Indirect nitrous oxide emissions from streams within the US Corn Belt scale with stream order

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N2O is an important greenhouse gas and the primary stratospheric ozone depleting substance. Its deleterious effects on the environment have prompted appeals to regulate emissions from agriculture, which represents the primary anthropogenic source in the global N2O budget. Successful implementation of mitigation strategies requires robust bottom-up inventories that are based on emission factors (EFs), simulation models, or a combination of the two. Top-down emission estimates, based on tall-tower and aircraft observations, indicate that bottom-up inventories severely underestimate regional and continental scale N2O emissions, implying that EFs may be biased low. Here, we measured N2O emissions from streams within the US Corn Belt using a chamber-based approach and analyzed the data as a function of Strahler stream order (5). N2O fluxes from headwater streams often exceeded 29 nmol N2O-N m⁻² s⁻¹ and decreased exponentially as a function of S. This relation was used to scale up riverine emissions and to assess the differences between bottom-up and top-down emission inventories at the local to regional scale. We found that the Intergovernmental Panel on Climate Change (IPCC) indirect EF for rivers (EF5r) is underestimated up to ninefold in southern Minnesota, which translates to a total tier 1 agricultural underestimation of N2O emissions by 40%. We show that accounting for zero-order streams as potential N2O hotspots can more than double the agricultural budget. Applying the same analysis to the US Corn Belt demonstrates that the IPCC EF5r underestimation explains the large differences observed between top-down and bottom-up emission estimates.

Significance

N2O emissions from riverine systems are poorly constrained, giving rise to highly uncertain indirect emission factors that are used in bottom-up inventories. Using a non-steady-state flow-through chamber system, N2O fluxes were measured across a stream order gradient within the US Corn Belt. The results show that N2O emissions scale with the Strahler stream order. This information was used to estimate riverine emissions at the local and regional scales and demonstrates that previous bottom-up inventories based on the Intergovernmental Panel on Climate Change default values have significantly underestimated these indirect emissions.


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Uncertainty in the EF$_{5r}$ can be attributed to a scarcity of studies (21, 22), poorly constrained water-air gaseous exchange relationships (23, 24), and high variability in river morphology (25, 26). Further, the EF$_{5r}$ assumes a linear relation between nitrate in water and N$_2$O emissions (14), the validity of which is the subject of considerable debate (27–30). Finally, N$_2$O fluxes derived from simple gas exchange models have been shown to underestimate the flux if stream channel hydraulics (i.e., stream flow velocity) are ignored (31), highlighting that stream chemistry alone is not an accurate predictor of N$_2$O fluxes.

We posit that the indirect N$_2$O fluxes in agricultural landscapes are highly dependent on stream hierarchy, which is semiquantitatively represented with the Strahler stream order ($S$), a numerical classification system. Here, we demonstrate that with detailed knowledge of $S$, N$_2$O fluxes can be scaled up to the region and help to resolve the discrepancy between top-down and bottom-up N$_2$O emission estimates in the US Corn Belt.

**Results and Discussion**

N$_2$O fluxes in southeastern Minnesota were measured in streams of varying $S$ over a 2-y period. A total of 19 stream systems, representing nine stream orders, were sampled. An exponential function was used to describe the relationship between observed N$_2$O fluxes ($F$, nmol N$_2$O-N·m$^{-2}$·s$^{-1}$) and $S$

\[ F = b_0 \exp\left(-b_1 S\right) \]

where $b_0 = 34 \pm 10.2$ (95% CI) and $b_1 = 0.73 \pm 0.2$, with $R^2 = 0.95$ and 0.58 for binned ($n = 9$) and raw data ($n = 200$), respectively (Fig. 1). Fluxes ranged from below the chamber system detection limit of 0.018 nmol N$_2$O-N·m$^{-2}$·s$^{-1}$ (i.e., for the Mississippi River; $S = 9$) to a maximum observed flux of 34.5 nmol N$_2$O-N·m$^{-2}$·s$^{-1}$ in a headwater stream ($S = 1$). A Kruskal–Wallis significance test revealed a significant mean rank difference ($P < 0.05$) in fluxes for headwater streams vs. all other stream orders. Further, there was a significant rank difference between fifth- and ninth-order streams, whereas there was no rank difference detected in second- to fifth-order streams. The differences were greatest when testing nonsequential stream orders.

