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Hyporheic Source and Sink of Nitrous Oxide

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Abstract Nitrous oxide (N₂O) is a potent greenhouse gas with an estimated 10% of anthropogenic N₂O coming from the hyporheic zone of streams and rivers. However, difficulty in making accurate fine-scale field measurements has prevented detailed understanding of the processes of N₂O production and emission at the bedform and flowline scales. Using large-scale, replicated flume experiments that employed high-density chemical concentration measurements, we have been able to refine the current conceptualization of N₂O production, consumption, and emission from the hyporheic zone. We present a predictive model based on a Damköhler-type transformation (τ) in which the hyporheic residence times (τ) along the flowlines are multiplied by the dissolved oxygen consumption rate constants for those flowlines. This model can identify which bedforms have the potential to produce and emit N₂O, as well as the portion and location from which those emissions may occur. Our results indicate that flowlines with τ<sub>up</sub> values between 0.54 and 4.4 are likely to produce and emit N₂O. Flowlines with τ<sub>up</sub> values of less than 0.54 will have the same N₂O as the surface water and those with values greater than 4.4 will likely sink N₂O (reference conditions: 17°C, surface dissolved oxygen 8.5 mg/L). N₂O production peaks approximately at f = 1.8. A cumulative density function of τ<sub>up</sub> values for all flowlines in a bedform (or multiple bedforms) can be used to estimate the portion of flowlines, and in turn the portion of the streambed, with the potential to emit N₂O.

1. Introduction

Nitrous oxide (N₂O) is a potent greenhouse gas that is of particular interest because of its role in the depletion of stratospheric ozone. On an equal mass basis, N₂O has 300 times the forcing potential as CO₂ (IPCC, 2007). Due to actions taken in response to The Montreal Protocol on Substances that Deplete the Ozone Layer (MP), the abundance of anthropogenically generated, ozone-depleting substances that are controlled by the MP have been steadily decreasing over the past few decades. However, N₂O is not among the substances included in the MP and in the time since its implementation, N₂O concentrations in the upper atmosphere have been steadily increasing, raising the prominence of N₂O as a cause for ozone depletion and as a forcing agent for atmospheric warming (Ravishankara et al., 2009; World Meteorological Organization (WMO), 2014; Wuebbles, 2009). Recent estimates indicate that N₂O is responsible for 9% of the current climate forcing (Rosamond et al., 2012). Streams and rivers have been identified as a significant source of N₂O emissions. Estimates of N₂O emissions from streams and rivers vary in range from 0.1 Tg N-N₂O/year (Anderson et al., 2012).
2010) to 0.95 Tg N-N2O/year (Seitzinger & Kroeze, 1998). In the middle of this range, Beaulieu (2011) estimated emissions from streams at 0.68 Tg N-N2O/year, which is approximately 10% of all anthropogenically generated N2O that is emitted into the atmosphere. These emissions are largely correlated to pollutant runoff from wastewater treatment plants and agricultural practices (Davidson, 2009) with excess nitrogen stimulating N2O production in rivers (McMahon & Dennehy, 1999; Park et al., 2012). However, field observations indicate that not all impacted streams emit N2O (Beaulieu, 2011).

Our current understanding of these emissions comes almost exclusively from reach or watershed-scale field studies (Beaulieu, 2011; Beaulieu et al., 2008; Laursen & Seitzinger, 2004; Zarnetske et al., 2011a, 2011b) or from numerical studies (Marzadri, Tonina, Bellin, et al., 2014; Marzadri et al., 2011), conducted at similar scales. While these studies and models have been quite useful in quantifying the regional and global impact of N2O emissions from streams, they have been unable to resolve the source points of emission at the hyporheic flowline scale or even bedform scale. Recently, Quick et al. (2016) presented a conceptual model in which only the portion of the hyporheic zone (HZ) that contains flowlines with intermediate residence times produce and emit N2O. Portions of the HZ with short or long residence time have dissolved oxygen (DO; short flowlines) or N2 (long flowlines) as their primary emissions. However, this work did not provide a method to delineate the emitting zone nor a procedure to identify and quantify short, intermediate, or long residence times. Having an understanding of N2O emissions at the flowline scale becomes important when trying to define the mechanisms that lead to and control N2O emissions from streams. This level of understanding could usefully supplement planning and assessment of remediation and restoration projects whose objectives include reducing N2O emissions (Herzog et al., 2016). Our goal in this study is to resolve the controls on N2O production and emission and to create a model (Figure 1) that resolves N2O production at the flowline scale and can be scaled up to the bedform, reach, or watershed scale.

