N₂O Emissions from Streams in the Neuse River Watershed, North Carolina

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We present N₂O emission data from 11 sites in the Neuse River watershed. Emissions were measured using a static surface enclosure technique deployed on eight sites on the main river channel and three tributary sites. Ancillary data collected included dissolved oxygen, nitrate, total nitrogen, ammonium, dissolved organic carbon, total phosphorus, and temperature. Analysis using standard linear models, and classification and regression trees (CART), indicated nitrate to be the primary driving variable associated with N₂O emission, although dissolved organic carbon concentration and water temperature were positively related with N₂O emission as well. Relationships between nitrate concentration and N₂O emission were consistent with those found in previous studies, although the data presented here represent the lower end of the range for both variables among published studies. Using our measured N₂O emission rates along with literature values for the ratio of nitrogen gas to N₂O produced during denitrification, we estimate N loss via denitrification in the Neuse River is approximately 17% of the annual N load delivered to the estuary.

Introduction

Nitrous oxide (N_2O) is an efficient greenhouse gas, with a global warming potential approximately 300 times that of carbon dioxide (1). It is inert in the troposphere with an average atmospheric residence time of approximately 120 years (2). N_2O is emitted as a byproduct from nitrification and denitrification, two microbial processes. Though these processes occur naturally their relative importance in global N_2O production is believed to have increased as more atmospheric nitrogen has been anthropogenically diverted into fertilizers and other biologically available nitrogen compounds. Quantifying N_2O sources and sinks is important for evaluating climate change scenarios and assessing mitigation and management options.

On the watershed-scale, mass accounting typically indicates a nitrogen surplus, with imports exceeding exports (3, 4). David and Gentry (5) estimated that denitrification could account for much of the missing nitrogen in Illinois watersheds, with approximately 60% of the denitrification occurring in rivers and streams. Thus, fed by nitrogen-rich runoff from agricultural and urban land, and nitrogen-rich effluents from municipal and industrial point-sources, rivers and streams may be important N₂O sources. Seitzinger et al. (6) estimated that >90% of riverine nitrous oxide emissions originate from anthropogenically sequestered nitrogen. Globally, rivers may contribute up to 25% of the total anthropogenic nitrous oxide emitted into the environment (7). However, to date, riverine N₂O emission has been reported from only a few systems (7– 9).

We measured N₂O emission rates in the Neuse River and three tributaries to further document the role of nitrogenrich rivers in the global N₂O budget, and to provide an estimate of N loss via denitrification in this particular system. The Neuse basin (Figure 1) is typical of many coastal watersheds. Increases in urban and suburban development and changes in agricultural practices, especially the proliferation of concentrated animal feeding operations, have stimulated concern about water quality degradation and eutrophication. Most of these concerns have focused on the downstream estuary where a series of large fishkills in the mid-1990s prompted a series of management actions to curb nitrogen inputs to the river. However, while nitrogen imports to the watershed have increased (10), and the ammonia-N concentration in precipitation has risen (11), the annual nitrogen load to the estuary, (\sim 4145 metric tons total N yr⁻¹, with 2410 as nitrate-N over the period 1979–2002) has not shown a discernible increase (12). The absence of an N load increase may result, in part, because losses via denitrification have buffered the effect of increased N imports. Many conditions in the river are favorable for denitrification; water temperature is warm through much of the year, the water travel time enroute to the estuary can be several weeks (13), and the river is generally shallow with a high wetted-perimeter to cross-sectional area ratio presenting a large potential reaction surface.

Methods

Sample Collection and Chemical Analysis. We sampled 11 sites in the Neuse watershed from 2001 to 2002. Air and water samples were collected monthly from October through December during 2001 and approximately every three weeks from May through October during 2002 for a total of 109 samples from 11 sites (the Falls Lake site was sampled nine times, all other sites were sampled 10 times) (Figure 1). The Middle Creek, Swift Creek (upper watershed), and Little River sites are on small tributaries, while the remaining eight sites are on the main-stem of the Neuse River.

