

An Empirical Model for Dinitrogen Gas Emission from Inland Waters

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Abstract

The motivation to calculate this empirical model resulted from often observing—at the time disconcerting—excess dinitrogen gas (N_2 concentration > background concentration) in bubble-gas emission samples, collected primarily for the purpose of carbon budget research, from Brazilian rivers and reservoirs sampled during roughly 100 field surveys lasting 4 days each on average and executed between years 2000 and 2012. We model the (serendipitously) measured dinitrogen gas above environmental concentration ($N_{2,aec}$) escaping in bubbles from Brazilian rivers as a function of dissolved nitrogen (N) in water. To this model, we mathematically add a pre-existing model of diffusively emitted denitrified dinitrogen (also as a function of dissolved N) from streams in the United States of America (USA). The resulting model predicts denitrified dinitrogen water-air emission from inland waters in the USA, China and Germany.

Keywords

Dinitrogen Gas Emission, Inland Waters, Bubbles, Diffusion, Nitrogen Cycle, Denitrification

1. Introduction

Gases evade water bodies through the diffusive, ebullitive and advective pathways [1] [2]. Diffusive emissions of greenhouse gases (GHG) such as carbon dioxide (CO_2), methane (CH_4), and nitrous oxide can be directly measured using the concentration increase rate of these gases in the headspace of floating static chambers. The thin boundary layer method is also used [3]. However, floating static

chambers are not used to sample diffusive emissions of our subject dinitrogen gas above environmental concentration ($N_{2,aec}$)—such as denitrified N_2 —because of the high concentration of atmospheric N_2 (78%) in the headspace and the difficulty to distinguish $N_{2,aec}$ from environmental N_2 [4]. As for bubble emissions of GHG, they are sampled carrying out a different procedure in which equipment similar to inverted funnels [5] [6] is used, thus allowing ebullitive emission sampling to be done independently of the diffusive one. While the difficulty to distinguish environmental N_2 from $N_{2,aec}$ in diffusively emitted gas samples exists for bubble-gas samples too, this can be dealt with by using argon (Ar) as a tracer of environmental N_2 in bubble-gas—a path here taken.

The ebullitive:diffusive water-air emission partition ratio for a certain gas can be explained in part by its solubility in water and atmospheric concentration. For instance, ebullitive water-air emission of CO_2 tends to be very small. Typically, there is less than 1% CO_2 in the gas composition of bubbles escaping tropical reservoirs [7]. On the other hand, CO_2 water-air emission occurs via the diffusive pathway mainly for two reasons. First, it is highly soluble in water (88 ml/100 ml H_2O at 20°C) [8]. Second, water bodies tend to be under saturated with dissolved CO_2 because of the small—although increasing—concentration of CO_2 in Earth's atmosphere (485 ppm in year 2015) [9]. (Dissolved CO_2 saturated water bodies exist under a 100% CO_2 atmosphere. Under this scenario, further generation of CO_2 would increasingly super saturate water bodies with dissolved CO_2 . Then, concentration of CO_2 in emitted bubbles would tend to increase with CO_2 production, simply because streams, rivers and reservoirs could not dissolve CO_2 indefinitely and therefore diffusively emitted CO_2 could not increase indefinitely).

Solubility of CH_4 (3.5 ml/100 ml H_2O at 17°C) [8] is much smaller compared to that of CO_2 . Because of the small concentration of CH_4 in air (1.84 ppm in year 2015) [9] water bodies are also under saturated with dissolved CH_4 concerning contact with the atmosphere. However, dissolved CH_4 from decomposition of organic matter can super saturate water to an extent that the ebullitive pathway can periodically overwhelm the diffusive one [7]. Compared to CO_2 and CH_4 and due to the overlying 78% N_2 atmosphere, $N_{2,aec}$ emission is potentially more straightforward to model. Solubility of N_2 ranges between 18.42 ml/l (in water at 0°C with 0‰ salinity) to 6.95 ml/l (40°C, 40‰) under one atmosphere total pressure [10]. As one mol of N_2 (28 g) occupies 22.4 liters, the solubility range can be expressed in molarity: 310 $\mu\text{mol/l}$ - 822 $\mu\text{mol/l}$, and the saturation concentration range is 397 $\mu\text{mol/l}$ - 1054 $\mu\text{mol/l}$. For higher altitudes, for instance, at pressure 0.9 atm the solubility range is 279 $\mu\text{mol/l}$ - 740 $\mu\text{mol/l}$ and the saturation concentration range is 357 $\mu\text{mol/l}$ - 949 $\mu\text{mol/l}$. Due to contact with the 78% N_2 atmosphere, the solubility ranges shown above are actually the background concentrations of dissolved N_2 in environmental water bodies. They are close to saturation. Difference between background and saturation are within the range 87 $\mu\text{mol/l}$ - 232 $\mu\text{mol/l}$ under one atmosphere and smaller at higher altitudes, in theory. A higher difference (250 $\mu\text{mol/l}$) has been measured in prac-

tice [11] possibly caused by sudden temperature and/or pressure gradients. Therefore, an inflexion in the diffusive emission of N_{2aec} is expected when dissolved N concentration in water is as high as ~ 87 to $250 \mu\text{mol/l}$. If a source of N_2 (such as denitrification) exists in the water, it will become increasingly unlikely that the N_2 thus produced will escape diffusively to the atmosphere and more probable that it will escape ebullitively. A “cat leap” realization led us to infer that, not only does the expected transition in the N_{2aec} diffusive flux in N-saturated waters exist [12] but that, the N_{2aec} diffusive emission is modeled fairly well [12] by either of two equations:

$$y = (640x)/(180 + x) \quad (1)$$

Alternatively:

$$y = (700x)/(320 + x) \quad (2)$$

Actually, Equations (1) and (2) represent diffusively emitted denitrified N_2 (y , $\mu\text{mol}\cdot\text{N}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$) as a function of above-background dissolved N in water (x , $\mu\text{mol}\cdot\text{N}\cdot\text{l}^{-1}$). Plots of saturation Equations (1) and (2) show how the rate of increase of diffusive denitrified N_2 emission with concentration undergoes an inflexion around roughly $x = 87$ to $x = 232 \mu\text{mol}\cdot\text{N}\cdot\text{l}^{-1}$ [12]. These concentrations added to background concentration (310 to 822) are the saturation concentrations (397 and $1054 \mu\text{mol}\cdot\text{N}_2\cdot\text{l}^{-1}$) of dissolved N_2 , discussed above. Equations (1) and (2) also show that at limit $x \rightarrow \infty$, diffusive emissions of denitrified N_2 can, in theory, increase no more than about $640 - 700 \mu\text{mol}\cdot\text{N}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$. In practice, one order of magnitude higher diffusive emission rates have been measured [12].

Given that diffusive emissions are limited to these maximum values one can expect an increasingly significant ebullitive pathway, especially if there is a source of N_2 (e.g. denitrification) in dissolved-N saturated waters. The penalty for disregarding N_{2aec} (e.g. denitrified N_2) emitted in bubbles is that the fate of anthropogenic N will appear to be uncertain [13] [14] because nitrogen will seem to be “missing”, in other words, not enough N output will be found to balance riverine N inputs and outputs. Several studies observed such imbalances [1] [11] [15]-[22].

The purpose of this work is to model our findings of excess N_2 in ebullitive emissions, complement it with the existing diffusive denitrified N_2 models described above, and predict denitrified N_2 emissions from inland waters with available data on total dissolved N.

2. Materials and Methods

2.1. Studied Sites and Rivers

Between years 2008 and 2012, we investigated 131 sites distributed among four tropical and two sub-tropical rivers, all in Brazil (Figure 1).

The geographic coordinates, depth, quantity of bubble-samplers (funnels) collectively deployed per site; surface water temperature and atmospheric pressure are in Table A1. Land cover surrounding the surveyed river reaches range

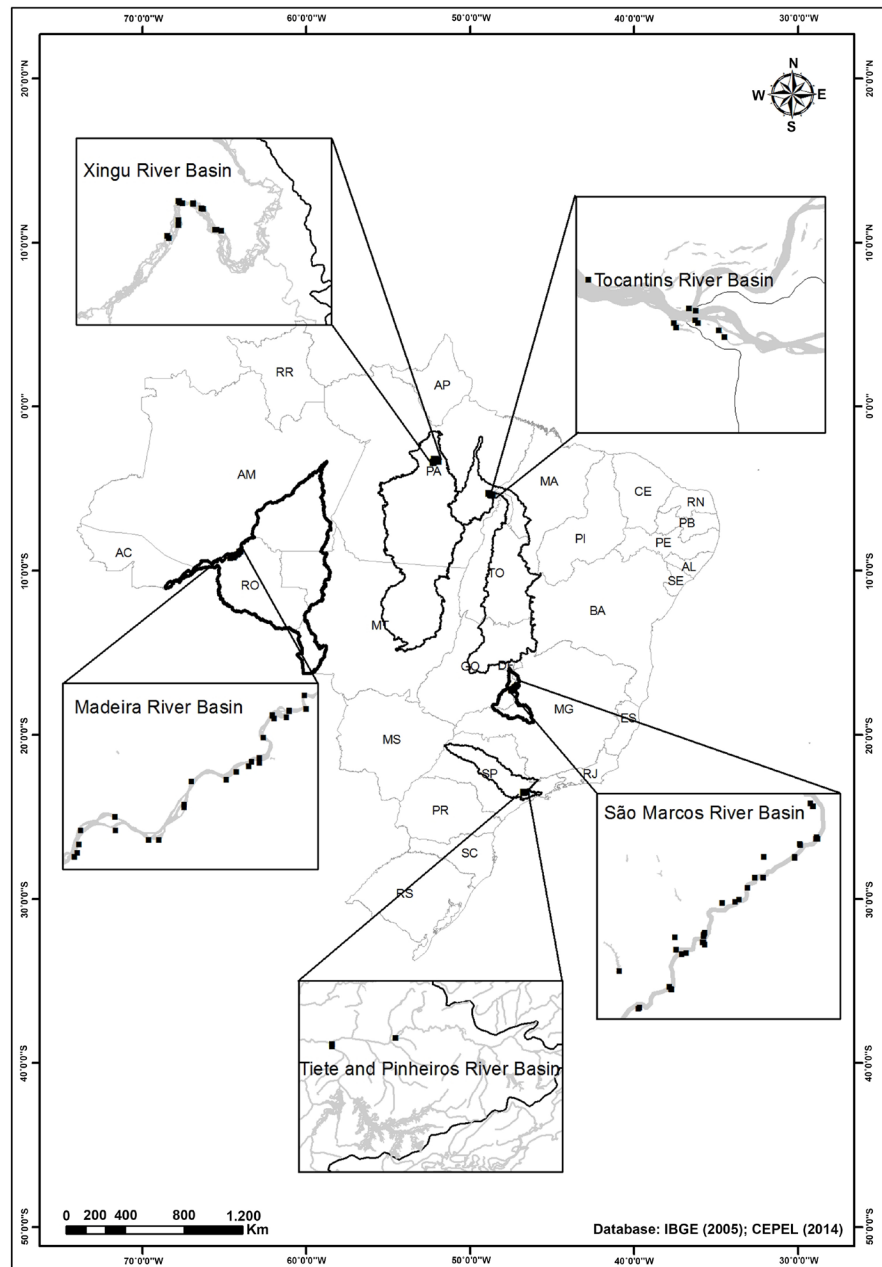


Figure 1. Catchments and sampled sites of the six Brazilian surveyed rivers.

from tropical rainforest typically subjected to periodic floods, to heavily urbanized land.

