

## THE ROLE OF HYPORHEIC PROCESSES ON CLIMATE CHANGE

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Streams and rivers represent the natural connectivity between terrestrial and marine environments through which solutes, nutrients, contaminants, and pathogens, move along both their surface and subsurface environments. In the recent decades, the importance of the subsurface environments, and particularly the benthic and hyporheic zones in contributing and controlling both water quantity and quality, has received more and more attention [see Boano et al., [1] and reference therein]. The benthic zone is the ecological region of the streambed located at the interface between water and sediment, where both aquatic fauna and flora can be found [2], [3]; while the hyporheic zone is the band of streambed material mainly saturated with stream water [see Tonina [4] and reference therein]. Field evidence confirm that within these surface and subsurface aquatic environments, the biogeochemical processes that control N cycle, contribute to the production of nitrous oxide, N<sub>2</sub>O, one of the most important greenhouse gas; which additionally is also responsible for stratospheric ozone destruction [5]. According to the IPCC report [6] CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>O account for the 94% of the global radiative forcing; with N<sub>2</sub>O that in terms of global warming potential (GWP) for the 100-year time horizon, is 300 times more potent (per molecule) than CO<sub>2</sub> [7]. Therefore, the role of riverine environments cannot be neglected in the perspective of characterizing their contribution on climate change. However, most of the available studies do not identify the linkage between hydro-morphological and biochemical characteristics of riverine environments on N<sub>2</sub>O emissions and very few provide predictive models at the regional and larger scales [8]–[10]. Here, we focused our attention on the contribution of riverine environments in controlling the fate of the dissolved inorganic nitrogen species (DIN) that enter within surface water in the form of ammonium (NH<sub>4</sub>) and nitrate (NO<sub>3</sub>) and are converted, mainly through microbially mediated processes of nitrification-denitrification, to N<sub>2</sub>O and dinitrogen (N<sub>2</sub>). We analyzed the production of N<sub>2</sub>O from riverine environments at different spatial scales (i.e., from local reach scale to global scale). Firstly, we characterized the local reach scale behavior under different streambed morphologies [11]–[13] considering also possible effects of streambed heterogeneity [14] and groundwater intrusion [14]. At this scale, the stream boundaries are extended beyond the surface water in order to include the interaction with benthic and hyporheic zones, but then in order to represent N<sub>2</sub>O emissions at the network scale we need to identify a framework able to account for local processes and at the same time based only on reach scale quantities.

The development of the upscaling procedure originates from the solution of the transport equation along each streamline that connect downwelling (i.e., the areas of the streambed where water enter within the hyporheic zone) and upwelling zones (i.e., the areas of the streambed where water exits from the hyporheic zone).

$$\frac{\partial C_i}{\partial t} + \frac{\partial C_i}{\partial \tau} = \frac{D_L}{u^2} \frac{\partial^2 C_i}{\partial \tau^2} \pm k_i C_i \quad (1)$$

where  $C_i$  is the concentration of the generic DIN species (i.e.  $i=1$  for NH<sub>4</sub>,  $i=2$  for NO<sub>3</sub>),  $\tau$  is the travel along the streamline,  $t$  is the current time,  $D_L$  is the longitudinal dispersion coefficient,  $u$  is the mean velocity along the streamline, and  $k_i$  is the generic first order reaction rate that can be seen as the inverse of the characteristic reaction time of the process analyzed (i.e.  $\tau_R$ ). Within Eq.(1): i) the space variable is replaced by the travel time ( $\tau$ ), ii) nitrification-denitrification processes are modeled by means of the first-order kinetics and iii) the transversal dispersion is neglected. Eq. (1) can be represented also in its dimensionless form:

$$\frac{\partial C_i^*}{\partial t^*} + \frac{\partial C_i^*}{\partial \tau^*} = \frac{1}{Pe} \frac{\partial^2 C_i^*}{\partial \tau^{*2}} \pm Da_{local} C_i^* \quad (2)$$

