



## RESEARCH LETTER

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## Nitrous Oxide Emissions From Drying Streams and Rivers

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## Key Points:

- Low flows lead to higher N<sub>2</sub>O emission per unit stream area in agricultural but not in forested reaches
- Total riverine N<sub>2</sub>O emissions decrease with low flow severity regardless of land use
- Increasing low flow severity does not induce positive feedback to climate change due to N<sub>2</sub>O emissions

## Supporting Information:

Supporting Information may be found in the online version of this article.

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**Abstract** Streams and rivers are suffering more extreme and prolonged low flows than those naturally occurring without human intervention with potential relevant worldwide effects on the production of nitrous oxide (N<sub>2</sub>O), a greenhouse gas 300 times more potent than carbon dioxide. Here, we address the question of whether droughts and management-induced low flows increase riverine N<sub>2</sub>O emissions causing positive feedback in response to climate change. Supported by field data, we model riverine N<sub>2</sub>O emissions for decreasing mean summer flows in a forested and agricultural watershed under chemostatic and chemodynamic dissolved inorganic reactive nitrogen (DIN) concentrations. Our results demonstrate that total N<sub>2</sub>O emissions decrease with increasing low flow severity in both watersheds regardless of DIN scenario; which imparts a form of climate resilience.

**Plain Language Summary** Emissions of the ozone-layer destructor and potent greenhouse gas nitrous oxide, N<sub>2</sub>O, from rivers are a function of both nitrate loads and stream flows. Here we answer the question of whether droughts and subsequent low flows may exacerbate climate change by increasing N<sub>2</sub>O emissions, thus forming positive feedback, which may self-reinforce the adverse effects of climate change. We demonstrate that total N<sub>2</sub>O emissions may remain similar or decrease with decreasing flows in both agricultural and forested watersheds. The reduction is mainly due to reduced water surface areas. However, N<sub>2</sub>O emissions per stream water surface unit area significantly increase in agricultural reaches due to both high nitrate concentrations and their morphological characteristics but remain constant or decrease in reaches flowing in forested watersheds.

## 1. Introduction

Streamflow, along with land use practices (e.g., agriculture), are important determinants of the export of carbon (Hotchkiss et al., 2015), nutrients (Rinaldo et al., 2006) and contaminants (Kaushal et al., 2014; Vidon & Cuadra, 2010) along riverine networks. In addition, low flows (i.e., discharges below the base flow, which is the flow other than runoff sustained primarily by springs and groundwater seepage, Smakhtin, 2001 and Supporting Information S1), caused by droughts or water uses (Miller et al., 2021), may influence stream biogeochemical processes, as well as the transformation and uptake of dissolved solutes. Drought is a significant stressor in agricultural lands, with significant socioeconomic implications (Overpeck, 2013; Sheffield et al., 2014), as well as direct impacts on the amount and timing of solutes and particles lost from landscapes to waterways. Among the dissolved constituents, dissolved reactive inorganic nitrogen (DIN), especially nitrate (NO<sub>3</sub><sup>-</sup>), plays an important role at the global scale. Because it fuels the emission of nitrous oxide N<sub>2</sub>O (Seitzinger et al., 2000) from riverine systems via the process of microbially-mediated denitrification (Beaulieu et al., 2011; Seitzinger, 1988). Moreover, N<sub>2</sub>O is a potent greenhouse gas that is also responsible for stratospheric ozone destruction (Ravishankara et al., 2009). However, limited research has examined N<sub>2</sub>O emissions from streams and rivers during low flow conditions (Audet et al., 2017). Even fewer studies have provided emission predictors at ecologically relevant scales (Baulch et al., 2011; Marzadri et al., 2017; Turner et al., 2015), due to the difficulties in upscaling local processes occurring in the hyporheic zone (subsurface streambed sediment), benthic zone (sediment-water surface), and water column, to the scale of river networks. We do not know whether N<sub>2</sub>O emissions will increase or decrease as river and stream flows (i.e., discharge) decrease below normal base flows, which will be critical in assessing the feedback between predicted impacts of climate change and N<sub>2</sub>O emissions from riverine systems. Low flows may exacerbate the effects of climate change, via a positive feedback in which extended low flow conditions increases N<sub>2</sub>O emissions, or attenuate drought effects due to reduction in N<sub>2</sub>O emissions, depending

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on local land cover, water use, and changes in surface hydraulics (Marzadri et al., 2017). River morphology may change with discharge, for instance, dune size adjusts to local discharge because fine sediments are typically mobile even at low flows (Yalin, 1964). These morphological changes, in turn, impact hyporheic hydraulics and thus the time for biogeochemical transformation within streambeds. Moreover, nutrient concentrations may be discharge-dependent or behave as chemostatic (similar concentration regardless of discharge) depending on land uses (Basu et al., 2010; Levi et al., 2018). Denitrification reaction rate constant also changes depending on both solute concentration and surface hydraulics (see, Supporting Information S1 and Beaulieu et al., 2011; Davis & Minshall, 1999; Mulholland et al., 2008). These complex dependence of N<sub>2</sub>O emissions on local processes, from river morphology to biological reactivity, hinder predicting N<sub>2</sub>O emissions with decreasing discharge and prevent simple extrapolation of N<sub>2</sub>O trends observed under natural base flows to more extreme low flows conditions.

Here, we used the N<sub>2</sub>O emission model developed by Marzadri et al. (2017) and successively modified by Marzadri et al. (2021), which accounts for biological processing within the riverine hyporheic benthic and water column environments, to identify the hydrological and environmental conditions that cause riverine systems to increase or decrease total N<sub>2</sub>O emissions during low flows, at areal and whole-river network scales. We applied the model to two low-gradient watersheds with contrasting land-use land-cover: the Manistee River (Michigan, USA; ~83% forested) and the Tippecanoe River (Indiana, USA; ~82% agricultural). We collected two sets of 80 synoptic samples, providing water temperature and concentrations of NO<sub>3</sub><sup>-</sup>, N<sub>2</sub>O, and ammonium (NH<sub>4</sub><sup>+</sup>), across both watersheds during a typical base flow condition during summer 2015. These model input data were supplemented by hydro-morphological measurements, including mean flow depth, velocity, width, substrate size, and bedform type at the same synoptic sites, thereby allowing the model to account for changes in stream hydraulics and morphology as discharge changes (Stewart et al., 2011) (see Supporting Information S1).