The purpose was to measure CH_4 and CO_2 emissions. We studied stretches of the tropical rivers: Xingu (surrounded mainly by tropical rainforest), Tocantins (forest and grassland), Madeira (forest and grassland) and São Marcos (grassland and agricultural land). Also of highly impacted sub-tropical stretches of rivers Tietê and Pinheiros, both surrounded by São Paulo city. Physical and chemical parameters of the investigated reaches are in **Table 1**.

We surveyed tropical rivers Xingu, Tocantins and Madeira along stretches located in the Brazilian Amazon, near Altamira, Marabá and Porto Velho cities,

Table 1. Median (1st quartile; 3rd quartile) (number of measurements) of physical and chemical parameters of the surveyed areas. Parameter measurements are contemporary with the ebullitive emission measurements reported in this work except for Tocantins River, where we measured bubble emissions in year 2008 but found parameter data only for year 2011.

River	Sampled riverine stretch/site		Dissolved Oxygen (mg·l ⁻¹)	pH	Temperature (°C)		Total Phosphorus (mg·l ⁻¹)	Ammonium (NH ₄ ⁺) (mg·N·l ⁻¹)	Nitrate (NO ₃ ⁻) (mg·N·l ⁻¹)	Nitrite (NO ₂ ⁻) (mg·N·l ⁻¹)	N ₂	Month and year of measurement	Reference
	Lat (°S)	Long (°W)			Water	Air							
Xingu	3.5140	51.7109	7.36	7.00	30.9		0.068	<0.0005	0.039			Nov 2008	[24]
	to 3.5805	to 51.7654	[4.70; 7.50] (5)	[6.94; 7.30] (5)	[30.0; 31.6] (5)	...	[0.021; 0.070] (5)	[<0.0005; 0.002] (5)	[0.005; 0.156] (5)	... ^b	...		
Tocantins	5.1263	49.3200	9.20 (1)	7.70 (1)	30.5 (1)	29.0 (1)	0.032 (1)	<DL ^a (1)	0.075 (1)	<DL (1)	0.488 (1)	Jun 2011	
Madeira	8.5056	63.597	6.92	6.76	28.1	27.4	0.172	0.020	0.131	0.001	0.60	May, Aug, Dec 2011, Feb, Mar 2012	BALCAR databank; Furnas Reports ^d
	to 9.289	to 64.62	[5.94; 7.69] (42)	[6.33; 7.31] (45)	[27.8; 29.5] (48)	[26.8; 28.6] (50)	[0.060; 0.236] (96)	[0.017; 0.030] (61)	[0.107; 0.171] (61)	[0.000; 0.001] (49)	[0.47; 0.67] (23)		
São Marcos	16.9017	47.1413	7.88	6.20	23.4	27.5	0.022	0.017	0.045	0.001	0.050	Mar, Jun, Oct 2011	
	to 17.4430	to 47.5217	[7.52; 8.65] (32)	[5.85; 6.68] (33)	[20.9; 24.3] (33)	[25.9; 29.0] (32)	[0.016; 0.032] (79)	[0.009; 0.058] (45)	[0.024; 0.071] (45)	[0.000; 0.001] (33)	[0.023; 0.410] (36)		
Tietê	23.5197	46.5592	0.21	7.2	20.5	24.5	1.71	16.1	<0.2	<0.1		May 2012	[23]
	to 23.5253	to 46.7464	[0.21; 0.26] (3)	[7.2; 7.2] (3)	[20.5; 20.8] (3)	[22.4; 25.8] (3)	[1.58; 1.76] (3)	[15.8; 17.5] (3)	[<0.2; <0.2] (3)	[<0.1; <0.1] (3)	...		
Pinheiros	23.5311	46.7483	<0.21 (1)	7.1 (1)	21.2 (1)	22.1 (1)	1.82 (1)	17.6 (1)	<0.2 (1)	<0.01 (1)	...	May 2012	

^aSmaller than (unspecified in original report) detection limit. ^bNo existing data. ^cMonth and year this table's parameters were measured. ^dBALCAR Carbon Balance Project private databank and Furnas Reports. Published with permission from Furnas.

respectively. Due to agriculture, only 30% of tropical river São Marcos catchment's original *cerrado* (a savanna-type biome) remains. Tietê and Pinheiros rivers are both located in the upper Tietê River basin; their studied sites are on a sub-tropical reach within São Paulo, a city with 11 million inhabitants. São Paulo city's municipal disposal service collects 97% of total sewage generated and 75% is treated, but this treatment does not remove N compounds such as organic N, ammonium, nitrite and nitrate from the effluents discharged into the rivers [23]. Dredged sediment volume from the studied areas in May 2012 for desilting, was 84383 m³ from the 24.5 km extension (3444 m³·km⁻¹) of Tietê River canal. And 50387 m³ from the 10.1 km extension (4988 m³·km⁻¹) of Pinheiros River canal (2016 email from Waters and Electrical Energy Department of São Paulo City to us).

References [6] and [25] discuss the design of the measurement campaigns.

2.2. Bubble Sampling

Bubble emissions were sampled using submerged inverted funnels (70 cm Ø × 70 cm height) using established sampling procedures [5] [6] [25] [26]. Engaged to the narrower opening of the funnel is a bubble-gas collecting vial (typically 500 ml volume). The narrower opening of a deployed funnel is typically about 15 cm below the water surface. We deployed more than one funnel per site at sites

closer to river shores and fewer funnels per site at sites closer to river thalwegs, because shallower sites tend to be more ebullitive [25]. Funnels collected ebullitive emissions for about 24 h, unattended, and then were retrieved. At funnel retrieval, transference of the collected ebullitive gas per site into one graduated vial permits total bubble-gas volume measurement. It was not of interest at the time to measure variability of bubble emission among the simultaneously deployed funnels within a same site. After volume measurement, an aliquot was transferred to a 37 ml glass ampoule (made by Construmaq São Carlos) and screw-capped. Bubble-gas sample harvest, total volume measurement and transference into glass ampoules were always done underwater (leaning over the boat), with no exposure of the bubble-gas samples to the atmosphere. Bubble-gas samples < 1.6 ml were discarded because, although sufficient for chromatographic analyses, they were insufficient for purging and transference. When sampling was done for the day and the boat returned to shore, the glass ampoules containing the samples were immediately taken to our field portable-laboratory for chromatographic analysis.

2.3. Bubble-Gas Sample Transference into a Syringe

In the laboratory, bubble-gas was transferred from the glass ampoule into a syringe (BD Ultra-fine™ 12.5 mm needle-length, purchased over the counter) using a 0.6 ml volume transfer equipment. This equipment consisted of 50 cm length tubing and a glass bulb, previously purged with sample. Tubing consisted of stainless steel tube 1.5 mm outside diameter (OD) × 1.0 mm inner diameter (ID) × 30 cm length, and PVC tubing 2.0 mm OD × 1.3 mm ID × 20 cm length. Connected to the PVC tubing was a small glass bulb, sealed with a small plug made with stationery-shop-purchased white vinyl eraser. (Sample transferring setup image is available at

<http://www.construmaq.ind.br/produtos/bulbo-de-vidro-selado-com-rolha-de-borracha-e-inserido-em-mangueira-flexivel/>)

2.4. Chromatographic Analyses

Samples were chromatographically analyzed for CH₄ and CO₂, within the first 24 hours after being harvested. Oxygen and N₂ peaks elute from the Molecular Sieve chromatographic column prior to methane's (peak area is proportional to gas concentration). The O₂ peak is in fact an O₂+Ar peak because these two gases elute together; chromatograms showed them as one combined peak. We used a Molecular Sieve 5A filled stainless steel chromatographic column of 3.2 mm (OD) × 1.6 mm (ID) × 1.95 m length and a thermal conductivity detector (TCD) chromatograph manufactured by Construmaq São Carlos. Carrier gas was hydrogen (H₂). Injector, column and detector operated at room temperature. Samples were injected by hand using the BD syringe mentioned above. Injected gas volumes were 0.1 milliliter (100 µl). Variability (average ratio of standard deviation divided by average peak area of 3 peaks) was ± 1.5% O₂ and ± 1.2% N₂. Detection limits were 0.5% O₂ and 1% N₂. Oxygen and Ar elute together from the

Molecular Sieve 5A column as one combined peak, followed by the N₂ peak and CH₄ peak. Reference [27] briefly mentions that 5% of the O₂+Ar peak is Ar.