We measured N₂O emissions using a 37-L 0.18-m⁻² static floating chamber. The chamber frame was welded aluminum and the top was made of flexible Teflon to minimize pressure changes when samples were extracted. The chamber was placed on the water and sample air was drawn into preevacuated 800-mL SUMMA canisters at t = 0, 1, 2, 4, 6, and 8 min using a computer-controlled sampling system. Nitrous oxide fluxes were calculated according to the relationship

$$F_t = \left(\frac{C_t - C_0}{t}\right) \frac{V_t}{A}$$

where F_t is the flux (μ g N m⁻² min⁻¹) at time *t* (min), C_t is the chamber concentration (μ g N₂O–N m⁻³) at time *t*, C_0

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FIGURE 1. Neuse River Basin showing sampling sites and land cover classifications: 1 =Swift Creek, 2 = Middle Creek, 3 = Little River, 4 = Falls Lake, 5 = Smithfield, 6 = Goldsboro, 7 = Kinston, 8 = Fort Barnwell, 9 = Watoosi Marker, 10 = Swift Creek at Neuse River, 11 = Narrows.

is the initial chamber concentration, V_t is the chamber volume (m³) at time *t*, and *A* is the surface area (m²) enclosed by the chamber. This calculation accommodates the chamber volume changes that occur as a result of drawing samples, and provides five flux measurements for each sample. Each reported sample value is the average of the last four measurements. Because we were concerned that the placement of the chamber on the water surface might cause a physical disruption, temporarily affecting the flux, we did not include the 0–1 min interval in the sample calculation. Fluxes are expressed in units of μ g N m⁻² d⁻¹.

The lateral positioning of the chamber within the channel was based largely on accessibility. A principal consideration was to get samples without disturbing the bottom sediments. We found that wading into the channel released gaseous bubbles, so to avoid sample contamination we deployed the chamber from the side. For the sites sampled by boat (8–11) physical disturbance of the bottom was less of a constraint, but to keep sampling consistent with the land-based sites, and to avoid possible bottom disturbance by anchor dragging, we also sampled near the side of the channel.

Nitrous oxide concentrations were determined using a Hewlett-Packard 5890 gas chromatograph with electron capture detection, Porapak Q column, (2-m length), and a 5-mL sample loop. The GC sample loop was flushed 10× with sample air before loading onto the column to prevent memory effects. Carrier gas was 90% argon/10% methane. The system was multi-point-calibrated with a 5-ppm N₂O standard (National Specialty Gases, Inc.) and TEI model 146C dilution system. Peak area response was linear from 100 ppb v/v to 5 ppm. System precision was less than 1% RSD at approximately ambient concentrations.

We collected water samples at each location (depth ~ 10 cm) for analysis of nitrate + nitrite, ammonium, total nitrogen, orthophosphate, total phosphorus, and dissolved organic carbon. Nitrate (14, Method 353.2), nitrite (14, Method 353.2), ammonium (14, Method 350.1), total nitrogen (14, Method 353.2), orthophosphate (15, Standard Method 4500-PE), and total phosphorus (15, Standard Method 4500-PE) were determined using standard colorimetric procedures.

Dissolved organic carbon was determined using a hightemperature combustion/total organic carbon method (*15*, Standard Method 5310-B). Water temperature, conductivity, dissolved oxygen, and salinity were also measured at a depth of 10 cm using a YSI probe model 85 (Yellow Springs Instruments, Yellow Springs, OH).

Statistical Analysis. To determine the major driving variable of N_2O flux we examined the data using both conventional linear models and the S+ software (*16*) implementation of classification and regression trees (CART). CART models are a relatively new method (*17*) consisting of an algorithm that recursively partitions the data into a succession of nodes or branches, based on values or categories of the predictor variables. The algorithm begins by defining the deviance of the first node (all of the data) as

$$D(\mu) = \sum (y_i - \mu)^2$$

where y_i are the observations within the node and μ is the node mean. Then each candidate predictor variable is examined to find a point that splits the response variable into two new nodes, a left and right, where

 $D(\mu_{\rm L}) = \sum (y_{\rm i} - \mu_{\rm L})^2$

and

$$D(\mu_{\rm R}) = \sum (y_{\rm i} - \mu_{\rm R})^2$$

are the respective deviances of the left and right nodes. The split that maximizes the deviance reduction

$$\Delta D(\mu) = D(\mu) - \{D(\mu_{\rm I}) + D(\mu_{\rm R})\}$$

is chosen, and the process begins again at the left and right nodes. The result, which is graphically depicted as a branching tree, is similar to a dichotomous key where successive choices are made regarding the value of the response variable, based on predictor characteristics. CART models have a number of features which make them a useful complement to more familiar data analysis methods. They are not based on assumptions of linearity, additivity, or multiplicative interactions, and are invariant to monotone transformations of the predictors. They are particularly applicable when the relationship between the response variable and the predictors is not homogeneous within the sample space. Predictor variable selection is implicit in the model procedure; many candidate predictors can be specified, but only those resulting in the greatest deviance reduction will be incorporated into the model. Interactions among predictors are not specified a priori, they are determined in the recursive partitioning procedure.