## 2. Methods

The Marzadri et al. (2021) model does not require calibration to predict the dimensionless N<sub>2</sub>O flux (F\*N<sub>2</sub>O) and it is fully characterized by reach-scale, hydro-morphological characteristics, such as roughness, streambed morphology and discharge, and how these metrics change as a function of flow regime, combined with stream water temperature, and stream dissolved inorganic nitrogen (DIN) concentrations (see Supporting Information S1). F\*N<sub>2</sub>O represents a type of N<sub>2</sub>O emission factor, at the reach scale resolution (Marzadri et al., 2021), and is defined as the ratio between the flux of N<sub>2</sub>O (FN<sub>2</sub>O) per unit stream area and the in-stream flux of DIN species per unit stream cross-section area (NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup>; FDIN = V·([NO<sub>3</sub><sup>-</sup>] + [NH<sub>4</sub><sup>+</sup>]), with V as the mean reach flow velocity. F\*N<sub>2</sub>O value depends on the dimensionless Damköhler number, Da<sub>D</sub>, which accounts for reach-scale hydro-morphological and biochemical characteristics. The Da<sub>D</sub> is defined as the ratio between the residence time  $\tau$  in the compartment where denitrification chiefly occurs and the characteristic time of denitrification  $\tau_D$ : Da<sub>D</sub> =  $\tau/\tau_D$ . Two relevant stream compartments are considered: (a) the hyporheic zone, including the overlying benthic zone, with a characteristic residence time defined as the median of the travel time within the hyporheic zone  $\tau_{50}$ , and (b) the water column, with a characteristic time identifiable as the turbulent vertical mixing time scale  $t_m = D/(0.067[g \cdot D \cdot s_0]^{0.5})$ , where g is the gravitational acceleration, D is the mean flow depth and s<sub>0</sub> is the friction slope (Rutherford, 1994). In small systems (i.e., streams), denitrification occurs chiefly in the benthic-hyporheic zone, but as systems widen (i.e., in rivers) and their slope declines, water depth increases and denitrification occurs mostly in the water column. These two situations are represented by using two different Da<sub>D</sub> numbers: Da<sub>DHZ</sub> =  $\tau_{50}/\tau_D$  for headwater streams, and Da<sub>DWS</sub> =  $t_m/\tau_D$  for rivers. River morphology (dunes but not pool-riffle, whose size depends on effective discharge [e.g., Tubino, 1991]) and local hydraulics are dynamically linked to discharge such that the model can account for direct impact of discharge to flow regime, and indirectly on stream bedform size (see Supporting Information S1). For both Da<sub>D</sub> numbers, the biological processes are represented via the denitrification time scale,  $\tau_D$ , which is the inverse of the denitrification reaction rate and is quantified as a function of the stream denitrification uptake rate,  $v_{\text{den}}$  (see Supporting Information S1). The  $v_{\text{den}}$  is a mass transfer coefficient, which is operationally defined as “demand relative to concentration” and its value decreases as NO<sub>3</sub><sup>-</sup> concentrations increase (Davis & Minshall, 1999) typically in the form of  $v_{\text{den}} = a \cdot [\text{NO}_3^-]^b$  with a and b being regression coefficients (Beaulieu et al., 2011; Mulholland et al., 2008).

The model consists of three equations, whose application depends on stream size, expressed as channel width, W, because the main source of N<sub>2</sub>O emissions shifts from the hyporheic zone in small streams (HZ Model), chiefly benthic zone for intermediate streams (BZ Model) and then to the water column for rivers (WC Model):

$$\begin{cases} \text{HZ : } F^*N_2O_{\text{HZ}} = 1.55 \cdot 10^{-7} (Da_{\text{DHz}})^{0.43}, & (r^2 = 0.48), & W \leq 10 \text{ m} \\ \text{BZ: } F^*N_2O_{\text{BZ}} = 1.91 \cdot 10^{-8} (Da_{\text{DHz}})^{0.57}, & (r^2 = 0.40), & 10 \text{ m} < W \leq 175 \text{ m} \\ \text{WC: } F^*N_2O_{\text{WC}} = 4.56 \cdot 10^{-6} (Da_{\text{DS}})^{0.72}, & (r^2 = 0.54), & W > 175 \text{ m} \end{cases} \quad (1)$$

Marzadri et al. (2017) derived the first two equations (Equation 1  $F^*N_2O_{\text{HZ}}$  and  $F^*N_2O_{\text{BZ}}$ ) by using a mechanistic model of emissions applied to the data collected in 12 stream reaches of the Kalamazoo (MI, USA) (Beaulieu et al., 2008, 2009) and 16 reaches from the second iteration of the Lotic Intersite Nitrogen eXperiment (LINXII) (Beaulieu et al., 2011; Hall et al., 2009; Mulholland et al., 2008). The obtained equations were validated against measured emissions from 400 reaches of streams and rivers worldwide during summer base flows with riverine water temperatures ranging between 11 and 36°C. The third equation of the model ( $F^*N_2O_{\text{WC}}$ ) was obtained analyzing measured emissions from streams and rivers with width larger than 30 m in terms of the Damköhler number that considers the major role played by the water column in controlling emissions ( $Da_{\text{DS}}$ ); this is expressed differently from the first two equations and is a regression-based model that we validated with independent data (Figure S1 in Supporting Information S1).

Stream  $N_2O$  measurements along with hydro-morphological data collected during drought conditions are scarce. To our knowledge, we collected and used all those measurements available in the literature: nine headwater streams from a small Swedish agricultural catchment (C6, Kyllmar et al., 2006; Figure S2 in Supporting Information S1) and eight reaches of the San Joaquin River (Hinshaw & Dahlgren, 2012). The performance of HZ model in predicting  $N_2O$  emissions during low flow conditions was tested with the data from the Swedish streams ( $r^2 = 0.53$ , Figure S3 in Supporting Information S1), and that of the BZ model with the data from San Joaquin River ( $r^2 = 0.43$ , Figure S3 in Supporting Information S1). In the two cases, only reaches within the HZ ( $W \leq 10$  m) and BZ bounds ( $W > 30$  m) were included in the analysis.

We quantified the role of low flows in  $N_2O$  emissions by applying the above framework to the Manistee River (MI, USA, forested) and the Tippecanoe River (IN, USA, agricultural). The Manistee River is forested over 83% of its 3,616 km<sup>2</sup> watershed, stream flow discharges range between 22 and 14,000 L/s and summer low-flow  $NO_3^-$  concentrations average 120 µg N/L. The Tippecanoe River has 82% of its 4,496 km<sup>2</sup> basin in row-crop agriculture, discharges range between 0.9 L/s and 22,500 L/s and summer low-flow  $NO_3^-$  concentrations average 1,860 µg N/L. Both watersheds have reaches with dune-like or pool-riffles morphologies with sediments composed by gravel and sand. Information from the grain size distribution allowed estimation of the hydraulic conductivity of the streambed sediment (Salarashayeri & Siosemarde, 2012).