2.5. N₂aec Bubble-Emission Calculation Method

Consider data from the third line of data in **Table A1(a)**. After a period of 22.33 sampling hours, four funnels at 5.5 m depth Xingu River site 3.3118°S 52.1960°W, collectively collected 520 ml of gas. Chromatographic analysis of an aliquot of the collected volume resulted 4.89% O₂+Ar and 26.5% N₂. The bubble sample had 0.2445% Ar (5% of the O₂+Ar mixture). Environmental N₂, in the bubble sample was 0.2445% Ar × 78.1% N₂/0.93% Ar = 20.5%. Emitted N₂aec concentration, in bubble sample was 26.5% – 20.5% = 6.0%. Emitted N₂aec volume, in the bubble sample was:

$$\frac{6.0\%N_{2aec} \times 520 \text{ ml}}{100\% \times 1000 \text{ ml} \cdot \text{l}^{-1}} = 0.0312 \text{ l} \quad (3)$$

Emitted N₂aec-N mass, in bubble sample was:

$$\frac{747.0 \text{ mmHg} \times 0.0312 \text{ l} \times 28 \text{ g} \cdot N_{2aec} - N \cdot \text{mol}^{-1} \times 1000 \text{ mg} \cdot \text{g}^{-1}}{62.4 \text{ l} \cdot \text{mmHg} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times 301.7 \text{ K}} = 34.6 \text{ mg} \quad (4)$$

Funnel area was 0.3848 m². Rate of emitted N₂aec-N from site 3.3118°S 52.1960°W was:

$$\frac{34.6 \text{ mg} \times 24 \text{ h} \cdot \text{d}^{-1}}{4 \times 0.3848 \text{ m}^2 \times 22.33 \text{ h}} = 24.1 \text{ mg} \cdot \text{m}^{-2} \cdot \text{d}^{-1} \quad (5)$$

Variability is 1.9% ($\sqrt{1.5^2 + 1.2^2}$). Had the collected volume been 1.6 ml rather than 520 ml, then, the minimum detectable ebullitive N₂aec emission in this case would have been 74.2 μg N₂aec-N·m⁻²·d⁻¹.

3. Results

All six sampled rivers were sources of ebullitive N₂aec (**Table A1, Appendix**). Two out of the 131 collected samples lacked data (e.g. bubble emission volume data) to calculate emission; even so, those 2 samples were chromatographically analyzed (**Table A1(b)** and **Table A1(d)**). From the 129 ebullitive emission samples which provided N₂ emission rates, 19 had insufficient volume (<1.6 ml) for transfer-tube purging and chromatographic analyses and were labeled “zero emission” (**Table A1(a)** and **Table A1(b)**). Thirty-eight samples had sub-environmental N₂ concentrations (**Tables A1(a)-(d)**). These 38 samples resulted in negative emission rates of N₂aec. They were also considered “zero emission”, for the purpose of N₂aec emission quantification. Therefore, less than half (44%) of the 129 samples yielded zero N₂aec ebullitive emission either because of too small sample volume or due to a negative emission result. **Table 2** summarizes bubble emission measurement results.

3.1. Ebullitive N₂aec Emission Model

Ebullitive N₂aec emission increased with dissolved (reactive + inert) N concentration in water (**Figure 2**). Using median emission rate per river (**Figure 2**), the

Table 2. Ebullitive N_2 aec-N medians given in both emission rate units used in this work, and dissolved N concentration in the studied rivers.

River	Quantity of measurements	Median N_2 aec-N ebullitive emission (first quartile; third quartile)		Median dissolved N concentration ($\mu\text{mol}\cdot\text{N}\cdot\text{l}^{-1}$)
		$\text{mg}\cdot\text{N}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$	$\mu\text{mol}\cdot\text{N}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$	
Xingu	38	0 (0; 1.50)	0 (0; 4.44)	2.79
São Marcos	37	0.54 (0; 9.73)	1.6 (0; 28.8)	8.07
Tocantins ^a	23	2.92 (0; 10.8)	8.7 (0; 32.2)	40.2
Madeira	26	40.5 (15.8; 79.6)	121 (47.2; 238)	53.7
Tietê	3	355 (293; 405)	1057 (872; 1206)	1150
Pinheiros	2	934 (858; 1011)	2780 (2554; 3009)	1257

^aTocantins River data are not used to model dinitrogen emission because ebullitive emission (measured in 2008) and dissolved N concentration (measured in 2011) are not contemporary.

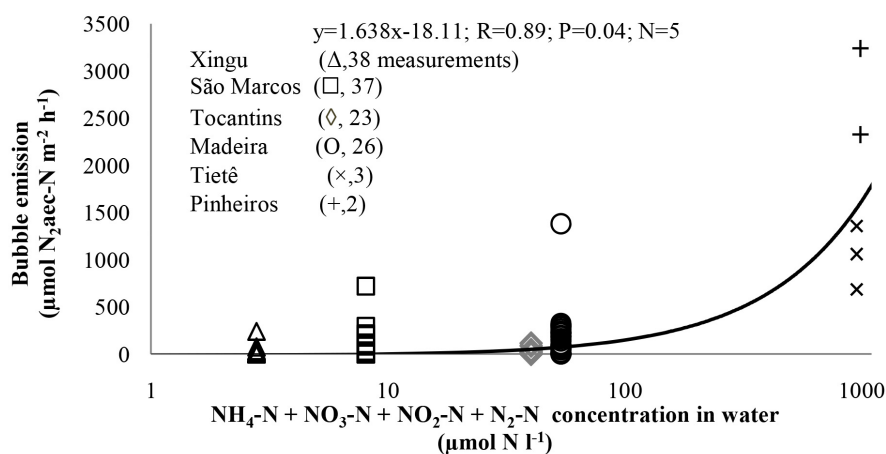


Figure 2. Data markers distant from clusters represent measured outliers. **Table A1**'s measured ebullitive N_2 aec emission rates (y) in unit $\mu\text{mol}\cdot\text{N}_2\text{aec}\cdot\text{N}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ ($1\text{ mg}\cdot\text{N}_2\text{aec}\cdot\text{N}\cdot\text{m}^{-2}\cdot\text{d}^{-1} \cong 3\ \mu\text{mol}\cdot\text{N}_2\text{aec}\cdot\text{N}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$), plotted against dissolved N ($\text{NH}_4\text{-N} + \text{NO}_3\text{-N} + \text{NO}_2\text{-N} + \text{N}_2\text{-N}$, x) median concentration (**Table 1**). Linear fit is curved “up” due to the log- X plot, and was calculated with median emission from Xingu ($0\ \mu\text{mol}\cdot\text{N}_2\text{aec}\cdot\text{N}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$), São Marcos (1.6), Madeira (121), Tietê (1057) and Pinheiros (2780), as functions of dissolved N concentration (2.79 ; 8.07 ; 53.7 ; 1150 ; $1257\ \mu\text{M N}$, respectively). Tocantins' 23 rates (\diamond) median ($8.7\ \mu\text{mol}\cdot\text{N}_2\text{aec}\cdot\text{N}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$) was not used to calculate linear fit because it is unlikely that year 2011's dissolved N, $40.2\ \mu\text{M N}$, was valid also back in year 2008, when N_2 aec bubble emission from Tocantins River was measured.

dependence of bubble emission on concentration is best (high R /small P) described by the first-order equation:

$$y = 1.638x - 18.11 \quad (6)$$

where y is N_2 aec bubble emission ($\mu\text{mol}\cdot\text{N}_2\text{aec}\cdot\text{N}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$) and x is total dissolved (reactive + inert) N concentration in water ($\mu\text{mol}\cdot\text{N}\cdot\text{l}^{-1}$). As bubble growth is a function of dissolved gas concentration in water [28], it is pertinent to know (besides reactive N concentration) how much dissolved N_2 is in the studied water.

If investigated N_2 emissions from swine farms [29] hold for rivers too then, for dissolved N concentrations $> 1200 \mu\text{mol}\cdot\text{N}\cdot\text{l}^{-1}$ ebullitive emissions increase at a smaller rate and, rather than by Equation (6), are better described by:

$$y = 0.4300x + 1430.7 \quad (7)$$

3.2. Total N_2 aec Emission Model

For a given total dissolved N concentration in water, the ebullitive emission (Equation (6) if dissolved N concentrations $< 1200 \mu\text{mol}\cdot\text{N}\cdot\text{l}^{-1}$ and Equation (7) if concentrations $> 1200 \mu\text{mol}\cdot\text{N}\cdot\text{l}^{-1}$) plus the diffusive emission (Equation (1) or (2)) results total N_2 aec emission (Figure 3).

Actually, diffusive emissions were originally [12] plotted against dissolved $\text{NO}_3\text{-N}$, which, for lack of more data on dissolved N, we assume roughly represents total dissolved N. The ready-to-use version of our model (Table 3) will be used while working through the five case studies.

3.3. Partition between Ebullitive and Diffusive N_2 aec Emissions

The ebullitive:diffusive partition ratio changes radically with increasing dissolved N. In river water with small concentrations ($< 11 \mu\text{mol}\cdot\text{N}\cdot\text{l}^{-1}$) of dissolved N, N_2 aec ebullitive emissions are not significant and diffusive emissions predominate (Figure 3(a), Table 3 and Figure 4).

In waters with $> 11 \mu\text{mol}\cdot\text{N}\cdot\text{l}^{-1}$ ebullitive N_2 aec emissions increase steadily, along with the diffusive ones. At concentrations between $140 - 240 \mu\text{mol}\cdot\text{N}\cdot\text{l}^{-1}$ ebullitive rate equal diffusive rate emissions (Figure 3(b) and Figure 4). At concentrations $> 250 \mu\text{mol}\cdot\text{N}\cdot\text{l}^{-1}$, ebullitive will tend to be higher than diffusive emissions (Figure 3(b) and Figure 3(c), and Figure 4). In the concentration range $300 - 1200 \mu\text{mol}\cdot\text{N}\cdot\text{l}^{-1}$ water is supersaturated with dissolved N and bubble emissions continue to increase, while diffusive emissions eventually saturate at $640 - 700 \mu\text{mol}\cdot\text{N}_2\text{aec}\cdot\text{N}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ (Figure 3(c) and Figure 4). In waters with dissolved N concentration $> 1200 \mu\text{mol}\cdot\text{N}\cdot\text{l}^{-1}$ ebullitive emissions predominate (Figure 3(d) and Figure 4).