2. Methods and Materials

2.1. Experimental Setup

The experimental setup and methodologies were described in detail in Quick et al. (2016). The key elements are described below. We conducted two sets of experiments in the large-scale flume (approximately 20 × 2 m) at the Center for Ecohyaulics Research Stream Laboratory (Budwig & Goodwin, 2012) at the University of Idaho, Boise, to test the impact of bed morphology, stream hydraulics, and surface water chemistry (reactive nitrogen loading) on DO and nitrogen consumption dynamics and the impact of those processes on N2O emissions from streams. The first experiment (Flume 1) ran continuously from August 2013 through December 2013, and the second (Flume 2) ran from February 2015 through June 2015. In both sets of experiments, the flume was divided into three stream channels (30 cm wide × 60 cm deep × 15 m long) which were...
separated by access corridors. Triangular dunes of various sizes were constructed from 90% quarry sand (D$_{50}$ ~1.5 mm) and 10% natural sand collected from the Boise River (Boise, ID, USA). The natural sand provided an inoculum to initiate bacterial communities, which were representative of those that typically reside in streambed sediments. To provide an organic carbon nutrient source, 0.15% by dry weight of finely divided (<5 mm) cottonwood leaves were uniformly added to the sand mix. Water for surface flow over the dunes was pumped and recirculated from a 190,000-L catch basin into a head box at the top of the flume and over individual sills into each of the three flume channels. We will consider three different dune variants. From Flume 1, we evaluate the response of a 9 cm tall by 1 m long dune (two replicates), hereafter referred to as the 9 cm dune. The energy slope for the 9 cm dune was 0.002. The concentration of nitrate in the surface water (from KNO$_3$ added to the catch basin) was approximately 3 mg/L in Flume 1. From Flume 2, we consider a 9 cm tall by 100 cm long dune and a 9 cm tall by 70 cm long dune, hereafter referenced as 100 cm dune and 70 cm dune, respectively. The three replicate channels in Flume 2 are referred to as Channels A, B, and C. Individual dunes in Flume 2 are identified by their channel and length, that is, a 70 cm dune in Channel C is identified as C70. The energy slope for the Flume 2 experiments was 0.003. In Flume 2, the surface-water nitrate concentration was approximately 10 mg/L. In both experiments, we surveyed bed surface and water surface profiles every 2 cm along the centerline of each dune with a laser and an ultrasonic sensor, respectively; both with better than 1 mm vertical resolution.

2.2. Pore Water Sampling

In situ pore-water-extraction ports (rhizon soil-moisture samplers, Rhizosphere Research Products, Netherlands) were embedded through the sidewalls of the flume channels and into the bulk of the dunes, allowing us to obtain high-density, repeatable pore water samples throughout the duration of the experimental runs. A typical placement of the in situ sampling ports is illustrated by the purple dots in Figure 2. The embedded portion of the rhizon sampling ports consisted of porous (0.45 $\mu$m) tubing (10 cm x 3 mm) that was supported by a stainless steel wire stiffener. The porous tube was connected through the sidewall of the flume channel and into the access corridors by silicon tubing that was terminated by a luer lock adapter and a cap. During sampling, the cap was replaced with a needle and, initially, the port was allowed to drip for a brief time to allow any stagnant water in the silicon tubing to be evacuated. For the actual pore water sample, a closed sampling method was used. The needle was inserted, under water, through the septa of an evacuated vial. Pore water was slowly pulled by the vacuum in the vial through the rhizon sampling port and into the vial. The vial was held under water for the duration of the sample extraction. Approximately 10 ml of pore water was collected in a 20 ml headspace vial. To measure dissolved N$_2$O, the samples were analyzed using an HP 7694 headspace autosampler and an Agilent 6890 gas chromatograph equipped with a GS_Carbon PLOT column (30 m x 0.53 mm) and a $^{63}$Ni microelectron capture detector. Dissolved concentrations of N$_2$O were calculated using Henry’s law (Hudson, 2004).

2.3. Bed-Surface Pressure Profiles and Hyporheic Flowlines

The interaction between surface flow velocities and streambed morphology creates the bed surface pressure profile that drives hyporheic flow (Elliott & Brooks, 1997). That pressure profile also constitutes the boundary.
conditions for the groundwater flow equations that describe hyporheic flows. Because of the low surface flow velocities used in the flume experiments (<0.1 m/s), the bed surface pressures were functionally unmeasurable. As a result, we modeled the pressure profiles (Cardenas & Wilson, 2007) using ANSYS Fluent CFD (ANSYS Inc., Canonsburg, PA, USA). Fluent provides a numerical solution to the Reynolds-Averaged, Navier Stokes equations. The Fluent models were meshed with between 65,000 and 95,000 triangular elements and used a $k-\omega$ turbulence closure with a Low-Reynolds-Number correction. Measured bed surface and water surface provided the physical boundary of the numerical domain. The inlets and outlets of the surface flow models were treated as periodic boundaries with the periodic pressure gradient defined by the energy slope. The water surface was modeled as a symmetry boundary and the bed surface as a no-slip wall boundary. Residual error for continuity, x-velocity, y-velocity, k, and $\omega$ was set to less than $1 \times 10^{-6}$ for convergence. The overall CFD modeling approach was validated against the pressure measurements provided by Fehlman (1985). Excellent agreement between the simulated and measured bed-pressures, over a broad range of discharges and energy head, gave us a high degree of confidence that our modeling approach was robust, accurate, and not overly sensitive to the applied boundary conditions (Reeder, Quick, Farrell, Benner, Feris, & Tonina, 2018).

Hyporheic flowlines (red and green lines, Figure 2) and the associated residence times ($\tau$) were quantified using the models of Marzadri (Marzadri, Tonina, McKeen, et al., 2014) and GMS ModFlow (Aquaveo, LLC, Provo, Utah). The Marzadri model provides a semianalytical solution to the groundwater flow equations and ModFlow provides a numerical solution. The two approaches were used as a crosscheck and to utilize the visual presentation of GMS ModFlow. Calculated residence times were calibrated (by adjusting hydraulic conductivity) against measured residence times from a post experiment salt pulse injection at the end of Flume 2. Salt solution was constantly added into the head box of the flume for approximately 30 min to raise the surface water salt concentration to approximately 100 mmol/L. Electrical conductivity was measured with electrical conductivity sensors placed at a subset of the sampling ports (purple dots, Figure 2). Measurements were recorded every 5 min for approximately 3 days using Model CR1000 data loggers (Campbell Scientific, Logan, UT, USA). Residence times were calculated from breakthrough curves at 9 locations in a 70 cm dune and 20 locations in a 100 cm dune (Reeder, Quick, Farrell, Benner, Feris, & Tonina, 2018).