We collected all the required hydro-morphological and water quality information during a synoptic sampling effort in summer 2015, at 80 locations in each watershed, collected within a 24-hr period, at baseflow conditions. To apply the model to each reach of the riverine network, we spatially distributed these original measurements of temperature,  $NH_4^+$  and  $NO_3^-$  concentrations along the two riverine networks using the Spatial Stream Network (SSN; R) (Ver Hoef et al., 2014) model and Spatial Tools for the Analysis of River Systems (STARS; ArcGIS) (Peterson & Ver Hoef, 2014), which uses a one-dimensional geostatistical interpolation along the streams. Mean flow velocity, depth and width were spatially distributed with a set of regime equations developed from the 80 locations at each watershed (Equations S9 and S10 in Supporting Information S1). Bedform type and size were derived by combining Montgomery and Buffington stream classification (Montgomery & Buffington, 1998) with hydro-morphological relationships for dune and pool-riffle. Bedform prediction was verified with visual inspection at the sites. Stream discharge was predicted at each reach of the river networks with the GIS tools ArcHydro and Hec-GeoHMS, which provided the input conditions for the Land Surface Model (Piccolroaz et al., 2016) that predicted the lateral inflows to the river network. Flow generation was accomplished with a continuous soil-moisture accounting model based on the SCS-CN methodology (Avesani et al., 2021). Stream flows were then routed with a validated (averaged Nash-Sutcliffe index larger than 0.7) Muskingum flow routing scheme (Cunge, 1969) at the reach scale.

The resolution of the model and input data allows us to explore the response of  $N_2O$  emissions longitudinally, from headwaters to mainstem reaches, along the forested and agriculture watershed, and at the watershed scale under different scenarios of decreasing low flows (i.e., increasing drought severity). The mean daily discharge ( $Q_{\text{sum}}$ ) in summer is a common statistic used for water resource planning with important ecological and water use implications (WMO, 2008). Thus, we used  $Q_{\text{sum}}$  as our reference discharge for current flows and selected three

alternative mean summer flows, which may replace the current  $Q_{\text{sum}}$  in future scenarios resulting from climate-induced increase in drought severity or low flows induced by water uses. These data represent current daily base flow conditions, and their 25th and 5th percentiles, which we quantify from daily discharges monitored at six US Geological Survey (USGS) gauging stations located within the two watersheds with the R package *lfstat* (Koffler & Laaha, 2012). We define these three alternative summer mean flows as moderate low  $Q_{\text{sum}}$ , very low  $Q_{\text{sum}}$ , and extremely low  $Q_{\text{sum}}$ . Current information on DIN concentration and temperature distributions were then used as reference values for simulating  $\text{N}_2\text{O}$  fluxes. We considered the two most likely end member scenarios for FDIN: constant DIN concentrations (i.e., chemostatic scenario) and constant FDIN (i.e., conservation of mass flux, chemodynamic scenario) (Basu et al., 2010; Levi et al., 2018). In chemostatic scenario, a flow reduction gives rise to a contemporaneous reduction in catchment inputs (Mosley, 2015) and thereby a reduction of FDIN (see example, Figure S4a in Supporting Information S1). However, in chemodynamic scenario, an increase in DIN concentrations may offset the lower flows resulting in a constant FDIN, rather than constant DIN concentrations, with decreasing discharge (Hinshaw & Dahlgren, 2012) (see example, Figure S4b in Supporting Information S1).

Total  $\text{N}_2\text{O}$  emissions (TE) at the watershed scale were quantified at daily time steps with:

$$\text{TE} = \sum_{r=1}^{N_r} \text{F}^*\text{N}_2\text{O}_r \cdot \text{FDIN}_r \cdot W_r \cdot L_r \quad (2)$$

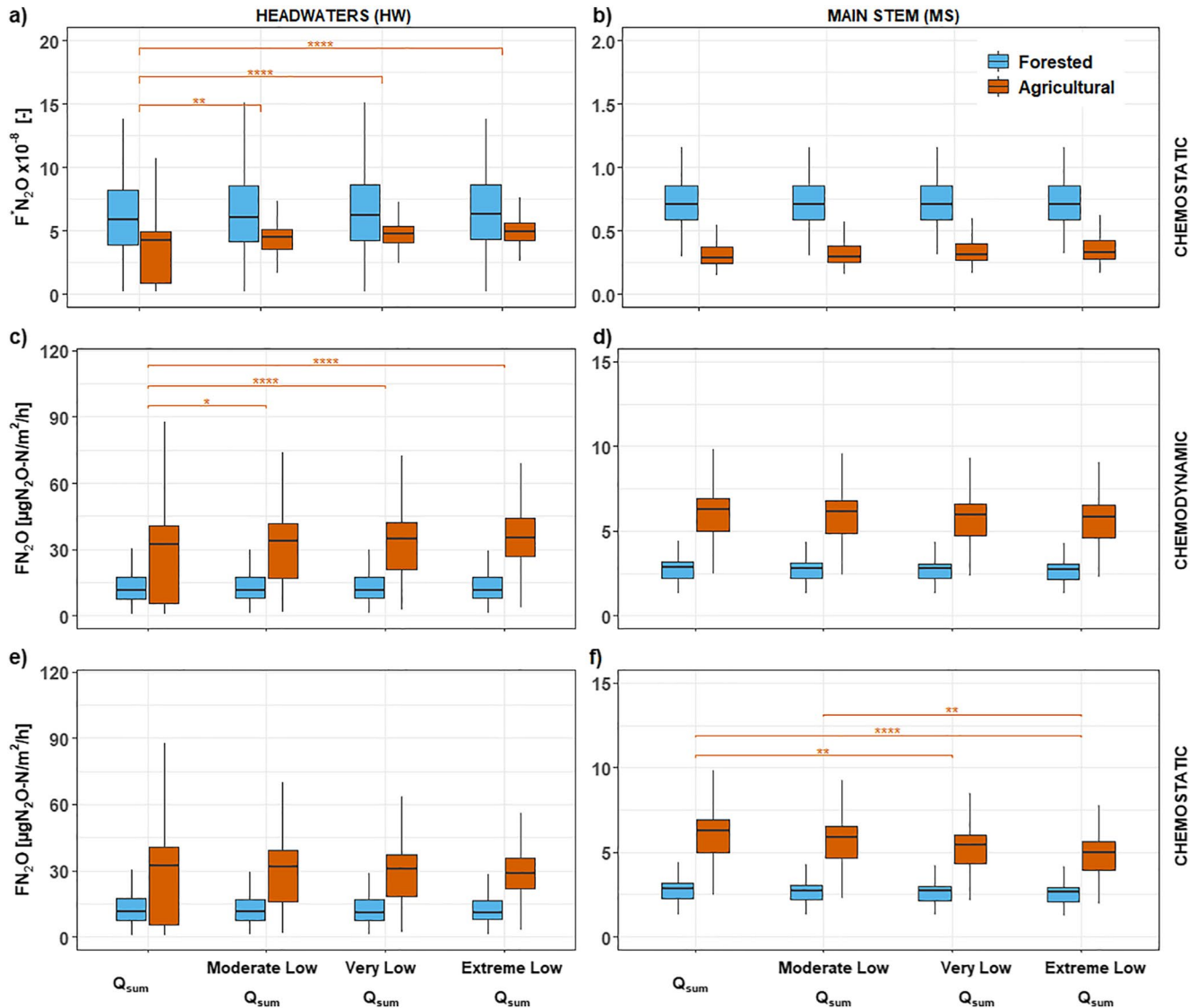
where  $N_r$  is the number of the reaches that compose the stream network,  $W_r$  is the width of the  $r$ -th reach,  $L_r$  is its length,  $\text{F}^*\text{N}_2\text{O}_r$  is its dimensionless  $\text{N}_2\text{O}$  emission estimated with the power law scaling model (Equation 1), and  $\text{FDIN}_r$  is its flux of DIN.

