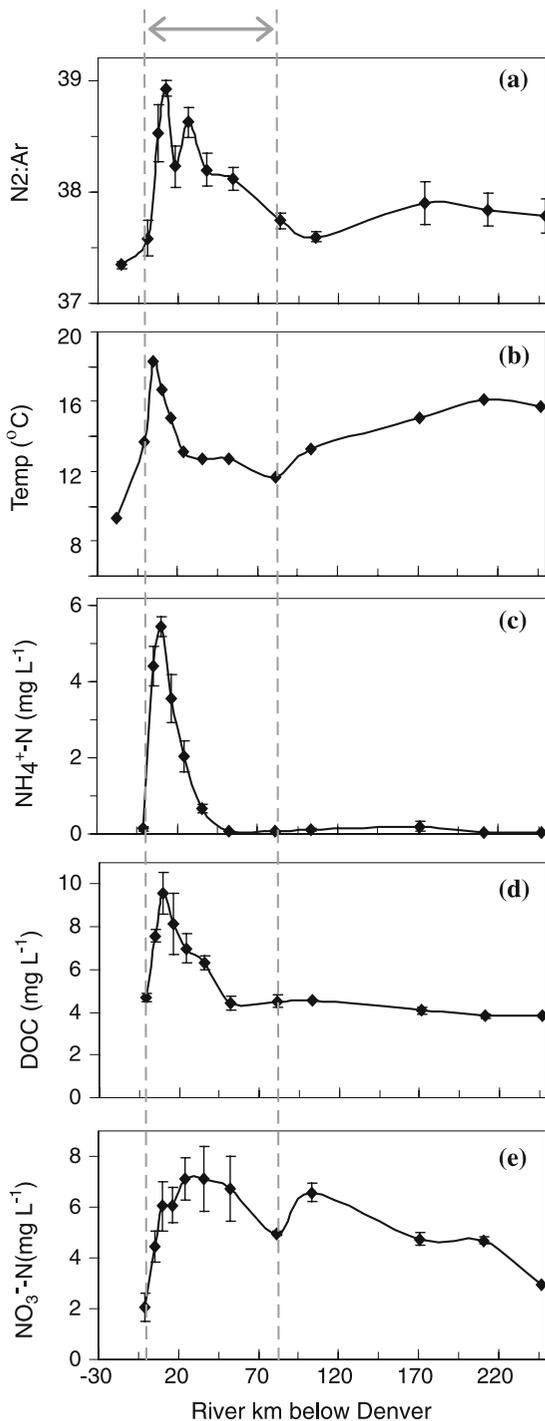
Fig. 3 Variation in (**a**) dissolved N_2:Ar ratio, (**b**) temperature, (**c**) ammonium, (**d**) dissolved organic carbon and (**e**) nitrate, along a 270-km reach of the South Platte river between Denver and Sterling, Colorado (July–September 2006, $n = 3$). The broken lines indicate the region in which ebullition was observed (detailed in Table 5)

Table 2 Characteristics of study sites A–D on the South Platte River

	Site A	Site B	Site C	Site D
Location (N)	39°51′	39°59′	40°10′	40°12′
(W)	104°56′	104°50′	104°50′	104°49′
Distance from Denver (river km)	5	24	44	52
Width (m)	33	18	40–50	30–40
Depth (m)	0.39	0.41	0.3–0.7	0.3–0.7
Discharge ($m^3 \, s^{-1}$)	10.4	9.6	9.4	9.5
Sediment size fractions (%)				
Pebble, >10 mm	17.6	10.3	5.5	2.3
Gravel, 2.36–10 mm	34.4	31.8	28.8	26.4
Coarse sand, 0.6–2.36 mm	27.9	27.3	42.7	42.5
Sand, 250–600 μm	14.2	23.0	17.0	20.5
Silt/clay, <250	5.9	7.6	6.0	8.3
Sediment porosity (%)	33.4	32.2	27.3	26.6
Sediment organic content (%)	0.35	0.31	0.43	0.56
Water temperature (°C)				
July (mean daily)	22.4	22.7	24	25
November (mean daily)	11.4	8.5	10.8	10.5
Nitrate, NO_3^-–N ($mg \, l^{-1}$)	3.99	5.79	5.83	5.10
Ammonium, NH_4^+–N ($mg \, l^{-1}$)	2.80	1.78	0.25	0.06
Dissolved organic carbon ($mg \, l^{-1}$)	7.4	6.9	5.9	5.0

alluvial groundwater of the South Platte declined steeply below Denver and nitrate concentrations increased (Fig. 4c). These trends in groundwater nutrient concentrations and N_2:Ar ratios suggest coupled nitrification-denitrification in this reach of the South Platte River.