2.4. Flowlines and Chemical Concentration Profiles

The measured N$_2$O concentration data were krigged and gridded (Surfer ® Version 10, Golden Software, Inc., Golden CO) to create N$_2$O concentration maps for each dune. The concentration profile for the C70 dune on Day 91 of the Flume 2 experiment is shown in Figure 2. The kriging operation creates a regular grid of X-Y locations and assigns an N$_2$O concentration that is interpolated from the measured values, to each location. The interpolation is constrained such that the measured values are not altered. For each of the dunes, flowlines (red and green traces, Figure 2) were calculated from the pressure profile for that particular dune. Those flowlines were mapped onto the associated N$_2$O concentration profile. The data stream for flowline traces consist of a series of X-Y locations with a residence time at each location. For each flowline, from these co-mapped data sets, we extracted a data string of paired residence time and the N$_2$O concentration ($\tau$, [N$_2$O]). The two profiles in Figure 3 are representative examples of individual flowline N$_2$O concentration profiles presented as a function of residence time. With these data, we can parse the chemical activity in the HZ to a fine level. For instance, we can locate the residence time and position of the peak of net production of N$_2$O along the flowline as well as the N$_2$O concentration and residence time at flowline exit. Additionally, by calculating an exponential fit to the rising and falling limbs of the [N$_2$O] versus $\tau$ profiles, we can calculate the apparent first-order reaction kinetics for N$_2$O production and consumption, respectively. It is likely that production and consumption are happening simultaneously and, thus, calculated rates should be viewed as apparent as opposed to thermodynamic. DO and other chemical constituents can be treated in a similar manner. We used the same procedure, with $\tau$ versus [DO] data streams, to calculate the rate constant of metabolic DO consumption ($K_{DO}$) for all flowlines (Reeder, Quick, Farrell, Benner, Feris, & Tonina, 2018).

2.5. Calculation Methodologies

2.5.1. Distributed K$_{DO}$ Transform

Following previous approaches (Ocampo et al., 2006), we define a Damköhler-type transformation that scales the residence times ($\tau$) along each of the individual flowlines by a characteristic reaction rate for each of the flowlines (Marzadri et al., 2011; Zarnetske et al., 2011a; Zarnetske et al., 2012). We used $K_{DO}$ the rate constant for
for the metabolic consumption of DO. The transformed residence times are designated as $\tilde{\tau}$, and the transform is calculated by

$$e^{\tau_i} = \tau_i K_{DO},$$

(1)

where $\tilde{\tau}_i$ is the collection of transformed residence times ($\tau$) from flowline ($i$) and $K_{DO}$ is the DO consumption rate constant for flowline ($i$). The $\tilde{\tau}$ transform is calculated for all flowlines using individual $K_{DO}$ values that have been calculated for each of the flowlines.

In Reeder, Quick, Farrell, Benner, Feris, and Tonina (2018), we showed that, for dune-like bedforms, $K_{DO}$ values are lognormally distributed and that flowline $K_{DO}$ values can be calculated from the mean $\mu_Y$, the log transform mean, and the standard deviation, $\sigma_Y$, from the inverse normal distribution:

$$K_{DO} = \exp\left(F^{-1}(X^*; \mu_Y, \sigma_Y)\right),$$

(2)

where

$$F(Y|\mu_Y, \sigma_Y) = \frac{1}{\sigma_Y \sqrt{2\pi}} \int e^{-\frac{(\ln(Y) - \mu_Y)^2}{2\sigma_Y^2}} d\xi,$$

(3)

where $\xi$ is a dummy variable of integration and $X^*$ is the dimensionless, horizontal distance along the upstream downwelling face of the bedform, defined as

$$X^* = x/x',$$

(4)

with $x'$ as the horizontal length of the downwelling face of the bedform. In a triangular dune, $x'$ is simply the streamwise distance from the trough to the crest of the dune such that $X^* = 0$ at the trough (position 0 m in Figure 2) and 1 at the crest (position 0.5 m in Figure 2). More simply, the flowline $K_{DO}$ values can be calculated in Excel or Matlab using the expression

$$K_{DO} = \exp(\text{norminv}(X^*; \mu_Y, \sigma_Y)).$$

(5)

### 2.5.2. Mean $K_{DO}$ Transform, $\overline{K}_{DO}$

Alternatively, the $\tilde{\tau}$ transform can be calculated using the mean $K_{DO}$ of a particular bedform for all flowlines in that bedform. This is less precise than the distributed transform but it may be useful in some situations. For this approach, the transform takes the form

$$\overline{\tilde{\tau}}_i = \tau_i \overline{K}_{DO},$$

(6)
2.5.3. N\textsubscript{2}O Flux Calculations

N\textsubscript{2}O flux for each flowline was calculated as

\[
f_i = \begin{cases} 
0, & \bar{t}_{up(i)} < 0.54 \\
 v_{dw(i)} \times A_{dw(i)} \times \frac{[N_2O]_{up}}{[N_2O]_{surf}}, & 0.54 \leq \bar{t}_{up(i)} \leq 4.4 \\
 v_{dw(i)} \times A_{dw(i)} \times \frac{([N_2O]_{min} - [N_2O]_{surf})}{[N_2O]_{surf}}, & \bar{t}_{up(i)} > 4.4
\end{cases}
\]  \hspace{1cm} (7)