### 3. Results and Discussion

The effect of the DIN scenario considered on  $\text{F}^*\text{N}_2\text{O}$  was large because DIN concentration influenced the calculation of  $\text{Da}_D$  via  $v_{\text{fden}}$ . For the chemodynamic scenario,  $\text{F}^*\text{N}_2\text{O}$  values remained almost constant (Figure S5 in Supporting Information S1), while values increased for the chemostatic scenario. In the latter case, the model predicted a statistically significant increase in  $\text{F}^*\text{N}_2\text{O}$  with lower flows in the agricultural headwater (HW, stream orders 1 to 3) and main stem (MS, stream order >3) reaches, but not for the forested headwater and mainstem reaches (Figure 1; Kruskal-Wallis non-parametric test results in Table S4 in Supporting Information S1). The impact of low flows on  $\text{F}^*\text{N}_2\text{O}$  in agricultural reaches reflects its land use footprint characterized by narrower streams (including ditches) compared to the forested watershed (Figure S5 in Supporting Information S1). As such, the hydro-morphological characteristics especially in HW are more sensitive to changes in discharge in the agricultural than in the forested watershed, as indicated by the 30% decline in mean  $W$  simulated for extreme low  $Q_{\text{sum}}$  (Figures S6 in Supporting Information S1). In contrast, forested HW streams have a less pronounced reduction in width (half of the agricultural, 15%) and smaller changes in Damkhöler numbers (1.4% increase) with low-flow severity than the agricultural HW, which shows a 26% increase in Damkhöler numbers (Figures S6 and S7 in Supporting Information S1). In contrast to HW, simulated low flow conditions have subtler impacts on main stem hydromorphology (e.g., mean  $W$  reductions of 7% and 13% from  $Q_{\text{sum}}$  to extreme low  $Q_{\text{sum}}$  for the forested and agricultural MS, respectively), which drives the non-significant changes in  $\text{F}^*\text{N}_2\text{O}$  in river forested MS, but still significant in the agricultural.

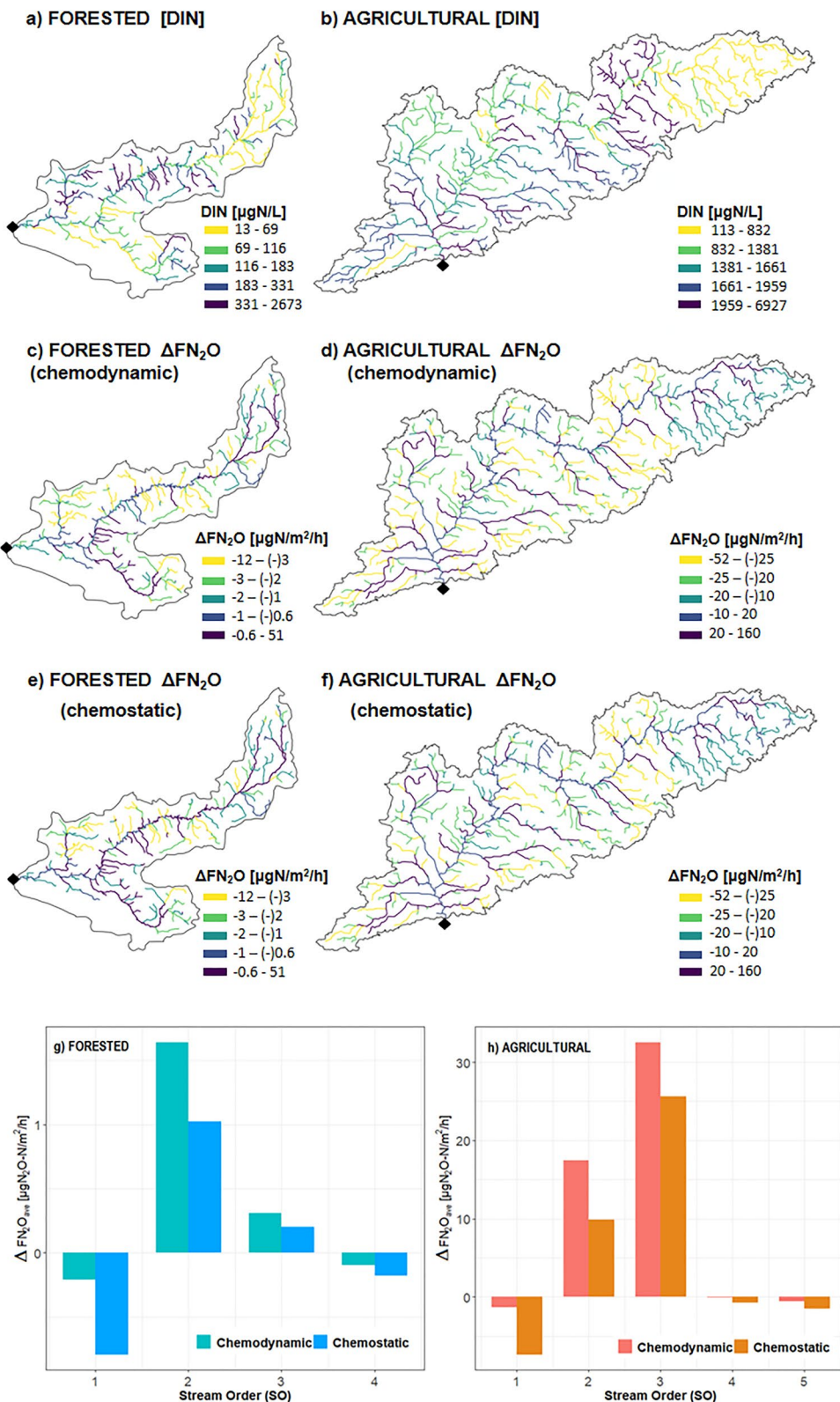
However, an increase in  $\text{F}^*\text{N}_2\text{O}$  does not necessarily lead to an increase of  $\text{FN}_2\text{O}$  from riverine systems, because changes in  $\text{FN}_2\text{O}$  depend also on DIN availability (FDIN), which is influenced by land use, land cover, and discharge (Basu et al., 2010; Marinos et al., 2020; Mosley, 2015). Both FDIN scenarios did not significantly change  $\text{FN}_2\text{O}$  in either HW or MS reaches in the forested watershed. Conversely, the chemodynamic scenario caused significant increase of  $\text{FN}_2\text{O}$  with decreasing low flows in the agricultural HW reaches, whereas the chemostatic scenario caused a significant reduction in  $\text{FN}_2\text{O}$  with low flow severity in the agricultural MS reaches (Figure 1 and Kruskal-Wallis test results in Table S4 in Supporting Information S1).