Finally, we used the measured N_2O emission rates from river sites 5–8 to estimate a probable range for the total annual N_2 loss via denitrification from the Neuse River. We estimated the loss as a percent of the total nitrogen delivered to the estuary as follows:

% N loss = $(ABC \times 1 \times 10^{-6}/D)/(GF)$

where A = average N₂O emission rate from sites 5–8 (g N m⁻² y⁻¹), B = river length (m), C = average river width (m), 1 × 10⁻⁶ ton g⁻¹ = conversion factor, D = estimated ratio of N loss via N₂O vs N₂, G = total nitrogen delivery to estuary measured at Fort Barnwell (ton yr⁻¹), and F = ratio of nitrogen at Fort Barnwell from Neuse River vs from Contentnea Creek (a tributary that enters the Neuse River just above Fort Barnwell). This last factor was included to discount nitrogen load at Fort Barnwell for the contribution from Contentnea Creek, because we did not measure emissions on this tributary and did not include it in the loss estimate.

Because most of these inputs are uncertain or vary temporally and spatially (18) we ran a Monte Carlo simulation, using a probability function for each input, to estimate the total uncertainty in the % N loss. We represented the probability functions as follows: A = Log-normal distributionwith $\mu = 0.195$, $\sigma = 0.145$, a shift of -0.065 (consistent with a mean emission rate of 0.13 g N $m^{-2} y^{-1}$) based on a fit of measured emission rates from sites 5-8; B was assumed known at 3 \times 10⁵ m; *C* = normal distribution with μ = 20 m and $\sigma = 2$, based on personal observation; D = gamma distribution with $\alpha = 2$, $\beta = 0.001$ and a shift of 0.001 (consistent with a mean of 0.003) based on values reported in refs 6 and 19; G = normal distribution with $\mu = 2424$ and $\sigma = 273$, based on total nitrogen load estimates at Fort Barnwell for 2001-2002 presented in ref 12; and F was represented as a uniform distribution ranging from 0.7 to 0.87 based on estimates in ref 12. We estimated these probability functions from fits to data using @Risk software. Similarly, we ran the simulation using @Risk, under the assumption of independence for the inputs.

Results

Measured water quality characteristics exhibited fairly typical values (Figure 2). Nitrate, total N, DOC, and total P displayed considerable site-to-site variability, while ammonia, dissolved oxygen, and temperature were more consistent among sites. Means and variances in the three tributary sites were similar to values at the eight river sites. The influence of municipal point source discharges from the City of Raleigh and nearby communities occurring between sites 4 (Falls Lake) and 5 (Smithfield) is evidenced by large increases in nitrate, total N, and total P.

 N_2O emissions ranged from $-221 \ \mu g \ N \ m^{-2}d^{-1}$ at site 1 (Swift Creek) to $1558 \ \mu g \ N \ m^{-2}d^{-1}$ at site 7 (Kinston) with an overall mean ($\pm 1 \ SE$) of 309.6 (± 32.6). Emissions exhibited considerable variability both across and within sites (Figure 2). The highest values were recorded during warmer months, though there was no clear seasonal pattern. Both mean and median values for all sites were positive, indicating they were

net atmospheric N₂O sources, however, approximately onethird of the measurements at sites 1 (Swift Creek), 4 (Falls Lake), and 6 (Goldsboro) were negative indicating periodic N₂O uptake. Low nitrate concentrations at sites 1 and 4 may be responsible for the overall low emission rates at these locations. Additionally, water levels at site 1 were frequently low, with much of the stream bed exposed, and minimal flow. However, site 6 had characteristics more consistent with the other river sites, but exhibited much lower emission rates. This site was located approximately 200 m downstream from the City of Goldsboro municipal discharge, a point source of approximately 7.7 mgd ($2.9 \times 10^4 \text{ m}^3 \text{d}^{-1}$), though it is unclear if characteristics of this effluent could be influencing emission rates. The overall highest emissions were recorded at site 7 (Kinston), though no measured or observed characteristics distinguish this site from the others.

Exploratory analysis with candidate linear models indicated considerable heteroscedasticity among model residuals, so to stabilize the error variance we used a generalized least squares approach with $1/NO_3^-$ as a weight. Our final model includes a categorical (nominal) variable to differentiate the 11 sites, and NO_3^- and DOC as covariates (Table 1).