In addition, ebullitive N_2 aec emission correlates significantly with CH_4 ebullitive emission ($R = 0.96$; $P = 0.002$; $n = 11$; data from Table A1; graph not shown) and CO_2 ebullitive emission ($R = 0.94$; $P = 0.005$; $n = 11$; data from Table A1; graph not shown), suggesting that the production of N_2 aec is associated with decomposition of organic matter.

4. Case Study Application

The following five case studies use the findings here reported to estimate N_2 aec emission across aquatic environments.

4.1. Case Study 1: The “Missing” Nitrogen

Approximately 50% of the net anthropogenic N input was unaccounted for in a watershed N budget, which included diffusive but not ebullitive emission [22].

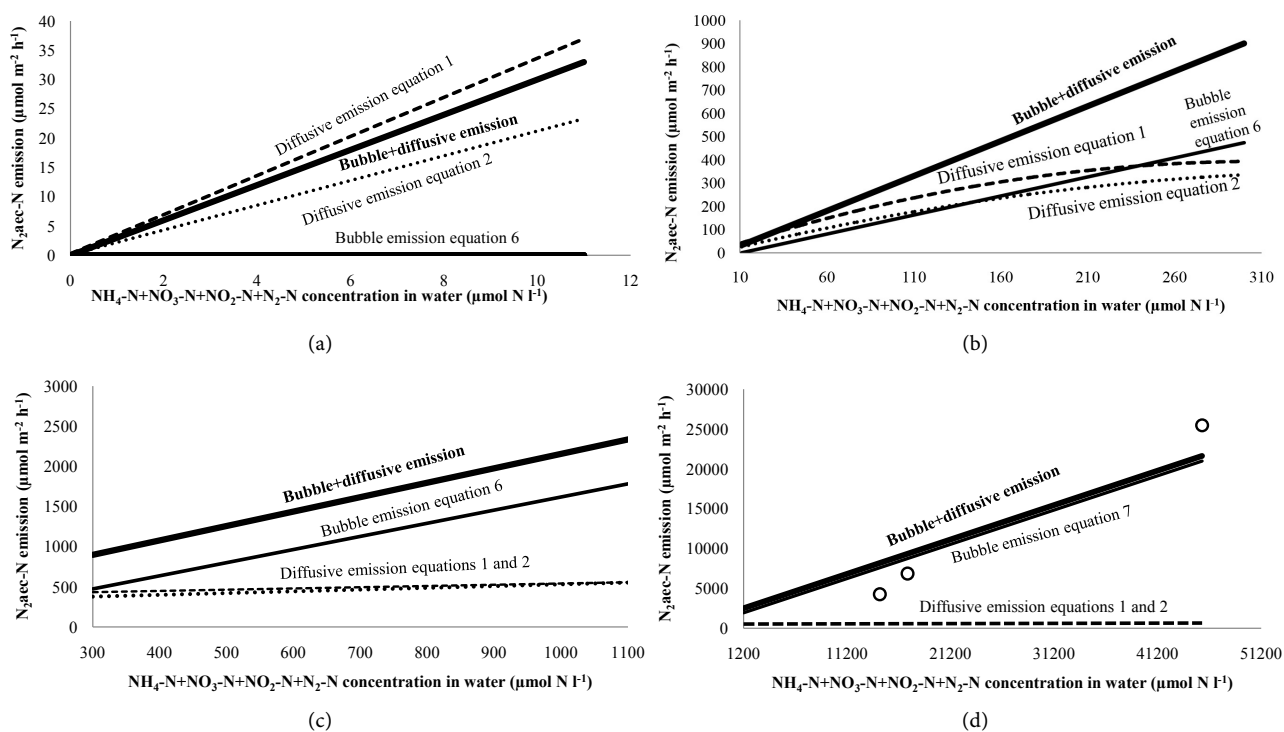


Figure 3. (a), (b), (c) and (d) Graphical representations of ebullitive (bubble), diffusive, and total (bubble + diffusive) N_2 aec water-air emission as a function of total N concentration in water. Circles in **Figure 3(d)** are reference [29]’s denitrified N_2 bubble emission data from swine farms.

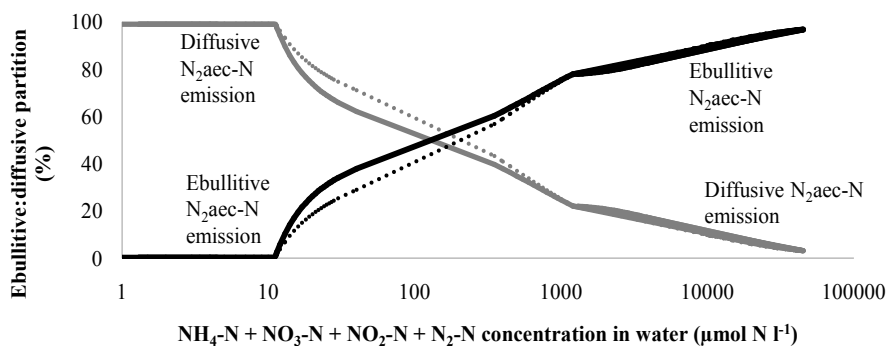


Figure 4. The “scissors-like” ebullitive:diffusive partition. N_2 aec emission percentage (%), y) as a function of dissolved total N in water ($\mu\text{mol}\cdot\text{N}\cdot\text{l}^{-1}$, x).

Figure 4 shows that ratio 63% - 65% ebullitive/37% - 35% diffusive N emission is predicted for stream waters with $500 \mu\text{mol}\cdot\text{N}\cdot\text{l}^{-1}$ such as those studied. Albeit a higher ebullitive loss (63% to 65%) than what was actually missing (~50%), this still shows that the fate of the missing N can be explained by ebullitive losses. See “Conclusion”.

4.2. Case Study 2: Nitrogen-Removal Rates

Nitrogen-removal rates were measured [30] with the membrane inlet mass spectrometry (MIMS) technique. Using the nitrate concentration data from Sugar Creek and Iroquois River [30] and our model, we find:

Table 3. N_2 aec emission ($\mu\text{mol}\cdot N_2\text{aec}\cdot N\cdot\text{m}^{-2}\cdot\text{h}^{-1}$, y) as a function of dissolved N concentration ($\mu\text{mol}\cdot N\cdot\text{l}^{-1}$, x) in water, within the 0 to 45,500 $\mu\text{mol}\cdot N\cdot\text{l}^{-1}$ concentration range.

Total dissolved N concentration range ($\mu\text{mol}\cdot N\cdot\text{l}^{-1}$, x)	Ebullitive emission ($\mu\text{mol}\cdot N_2\text{aec}\cdot N\cdot\text{m}^{-2}\cdot\text{h}^{-1}$, y) (A)	Diffusive emission ($\mu\text{mol}\cdot N_2\text{aec}\cdot N\cdot\text{m}^{-2}\cdot\text{h}^{-1}$, y) (B)	Total emission ($\mu\text{mol}\cdot N_2\text{aec}\cdot N\cdot\text{m}^{-2}\cdot\text{h}^{-1}$, y) (A + B)
0 - 11	0		$y \approx 3x$
11.1 - 300	$y = 1.638x - 18.11$	Either $y = (640x)/(180 + x)$	$y \approx 3x$
300 - 1200	$y = 1.638x - 18.11$	or $y = (700x)/(320 + x)$	$y = 1.797x + 360.6$
1200 - 45,500	$y = 0.4300x + 1430.7$		$y = 0.4315x + 1999.2$

1) How denitrified N_2 -emission is partitioned between ebullition and diffusion. For example, we estimated 83 to 123 $\mu\text{mol}\cdot N\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ diffusive emission (Table 4, line “Sugar Creek Sep 1999”, column “Diffusive estimated by us”); and 52 $\mu\text{mol}\cdot N\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ ebullitive emission (column “Ebullitive estimated by us”);

2) Significant discrepancy between predicted and measured rates for the high dissolved [N] range. For example, in June 2001 Sugar Creek’s sampled waters had the relatively high dissolved N concentration 1096 $\mu\text{mol}/\text{l}$ (Table 4). While a relatively small denitrification rate range $290 \pm 151 \mu\text{mol}\cdot N\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ (Table 4) was found, we estimated eight times higher rates 2319 to 2327 $\mu\text{mol}\cdot N\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ (Table 4).

4.3. Case Study 3: Nitrogen Budget

Estimation of total annual N_2 emitted and N buried in a subtropical river reservoir (Xipi) in southeast China with 8.5 km channel length and mean width of 125 m. For Xipi an annual $80\cdot 10^3$ kg gaseous N total emission was estimated [31], while we obtained $88\cdot 10^3$ kg-N (“TOTAL” line, Table 5). However, assuming permanent carbon sedimentation median rate $78 \text{ mg}\cdot\text{C}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ [32] and that the Redfield ratio 6.625 (106 C:16 N) roughly holds, we estimate sedimentation rate is:

$$78/6.625 = 11.77 \text{ mg}\cdot\text{N}\cdot\text{m}^{-2}\cdot\text{d}^{-1} \quad (8)$$

In addition, annual buried N is:

$$8500 \text{ m}\times 125 \text{ m}\times (11.77 \text{ mg}\cdot\text{N}\cdot\text{m}^{-2}\cdot\text{d}^{-1})\times (1 \text{ g}/1000 \text{ mg}) \quad (9)$$

$$\times (1 \text{ kg}/1000 \text{ g})\times (365 \text{ d}/\text{yr}) = 4564 \cdot 10^3 \text{ kg}\cdot\text{N}\cdot\text{yr}^{-1}$$

It follows that the total annual retention $(88.260 + 4.564) \times 10^3 \approx 93 \times 10^3$ kg estimated by us, is equal to 93×10^3 kg-N annual retention of dissolved inorganic N, estimated by using a different approach [31].