N_2 comprised >98% of the bubbles at sites A, B and C (Table 3). Bubbles at site D contained a mixture of N_2 (62%) and methane (38%). Site D had higher DOC and lower nitrate concentrations as well as finer sediments with more organic matter. Ebullition ceased at this site when the organic deposits were washed away during a high flow event in mid-July 2006 and subsequently recommenced as organic matter accumulated. N_2O was present in bubbles analyzed from sites A and B on 5 December 2006 at
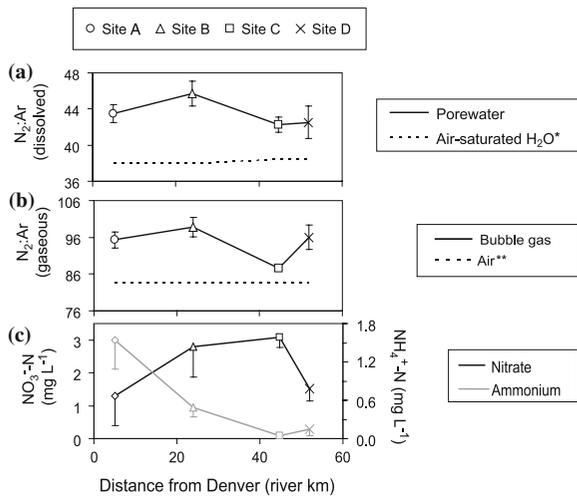
Fig. 4 (a) N_2:Ar ratio of interstitial pore water, (b) N_2:Ar ratio of bubble gas, and (c) groundwater concentrations of nitrate and ammonium at 4 sites (A–D) on the South Platte River downstream from Denver. Values shown are mean (April–September 2006, $n = 14$); error bars give standard errors. (*air-calibrated water at ambient temperature and pressure; **interstitial air collected from dry river sediments at ambient temperature and pressure)

Table 3 Mean % composition of bubble gas at sites A–D on the South Platte River (April–September 2006, $n = 14$)

	n	%N_2	%CH_4	%N_2O[a]
Site A	33	98.1	1.52	0.00115
Site B	23	99.6	1.68	0.00036
Site C	15	98.9	1.10	–
Site D	10	61.9	38.1	–
Air[b]	4	78.0	0.00018	0.00003

[a] Bubbles from Dec 5th 2006 ($n = 5$)

[b] Interstitial air taken from dry, air-saturated river sediments

10–30 times its concentration in the atmosphere (Table 3).

Rates of ebullition in the South Platte River varied both spatially and seasonally. Average ebullition rates were 35% higher at site A than 19 km downstream at site B (Fig. 5 and Table 4). This difference was greatest in May, October and November, when ebullition rates at site B declined while rates at site A remained high, possibly reflecting warmer year-round temperatures at Site A caused by effluent discharges from Denver. The highest ebullition rates for sites A and B were recorded in August.
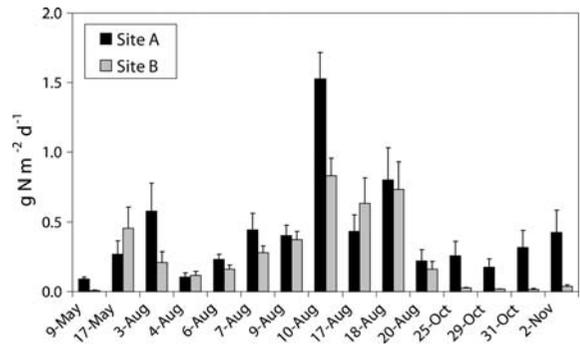

Fig. 5 Ebullition rates at two South Platte River sites on 15 sampling dates between May and November 2006. Values are the mean of multiple gas chamber measurements ($n = 15$–24) made at sites A and B; error bars show the standard error of the mean. (*Note*: x-axis is not a time scale)

Table 4 Mean gas ebullition rates at two South Platte River sites downstream from Denver (May–November 2006, $n = 15$). Values in parentheses are standard errors