Comparing site-wise parameter estimates gives an indication of the relative N₂O emission rates among sites, adjusted for differences in NO3⁻ and DOC concentration. The highest values are generally in the lower section of the river at sites 7 (Kinston), 10 (Swift Creek at Neuse River), and 11 (Narrows), with lower values in the three tributary streams (sites 1-3), and below the Falls Lake dam (site 4). Site 6 (Goldsboro) has the lowest value, indicating that the low emission rates at this site are not caused by low NO3⁻ or DOC levels, reinforcing our speculation that another factor, such as proximity to the City of Goldsboro municipal discharge, may be influencing emissions. The model R² of 0.48 indicates only about half of the marginal N₂O variance is resolved by this model. The unresolved variance may be associated with factors that were not measured in this study such as water depth, turbulence, or bottom composition, or may reflect nonlinear relationships among the variables.

A CART analysis indicates some structure not easily revealed in a standard linear model (Figure 3). NO_3^- is the first split in this tree, underscoring the relative importance of the $N_2O-NO_3^-$ relationship. At NO_3^- values $<74.55 \ \mu g \ L^{-1}$ the mean N_2O emission rate was $159.2 \ \mu g \ N \ m^{-2}d^{-1}$, while at NO_3^- values above $74.55 \ \mu g \ N \ m^{-2}d^{-1}$ another split is indicated, based on the DOC value. At DOC below 9 mg L^{-1} NO_3^- appears again as a node in the tree with a mean N_2O emission of $411.6 \ \mu g \ N \ m^{-2}d^{-1}$ at NO_3^- less than $742.45 \ ug \ L^{-1}$ and $929.5 \ \mu g \ N \ m^{-2}d^{-1}$ at NO_3^- above 742.45. When NO_3^- is greater than 74.55 and DOC >9 temperature enters the model as a predictor. Our results indicate a split at a temperature of $24.05 \ ^\circ$ C, with higher emission rates at the higher temperatures.

The mean estimated proportional N loss via denitrification in the Neuse River was 0.17 (Figure 4). However, uncertainty in the inputs causes this estimate to range from just below zero to just above one. Approximately 9% of the probability lies below zero, while approximately 5% is above 0.57. The 25th and 75th percentiles (representing the bounds of the middle 50%) correspond to 0.04 and 0.22, respectively. A sensitivity analysis indicated that the outcome is most sensitive to inputs for the N₂O emission rate (r = 0.92), secondarily to the ratio of N loss via N₂O vs N₂ (r = -0.32), and relatively insensitive to all the other inputs ($|r| \le 0.08$).

Discussion

Of the variables that we measured, the most important factor associated with river/stream N_2O emission was NO_3^- concentration. This outcome is consistent with results from



FIGURE 2. Box and whisker plots depicting site-wise measured N₂O emission rates and ambient water quality data. Vertical line separates tributary from river sites. Horizontal dashed line in N₂O plot at 0 μ g N m⁻² d⁻¹ included for reference.

Garcia-Ruiz et al. (20) who reported water column NO₃⁻ and sediment denitrification to be positively correlated, and also with the results of Richardson et al. (21) who concluded that denitrification was NO₃⁻ limited in the upper Mississippi River. We emphasize that in our data this relationship occurs mainly across sites, not necessarily within sites. This result is also consistent with the broader across-site pattern (Figure 5) established by Cole and Caraco (7). Our measurements extend this pattern to lower values than previously reported. If this pattern persists into even lower ranges it could imply that waters with extremely low NO₃⁻ concentrations are net N₂O sinks, an idea with possibly important implications when estimating the role of open oceans and inland seas in the global N₂O cycle.

Though the reported spatial/temporal scales of aggregation differ across studies, the persistence of this N_2O/NO_3^-

pattern suggests that water column NO_3^- concentration may be a useful surrogate for estimating the role of rivers in the global N_2O budget. NO_3^- concentration data are widely available, while N_2O emission data are fairly sparse. A simple linear regression (Figure 5) resulted in the following relationship:

$$Log_{10} N_2 O = -1.55 + 0.54 \log_{10} NO_3^- + \epsilon$$
 (1)

parameter se =
$$(0.19)$$
 (0.12) mse = 0.2

Equation 1 provides a starting point to quantify this relationship, and the inherent uncertainty, for development of emission inventories. This relationship can be easily updated as more data accrue, or modified if accumulating observations suggest significant nonlinearity. TABLE 1. N₂O Emissions Model Summary Statistics