4.4. Case Study 4: N_2 Emission Estimation

The Jiulong River is a large agricultural river in southeast China. We use N concentration data (Table 6) to estimate its N_2 water-air emissions. These estimates are then compared to those of co-workers [33]:

1) The North River median area-weighted N_2 flux range 812 - 873 $\mu\text{mol}\cdot N\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ (estimated by us, Table 6) expressed in $\text{kg}\cdot\text{N}\cdot\text{ha}^{-1}\cdot\text{yr}^{-1}$ is:

Table 4. Source data (from reference [30]) are shown in bold font.

Date	NO ₃ (μmol N/l) (A)	Denitrified N ₂ (μmol·N·m ⁻² ·h ⁻¹)			N (% d ⁻¹) ^c		
		Diffusive estimated by us ^a (B)	Ebullitive estimated by us ^b (C)	B + C	Smith <i>et al.</i> [30]	Estimated by us	Measured by Smith <i>et al.</i> [30]
Sugar Creek							
Sep 1999	43	83 - 123	52	135 - 176	76 ± 78	25 - 32	14
May 2000	717	484 - 512	1156	1640 - 1668	1277 ± 1201	14 - 14	11
June 2001	1096	542 - 550	1777	2319 - 2327	290 ± 151	13 - 13	2
Sep 2001	135	208 - 274	203	411 - 477	327 ± 300	24 - 28	19
Iroquois River							
Sep 1999	42	81 - 121	51	132 - 172	100 ± 67	9 - 12	7
May 2000	840	507 - 527	1358	1865 - 1885	711 ± 305	5 - 5	2
Sep 2001	79	139 - 195	111	250 - 307	181 ± 261	23 - 28	17

^aUsing Equations (2) and (1). E.g.: $[(700 \times A)/(320 + A)]$ and $[(640 \times A)/(180 + A)]$. ^bUsing Equation (6). E.g.: $[(1.638 \times A) - 18.11]$. ^cN (% d⁻¹) is the percentage of water-column nitrate removed by denitrification. E.g.: $((135 \text{ to } 176) \times 14)/76 = (25 \text{ to } 32)\% \text{ N} \cdot \text{d}^{-1}$.

Table 5. Source data (from reference [31]'s Figure 5) are shown in bold font.

Time interval	DIN (μmol·N·l ⁻¹) (A)	ΔN ₂ -N (μmol·l ⁻¹) ^a (B)	ΔN ₂ O-N (10 ⁻³ μmol·l ⁻¹) (C)	Total (μmol·N·l ⁻¹) A + B + C	Our estimate of emitted N ₂ (μmol·N·m ⁻² ·h ⁻¹)	Number of interpolated days	Our estimate for total N ₂ emitted (kg·N)
May Jun 2012	120	12	5.727	132.0057	396.0172 ^b	61	8624.066 ^d
Jul Aug Sep 2012	150	70	12.727	220.0127	660.0382 ^b	92	21,678.29
Oct Nov Dec 2012 Jan 2013	200	16	13.364	216.0134	648.0401 ^b	123	28,456.09
Feb Mar Apr 2013	300	16	31.818	316.0318	928.5091 ^c	89	29,501.52
			TOTAL				88,259.97

^aDissolved N₂, in excess of environmental (background) dissolved N₂. ^b $3 \times (A + B + C)$, see **Table 3**. ^c $[(1.797 \times (A + B + C)) + 360.6]$, see **Table 3**. ^d8500 m × 125 m × (396.0172 μmol·N·m⁻²·h⁻¹) × (24 h·d⁻¹) × (61 d) × (1 mmol/1000 μmol) × (1 mol/1000 mmol) × (14 g/mol) × (1 kg/1000 g) = 8624.066 kg N per 61 days.

$$(812 \mu\text{mol} \cdot \text{N} \cdot \text{m}^{-2} \cdot \text{h}^{-1}) \times (10^{-6} \text{ mol} \cdot \mu\text{mol}^{-1}) \times (100 \text{ m}^2 \cdot \text{ha}^{-1}) \times (24 \text{ h} \cdot \text{d}^{-1}) \times (365 \text{ d} \cdot \text{yr}^{-1}) \times (14 \text{ g} \cdot \text{mol}^{-1}) \times (0.001 \text{ kg} \cdot \text{g}^{-1}) = 9.96 \text{ kg} \cdot \text{N} \cdot \text{ha}^{-1} \cdot \text{yr}^{-1} \quad (10)$$

or 9.96 - 10.7 kg·N·ha⁻¹·yr⁻¹, and similar to 9.88 kg·N·ha⁻¹·yr⁻¹ estimated by co-workers (in reference [33]'s **Table 3**);

2) Likewise, West River median area-weighted N₂ flux range 1100 - 1149 μmol·N·m⁻²·h⁻¹ (**Table 6**) or 13.49 - 14.09 kg·N·ha⁻¹·yr⁻¹, is similar to 14.06 estimated by co-workers (in Reference [33]'s **Table 3**).

4.5. Case Study 5: Comparison between Denitrification Rates (Median and Interquartile) Measured on the Elbe River with Rates Predicted by Our Model

Elbe River denitrification rates were obtained by measuring dissolved N₂ “super-saturation” (measured dissolved N₂ minus equilibrium dissolved N₂) and

Table 6. Source data (from Reference [33]'s Figure 3) are shown in bold font. Data from tributary sites' (W1, W2 and W3) were not used here.

Site	(NH ₄ -N) + (NO ₂ -N) + (NO ₃ -N) (μmol·N·l ⁻¹) (A)	Δ N ₂ (μmol·N·l ⁻¹) ^a (B)	A + B	Denitrification (μmol·N·m ⁻² ·h ⁻¹),		C + D
				Diffusive estimated by us ^b (C)	Ebullitive estimated by us ^c (D)	
North River						
N1	670	160	830	505 - 526	1341	1847 - 1867
N2	630	163	793	499 - 522	1281	1780 - 1802
N3	538	130	668	473 - 504	1076	1549 - 1580
N4	600	110	710	483 - 511	1145	1627 - 1655
N5	268	64	332	356 - 415	526	882 - 941
N6	200	52	252	308 - 373	395	703 - 768
N7	235	50	285	330 - 392	449	778 - 841
N8	223	62	285	330 - 392	449	778 - 841
N9	240	44	284	329 - 392	447	776 - 839
N10	248	46	294	335 - 397	463	799 - 860
N11	238	54	292	334 - 396	460	794 - 856
N12	250	50	300	339 - 400	473	812 - 873
N13	245	48	293	335 - 396	462	796 - 858
N14	300	50	350	366 - 423	555	921 - 978
N15	295	54	349	365 - 422	554	919 - 976
North River median emission range						812 - 873
West River						
W4	670	72	742	489 - 515	1187	1686 - 1712
W5	725	76	801	500 - 523	1286	1794 - 1816
W6	180	86	266	318 - 382	395	735 - 799
W7	190	74	264	316 - 381	404	731 - 795
W8	250	88	338	360 - 418	526	895 - 953
W9	140	72	212	279 - 346	300	608 - 675
W10	243	86	329	355 - 414	504	876 - 934
W11	350	100	450	409 - 457	701	1128 - 1176
W12	340	96	436	404 - 453	667	1100 - 1149
W13	340	100	440	405 - 454	671	1108 - 1157
W14	400	106	506	429-472	785	1240 - 1283
West River median emission range						1100 - 1149

^aDissolved N₂, in excess of environmental (background) dissolved N₂. ^b $[(700 \times (A + B))/(320 + (A + B))]$ and $[(640 \times (A + B))/(180 + (A + B))]$, see **Table 3**. ^c $[(1.638 \times (A + B)) - 18.11]$, see **Table 3**.

using varying reaeration-rate coefficient gas exchange equations [34]. Comparison shows:

1) The decreasing N_2 emission tendency from upstream (Reach A) to downstream (Reach C) is observed in both works, here and [34], (Table 7).

2) Median (and interquartile) total N in the Elbe River water between years 2011 and 2012 was 5.0 (4.0; 6.1) mg N/l based on 863 measurements (<http://www.fgg-elbe.de>) performed on the about 105 km² studied river area. Using this data and the model here proposed we estimate a nitrogen removal of 12,910 (11,038; 14,728) t·N·yr⁻¹. These rates are compatible with the ~10,000 t·N·yr⁻¹ extrapolated annual estimate, based on annual temperature changes [34].

5. Discussion

To the best of our knowledge, this is the first work to report N_{2aec} in ebullitive emission samples using Ar as a tracer of environmental N_2 . Furthermore, this approach can be used to quantify ebullitive N_{2aec} in bubbles sampled elsewhere (Table 8 and Table 9).

Using a different analytical approach—headspace equilibration—gaseous $N_2:Ar$ in the collected bubbles at sites from South Platte River within 81 km of Denver (Colorado, USA) were quantified [35]. The collected bubbles were injected into a vial containing 40 ml of N_2 -saturated water and shaken for 1 minute. Dissolved N_2 and Ar concentrations in the liquid fraction, measured via MIMS [36] [37], were used to back-calculate gas concentrations in the collected bubbles. The N_{2aec} —possibly denitrified N_2 in fact—in those bubbles ranged from 0% to 13.9% (Table 9).

The rate of increase of total N_{2aec} emission weakens with dissolved N concentration: from 3 $\mu\text{mol } N_{2aec}\cdot\text{N}\cdot\text{m}^{-2}\cdot\text{h}^{-1}/\mu\text{mol}\cdot\text{N}\cdot\text{l}^{-1}$ (Table 3) to 1.797 (Table 3) to 0.4315 (Table 3). The denitrification (a source of N_{2aec}) model from co-workers also points to a decrease in denitrification capability of streams with increasing nitrate loads: “higher loading rates stimulate NO_3^- uptake and denitrification, but yield an associate disproportionate increase in downstream NO_3^- export to receiving waters” [38].

While it is possible that the N_2 gas in bubbles is due to “excess air” from groundwater recharge, the fact that the ratio N:Ar in this “excess air” is close to that in the atmosphere [39] excludes the N_2 of this source to be accounted as denitrified N_2 . This suggests denitrification is the source of excess N_2 in the bubbles here reported.