We found that the distribution of DIN concentrations measured during the summer synoptic sampling showed a clustering of high and low concentrations within sub-basins, rather than a longitudinal pattern from headwater to mainstem reaches (Figures 2a and 2b). As such, the change in  $\text{N}_2\text{O}$  emissions per unit streambed area ( $\Delta\text{FN}_2\text{O}$ ) induced by the extreme low flow scenario showed a systematic decrease from HW to MS reaches (except for order 1), suggesting that low flows accentuate increases in  $\text{FN}_2\text{O}$  from headwater reaches, especially from stream

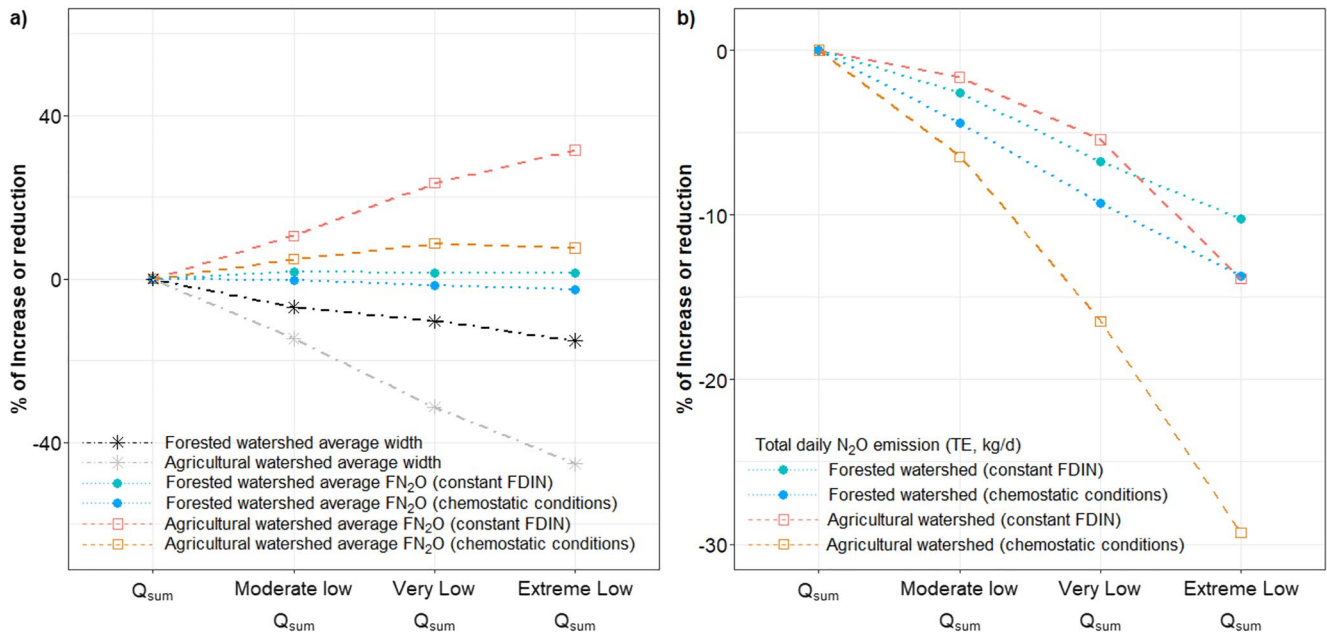


**Figure 1.** Box plot (15th, 50th and 75th quartiles with the 10% and 90% within the whiskers) of  $N_2O$  emissions from forested (light blue fill) and agricultural (red fill) reaches. The scale of the Y-axis changes among panels to better present the data. The top panels (a) and (b) show the dimensionless areal emission  $F*N_2O$  for the chemostatic case, whereas the middle and bottom panels show the actual areal emission  $FN_2O$  for constant FDIN (conservation of mass flux, i.e., chemodynamic scenario) (c) and (d), and constant DIN concentrations (chemostatic FDIN scenario) (e) and (f) from headwaters (HW, left panels) and the mainstem (MS, right panels). Brackets report the  $p$  value significance ( $*p < 0.05$ ,  $**p < 0.01$ ,  $***p < 0.001$  and  $****p < 0.0001$ ) of the statistically significant changes in  $F*N_2O$  and  $FN_2O$  with low flow severity with the non-parametric Wilcoxon test. If not reported the trend is not statistically significant. Only the agricultural watershed has some scenarios with statistically significant changes:  $F*N_2O$  from headwaters and main stems for the chemostatic scenario and  $FN_2O$  from headwaters for the chemodynamic scenario significantly increase with increasing low flow severity, but  $FN_2O$  values decrease for the main stems with the chemostatic scenario (also see Kruskal-Wallis test in Table S4 in Supporting Information S1).

orders 2 and 3 (Figures 2g and 2h). The same results were found for total emissions quantified from headwater or mainstream reaches, which further underscores the importance of headwater streams in controlling  $N_2O$  emissions at the watershed scale (Table S5 in Supporting Information S1). We found that this pattern was accentuated in agricultural reaches compared to forested ones (Figures 2c, 2h and Figure S8 in Supporting Information S1), likely because the former had a stronger reduction in width, which contributed to decrease  $FN_2O$  (Figure S6 in Supporting Information S1). This size change is critical because the hyporheic zone is the dominant source of  $N_2O$  yield in HW streams, but its role decreases rapidly as size increases, from HW to MS.