where \(i\) refers to the \(i\)th flowline such that \(f_i\) is the flux from the \(i\)th flowline, \(v_{dw(i)}\) is its downwelling velocity, \(A_{dw(i)}\) is its downwelling surface area, \([N_2O]_{up}\) is its N\textsubscript{2}O concentration as the \(i\)th flowline exits the HZ, \([N_2O]_{surf}\) is the N\textsubscript{2}O concentration of the surface water, and \([N_2O]_{min}\) is the minimum N\textsubscript{2}O concentration along flowline \((i)\). Total flux from a bedform is calculated by summing the fluxes from all flowlines. The derivation for the thresholds \((\bar{t}_{up} = 0.54 \text{ and } 4.4)\) is presented in section 3.2.2.

3. Results and Discussion

3.1. N\textsubscript{2}O Production and Consumption Profiles

The blue profiles in Figure 2 show the krigged N\textsubscript{2}O concentrations for the C70 on Day 91 of the Flume 2 experiment. Compared to the other dunes, the C70 dune experienced higher levels of bioactivity, and as a result, its profile map is somewhat more spatially extensive and continuous than the other dunes. Nonetheless, the morphology, extent, and location of all the N\textsubscript{2}O plumes is quite similar to the C70 profile. Residence time versus N\textsubscript{2}O concentration profiles \((\tau, [N_2O])\) were extracted for all flowlines that intersected the various N\textsubscript{2}O plumes. Two representative profiles are shown in Figure 3. The concentration profile in Figure 3a is from a long flowline (dark green flowline, Figure 2). The rising limb of the profile traces production of N\textsubscript{2}O and the falling limb is consumption. The N\textsubscript{2}O concentration at the entry point of the flowline was 0.55 \textmu g/L and peaked at about 65 \textmu g/L. All N\textsubscript{2}O was consumed before the flowline exited the HZ. This flowline functions as a sink of N\textsubscript{2}O. The concentration profile in Figure 3b is for an intermediate length flowline. As with the long flowline (Figure 3a), both production and consumption are occurring along this flowline. However, this flowline exits the bed before all N\textsubscript{2}O is consumed and, at least on this date, was acting as a source of N\textsubscript{2}O to the surface flow.

The N\textsubscript{2}O concentration profiles for all flowlines from all dunes are shown in Figure 4. Within this collection of N\textsubscript{2}O concentration profiles, there is a wide range of production and consumption responses. From flowline to flowline, the initiation of production and peak production occurs at different points in (residence) time. The magnitude of the peak and terminal concentrations vary by flowline. The apparently tight grouping of the profiles is somewhat deceptive. The large number of data points (\(>100,000\)) and the inherent similarity between the experiments tend to obscure the broad diversity of responses. When the flowlines are evaluated against the tendency to emit N\textsubscript{2}O, it is difficult to identify a concise range of residence times \((\tau)\) and flowlines that have a high probability to emit N\textsubscript{2}O. The concentration data in this format is not particularly useful as a predictive tool.

3.2. Scaling and Classifying the N\textsubscript{2}O Profiles

3.2.1. Distributed (Lognormal) Transform

Most of the variability among the concentration profiles in Figure 4 comes from variability between flowlines as opposed to variability between dunes. Reeder, Quick, Farrell, Benner, Feris, and Tonina (2018) showed that, when evaluated at the flowline level, the metabolic DO consumption rate, expressed as \(K_{DO}\), is a linear function of the downwelling velocity of that flowline. Flowline downwelling velocities, for a bedform, are lognormally distributed and, thus, so too are the values expressed by \(K_{DO}\) indicating that biological activity within a dune is likely to be lognormally distributed. Based upon these observations, it seemed a reasonable possibility that scaling the residence times \((\tau)\) by a characteristic reaction rate would yield a nondimensional residence time that would tend to group similar events together. To test this idea, we multiplied the flowline residence times \((\tau)\) by the DO consumption rate constant \((K_{DO} (1/s))\) for each flowline. \(K_{DO}\) values were calculated from the lognormal distribution of \(K_{DO}\) values for the dune in which a particular flowline resided. We designate the transformed, nondimensional residence times as \(\bar{\tau}\). The results of the \(\bar{\tau}\) transform are shown in Figure 5. N\textsubscript{2}O production for the majority of the profiles initiates within relatively small range of \(\bar{\tau}\) values (\(\sim 0.5\) to 1). The N\textsubscript{2}O concentration peaks are reasonably well aligned, as are the falling limbs of the profiles,
indicating consumption. Collectively, these profiles potentially define a concise range of \( \bar{\tau} \) values that encompass N\(_2\)O production and consumption for a broad range of bedforms.