Possible causes for negative emission rates are: N consumption, N fixation in excess of production, excess O_2 (possibly from photosynthesis), and/or Ar gas seeping into the bubble faster than O_2 or N_2 . If the cause was N consumption or N fixation in excess of production, then inclusion of the negative rates in median calculation would yield net N_2 “production”. However, median emission results for each one of the eleven surveys would not be impacted by this inclusion except for São Marcos’ River June 2011 survey 2/3 (median would be

Table 7. Dissolved N and N₂ emissions from Elbe River (source data [34] in bold).

Campaign-Reach	Total N (mg/l) ^a	n ^b	Median rate and ranges estimated here ^c (mg·N·m ⁻² ·h ⁻¹)	Median rate and ranges estimated by Ritz <i>et al.</i> [34] (mg·N·m ⁻² ·h ⁻¹)
Summer 2011-A	5.8 (5.2; 6.1)	22	15 (14; 16)	14 (11; 22)
Summer 2011-B	4.8 (4.5; 4.9)	6	14 (13; 14)	25 (16; 34)
Summer 2011-C	2.6 (2.6; 2.9)	3	8 (8; 9)	6 (2; 6)
Spring 2012-A	4.9 (4.3; 5.2)	18	14 (13; 14)	21 (18; 33)
Spring 2012-B	4.3 (4.1; 4.3)	5	13 (12; 13)	11 (1; 12)
Spring 2012-C	2.8 (2.6; 2.9)	3	8 (8; 9)	10 (-1; 13)

^a<http://www.fgg-elbe.de>. ^bQuantity of measurements. ^cTotal N is multiplied by 71.4 (1 mg N = 71.4 μmol N). The appropriate equation is selected from “Total emission” column in **Table 3**. The result is divided by 71.4.

Table 8. Columns “Site”, “% O₂+Ar” and “% N₂” are from reference [27]. There it is stated that 5% of the O₂+Ar mixture is Ar (calculated in the “% Ar” column). Assuming environmental concentrations 78% N₂ and 0.93% Ar, we used Ar as a tracer of environmental N₂ to calculate the concentration (%) of N₂aec (possibly denitrified N₂) in bubbles (results in “% N₂aec-N” column). Example of calculation (using data from line 1, Site DC): 5.40 = 7.5 - (0.025%Ar × 78%N₂/0.93%Ar). We assumed negative values indicated zero N₂aec in bubbles (see **Table A1** header). Median (24.12) was not changed by including negative (rather than zero) value observed in site CLB.

Site	% (O ₂ + Ar)	% N ₂	% Ar [†]	% N ₂ aec-N
DC	0.5	7.5	0.025	5.40
BB	1.2	36.4	0.06	31.37
HC	0.3	11.1	0.015	9.84
CLB	0.9	3.4	0.045	-0.37 (0)
UF	1.1	29.5	0.055	24.89
GI	1.3	24.4	0.065	18.95
S	1.2	12	0.06	6.97
F	1.3	28.8	0.065	23.35
Br	1	42.7	0.05	38.51
LF	1.4	49.8	0.07	43.93
HL	0.6	19.4	0.03	16.88
<i>Pelt.</i>	2.1	64.4	0.105	55.59
<i>Spar.</i>	2.4	84.5	0.12	74.44
DFC	1.2	52.1	0.06	47.07
		Median		24.12 (24.12)

[†]5% of (O₂ + Ar).

-3.27 mg·N₂-N·m⁻²·d⁻¹, rather than zero) as shown in **Table A1**, indicating that in the six rivers here studied N production would exceed N fixation. Excess N₂ was also found in most bubble samples collected in the White Oak River estuary USA (**Table 8**) and South Platte River USA (**Table 9**).

Table 9. Columns “Site”, “Distance” and “Gaseous N₂:Ar” were copied from Reference [35]. Sites are situated on South Platte River downstream from the point of discharge from the largest wastewater treatment plant from Denver, serving 1.3 million people. Concentration of N₂aec was calculated using environmental ratio 78% N₂:0.93% Ar. Calculation example for the South Platte site: $(79.93 \times 0.93) - 78 = -3.67$ (0). Median (7.51) was not changed by inclusion of negative value observed in South Platte site.

Site	Distance from wastewater discharge (river km)	Gaseous N ₂ :Ar	N ₂ aec-N in bubbles (%)
South Platte	-18	79.93	-3.67 (0)
	+5	95.28	10.6
Site A	+10	97.07	12.3
	+16	97.51	12.7
Site B	+24	98.86	13.9
Site C	+44	88.62	4.42
Site D	+52	87.64	3.51
	+81	87.55	3.42
	Median		7.51 (7.51)

Synthetically stirred bubbles from bubble-enriched sediment sites [27] showed higher median concentration (24.1 % N₂aec-N, n = 14, Table 8) of N₂aec than ours (5.75 % N₂aec-N, n = 112, data from Table A1) and, than the median (7.51 % N₂aec-N, n = 8, Table 9) for naturally emerging bubbles from a high nutrient segment of South Platte River. The relatively small median (5.75%) obtained here could be due to partial bubble dissolution during the diel harvest, or greater variety of sampled aquatic environments.

The significant rates of ebullitive gas water-air emission from the heavily urbanized stretches of Pinheiros and Tietê rivers here observed support the finding that urban streams and rivers should be included in river nitrogen cycling models [40].

Bubble occurrence in the eyes and inwards of fish [41] is a condition known as “gas bubble disease” also referred to as “gas bubble trauma”. This can possibly be explained by super saturation levels of dissolved N concentration ($> \sim 250 \mu\text{mol}\cdot\text{l}^{-1}$) because this favors excessive bubble formation while promoting the ebullitive escape discussed here.

6. Conclusions

In waters with small concentrations of dissolved N ($< 10 \mu\text{mol}\cdot\text{N}\cdot\text{l}^{-1}$) ebullitive N₂aec water-air emissions are practically insignificant and diffusive N₂aec emissions predominate. Ebullitive and diffusive N₂aec emissions increase with dissolved N concentration but diffusive N₂aec emissions saturate at $\sim 700 \mu\text{mol}\cdot\text{N}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ in waters with $> \sim 1000 \mu\text{mol}\cdot\text{N}\cdot\text{l}^{-1}$, while ebullitive continue to grow.

While the chromatographic analyses of N₂ and O₂ (although CH₄ and CO₂

were the main gases of interest at the time) were carefully done, the Ar concentration in the ebullitive emission sample hinges on a statement, *i.e.* that 5% of the “O₂” peak is Ar. Here, there is margin for refinement because the Ar concentration in each ebullitive emission sample can easily be done chromatographically, using O₂ as a carrier gas, with the precision required for this work.

As dissolved N is a predictor of N₂ae emission, denitrified N₂ emission models would benefit from data of simultaneous measurements of total dissolved N concentration (NH₄-N + NO₃-N + NO₂-N + N₂-N) and denitrified N₂ ebullitive and diffusive emission (rather than not measuring total dissolved N along with the ebullitive and diffusive measurements).

Our N₂ae emission model predicted 13% - 15% (63 - 50 = 13 and 65 - 50 = 15) more ebullitive N losses than the actual “missing N”, in Case Study 1. Causes for this overestimation could probably be understood with more bubble emission measurements in other river systems, considering local variability such as slope, sediment types, N inputs and biochemistry. In Case Study 2, the nitrogen-removal range predicted by our model tends to be within the measured range by MIMS, except when nitrate concentrations are highest (840 and 1096 µmol N/l) then, our model overestimates the measured nitrogen-removal rates. This could be due to local conditions and/or underestimation by MIMS of the ebullitive nitrogen-removal pathway. In Case Studies 3, 4 and 5 the measured values by co-workers are predicted relatively well by our model.

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Conflicts of Interest

The authors declare no conflict of interest, financial or otherwise.

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Appendix

Table A1 Each of the six rivers' surveyed sites. ^aSite depth. ^bVolume of collected bubble gas. ^cQuantity of 70 cm diameter funnels at sampled site. ^dSampling time interval. ^eSurface water temperature, at ~10 cm depth. ^fAtmospheric pressure in field laboratory. ^gO₂+Ar, N₂, CO₂ and CH₄ concentrations in bubble gas samples. ^hSee 2.5 N₂aec bubble-emission calculation method (main text). ⁱExcluded, river flow probably tilted the funnels and air entered bubble-gas vial. ^jNo existing data. ^kMedian temperature; temperature probe had faulty contact. ^lUnderestimated volume due to bubble-gas overflow. ^mNot analyzed. ⁿFirst and third quartiles are the nonparametric statistics' numerical equivalents to the normal distribution's two values in between which the central 50% of the area under the normal curve lies. First and third quartiles were calculated assuming: ebullitive N₂aec emission rate histograms of polluted rivers display normal distributions; ±1 standard deviation from the mean were 293 and 405 (Tietê River) and 858 and 1011 (Pinheiros River). [†]Negative emissions, and results of calculations using negative emissions, are italicized. This parallel calculation was done for the following reason: if the assumption that negative N₂ emission rates indicate N fixation is true, then their inclusion in median calculation would yield either net N₂ production (positive median) or net uptake of N *i.e.* consumption (negative median).

Table A1. (a) Xingu River; (b) Tocantins River; (c) Madeira River; (d) São Marcos River; (e) Tietê River; (f) Pinheiros River.