**Figure 2.** In-stream dissolved inorganic nitrogen concentration (DIN) distributions derived from the 2015 summer synoptic measurements along the forested (a) and the agricultural (b) watersheds, and distribution of differences,  $\Delta\text{FN}_2\text{O}$ , between  $\text{FN}_2\text{O}$  for extreme low and current  $Q_{\text{sum}}$  for constant FDIN (conservation of mass flux, i.e., chemodynamic scenario) (c) and (d), and constant DIN concentrations (chemostatic scenario) (e) and (f), along the forested (right panels) and the agricultural (left panels) watersheds. Histograms of  $\Delta\text{FN}_2\text{O}$  as a function of stream order for the forested (g) and agricultural (h) watersheds.



**Figure 3.** Relative changes in (a) average  $N_2O$  flux (FN<sub>2</sub>O open squares and solid circles) and average channel width ( $W$ , star symbols) and (b) total daily emission (TE) of  $N_2O$ , for the current, moderate low, very low and extreme low  $Q_{sum}$  scenarios for the forested (solid circles) and agricultural (open squares) watersheds for constant FDIN (conservation of mass flux, i.e., chemodynamic scenario) and constant DIN concentrations (chemostatic scenario).

Mean FN<sub>2</sub>O increased for the chemodynamic scenario (i.e., constant DIN flux) regardless of watershed type, but FN<sub>2</sub>O decreased for the chemostatic case for the forested watershed (Figure 3a). Overall, the FN<sub>2</sub>O patterns for the forested watershed showed less dependence on the DIN scenario considered compared to the agricultural watershed, suggesting that forested watersheds are more resilient to increasing the occurrence of low flows.

The spatial distribution of changes in FN<sub>2</sub>O demonstrates how biogeochemistry, hydrology, and land use practices interact to influence  $N_2O$  emissions from different reaches within a stream network (Figures 2c–2h). However, it is essential to understand the response of entire watersheds to increasing low flow conditions by transitioning  $N_2O$  emissions from a reach-to-a whole fluvial network-scale perspective. We calculated the total  $N_2O$  emissions (TE) over the entire watershed at daily time scale by accounting for each reach surface area (See Equation 2 in Section 2). Whereas average FN<sub>2</sub>O may slightly decrease or increase up to 38% depending on the DIN concentration scenario and watershed considered (Figure 3a), channel width, which controls the riverine surface areas (reach length is fixed), is expected to decrease or at the most remain constant with increasing low flow severity (Figure 3a, star symbols). For the three low flow scenarios, the model predicts a decrease in total daily  $N_2O$  emissions for both watersheds regardless of the DIN scenario considered (i.e., chemodynamic or chemostatic), primarily driven by the reduction in channel width (Figure 3b).

All scenarios result in a decrease of TE emission between 10% and 20%. The reduction in stream width (grey star symbol Figure 3a) compensate the almost 40% increase in FN<sub>2</sub>O (Figure 3a pink square open symbols). This effect is stronger in headwater than main stem reaches (Table S5 in Supporting Information S1). Our analysis indicates that the compensatory role of changes in channel morphology is critical if we are to understand the feedback between climate change and its effect on the biogeochemistry of streams and rivers. Whereas the results obtained at the reach scale may suggest that lower flows, and eventually higher DIN concentrations in headwater reaches, could lead to overall higher  $N_2O$  emissions (Figures 2g and 2h and Figure 3a), our watershed-scale analysis points toward the opposite direction: total emissions of  $N_2O$  at the watershed scale would likely decrease with increasing drought conditions in the future because reduction in flow and stream width will hold down  $N_2O$  emissions even in agricultural watersheds where increases in DIN concentration are expected (Figure 3b).

#### 4. Conclusions

Our results highlight that the impact of drought on  $N_2O$  emission factor expressed as  $F \cdot N_2O$  and emissions per unit area of stream ( $FN_2O$ ) was maximized in headwater reaches but decreased with increasing stream size in the river mainstems. This finding underscores the importance of managing (e.g., DIN runoff and channelization) small headwater streams, especially in agricultural lands. Drought conditions significantly decrease  $FN_2O$  in those reaches where no changes in DIN concentration are expected (i.e., chemostatic scenario). Yet, in most stream reaches, the increase in low flow condition (i.e., drought severity) lead to increases in  $FN_2O$  for the scenario of future increases in DIN concentrations and constant DIN fluxes, which is the most critical situation in streams draining agricultural lands with long-lasting legacy effects. Conversely, changes in  $FN_2O$  are subtle, and not statistically significant for stream reaches at the forested watershed. However, our conclusions on the implications of increasing drought conditions for  $N_2O$  emissions drastically change when results are integrated at the whole fluvial network scale because of the interplay between changes in  $FN_2O$  and channel width. While  $FN_2O$  at the reach scale may increase or decrease with drought conditions, channel width will mostly decrease. The combined effect of these two variables results in an amplified reduction of  $N_2O$  emissions from forested and agricultural networks regardless of the DIN scenario. These results stress the intertwined link between in-stream biological processing and hydrological conditions; hydrology does not only control the mean residence time of water, and with that, the Damköhler number and the characteristic time of denitrification, but also drives the expansion and contraction of the fluvial network, which is a fundamental feature for understanding how changes in biogeochemical fluxes per unit stream area resonate at the whole fluvial network scale. Overall, our results show no evidence that climate change-induced drought would cause positive feedback on  $N_2O$  emissions, but rather suggests that low flow conditions would contribute to a decrease watershed-scale  $N_2O$  emissions in both agricultural and forested landscapes.

#### Conflict of Interest

The authors declare no conflict of interest relevant to this study.

#### Data Availability Statement

Data are available at Tonina et al. (2021), <http://www.hydroshare.org/resource/70a1078d0ca14839aeca8e0f-4082cb81>.