To generalize the collective data shown in Figure 5 and to define beginning and ending points for N\(_2\)O production and consumption as well as the peak production point, we calculated a mean profile for the collective flowline data. However, the various dunes and their flowlines present a broad range of amplitudes for the N\(_2\)O concentration profiles. We were concerned that the high amplitude profiles would dominate and bias the mean profile. To test this concern, we calculated the mean profile using two different approaches. In the first approach, the N\(_2\)O concentrations (Figure 5) were binned by their \( \bar{\tau} \) values, with each bin having a width of 0.1 (number of observations in each bin was \( \approx 100,000 \)). All N\(_2\)O values in each bin were averaged and plotted to the midpoint of the bin (orange line, Figure 6). In the second approach, the amplitudes of all flowlines were normalized to the maximum values of each of the individual flowlines. Thus transformed, each of the normalized flowlines exhibited values that ranged from 0 to 1. The normalized values were binned, averaged, and plotted in the same manner as used in the first approach (blue line, Figure 6). We calculated the mean and standard deviation using the expressions

\[
\bar{\tau} = \frac{1}{\sum C_i} \sum C_i \bar{\tau}_i \tag{8}
\]

for the mean and

\[
\sigma^2 = \frac{1}{\sum C_i} \sum C_i (\bar{\tau}_i - \bar{\tau})^2 \tag{9}
\]

for the variance. The mean and standard deviation (square root of the variance) for the non-normalized data were 1.82 and 0.64, respectively. For the normalized data, the mean and standard deviation were 1.65 and 0.91, respectively. For both approaches, the mean and standard deviation were quite similar, suggesting that differing amplitudes among the flowlines was not overly biasing to the result. Using the non-normalized data, we define lower and upper boundaries for N\(_2\)O production and consumption. The lower boundary for production is defined as the mean (1.82) minus two standard deviations giving a lower limit of N\(_2\)O production at \( \bar{\tau} = 0.54 \) (gray vertical line, Figures 5 and 6). The upper limit of consumption is defined as the mean (1.82)
plus four standard deviations giving an upper limit of production at $\bar{\tau} = 4.4$ (black vertical line, Figures 5 and 6). The reason for unbalanced use of standard deviations is the relatively long tail on the consumption side of the profile. This unbalanced approach creates limits that match well to a threshold line (black, horizontal, dashed line, Figure 6) set at $[N_2O] = 0.65 \ \mu g/L$, just above surface water equilibrium concentration. The meaning of these limits is that, on average, for any particular flowline, $N_2O$ production will be initiated at $\bar{\tau} = 0.54$, the $N_2O$ concentration will peak at $\bar{\tau} = 1.8$ and, if the flowline is long enough, all $N_2O$ will be consumed by $\bar{\tau} = 4.4$. The $\bar{\tau}_{up}$ is the transformed residence time at the point where a flowline exits the bed and reenters the surface water. If a flowline has a $\bar{\tau}_{up}$ between $\bar{\tau} = 0.54$ and $\bar{\tau} = 4.4$, it has the potential to emit $N_2O$. The physical events tied to these boundaries are, at the lower boundary ($\bar{\tau} = 0.54$), the consumption of DO to a sub oxic state (though not necessarily anoxic), causing the initiation of metabolic consumption of reactive nitrogen compounds and, at the upper boundary ($\bar{\tau} = 4.4$), the completion of the denitrification reaction sequence.

Figure 5. $N_2O$ concentration profiles for all flowlines and all dunes plotted against the nondimensional residence time, $\bar{\tau}$. In this case, the tight grouping of the concentration profiles is a result of the $\bar{\tau}$ transform. This provides a useful tool for predicting $N_2O$ production and consumption. For this chart, each flowline was transformed using the $K_{DO}$ value calculated for that specific flowline. $N_2O =$ nitrous oxide.

Figure 6. Mean $N_2O$ concentration profiles (for all dunes) by two different approaches. In both approaches, $N_2O$ concentration values were binned by $\bar{\tau}$, with each bin having a width of 0.1. All $N_2O$ values in each bin were averaged and plotted to the midpoint of the bin. In Approach 1 (orange line), averages were calculated against the raw (un-normalized data). In Approach 2 (blue line), the $N_2O$ values for all flowlines were normalized by the peak $N_2O$ value for each of the flowlines. $N_2O =$ nitrous oxide.
Interestingly, the production of N₂O spans τ_{up} pore water conditions between bulk aerobic and anaerobic and peaks at times or locations well in anoxic conditions (τ_{up} = 1.8). Values of τ_{up} less than 1 indicate that the bulk pore water has DO concentrations higher than the threshold concentration for anaerobic conditions, suggesting that N₂O production consistently and systematically starts in the oxic zone of the HZ. This production could be due to different mechanisms that may include denitrification in microanoxic zones, nitrification (oxidation of ammonia to nitrite and nitrate, Hydroxylamine Oxidation) and chemodenitrification (Otte et al., 1996, 1999; Schreiber et al., 2012). However, the highest N₂O concentrations occur in the anoxic zone of the HZ, suggesting that denitrification is probably the main mechanism producing N₂O in this environment.

### 3.2.2. Adapting to Surface DO and Temperatures that Vary From the Reference Conditions

For our experiments, surface water temperatures were substantially constant at around 17 °C, as were DO concentrations at around 8.5 mg/L. The N₂O production and consumption limits are referenced to those conditions. It is possible that a significant shift to those reference conditions, particularly the surface water DO concentration, could cause a shift to those limits. If, for example, the surface water DO concentration were 10 mg/L and all other factors were held the same, the initiation of denitrification could be delayed as compared to the 8.5 mg/L condition. This may cause the limits of production and consumption to shift to higher values of τ. To accommodate significant variations in DO concentration and following the work of Marzadri et al. (2011), we suggest that τ transform (from equation (1)) could be modified to the following form:

\[
\bar{\tau} = \frac{\tau_{DO}}{\ln\left[\frac{[DO]_s}{[DO]_{lim}}\right]}
\]

where [DO]_s is the surface water DO concentration and [DO]_{lim} is the limiting concentration for aerobic activities, typically 2 mg/L, and the reaction rate constant could be adjusted by the local water temperature, T, with an Arrhenius equation like

\[
K_{DO} (T) = K_{DO} (T=20°C) e^{\left(\frac{T-20}{T_{KDO}}\right)}
\]

with the temperature coefficient for respiration of \(\phi_{KDO} = 1.047\) (Marzadri et al., 2013).