	Site A ($n = 231$)	Site B ($n = 209$)
Ebullition rate, ml m^{-2} d^{-1}	368 (34)	239 (23)
N_2 Ebullition rate, g N m^{-2} d^{-1}	0.44 (0.1)	0.29 (0.08)
N_2O Ebullition rate, µg N_2O m^{-2} d^{-1}	8.27	1.67
Fraction of diffusive N_2 flux[a]	9–16%	6–11%
Fraction of diffusive N_2O flux[b]	0.6%	0.1%

[a] Based on previous diffusive N_2 flux measurements by (McCutchan et al. 2003) and J. McCutchan unpublished data

[b] Based on measurement of diffusive N_2O fluxes in the South Platte River by McMahon and Dennehy (1999)

Table 5 Summary of stepwise multiple regression analysis predicting of relationships between N_2 ebullition rates (g N m^{-2} d^{-1}) and other environmental variables at sites A and B. All analyses were performed on log$_{10}$-transformed data sets ($n = 26$). Depth and nitrate concentration were found not to be significant (data not shown)

Variable	Slope	Change in R^2	Cumulative R^2, Adj.	P
Temperature, °C	3.93	0.71	0.48	0.000
DOC, mg l^{-1}	4.33	0.08	0.59	0.010

Log-transformed temperature and DOC together explained 62% of the variance in log-transformed ebullition rates at sites A and B (Table 5).

Discussion

High concentrations of nitrate and labile organic carbon in combination with warm temperatures support high rates of denitrification in the South Platte River below Denver (McCutchan and Lewis 2008; Pribyl et al. 2005; Sjodin et al. 1997). Production of N_2 associated with denitrification elevated N_2:Ar ratios (>38) in both the sedimentary porewater and the overlying channel water in the present study, especially just downstream of Denver where coupled nitrification-denitrification enhanced denitrification rates. Denitrifying bacteria are probably dependent on nitrifiers to provide nitrate in support of high denitrification rates in this reach of the South Platte River. Diffusive flux of dissolved N_2 has been widely assumed to be the only significant pathway for N_2 transport from riverbed sediments to the atmosphere. The current data indicate that ebullition also can be important for N_2 export, much as it is for methane in wetlands (Chanton and Whiting 1995; Chareonsilp et al. 2000; Tokida et al. 2005). Ebullition of N_2 from South Platte River sediments up to 52 km downstream from Denver released N_2 gas (>98%) at rates of 239–368 ml m^{-2} d^{-1}. Comparing these measurements with previous values for diffusive N_2 flux for this region (McCutchan and Lewis 2008; Pribyl et al. 2005) indicates that ebullition accounts for 6–16% of diffusive N_2 losses. Thus, not accounting for ebullitive N_2 losses would lead to a considerable underestimation of denitrification rates in this reach of South Platte River. Our data for the South Platte suggest that ebullition can cause spikes in N_2 emission associated with the release of accumulated gas. This ebullition pathway represents a more direct transport of N_2 to the atmosphere as intense fluxes of relatively short duration. It is unknown what fraction of the total N_2 efflux ebullition may represent in systems with lower diffusive N_2 losses than the South Platte (e.g. Piña-Ochoa and Álvarez-Cobelas 2006).

Ebullition may also bias open-channel measurements of oxygen metabolism in rivers (McCutchan et al. 1998), which rely solely on the measurement of dissolved O_2 concentrations and assume that the contribution of gas bubbles to O_2 transport is negligible. Oxygen bubbles frequently form directly on biofilms or algal mats when rates of photosynthesis are high, but the contribution of ebullitive O_2 losses to total oxygen efflux in such systems is not well known. Where oxygen ebullition is high and bubbles remain attached for some time to algae or aquatic macrophytes, other gases would also be stripped from the water column; this might also be an additional pathway for the ebullitive loss of N_2 from river beds.