We hypothesize that the exponential decline in N$_2$O flux is the result of both weakened concentration gradient and lower piston velocities ($k$) in higher-order streams. Riverine N$_2$O fluxes are a product of the concentration gradient between the surface water and the overlying atmosphere and a physical gas transfer coefficient (32). We propose two possible mechanisms underlying the emergent pattern shown in Fig. 1 including decreased in situ N$_2$O production and loading and decreased gas exchange rates.

**Mechanism 1.** Headwater streams form from surface and subsurface runoff that, in regions with a high density of row crop agriculture, have high nitrate and ammonium loads, and as a consequence, ~45–50% of a watershed’s inorganic nitrogen transport can occur in these systems (33, 34). Nitrogen is rapidly transformed via nitrification and removed through denitrification (35) in headwater streams (33), and these processes can quickly produce a surplus of N$_2$O in the water column. However, the average first-order rate of nitrogen loss within stream channels declines by as much as 90% down the stream order continuum (36). Therefore, production potential declines as stream order increases. Accordingly, we observed a decline in surface water N$_2$O concentrations from supersaturated (>1,000%) in second-order streams to near equilibrium with atmospheric N$_2$O in fourth-order streams. Groundwater dissolved gas inputs are an additional N$_2$O source and are most impactful in low flow headwater systems (37). However, groundwater loading has less of an effect on stream water chemistry with rising stream order (i.e., due to the water volume dilution effect) (37). Collectively, with increasing stream order, N$_2$O production potential and loading progressively decline, which could account for the pattern shown in Fig. 1.

**Mechanism 2.** Exchange across the water-atmosphere interface of supersaturated gases is governed by $k$, which describes the turbulent nature of the stream. An inverse relationship between $k$CO$_2$ and $S$ has been observed (38–40), and as a consequence, the highest $k$CO$_2$ values are frequently observed in headwater streams (38, 40–42). The same relationship after adjusting for the Schmidt number should be applicable to N$_2$O, implying that $k$N$_2$O increases with declining stream order. Localized areas with high $k$ values (i.e., riffles) have been shown to be strong emission sources (31) if streams are supersaturated (c.g., mechanism 1). However, if the stream is not supersaturated, a high $k$ value alone cannot generate a large flux. Further, a lower $k$ implies a longer total residence time (age) and therefore a greater probability of N$_2$O reacting with nitrous oxide reductase (nosi), the enzyme that catalyzes the final step in the denitrification reaction sequence: the reduction of N$_2$O to N$_2$ (43). Although this has not been documented in river systems, this potential mechanism merits further research to determine its importance and its ability to weaken the water-atmosphere N$_2$O concentration gradient. We posit that these two mechanisms, individually or combined, account for the relationship observed in Fig. 1 and require further study to elucidate their relative importance.

In our study, the variability of N$_2$O flux (i.e., the SD) scaled with stream order, leading to a tightly constrained relation for high order systems (Fig. 1). These observations imply a robust constraint on high-order (fifth-order and higher) emissions and that this pattern could be applied to similar systems (44). Conversely, much larger uncertainty in low-ordered systems (45, 46) exists, indicating that caution must be taken before generalizing our scaling function outside of the US Corn Belt. Headwater streams displayed the greatest uncertainty and their high variability has also been noted in CO$_2$ evasion work (41). Low-order streams receive tile drainage outflow and groundwater from springs giving rise to localized “hotspots” of N$_2$O loss (45), similar to those seen in methane evasion work (41). To test the appropriateness of the default IPCC EF$_{5r}$ value, we used Eq. 1 to up-scale emissions within the observed concentration footprint (50-km radius) of our tall-tower N$_2$O flux station (9). Land use in this study area consists of 70% crops and pasture, 14%
mixed vegetation, 11% forest, 3% developed, and 2% open water and is representative of the US Corn Belt. Streams in the area represent only a small fraction (0.16%) of the total surface area. Using default IPCC EFs for direct and indirect emissions, we provide a conservative estimate of the local agricultural N2O budget in addition to our up-scaled riverine emissions.

Whole-river emissions are the product of our scaling function and river area over a predicted ice-free period. We estimated the annual riverine N2O loss by coupling Eq. 1 with detailed geospatial datasets on stream length and width. Headwater streams (S = 1) were the strongest sources, emitting 60% of the riverine budget. The remaining streams in the study area (S = 2–5) contributed 14%, 8%, 10%, and 8% to the up-scaled riverine emission budget, respectively. This disproportionate flux distribution was a result of a threefold greater mean flux density from headwater streams (17.1 nmol N2O-N · m⁻² · s⁻¹) than second-order streams (5.7 nmol N2O-N · m⁻² · s⁻¹).