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#### References

- Audet, J., Wallin, M. B., Kyllmar, K., Andersson, S., & Bishop, K. (2017). Nitrous oxide emissions from streams in a Swedish agricultural catchment. *Agriculture, Ecosystems & Environment*, 236, 295–303. <https://doi.org/10.1016/j.agee.2016.12.012>
- Avesani, D., Galletti, A., Piccolroaz, S., Bellin, A., & Majone, B. (2021). A dual-layer MPI continuous large-scale hydrological model including Human Systems. *Environmental Modelling & Software*, 139, 105003. <https://doi.org/10.1016/j.envsoft.2021.105003>
- Basu, N. B., Destouni, G., Jawitz, J. W., Thompson, S. E., Loukinova, N. V., Darracq, A., et al. (2010). Nutrient loads exported from managed catchments reveal emergent biogeochemical stationarity. *Geophysical Research Letters*, 37, 1–5. <https://doi.org/10.1029/2010GL045168>
- Baulch, H. M., Schiff, S. L., Maranger, R., & Dillon, P. J. (2011). Nitrogen enrichment and the emission of nitrous oxide from streams. *Global Biogeochemistry*, 25. <https://doi.org/10.1029/2011GB004047>
- Beaulieu, J. J., Arango, C. P., Hamilton, S. K., & Tank, J. L. (2008). The production and emission of nitrous oxide from headwater streams in the midwestern USA. *Global Change Biology*, 14, 878–894. <https://doi.org/10.1111/j.1365-2486.2007.01485.x>
- Beaulieu, J. J., Arango, C. P., & Tank, J. L. (2009). The effects of season and agriculture on nitrous oxide production in headwater streams. *Journal of Environmental Quality*, 38, 637–46. <https://doi.org/10.2134/jeq2008.0003>
- Beaulieu, J. J., Tank, J. L., Hamilton, S. K., Wollheim, W. M., Hall, R. O., Mulholland, P. J., et al. (2011). Nitrous oxide emission from denitrification in stream and river networks. *Proceedings of the National Academy of Sciences of the United States of America*, 108, 214–219. <https://doi.org/10.1073/pnas.1011464108>
- Cunge, J. A. (1969). On the subject of a flood propagation computation method (Muskingum method). *Journal of Hydraulic Research*, 7, 205–230. <https://doi.org/10.1080/00221686909500264>
- Davis, J. C., & Minshall, G. W. (1999). Nitrogen and phosphorus uptake in two Idaho (USA) headwater wilderness streams. *Oecologia*, 119, 247–255. <https://doi.org/10.1007/s004420050783>
- Hall, R. O., Tank, J. L., Sobota, D. J., Mulholland, P. J., O'Brien, J. M., Dodds, W. K., et al. (2009). Nitrate removal in stream ecosystems measured by N-15 addition experiments: Total uptake. *Limnology & Oceanography*, 54, 653–665. <https://doi.org/10.4319/lo.2009.54.3.0653>
- Hinshaw, S. E., & Dahlgren, R. A. (2012). Dissolved nitrous oxide concentrations and fluxes from the Eutrophic San Joaquin River, California. *Environmental Science & Technology*, 47, 1313–1322. <https://doi.org/10.1021/es301373h>
- Hotchkiss, E. R., Hall, R. O., Jr, Sponseller, R. A., Butman, D., Klaminder, J., Laudon, H., et al. (2015). Sources of and processes controlling CO<sub>2</sub> emissions change with the size of streams and rivers. *Nature Geoscience*, 8, 696–699. <https://doi.org/10.1038/NGEO2507>