### 3.2.3. Single-Value Transform

Recognizing that it is difficult to obtain \(K_{DO}\) values for individual flowlines, it is also possible to transform the residence time (τ) values for a bedform using a single value of \(K_{DO}\). This might be single measured value for a particular bedform or the mean of a few measured values. While this transform approach is somewhat easier than the lognormally distributed transform, the distribution of the transformed curves is wider and more dispersed, and as a result, this approach is less precise.

### 3.3. Modeling N₂O Emissions

#### 3.3.1. Identifying Potential Emissions

Potentially, the τ transformation allows us to extend our findings to virtually any bedform. More research needs to be done to define clearly just how widely these results can be applied. However, the consistency and repeatability of the responses across bedform geometries, bedform replicates, and the two experiments suggest that, if the residence times within the HZ are known, the τ_{up} values can be used to evaluate the potential of a particular bedform or for a collection of bedforms to produce and emit N₂O across a broad range of bed morphologies. Flowlines that have a τ_{up} value of less than 0.54 are too short to produce N₂O. These flowlines will likely remain relatively oxic and are unlikely to have a significant impact on the overall nitrogen chemistry of the stream or HZ. Flowlines that have a τ_{up} value that is greater than 4.4 will produce N₂O but, for the most part, all N₂O will have been consumed before the flowline exits the bed. These flowlines have the potential to act as a sink of N₂O by consuming it to concentrations below that of the surface water. Flowlines that have a τ_{up} between those two limits have a significant potential to produce and emit N₂O. The above classifications all assume that the concentration of nitrate and/or ammonium in the surface water and the sediments is sufficient to produce significant levels of nitrification and denitrification. It is also assumed that the bed sediments contain sufficient levels of bioavailable carbon to support the anaerobic metabolic activities that drive the denitrification reaction sequence.
This classification approach for identifying N₂O-emitting flowlines is illustrated in Figure 7. The green lines in this figure are flowlines that have been identified as being too short (τ_up < 0.54) to produce and emit N₂O. The black lines are flowlines that are identified as being too long (τ_up > 4.4). The red lines are the flowlines that have the potential to emit N₂O. The two panels compare the flowline classifications using the distributed and single-value KDO transform techniques. In Figure 7a, the τ_up values and flowline classifications are derived from the (lognormally) distributed KDO transform—all flowlines are transformed by a KDO value that is specific to that flowline. In Figure 7b, all flowlines were transformed by the single-value (mean) KDO transform using the mean KDO value for that dune. The same τ_up limits were applied to the flowlines from both transforms and it is interesting to note, at least for this bedform, that the two classifications are remarkably similar. This is a bit surprising given the broad dispersion of the mean KDO transform relative to the distributed KDO transform. The mean KDO transform classifies fewer flowlines as potential emitters of N₂O, but, nonetheless, gives a useful estimation of which flowlines have the potential to emit. The idea of potential to emit needs to be stressed. Not every red flowline, from either classification scheme, is certain to emit N₂O. While our model focuses on the hydraulic controls over biological processes, it is clear that, for instance, nitrate loading in the stream water or the state of the biological communities at a point in time will have an impact on the final chemistry that exits a flowline. The model defines an upper limit on what is possible based upon the ambient chemistry and the stream hydraulics. We know, for instance, that the flowlines on the left side of the dune near the upstream trough (between x = 0 and 0.2, Figure 7), which have been classified as potential emitters, actually do not emit N₂O. On the date captured by this figure, that area was oxic (Reeder, Quick, Farrell, Benner, Feris, & Tonina, 2018) and, thus, anaerobic respiration and denitrification processes were not active. The power of classifying flowlines is twofold. First, this approach can be used in natural streams, in which the hydraulics and hyporheic residence times are known, to connect measured N₂O emissions to the source locations. Second, if the analysis is done prior to restoration or experimental work, it can be used to improve the effectiveness of those efforts.

If it is only desired to estimate the portion of the flowlines from a bedform or collection of bedforms that have the potential to emit N₂O, then a procedure somewhat simpler than mapping the flowlines can be used. A cumulative density function (CDF) of the τ_up values can be constructed (Figure 8). The portion of the CDF that falls between the lower and upper limits for N₂O production and consumption will be the portion of the
flowlines that have the potential to emit N₂O. The two CDFs presented in Figure 8 are from the same dune (C70, Day 91) and are the CDFs for the flowline classification schemes shown in Figure 7. Consistent with the flowline classifications in Figure 7, the CDF for the distributed KDO transform (blue line) classifies approximately 34% of the flowlines as potential emitters, while the CDF for the mean KDO transform (orange line) nominates only 26% as potential emitters. This approach does not identify which flowlines or bedforms have the potential to emit.

3.3.2. Scaling the Model
Whereas the proposed method does not predict the magnitude of N₂O emission from the HZ, it does identify the flowlines that may produce or remove N₂O concentrations at the upwelling zones. Additionally, it provides a powerful method to upscale processes at the local flowline scale to bedform and eventually to reach scale production of N₂O emissions once the residence time distribution within the HZ is known. Presently, available predictive models, with their own limitations, for the distribution of hyporheic residence time for streams are limited to dune-like (Elliott & Brooks, 1997) and pool-riffle (Marzadri et al., 2011) morphologies.