Using the IPCC tier 1 methodology (15), the total agricultural (direct + indirect) N2O emissions from the tall-tower footprint were 0.2 Gg N2O-N · y⁻¹, which corresponds to a flux density of 0.25 (0.08–0.6) nmol N2O-N · m⁻² · s⁻¹. Indirect and direct sources contributed 22% and 78%, respectively, to the tier 1 budget. Here, the default EF₅₅ predicts that rivers emitted 0.01 Gg N2O-N · y⁻¹, which represents just over 5% of the total N₂O-N emissions. Our scaling method predicted a riverine source of 0.09 (0.04–0.15) Gg N₂O-N · y⁻¹ (Fig. 2A), an estimate that is nine times greater than the source predicted by the default EF₅₅, signaling a significant bottom-up bias in the EF₅₅. Replacing the EF₅₅ with our scaling function suggests that the total tier 1 bottom-up agricultural emissions have been underestimated by 40%. Accounting for this potential bias increases the predicted bottom-up flux density within the tall-tower source footprint to 0.36 nmol N₂O-N · m⁻² · s⁻¹ (Fig. 2C). This estimate is in excellent agreement with the top-down tall-tower measured ensemble flux of 0.35 (0.3–0.4) nmol N₂O-N · m⁻² · s⁻¹ (9), indicating that top-down and bottom-up budgets can be reconciled by applying our stream order scaling function. Our study suggests that an appropriate EF₅₅ for the tall-tower source footprint should be closer to 2%, assuming the average application rate of nitrogen fertilizer (88.8 kg N · ha⁻¹) (47), which is in agreement with a recent independent investigation (18).

Based on the tier 1 methodology, we estimated the agricultural N₂O budget of the US Corn Belt at 58 (15–256) Gg N₂O-N · y⁻¹, of which 6% or 3.5 Gg N₂O-N · y⁻¹ emanates from rivers (Fig. 2B). In this region, watersheds with high agricultural land use (>40%) occupy 93 million ha (58 million ha under active row-crop cultivation). Applying Eq. 1 to these watersheds and using river area data, we obtained a riverine emission of 19.5 (9.3–41.2) Gg N₂O-N · y⁻¹. Our findings suggest that riverine N₂O emissions are underestimated by at least 16 Gg N₂O-N · y⁻¹ for the Corn Belt and on average by 29 kg N₂O-N · km⁻² · y⁻¹ in watersheds whose cropland fractions are greater than 40% (Fig. 3). Including this source results in a 27% increase in the total tier 1 emission estimate from 58 to 75 Gg N₂O-N · y⁻¹ (Fig. 2B). These findings indicate that a more appropriate regional EF₅₅ is closer to 1.5% (0.7–3%) if the average nitrogen inputs, agricultural coverage (48), and runoff scaling factor (15) are used.

It is important to note that our revised EF₅₅ may not be applicable to areas that are nitrogen limited. Our conservative land use threshold of >40% cropland was chosen because the
cropland systems with nitrogen inputs greater than 48 kg N ha\(^{-1}\) in Fig. 1 is likely applicable to watersheds that are dominated by limited by two main factors. First, the scaling relation described riverine N\(_2\)O budget will originate from those watersheds and served in this study. We believe that the majority of the annual subject to similar indirect emissions and emission factors as ob-

emissions double to 129 Gg N\(_2\)O-N and low spatial coverage, N\(_2\)O flux observations are severely order stream systems form at the intersection of terrestrial and agricultural production including corn (e.g., China, India, Brazil, and others).

The application of our methodology to the global scale is limited by two main factors. First, the scaling relation described in Fig. 1 is likely applicable to watersheds that are dominated by cropland systems with nitrogen inputs greater than 48 kg N ha\(^{-1}\). Second, our stream order width was estimated using methodologies limited to the contiguous United States and Africa (51). At this time, we are unaware of an existing accurate global river width dataset, and this represents an important limitation for application of our method to other regions. We believe this is an important research need, especially in countries with significant agricultural production including corn (e.g., China, India, Brazil, and others).