- Kaushal, S. S., Mayer, P. M., Vidon, P. G., Smith, R. M., Pennino, M. J., Newcomer, T. A., et al. (2014). Land use and climate variability amplify carbon, nutrient, and contaminant pulses: A review with management implications. *Journal of the American Water Resources Association*, 50, 585–614. <https://doi.org/10.1111/jawr.12204>
- Koffler, D., & Laaha, G. (2012). LFSTAT- an R-package for low-flow analysis. Retrieved from <http://cra>
- Kyllmar, K., Carlsson, C., Gustafson, A., Ulén, B., & Johnsson, H. (2006). Nutrient discharge from small agricultural catchments in Sweden: Characterization and trends. *Agriculture, Ecosystems & Environment*, 115, 15–26. <https://doi.org/10.1016/j.agee.2005.12.004>
- Levi, L., Cvetkovic, V., & Destouni, G. (2018). Data-driven analysis of nutrient inputs and transfers through nested catchments. *The Science of the Total Environment*, 610–611, 482–494. <https://doi.org/10.1016/j.scitotenv.2017.08.003>
- Marinos, R. E., Van Meter, K. J., & Basu, N. B. (2020). Is the river a chemostat?: Scale versus land use controls on nitrate concentration-discharge dynamics in the upper Mississippi river basin. *Geophysical Research Letters*, 47, 1–11. <https://doi.org/10.1029/2020GL087051>
- Marzadri, A., Amatulli, G., Tonina, D., Bellin, A., Shen, L. Q., Allen, G. H., et al. (2021). Global riverine nitrous oxide emissions: The role of small streams and large rivers. *The Science of the Total Environment*, 776, 145148. <https://doi.org/10.1016/j.scitotenv.2021.145148>
- Marzadri, A., Dee, M. M., Tonina, D., Bellin, A., & Tank, J. L. (2017). Role of surface and subsurface processes in scaling N<sub>2</sub>O emissions along riverine networks. *Proceedings of the National Academy of Science of the United States of America*, 114, 4330–4335.
- Miller, O. L., Putman, A. L., Alder, J., Miller, M., Jones, D. K., & Wise, D. R. (2021). Changing climate drives future streamflow declines and challenges in meeting water demand across the southwestern United States. *Journal of Hydrology X*, 11, 100074. <https://doi.org/10.1016/j.hydroa.2021.100074>
- Montgomery, D. R., & Buffington, J. M. (1998). Channel processes, classification, and response. In R. J. Naiman, & R. Bilby (Eds.), *River ecology and management* (pp. 13–42). Springer-Verlag, New York.
- Mosley, L. M. (2015). Drought impacts on the water quality of freshwater systems; review and integration. *Earth-Science Reviews*, 140, 203–214. <https://doi.org/10.1016/j.earscirev.2014.11.010>
- Mulholland, P. J., Helton, A. M., Poole, G. C., Hall, R. O., Hamilton, S. K., Peterson, B. J., et al. (2008). Stream denitrification across biomes and its response to anthropogenic nitrate loading. *Nature*, 452, 202–205. <https://doi.org/10.1038/nature06686>
- Overpeck, J. T. (2013). The challenge of hot drought. *Nature*, 503, 350–351.
- Peterson, E. E., & Ver Hoef, J. M. (2014). STARS: An ArcGIS toolset used to calculate the spatial information needed to fit spatial statistical models to stream network data. *Journal of Statistical Software*, 56, 1–17. <https://doi.org/10.18637/jss.v056.i02>
- Piccolroaz, S., Di Lazzaro, M., Zarlenga, A., Majone, B., Bellin, A., & Fiori, A. (2016). HYPERstream: A multi-scale framework for streamflow routing in large-scale hydrological model. *Hydrology and Earth System Sciences*, 20, 2047–2061. <https://doi.org/10.5194/hess-20-2047-2016>
- Ravishankara, A. R., Daniel, J. S., & Portmann, R. W. (2009). Nitrous oxide (N<sub>2</sub>O): The dominant ozone-depleting substance emitted in the 21st century. *Science*, 326, 123–125. <https://doi.org/10.1126/science.1176985>
- Rinaldo, A., Botter, G., Bertuzzo, E., Uccelli, A., Settin, T., & Marani, M. (2006). Transport at basin scales: 1. Theoretical framework. *Hydrology and Earth System Sciences*, 10, 19–29.
- Rutherford, J. C. (1994). *River mixing*. John Wiley & Sons.
- Salarashayeri, A. F., & Siosemarde, M. (2012). Prediction of soil hydraulic conductivity from particle-size distribution. *World Academy of Science Engineering and Technology*, 61, 454–458.
- Seitzinger, S. P. (1988). Denitrification in freshwater and coastal marine ecosystems: Ecological and geochemical significance. *Limnology & Oceanography*, 33, 702–724. [https://doi.org/10.4319/lo.1988.33.4\\_part\\_2.0702](https://doi.org/10.4319/lo.1988.33.4_part_2.0702)
- Seitzinger, S. P., Kroeze, C., & Styles, R. V. (2000). Global distribution of N<sub>2</sub>O emissions from aquatic systems: Natural emissions and anthropogenic effects. *Chemosphere - Global Change Science*, 2, 267–279. [https://doi.org/10.1016/S1465-9972\(00\)00015-5](https://doi.org/10.1016/S1465-9972(00)00015-5)
- Sheffield, J., Wood, E. F., Chaney, N., Guan, K., Sadri, S., Yuan, X., et al. (2014). A drought monitoring and forecasting system for sub-sahara african water resources and food security. *Bulletin of the American Meteorological Society*, 95, 861–882. <https://doi.org/10.1175/BAMS-D-12-00124.1>
- Smakhtin, V. U. (2001). Low flow hydrology: A review. *Journal of Hydrol.*, 240, 147–186.
- Stewart, R. J., Wollheim, W. M., Gooseff, M. N., Briggs, M. A., Jacobs, J. M., Peterson, B. J., et al. (2011). Separation of river network-scale nitrogen removal among the main channel and two transient storage compartments. *Water Resource Research*, 47, W00J10.
- Tonina, D., Marzadri, A., Alberto, B., Deed, M., Bernal, S., & Tank, J. (2021). Data: Riverine N<sub>2</sub>O emissions from drying streams and rivers, *HydroShare*. Retrieved from <http://www.hydroshare.org/resource/70a1078d0ca14839aea8e0f4082cb81>
- Tubino, M. (1991). Growth of alternate bars in unsteady flow. *Water Resource Research*, 27, 37–52.
- Turner, P. A., Griffis, T. J., Lee, X., Baker, J. C., Venterea, R. T., & Wood, J. C. (2015). Indirect nitrous oxide emissions from streams within the US Corn Belt scale with stream order. *Proceedings of the National Academy of Sciences of the United States of America*, 112(32), 9839–9843. <https://doi.org/10.1073/pnas.1503>
- Ver Hoef, J. M., Peterson, E. E., Clifford, D., & Shah, R. (2014). SSN: An R package for spatial statistical modeling on stream networks. *Journal of Statistical Software*, 56, 1–45. <https://doi.org/10.18637/jss.v056.i03>
- Vidon, P. G., & Cuadra, P. E. (2010). Impact of precipitation characteristics on soil hydrology in tile-drained landscapes. *Hydrological Processes*, 24, 1821–1833. <https://doi.org/10.1002/hyp.7627>
- WMO. (2008). *Manual on low-flow estimation and prediction: Operational hydrology report no. 50 WMO-No. 1029*.
- Yalin, M. S. (1964). Geometrical properties of sand waves. *Proceedings of American Society of Civil Engineers, Journal of Hydraulics Division*, 90, 105–119.

## References From the Supporting Information

- Elliott, A. H., & Brooks, N. H. (1997). Transfer of nonsorbing solutes to a streambed with bed forms: Theory. *Water Resource Research*, 33, 123–136. <https://doi.org/10.1029/96WR02784>
- Gillihan, T. (2013). *Dynamic vegetation roughness in the riparian zone*. University of New Mexico.
- Jähne, B., Münnich, K. O., Börsinger, R., Dutzi, A., Huber, W., & Libner, P. (1987). On the parameters influencing air-water gas exchange. *Journal of Geophysical Research*, 92(C2), 1937–1949. <https://doi.org/10.1029/JC092iC02p01937>
- Ikedo, S. (1984). Prediction of alternate bar wavelength and height. *Journal of Hydraulic Engineering* 110, 371–386.
- Leopold, L. B., & Maddock, T. (1953). *The hydraulic geometry of stream channels and some physiographic implications*.
- Marineau, M., Wright, S. A., Whealdon-Haught, D. R., & Kinzel, P. J. (2017). *Physical characteristics of the lower san Joaquin River, California, in relation to white sturgeon spawning scientific investigations. Report 2017 – 5069*. <https://doi.org/10.3133/sir20175069>

- Marzadri, A., Tonina, D., & Bellin, A. (2020). Power law scaling model predicts N<sub>2</sub>O emissions along the Upper Mississippi River basin. *The Science of the Total Environment*, 732, 138390. <https://doi.org/10.1016/j.scitotenv.2020.138390>
- Raymond, P. A., Zappa, C. J., Butman, D., Bott, T. L., Potter, J., Mulholland, P. J., et al. (2012). Scaling the gas transfer velocity and hydraulic geometry in streams and small rivers. *Limnology & Oceanography*, 2, 41–53. <https://doi.org/10.1215/21573689-1597669>
- Wanninkhof, R. (1992). Relation between wind speed and gas exchange over the ocean. *Journal of Geophysical Research* 97, 7373–7382. <https://doi.org/10.1029/92JC00188>
- Zambrano-Bigiarini, M. (2020). *hzambran/hydroGOF: v0.4-0*. <https://doi.org/10.5281/ZENODO.3707013>