By applying the analysis reported in the previous section, the method quantifies the percent of flowlines with the potential to emit N₂O. The constrains on $\bar{\tau}_{up}$ can allow quantifying whether a reach can remove or emit N₂O. The latter will be true if all $\bar{\tau}_{up}$ are longer than 4.4.

In idealized streambed conditions, (perfect dune-like and pool-riffle bedforms) this also implies mapping the sources or sinks of N₂O over the streambed. For other bedforms, for which predictive models of the hyporheic residence time are not available, the process may require to develop a hyporheic model supported by stream and river bathymetry and hydraulic conductivity distribution. Whereas the former is potentially at reach with the advances in remote sensing techniques, including structure from motion photogrammetry (Dietrich, 2017; Javernick et al., 2014; Storlazzi et al., 2016; Woodget et al., 2015) and bathymetric light detection and ranging (Hilldale and Raff, 2008; Kinzel et al., 2013), as applied by Benjankar et al. (2016), the latter is more challenging as mapping hydraulic conductivity is still difficult and there is not yet a viable field methodology. The current approach is to apply stochastic analysis by considering the physical variables (e.g., emissions and hyporheic residence time) as stochastic variables and assume that their spatial variability behave as a stochastic variability at the reach scale, such that ensemble analysis can provide reach scale values as proposed by Tonina et al. (2016).

3.3.3. Estimating N₂O Fluxes
In cases where the N₂O concentration profiles and flowline residence times are known or can be modeled, the $\bar{\tau}$ can be used to refine estimations of N₂O emissions. This can be easily accomplished by coding equation (7) and summing the fluxes from the individual flowlines. Using this procedure and the classifications from the distributed KDO transform, the net fluxes were calculated for all of dunes examined in this study.
experiment (Figure 9). The blue bars represent the flux estimations, with all of the flowline flux calculations based strictly upon the $\tau_{\text{up}}$ classifications in equation (7). However, not all flowlines in the possible emissions class will emit $\text{N}_2\text{O}$. In our data sets, it was observed that some of the flowlines included in that class did not exhibit a significant level of $\text{N}_2\text{O}$ production. For possible emissions flowlines whose peak $\text{N}_2\text{O}$ concentrations did not exceed the surface concentration by at least 5%, the effluent flux was set to zero. The result of the adjustment is shown by the orange bars in Figure 9. For the 70 cm dunes, the difference between the adjusted and unadjusted fluxes was negligible. For the 100 cm dune and the 9 cm dunes, the difference was slightly more than that of the 70 cm dunes but still quite modest. Overall, the upper and lower $\tau$ limits seem to be correctly placed and the potential error in the model is small. The dunes in the Flume 2 experiment (Channels A, B, and C, 70 and 100 cm dunes) exhibited significantly higher $\text{N}_2\text{O}$ emissions than the Flume 1 experiment (9 cm dune). The higher emissions from Flume 2 are consistent with the higher nitrate loading in that experiment. These flux estimations also point up the importance of experimental replicates in biochemical experiments. In Flume 2, the $\text{N}_2\text{O}$ concentrations and the estimated $\text{N}_2\text{O}$ fluxes exhibited significant variability across the replicates, both for the 70 and 100 cm dunes. This is not particularly surprising. If one were to imagine multiple biological systems, all with similar starting points, over time it would be expected that these systems would exhibit a range of responses that are likely driven by relatively small differences between the individual systems. Given this apparently inherent variability, estimations based upon measurements from a single source and extrapolated to a larger context might be poorly representative of the larger context. For instance, if we were to have made an estimate of the flux from all of our dunes base solely upon the C70 measurements, we would have likely overstated the overall flux. The specific reason(s) for the high flux value (and high $\text{N}_2\text{O}$ concentrations) for dune C70 are not explained by any specific observation that we can offer at this time.

The spatial distribution of $\text{N}_2\text{O}$ emissions from the HZ has not been previously described. The actual behavior may be a bit counterintuitive. Figure 10 shows the spatial distribution, in the dimensionless coordinate $X^*$, of $\text{N}_2\text{O}$ emissions from all dunes considered in this study. The brown line at the bottom represents a simplified dune-surface profile. For this diagram, emissions were assigned to the horizontal dimensionless position ($X^*$) of entry point of the flowline into the bed for which the emissions were calculated. This was done to highlight which flowlines and portions of the bedform are responsible for specific outcomes. Actual emissions occur downstream of the crest (Figure 10). Net $\text{N}_2\text{O}$ consumption (negative emissions) occurs mostly along the flowlines that enter the bed between $X^* = 0.2$ and $X^* = 0.55$. Most $\text{N}_2\text{O}$ sourcing occurs between $X^* = 0.55$ and $X^* = 1$ (the dune crest). There is a generally rising trend in $\text{N}_2\text{O}$ emissions from flowlines that enter at $X^* = 0.55$ to those that enter at $X^* = 1$, with the strongest emissions coming from flowlines that enter
between $X^* = 0.8$ and $X^* = 0.9$. It is not intuitively obvious that the maximum emissions should come from flowlines that enter the bed near the crest of the dune. This is not where the highest N$_2$O concentrations are observed. However, N$_2$O emissions are the product of the velocity along the flowline and the N$_2$O concentration at flowline exit. Concentrations vary by a factor of three or four, whereas downwelling velocities vary by an order of magnitude (Reeder, Quick, Farrell, Benner, Feris, & Tonina, 2018). Thus, peak production is a result of the synergy between strong flowline flux and N$_2$O concentration. This also suggests that while anaerobic denitrification may produce the highest N$_2$O concentrations within the bulk of the HZ (Figures 5 and 7), the processes within the oxic zone with $\tau_{\text{up}}$ values from 0.5 to 1 because of their high velocities (flowpath near the crest; Figures 7 and 10) may be the main sources of N$_2$O fluxes to the stream water. This could potentially explain the lower sensitivity of a Damköhler number based on DO consumption time scale (Marzadri, Tonina, Bellin, et al., 2014) than that based on denitrification time scale (Marzadri et al., 2017) to predict N$_2$O emissions at the reach scale, because denitrification time scale will be the limiting factor rather than DO.