Bubbles are formed when the concentration of a gas is above saturation for a given temperature and pressure. Supersaturation for N_2 can occur when excess N_2 is produced by denitrification, when pressure or temperature changes, or through a combination of these two mechanisms. Lamontagne and Valiela (1995) estimated potential temperature-driven, non-denitrification N_2-fluxes from porewaters over a 10°C temperature gradient of 43 μmol N_2 m^{-2} h^{-1} (or 0.0143 g N m^{-2} d^{-1}), which is <5% of the ebullitive N_2 fluxes calculated here. This 10°C temperature differential approximates the maximum differences between incoming alluvial groundwater and overlying channel water in the South Platte. Diel temperature variations within the riverbed sediments themselves, where most denitrification occurs, are typically much less (approximately 2°C at 5 cm; J. McCutchan, unpublished data). Moreover, ebullition was observed even in winter, when the temperature difference between the channel and hyporheic zone is much less. Thus, it appears that temperature-driven solubility changes do not contribute significantly to N_2 effluxes from the South Platte River. Neither was the release of air trapped in the sediments significant, as shown by N_2:Ar ratios in the sediment pore waters. Degassing (i.e. decreased water pressure causing dissolved gases to come out of solution) has been shown to account for significant losses of denitrification-produced N_2 in other riparian groundwaters (Blicher-Mathiesen et al. 1998). However, the contribution of degassing to bubble formation in the South Platte River would be small because groundwater contributions to flow are low. The high content of N_2 in gas bubbles released from marsh and marine sediments has been attributed to the stripping of 'pre-formed' atmospheric N_2 from pore waters by methane ebullition (Chanton et al. 1989; Chanton and Whiting 1995; Kipphut and Martens 1982; Lamontagne and Valiela 1995). The very low (<2%) methane content of the bubbles at Sites A–C indicates that the potential for bubble stripping via methanogenesis was not widespread in the South Platte downstream of Denver, except perhaps at Site D where the methane content of the bubbles was moderately

high (38%) and sediments were finer, containing a higher fraction of mud. Stripping of atmospheric N_2 via methanogenesis may dominate over denitrification-derived N_2 ebullition in localized areas of the South Platte and in other river systems where conditions are favourable (anoxic organic-rich sediments, low or moderate NO_3). In the absence of temperature-driven solubility changes, degassing and widespread bubble stripping, high denitrification rates in the riverbed are the most reasonable explanation for the production and release of N_2-rich bubbles from the sediments of the South Platte river below Denver. Others have observed that high N_2 production rates and high N_2 sediment porewater concentrations may favor bubble transport in rivers (Walter and Heimann 2000) and in laboratory cores and microcosms (Liikanen et al. 2002). Ebullition in the South Platte was strongly related to temperature and DOC concentration but not to nitrate concentration. The same is true of total denitrification in the South Platte River (McCutchan and Lewis 2008; Pfenning and McMahon 1996); nitrate consistently saturates denitrification potential and therefore does not control variances in denitrification rates.

Bubbles released from South Platte sediments downstream of Denver were generally >98% N_2. Methane was a dominant component only in bubbles released from areas of organic-rich sediments with low redox potential (site D). Methane content was moderately high (17%) in bubbles produced upstream of the Denver wastewater discharge where nitrate concentrations were lower. Bubble concentrations of N_2O were high in areas of highest ebullition (site A), supporting previous findings correlating increasing N_2O production with high rates denitrification (Thomas and Lloyd 1995). This association has wider implications for global warming (Liikanen et al. 2002). Overall, ebullitive release of N_2O is a very minor fraction of either diffusive N_2O fluxes (0.6% and 0.1% at Sites A and B; see also McMahon and Dennehy 1999) or total gaseous fluxes of N (0.001% and 0.004% at Sites A and B). More data are required to determine the role that the South Platte, and rivers generally, play in the global N_2O budget.

Ebullition was not observed in four South Platte tributaries, despite their moderate to high concentrations of nitrate and organic carbon. The occurrence of N_2 ebullition in the South Platte is likely the result of a combination of geophysical, hydrological, and chemical conditions: very high denitrification rates which are facilitated by rich supplies of nitrate and labile organic carbon causing supersaturation of the sediment porewater with N, an extensive porous alluvium that facilitates exchange between nitrate-rich groundwater and organic-rich surface waters, as well as fluctuations in flow and topographic irregularities (sand bars) that cause changes in hydrostatic pressure conducive to bubble formation and release. Areas of bubble formation probably represent biogeochemical 'hot spots' in the riverbed sediments, described by McClain et al. (2003) as patches that show disproportionately high reaction rates relative to the surrounding matrix. At these local 'hot spots', supersaturation of N_2 causes bubble formation. While the current data provide the first evidence that ebullition can contribute significantly to N_2 effluxes in rivers, the data also demonstrate that ebullition rates are heterogeneous in both space and time. Additional studies are required to accurately quantify spatial and temporal variations in the magnitude of ebullitive N_2 losses in running waters exhibiting high rates of denitrification.

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