	DF	sum of squares	mean square	F	Pr > <i>F</i>
model error <i>R</i> ² = 0.48	13 95 root N	196059.9 95115.2 VISE = 31.6	15081.5 1001.2	15.06	<0.0001

	DF	sum of squares	mean square	F	Pr > <i>F</i>
site	11	47488.3	4317.1	4.31	< 0.0001
NO_3^-	1	6455.6	6455.6	6.45	0.01
DOC	1	4115.9	4115.9	4.11	0.05

	parameter estimate	standard error	t	Pr > <i>t</i>
1	-250.8	154.2	-1.63	0.11
2	-123.9	297.0	-0.42	0.68
3	-72.7	135.6	-0.54	0.59
4	-181.9	116.0	-1.57	0.12
5	55.9	285.3	0.20	0.85
6	-440.2	245.1	-1.80	0.08
7	470.9	234.9	2.01	0.05
8	73.2	169.0	0.43	0.67
9	-109.6	198.9	-0.55	0.58
10	262.5	197.1	1.33	0.19
11	206.1	172.0	1.20	0.23
NO_3^-	0.76	0.29	2.54	0.01
DOC	31.8	15.7	2.03	0.05



FIGURE 3. CART model results. Mean emission rates for each group are depicted at the terminal nodes of the tree.

Our results also indicate that DOC may influence N₂O emission (Table 1), possibly as an energy source for denitrifying bacteria. The importance of organic carbon in the water may be contingent on the properties of the bottom sediments. Systems with highly organic sediments may be less reliant on the overlying water as a carbon source. CART results (Figure 3) suggest a combination of high DOC, high NO₃⁻, and warm water is associated with the highest emission rates. And even at low DOC levels ($<9 \text{ mg L}^{-1}$), high NO₃⁻ is associated with high emission rates. Though the structure in the CART analysis seems plausible, the interactions revealed can be difficult to detect with the more conventional linear regression and analysis of variance models.

The mean estimated proportional N loss of 0.17 indicates that denitrification is likely an important N sink in the Neuse River (Figure 4). It is important to recognize that this estimate is spatially aggregated, representing an average over the whole river. Thus, it is likely to underestimate N loss from inputs in the upper watershed, which travel the full length of the river, and overestimate the N loss from inputs in the lower watershed, which pass through only a portion of the river.

Estimated Proportional N Loss via Denitrification



FIGURE 4. Histogram from the Monte Carlo uncertainty analysis depicting estimated proportional nitrogen lost via denitrification on the main stem of the Neuse River. The histogram results from 50 000 sets of values drawn from the probability functions for each uncertain input. Approximately 5% of the probability mass is <-0.13 while approximately 5% is >0.57. The interquartile range (middle 50%) is 0.04-0.22.



FIGURE 5. Cross-sectional relationship of N₂O emission rates vs nitrate concentrations based on results reported by Cole and Caraco (7) (blue circle), Harrison and Matson (9) (green square), and this study (red dot). The blue line is the simple linear regression model fit (log metric) to these results.

Additionally, this estimate pertains only to losses directly from the surface of the Neuse River and does not include losses that have been documented in other portions of the drainage basin or upper estuary (22). We have tried to fairly convey the inherent uncertainty in this estimate by expressing the result probabilistically (Figure 4). Uncertainty, though often ignored, is important information for decision-makers who need to hedge decisions to avoid ineffective or disastrous outcomes (23). Additionally, quantifying uncertainty can help identify the decision-sensitive inputs so that resources can be appropriately directed to reducing the overall uncertainty. In this case, a sensitivity analysis indicated that further refinements in N₂O loss estimates and the ratio of N loss via N₂O would have the greatest returns for reducing the uncertainty in this estimate. In particular, the ratio of N loss via N2O in aquatic systems is not well-documented. Our probabilistic representation was based on values reported in Seitzinger (19) and Seitzinger et al. (6) who indicated a ratio generally in the 0.1-0.5% range. More precision in this value would reduce the uncertainty in our N loss estimate. We also emphasize that our measurements excluded the colder months of year, and that the survey was conducted during a relatively dry period, factors that could both influence the estimated losses.

While the relationship between N_2O emission and nitrate concentration is consistent with that found in other studies, data on this relationship are still sparse. Much additional

work is needed to further elucidate the primary factors controlling aquatic N_2O emission and its temporal and spatial variability.

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