4. Conclusions

Our results show that only a portion of the flowlines through the HZ are likely to emit N$_2$O, while others will sink N$_2$O to below instream concentrations. The primary factors that determine whether a particular flowline will emit N$_2$O are the residence time and biological activity level (reflected by $K_{DO}$) along that flowline, with the latter being influenced by the distribution and reactivity of organic carbon and denitrifying bacterial communities. Our results support and quantify the conceptual model proposed by Quick et al. (2016) that short or long flowlines are unlikely to emit N$_2$O. Short flowlines may have not started denitrification, thus will not produce N$_2$O but pass through the dissolved concentration from the flow. For long flowlines, the denitrification reaction sequence will likely be carried to completion and the primary effluent from those flowlines will be nitrogen gas (N$_2$), assuming reactive carbon is not limiting. Long flowlines may act as a sink by consuming N$_2$O to below the concentration of the surface water that entered the HZ. Because reaction rates (DO consumption, N$_2$O production, and N$_2$O consumption) are variable from flowline to flowline, by itself, is not an adequate predictor of N$_2$O emissions. However, as a general predictor of N$_2$O emissions for most bedforms, we propose to transform the residence times ($\tau$ (s)), for the individual flowlines, to a non-dimensional, Damköhler number, $\bar{\tau}$, by multiplying the $\tau$ values by a characteristic reaction rate for that
flowline, in this case $K_{DO}$ (1/s) ($\tau = \frac{r}{K_{DO}}$). Through the $\tau$ transform, we can predict the locations and portions of a bedform that will act as source or sink for $N_2O$. Our results suggest that the initiation of denitrification occurs at values of $\tau > 0.54$. Peak $N_2O$ production occurs at $\tau \approx 1.8$. $N_2O$ consumption is complete at values of $\tau > 4.4$. Flowlines for which $\tau_{up}$ (the nondimensional residence time, $\tau$, at which a flowline exits back into the surface water) is between 0.54 and 4.4 will produce and potentially emit $N_2O$. An adequate estimation of $\tau$ can be calculated by multiplying the $\tau$ values for all flowlines in a bedform by the mean $K_{DO}$ value for that bedform. However, if the mean $K_{DO}$ value and standard deviation are known, or can be estimated, individual $K_{DO}$ values can be calculated for each flowline refining the predictive power of the $\tau$ transform. $K_{DO}$ values are associated with hyporheic downwelling flows and are lognormally distributed for dune-like bedforms. In either case, mean $K_{DO}$ or distributed $K_{DO}$, a CDF of the $\tau_{up}$ values for all flowlines in a bedform (or multiple bedforms) can be constructed and the portion between 0.54 and 4.4 is a direct estimate of flowlines that have the potential of emitting $N_2O$. These constrains on the hyporheic residence time CFD allows upscaling the results to other bedforms and to reach scale processes as long as there is a model for the hyporheic hydraulics like that for dune-like or pool-riffle.

The range of $\tau$ spans both aerobic ($\tau < 1$) and anaerobic ($\tau > 1$) bulk pore water conditions, indicating that $N_2O$ production systematically starts in the HZ with bulk pore water oxic conditions. Our results show that for a given nutrient load, hyporheic hydraulics and thus stream flow/bedform interactions exert control on biological activity and are, at a significant level, responsible for hot spots of high production rates of transformed products occur. In fact, flowlines with high downwelling flow velocities identify or cause the biogeochemical hot spots. Most $N_2O$ emitted from a dune-like bedform is produced from hyporheic flows that enter the bed within a narrow downwelling band just upstream of the dune crest (0.8 < $X^*$ < 0.9), where downwelling velocities are high. This highlights our suggestion that hyporheic hydraulics plays a key role on biogeochemical processes and that the most important portion of the HZ is the zone with fast flows. The physical reasons for this dependence of production and reaction rates upon the local flux are unknown but we can speculate that it is related to the availability and delivery of resources (high velocities deliver resources more efficiently) and possibly due to the modification of and more efficient diffusion of nutrients through biofilms at high ambient velocities and turbulent flows (Hödl et al., 2014; Stewart, 2012). Our results also indicate that the processes within the oxic HZ with $\tau_{up}$ values from 0.5 to 1 because of their high velocities (flowpaths near the crest) may be the main sources of $N_2O$ fluxes to the stream water, whereas anaerobic HZ ($\tau_{up}$ around 1.8) may produce the highest $N_2O$ concentrations within the bulk of the HZ but may not contribute substantially to $N_2O$ emissions to the stream, at least within the constraints of our experimental setup.

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