(a)

Site		SD ^a (m)	VCBG ^b (ml)	QF ^c	STI ^d (h)	WT ^e (K)	AP ^f (mm Hg)	O ₂ +Ar ^g (%)	N ₂ ^h (%)	CH ₄ ^g (%)	CO ₂ ^g (%)	Ebullitive N ₂ aec-N (mg·m ⁻² ·d ⁻¹)
Latitude (°S)	Longitude (°W)											
3.3118	52.1960	3.5	2000	4	22.18	301.7	747.0	4.11	13.0	84.4	0.46	0 (-66.5) [†]
3.3118	52.1960	4.5	583	3	22.72	301.7	747.0	6.40	25.1	68.3	0.14	0 (-10.5)
3.3118	52.1960	5.5	520	4	22.33	301.7	747.0	4.89	26.5	68.3	0.21	24.1 ^h
3.4145	52.2497	3	320	4	22.72	301.6	746.0	5.49	19.4	75.0	0.19	0 (-8.90)
3.4145	52.2497	4.5	<1.6	3	22.75	301.6	746.0	na ^m	na	na	na	0
3.4145	52.2497	5.5	957	4	21.95	301.6	746.0	22.6	77.1	0.20	0.13	0 (-134)
3.3668	51.9870	4.5	<1.6	4	20.47	301.5	748.0	na	na	na	na	0
3.3668	51.9870	3.5	1464	4	20.35	301.5	748.0	4.31	24.5	71.2	0.57	80.0
3.3668	51.9870	4.5	29	3	19.83	301.5	748.0	8.96	43.4	49.4	0.18	1.96
3.2159	52.1114	3.5	135	4	22.50	301.8	761.0	6.34	36.5	56.3	0.23	10.5
3.2159	52.1114	4.5	20	4	21.92	301.8	761.0	11.8	60.8	26.9	0.17	1.81
3.2159	52.1114	4	<1.6	3	21.93	301.8	761.0	na	na	na	na	0
3.2129	52.1874	4	38	3	22.63	302.8	745.0	12.3	65.3	23.9	0.46	5.26
3.2129	52.1874	2.5	10	2	22.92	302.8	745.0	2.68	79.0	17.9	0.42	10.2
3.2020	52.1946	4	14	4	23.20	301.0	745.0	14.2	83.2	1.36	0.22	2.46
3.2020	52.1946	2	<1.6	2	23.25	301.0	745.0	na	na	na	na	0
Xingu River (1/2) May 13 to 18, 2008 survey N ₂ aec bubble-emission median (n = 16)												0.91 (0.91)
3.4032	52.2597	1.5	<1.6	2	23.07	304.0	746.0	na	na	na	na	0
3.4032	52.2597	2	<1.6	3	23.72	304.0	746.0	na	na	na	na	0
3.4032	52.2597	3	8	3	23.90	304.0	746.0	21.5	78.3	0.17	0.04	0 (-0.92)
3.3402	52.1960	1.5	4	3	24.33	304.5	746.0	18.5	81.5	na	na	0.14
3.3402	52.1960	3	11	2	24.20	304.5	746.0	19.8	80.1	0.01	0.06	0 (-0.47)
3.3402	52.1960	4	<1.6	2	24.23	304.5	746.0	na	na	na	na	0
3.2183	52.1119	1.5	<1.6	2	17.55	306.0	747.0	na	na	na	na	0
3.2183	52.1119	2	5	2	17.42	306.0	747.0	20.9	81.7	0.03	0.05	0 (-0.59)
3.2183	52.1119	3	<1.6	2	17.12	306.0	747.0	na	na	na	na	0
3.2157	52.1741	1.5	6	3	16.28	306.4	747.0	19.8	80.3	0.87	0.05	0 (-0.24)
3.2157	52.1918	2.5	<1.6	2	15.82	305.3	747.0	na	na	na	na	0
3.2157	52.1918	5	6	2	15.55	305.3	747.0	21.7	78.0	0.02	0.09	0 (-1.73)
3.3729	51.9495	1.5	39	3	22.05	304.8	745.0	10.2	61.2	28.5	0.12	7.41
3.3729	51.9495	2.5	3	2	22.22	304.8	745.0	15.6	78.0	6.32	0.08	0.58
3.3729	51.9495	3.5	<1.6	3	22.10	304.8	745.0	na	na	na	na	0
3.3681	51.9773	1.5	8	4	21.03	305.4	745.0	21.8	78.1	0.08	0.05	0 (-0.87)
3.3681	51.9773	4	<1.6	3	20.62	305.4	745.0	na	na	na	na	0
3.2491	52.0549	1.5	23	3	18.08	304.9	746.0	21.5	78.4	0.03	0.09	0 (-3.45)
3.2491	52.0549	2	<1.6	2	18.30	304.9	746.0	na	na	na	na	0
3.2491	52.0549	3.5	11	2	17.90	304.9	746.0	19.3	80.6	0.03	0.10	0 (-0.09)
3.2453	52.0639	1.5	31	4	17.92	305.1	746.0	6.79	64.2	28.6	0.37	10.6
3.2453	52.0639	2.5	<1.6	3	18.22	305.1	746.0	na	na	na	na	0
Xingu River (2/2) Oct 16 to 21, 2008 survey N ₂ aec bubble-emission median (n = 22)												0 (0)
Xingu River N₂aec bubble-emission median (n = 38)												0 (0; 1.50)
(first quartile; third quartile)												0 (-0.41; 1.50)

(b)

Site		SD ^a (m)	VCBG ^b (ml)	QF ^c	STI ^d (h)	WT ^e (K)	AP ^f (mm Hg)	O ₂ +Ar ^g (%)	N ₂ ^h (%)	CH ₄ ⁱ (%)	CO ₂ ^j (%)	Ebullitive N ₂ aec-N (mg·m ⁻² ·d ⁻¹)
Latitude (°S)	Longitude (°W)											
5.3942	48.7397	5.3	331	6	21.83	302.9	746.3	2.26	31.2	66.7	0.85	37.8
5.3942	48.7397	6.8	26	5	21.92	302.9	746.3	3.40	95.6	2.28	0.83	13.3
5.4084	48.6658	3	48	3	22.50	301.6	747.1	21.5	76.2	2.09	0.19	0 (-6.94)
5.4084	48.6658	3	740 ⁱ	2	22.50	301.6	747.1	22.2	75.6	0.03	0.14	... ^j
5.3874	48.7065	6.5	<1.6	6	22.80	304.0	744.8	na	na	na	na	0
5.3874	48.7065	6.8	13	4	22.80	304.0	744.8	12.0	80.3	7.27	0.38	2.92
Tocantins River (1/2) Apr 7 to 11, 2008 survey N ₂ aec bubble-emission median (n = 5)												2.92 (2.92)
5.3210	48.8745	2	14	5	22.05	303.6	744.8	22.3	76.4	1.16	0.09	0 (-1.50)
5.3210	48.8745	2.5	5	4	21.62	303.6	744.8	23.0	77.9	0.01	0.07	0 (-0.74)
5.3210	48.8745	3	<1.6	5	21.52	303.6	744.8	na	na	na	na	0
5.3869	48.7434	1.5	52	5	23.78	306.0	743.3	20.1	79.5	0.06	0.34	0 (-1.46)
5.3869	48.7434	2	8	5	23.80	306.0	743.3	14.1	70.8	14.9	0.23	0.53
5.3869	48.7434	3.5	50	4	23.87	306.0	743.3	9.89	57.6	32.1	0.39	5.72
5.3832	48.7110	2.1	53	2	23.23	306.8	744.8	7.99	46.9	44.8	0.29	10.3
5.3832	48.7110	3	62	2	22.97	306.8	744.8	8.11	44.1	47.6	0.20	9.21
5.3832	48.7110	4	217	2	22.90	306.8	744.8	3.95	25.3	70.5	0.28	28.1
5.3982	48.6742	2	432	3	22.98	306.5	744.8	3.37	16.8	78.4	1.39	11.3
5.3982	48.6742	3	<1.6	2	23.27	306.5	744.8	na	na	na	na	0
5.3982	48.6742	4	<1.6	2	22.87	306.5	744.8	na	na	na	na	0
5.3679	48.7094	1.9	80	3	20.77	305.8	744.1	6.75	22.9	70.0	0.37	0 (-4.76)
5.3679	48.7094	2.5	81	2	21.20	305.8	744.1	5.57	32.8	61.3	0.33	12.2
5.3679	48.7094	3.5	36	2	20.95	305.8	744.1	8.66	47.8	43.2	0.35	6.69
5.3649	48.7205	1.6	<1.6	3	20.93	306.2	744.1	na	na	na	na	0
5.3649	48.7205	2.6	43	2	21.08	306.2	744.1	8.36	55.7	35.8	0.15	14.3
5.3649	48.7205	3	18	2	20.95	306.2	744.1	13.4	67.3	19.2	0.10	3.22
Tocantins River (2/2) Nov 10 to 14, 2008 survey N ₂ aec bubble-emission median (n = 18)												1.88 (1.88)
Tocantins River N₂aec bubble-emission median (n = 23)												2.92 (0; 10.8)
(first quartile ; third quartile)												2.92 (0; 10.8)

(c)

Site		SD ^a (m)	VCBG ^b (ml)	QF ^c	STI ^d (h)	WT ^e (K)	AP ^f (mm-Hg)	O ₂ +Ar ^g (%)	N ₂ ^h (%)	CH ₄ ⁱ (%)	CO ₂ ^j (%)	Ebullitive N ₂ aec-N (mg·m ⁻² ·d ⁻¹)
Latitude (°S)	Longitude (°W)											
8.8516	64.0644	3	790	2	20.50	301.1	750.8	9.69	42.4	46.7	1.23	23.0
8.8621	64.0593	3	1370	3	23.10	300.6	750.8	17.4	80.3	1.13	0.58	100
8.8584	64.0241	4.7	1430	2	22.62	300.8	750.8	16.5	74.2	8.57	0.69	109
8.9153	64.0899	4	620	3	19.25	298.4	748.6	4.86	28.8	65.1	1.25	63.3
8.9855	64.1237	3.9	310	1	19.25	302.5	748.6	5.59	65.1	28.3	0.96	464
8.9983	64.1323	5.6	210	3	19.33	302.5	748.6	6.89	41.8	50.7	0.61	32.3
9.0368	64.1954	2.2	350	3	20.33	300.8	747.8	5.38	34.3	58.2	2.10	46.8