The above analyses did not consider the role of fine-scale drainage features. Zero-order streams, or microflow stream channels, extend upland of headwater streams, are highly episodic, and are likely hot spots of nitrogen processing (52). Zero-order stream systems form at the intersection of terrestrial and aquatic environments. However, because of their episodic nature and low spatial coverage, N\(_2\)O flux observations are severely lacking. Advancements in Light Detection and Ranging (LiDAR) remote sensing have made it possible to identify episodic microflow paths that may activate following snowmelt and precipitation events. The microflow paths are produced from high resolution (1 m) elevation maps that predict surface water movement. From these data, zero-order streams represent the most common stream order. We estimate that their length is 33 times that of first-order streams and that their total area globally exceeds 235 million ha. Following the United States (93 million ha), the largest regions meeting these criteria are China (69 million ha), Europe (43 million ha), and India (30 million ha). The remaining watersheds are likely to be small N\(_2\)O sources, and the default 2006 IPCC EF\(_\text{5r}\) value should be appropriate for these cases (50).

Upscaling. Nonlinear regression analysis was performed using the “fitnlm” function in Matlab. Local stream order data were downloaded from the Minnesota Department of Natural Resources. Mean North American stream order width (51) was used to generate stream area. Stream order area es-

imates were applied to our nonlinear function to predict river emissions over a 214-d period (Day of Year 91–305).

The extent of the Corn Belt is subjective and lacks boundaries. Our de-
nition was determined by selecting HUC12 subwatersheds with greater than 40% agriculture from 13 states in the Midwest (North Dakota, South Dakota, Nebraska, Kansas, Minnesota, Iowa, Missouri, Arkansas, Wisconsin, Illinois, Ohio, Indiana, and Michigan). Regional stream order data (NHDPPlus, V.2; Horizon Systems Corp.) were used in our nonlinear model. The regional dataset is at a lower resolution than the local stream order and as a con-
sequence underestimated stream length. A comparison of Minnesota streams determined a scaling factor (1.4) was appropriate to apply to the regional data to correct for this underestimation.

Default tier 1 IPCC methodologies were used to estimate N\(_2\)O emissions (15). This budget included direct emissions from soils from synthetic and organic nitrogen application, indirect emissions from the volatilization of synthetic and organic fertilizer, rivers, and groundwater. We did not account for emissions from natural systems, industry, grazing livestock, organic soils, crop residues, and legumes. Annual rates of synthetic and organic fertilizer application were used.

Zero-order streams were estimated from LiDAR data provided by the Minnesota Geospatial Information Office that was processed using ArcMap. A threshold of 1,500 m\(^2\) was before a stream would be “activated.” We assumed a period of 2 mo of active emissions that would include spring thaw and pe-
griod precipitation events. Zero-order width was estimated using a re-
gression equation from North American stream width data (51).

Materials and Methods

N\(_2\)O Flux Sampling. N\(_2\)O fluxes were measured in the field using a flow-through non–steady-state chamber system adapted for deployment in rivers. The floating chamber consisted of an aluminum lid with a pressure equili-

bration vent buoyed by foam insulation and covered with reflective mate-

rial. The chamber enclosed a surface area of 0.145 m\(^2\) with a headspace volume of -0.0147 m\(^3\).

Harvest gas was pulled through a Teledyne gas filter correlation N\(_2\)O analyzer (Model M320EU2; Teledyne Instruments), and the dry mole fraction was recorded at a sampling frequency of 1 Hz using a data-logger (model 23X; Campbell Scientific). The analyzer was powered in the field by deep cycle 12 V batteries wired in parallel to a DC-to-AC inverter. The chamber system has a minimum detectable flux of 0.028 nmol N\(_2\)O-m\(^{-1}\)-s\(^{-1}\) (53). The analyzer was calibrated at the beginning of the season using an analytical grade standard and zeroed two times per month using N\(_2\) gas. The concentration precision of the analyzer was 1.5 nmol-m\(^{-1}\), and the flux mea-

urement precision was 0.003 nmol-m\(^{-2}\)-s\(^{-1}\) (53).

The raw data were processed in Matlab (Matlab, Version R2012a; Math-

works). Fluxes were calculated according to

\[ F = \frac{\nu A}{A} \]

where \(\nu\) (mol m\(^{-1}\)) is the molar density of dry air, \(A\) (m\(^2\)) is the surface area enclosed by the chamber, \(V\) (m\(^3\)) is the chamber volume, and \(\Delta\) (nmol N\(_2\)O-m\(^{-1}\)-s\(^{-1}\)) is the rate of change of N\(_2\)O concentration in the chamber headspace determined from linear regression (53). Before calculating the chamber N\(_2\)O fluxes, a wavelet denoising technique was applied to the raw concentration data. This technique reduced the effect of instrument noise and improved the signal to noise ratio (53). We eliminated all chamber flux data when the linear regression \(R^2\) value was less than 0.9.

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Fig. S1. Photograph and diagram of the system used in this study to sample N$_2$O flux.