Continued

9.1160	64.3176	4	230	4	19.92	300.5	747.8	4.4	51.1	43.7	0.83	65.6
9.2094	64.3897	5	500	1	19.42	300.9	747.8	3.46	18.7	74.9	2.99	74.7
9.1818	64.5136	6	78	1	19.55	300.9 ^k	748.6	22.2	77.5	0.06	0.06	0 (-43.7)
9.2458	64.6233	3	110	3	24.00	300.9 ^k	748.6	22.2	78.4	0.41	0.06	0 (-15.8)
8.8390	64.0155	9.6	365	2	20.28	301.1	750.8	15.5	77.9	6.07	0.50	80.5
8.9883	64.1015	3.5	25	2	19.25	302.8	748.6	15.9	71.0	12.7	0.45	1.90
Madeira River (1/2) May 27 to 30, 2011 survey N ₂ aec bubble-emission median (n = 13)												63.3 (63.3)
8.8396	64.0159	9.9	30	2	23.92	299.7	750.1	5.9	38.0	55.6	0.56	5.81
8.8527	64.0647	7.1	280	3	23.95	301.4	750.1	11.9	70.0	17.7	0.46	54.4
8.8343	63.9674	4.8	90	1	24.03	300.3	750.1	6.1	31.2	62.1	0.63	14.6
8.7950	63.9716	11.0	210	2	23.93	299.9	750.1	8.5	67.3	23.9	0.44	97.1
9.0417	64.2963	1.2	160	2	21.13	300.7	749.3	3.87	45.3	50.2	0.63	76.7
9.1083	64.3161	5.5	380	2	22.30	300.1	749.3	7.87	38.8	52.8	0.46	34.3
8.9748	64.1008	6.0	500	1	23.50	299.9	749.3	4.42	20.3	74.8	0.48	25.9
9.0145	64.1675	4.3	300 ^l	3	20.25	300.4	749.3	2.17	17.4	79.3	1.21	28.6
9.2101	64.4191	4.9	500 ^l	2	22.68	300.0	750.1	2.13	20.5	75.5	1.83	89.1
9.1438	64.5152	2.3	420	2	21.43	299.8	750.1	18.5	70.6	10.5	0.43	0 (-48.6)
9.1827	64.6129	7.0	60	2	20.37	299.7	750.1	7.89	51.7	40.0	0.42	19.2
9.2582	64.6313	3.0	10	2	19.13	299.7	750.1	13.2	82.5	3.91	0.43	4.96
9.2226	64.6192	2.0	1000 ^l	2	19.13	299.9	750.1	1.8	13.3	82.3	2.49	105
Madeira River (2/2) March 7 to 9, 2012 survey N ₂ aec bubble-emission median (n = 13)												28.6 (28.6)
Madeira River N₂aec bubble-emission median (n = 26)												40.5 (15.8; 79.6)
(first quartile ; third quartile)												40.5 (15.8; 79.6)

(d)

Site		SD ^a	VCBG ^b	QF ^c	STI ^d	WT ^e	AP ^f	O ₂ +Ar ^g	N ₂ ^h	CH ₄ ⁱ	CO ₂ ^g	Ebullitive N ₂ aec-N (mg·m ⁻² ·d ⁻¹)
Latitude (*S)	Longitude (*W)	(m)	(ml)		(h)	(K)	(mm·Hg)	(%)	(%)	(%)	(%)	
17.0235	47.1476	4.2	275	5	21.28	297.3	699.1	20.9	77.4	1.38	0.32	0 (-17.6)
17.0618	47.1892	5.9	80	4	14.85	296.9	697.6	15.4	59.4	15.4	0.34	0 (-4.66)
17.0600	47.1894	4.0	280	7	14.28	297.1	697.6	9.02	32.4	57.8	0.78	0 (-10.1)
17.0991	47.2483	6	410	6	16.73	297.3	697.6	4.35	31.0	64.3	0.38	34.2
17.1000	47.2653	3	1060	4	18.10	296.0	697.6	4.86	30.6	63.6	0.97	98.4
16.9594	47.1598	2	1199	7	21.53	297.3	699.1	7.55	77.8	14.3	0.30	241
16.9594	47.1599	4	1075	6	21.85	297.1	699.1	4.74	33.1	61.3	0.81	71.3
16.9641	47.1550	4.5	2375	6	21.95	297.4	699.1	3.07	15.9	80.4	0.64	35.7
17.1418	47.2958	5	340	5	21.58	297.2	698.3	4.54	23.2	72.0	0.30	8.57
17.2092	47.3629	4.8	30	5	20.27	297.1	698.3	17.7	65.6	16.5	0.24	0 (-1.70)
17.2047	47.3602	4.6	760	5	19.32	297.1	698.3	7.17	26.1	66.4	0.35	0 (-20.7)
17.2271	47.3609	1.5	100	6	22.17	295.8	698.3	4.95	27.6	65.8	1.64	3.39
17.2229	47.3650	6	2000	4	21.20	295.7	698.3	4.01	13.5	81.7	0.76	0 (-52.0)
17.2369	47.4148	3	65	7	20.92	297.1	697.6	12.9	59.2	27.4	0.52	1.47

Continued

17.2125	47.4170	3	30	3	20.70	296.5	697.6	18.2	69.9	10.9	0.17	0 (-2.07)
17.3114	47.4242	6.6	575	6	20.85	296.7	697.6	4.38	27.9	67.3	0.47	28.8
17.2769	47.5227	4.5	153	3	21.30	297.1	697.6	3.75	21.0	74.8	0.48	8.27
17.3470	47.4844	5.2	510	3	21.33	297.1	697.6	21.2	78.4	0.24	0.19	0 (-55.6)
São Marcos River & tributaries (1/3) Mar 21 to 25, 2011 survey N ₂ aec bubble-emission median (n = 18)												2.43 (2.43)
17.0269	47.1462	2	480	2	20.28	292.6	702.1	17.8	68.5	13.6	0.10	0 (-49.6)
17.0382	47.1791	1	190	3	19.13	293.2	702.1	15.8	81.6	1.86	0.14	33.9
17.0626	47.1902	3.9	260	3	20.42	292.7	702.1	6.79	51.4	41.6	0.27	65.2
17.1000	47.2492	4.6	130	3	19.23	292.6	702.1	6.77	46.7	46.4	0.18	27.7
16.9646	47.1546	2.6	70	3	20.75	292.3	702.1	19.4	76.0	4.44	0.11	0 (-4.13)
17.1461	47.3026	3	10	3	21.03	292.2	700.6	19.9	78.4	1.60	0.10	0 (-0.55)
17.2068	47.3618	4.3	10	3	21.15	292.5	700.6	20.4	79.5	na	0.07	0 (-0.65)
17.2106	47.3623	5	45	3	21.15	292.6	700.6	20.5	79.2	0.04	0.12	0 (-3.27)
17.2428	47.3960	1.8	80	3	21.00	292.8	700.6	20.8	78.6	2.22	0.10	0 (-7.43)
17.3128	47.4241	2.5	1000	2	21.87	292.1	701.3	2.82	9.66	80.3	7.25	0 (-33.5)
17.3486	47.4869	4.8	180	3	21.30	292.3	701.3	16.6	59.6	23.2	0.51	0 (-19.1)
São Marcos River & tributaries (2/3) June 13 to 17, 2011 survey N ₂ aec bubble-emission median (n = 11)												0 (-3.27)
17.0258	47.1488	1.8	35	2	23.07	295.5	696.8	17.1	76.1	6.56	0.23	2.15
17.0620	47.1895	1.9	30	3	22.90	296.7	696.8	3.61	23.8	71.5	1.12	2.48
17.0357	47.1798	2	...	3	22.82	295.9	696.8	3.65	39.8	56.1	0.46	...
17.1000	47.2492	4.1	10	3	22.75	297.5	696.8	5.53	50.3	43.8	0.31	2.60
17.1188	47.2798	2	20	3	24.42	296.0	696.8	19.5	80.2	0.05	0.30	0 (-0.30)
17.1482	47.3272	2.3	240	3	24.48	296.5	696.8	19.2	80.5	0.04	0.25	0 (-0.26)
17.2224	47.3629	3.2	60	2	27.35	297.4	698.3	4.52	27.5	66.3	1.62	6.14
17.2449	47.4044	1.2	30	3	18.83	296.3	698.3	14.9	64.1	20.8	0.26	0.54
17.3071	47.4276	2	200	3	22.98	297.1	698.3	18.1	81.1	0.55	0.24	9.73
São Marcos River & tributaries (3/3) Sept 26 to 30, 2011 survey N ₂ aec bubble-emission median (n = 8)												2.32 (2.32)
São Marcos River and tributaries N₂aec bubble-emission median (n = 37)												0.54 (0; 9.73)
(first quartile; third quartile)												0.54 (-4.66; 9.73)

(e)

Site		SD ^a (m)	VCBG ^b (ml)	QF ^c	STI ^d (h)	WT ^e (K)	AP ^f (mm Hg)	O ₂ + Ar ^g (%)	N ₂ ^h (%)	CH ₄ ⁱ (%)	CO ₂ ^j (%)	Ebullitive N ₂ aec-N (mg·m ⁻² ·d ⁻¹)
Latitude (°S)	Longitude (°W)											
23.5254	46.7501	1.7	564	3	2.33	294.2	699.8	1.02	10.9	84.2	3.92	355
23.5067	46.5474	2.3	855	2	9.00	294.2	699.8	1.65	14.2	80.8	3.41	230
23.5255	46.7501	1.7	5400	3	18.75	294.2	696.1	1.58	13.8	79.7	4.95	456
Tietê River (1/1) May 8 to 9, 2012 survey N₂aec bubble-emission median (n = 3)												355 (293; 405)^a
(first quartile; third quartile)												

(f)

Site		SD ^a (m)	VCBG ^b (ml)	QF ^c	STI ^d (h)	WT ^e (K)	AP ^f (mm Hg)	O ₂ + Ar ^g (%)	N ₂ ^h (%)	CH ₄ ⁱ (%)	CO ₂ ^j (%)	Ebullitive N ₂ aec-N (mg·m ⁻² ·d ⁻¹)
Latitude (°S)	Longitude (°W)											
23.5255	46.7494	3	4200	3	0.85	293.9	699.8	1.10	5.61	80.7	12.6	1088
23.5332	46.7488	1.9	305	3	1.08	293.9	696.1	1.02	16.8	80.4	1.80	781
Pinheiros River (1/1) May 8 to 9, 2012 survey N₂aec bubble-emission median (n = 2)												934 (858; 1011)^a
(first quartile ; third quartile)												