where  $C_i^* = C_i/C_{ri}$  (with  $C_{ri}$  a reference concentration of the  $i$ -th species),  $t^* = t/\tau_T$  and  $\tau^* = \tau/\tau_T$  (with  $\tau_T$  a reference time controlling the transport),  $Pe$  is the Péclet number ( $Pe = (\tau_T u) u/D_L$ ) and  $Da_{local}$  is the local Damköhler number (i.e., the ratio between the local travel time and the time of reaction:  $Da_{local} = \tau_T/\tau_R$ ). At the local scale, using this framework, we are able to track each particle from the entry points into the downwelling areas to the exit points at the upwelling area with the aim to characterize the travel time distribution (i.e. its probability density function - pdf), its cumulative density function (CDF) and the statistical parameters that control the shape of the distribution (mainly mean, median and variance) [15]. Within this framework, we can use the median hyporheic residence time ( $\tau_{50}$ ) as a characteristic time scale of transport ( $\tau_T$ ).  $\tau_{50}$  represents an “average reach behavior” and it is related to hydro-morphodynamic that controls the delivery of reactants to microbial assemblages and determines residence times for reactions to occur. Specializing Eq. (2) for denitrification (i.e., the conversion of  $NO_3$  to  $N_2O$  and  $N_2$ ), the characteristic time scale of reaction ( $\tau_R$ ) assumed equal along each streamline, can be seen as the time of denitrification:  $\tau_R = \tau_D$ . Consequently, we can define a denitrification Damköhler number representative of the reach ( $Da_D$ ) as the ratio between the characteristic time of transport ( $\tau_T = \tau_{50}$ ) and a characteristic time of reaction ( $\tau_R = \tau_D$ ).

To analyze the capability of this approach to represent real observations of  $N_2O$  emissions from streams and rivers, we analyzed available literature data and we observed that the trend of variation of the average  $N_2O$  emissions per unit area ( $FN_2O$ ,  $\mu gN_2O-N/m^2/d$ ) decrease according to the system size (represented as the mean width,  $W$ ) [16]. We capitalized on these results by assuming that this reduction is caused by a shift from  $N_2O$  production that occurs primarily in the hyporheic zone of small headwater streams ( $W < 10$  m) to  $N_2O$  production occurring mainly in the benthic zone for intermediate systems ( $10m < W < 175$  m) and directly within the water column in large rivers ( $W > 175m$ ). We assumed that this shift is caused by a reduction in hyporheic exchange rate with increasing stream/river discharge in favor of a major role played by the benthic zone and the water column as the stream/river size (i.e., mean width) increases. In headwater streams that are typically small and shallow, microbially mediated denitrification occurs mainly within the benthic–hyporheic zone. Headwater stream hydrodynamics at and within the streambed (hyporheic flows) is the main factor controlling the flux of dissolved nutrients to the microbial assemblages that control biogeochemical transformations. Here, the denitrification Damköhler number is defined as  $Da_D = \tau_{50}/\tau_D$ . In intermediate systems as stream size increases, the ratio of the hyporheic to surface flow declines, reducing the relative contribution of hyporheic zone to biogeochemical transformations, solely to its upper part: the benthic zone, maintaining  $Da_D = \tau_{50}/\tau_D$ . In rivers water column transformations combined with benthic processes at the sediment–water interface dominate denitrification, overwhelming the benthic–hyporheic contribution. To describe this behavior the characteristic time of transport is represented as the time of turbulent vertical mixing,  $t_m$ , which is the average time for any neutrally buoyant particle to sweep through the entire water column because of turbulence [17].  $t_m = D/(0.067(g \cdot D \cdot s_0))$  can be represented as a function of the mean flow depth,  $D$ , the stream slope,  $s_0$ , and the gravitational acceleration,  $g$ . According to this new formulation, we can define a denitrification Damköhler number valid for large rivers:  $Da_{DS} = t_m/\tau_D$ .

All these considerations are summarized within the process based model proposed by Marzadri et al. [16]:

$$\begin{cases} F^*N_2O_{HZ} = 1.55 \cdot 10^{-7} \cdot (Da_{D_{HZ}})^{0.43}, W \leq 10m \\ F^*N_2O_{BZ} = 1.91 \cdot 10^{-8} \cdot (Da_{D_{HZ}})^{0.58}, 10m < W \leq 175m \\ F^*N_2O_{WC} = 4.56 \cdot 10^{-6} \cdot (Da_{DS})^{0.72}, W > 175m \end{cases} \quad (3)$$

where  $F^*N_2O_{HZ}$ ,  $F^*N_2O_{BZ}$  and  $F^*N_2O_{WC}$  are the dimensionless fluxes of  $N_2O$  from the three different zones obtained as the ratio of the  $N_2O$  flux per unit area ( $FN_2O$ ) and the in-stream flux of DIN ( $F_{DIN} = V \cdot ([NO_3] + [NH_4])$ , with  $V$  the mean stream velocity). Consequently,  $FN_2O$  can be evaluated by multiplying its dimensionless value (from Eq (3)) by the in-stream flux of DIN ( $FN_2O_i = F^*N_2O_i \cdot F_{DIN}$ , with the sub-index  $i$  identifying HZ, BZ and WC, respectively depending on the reach size).

The developed model was tested considering available field data under mean annual streamflow [16], and N load conditions as well as under extreme events such as drought conditions [19]. The scalable nature of the proposed modeling approach has the potential to estimate  $N_2O$  emissions from streams and rivers based on easily retrievable stream flow and stream channel morphology datasets. The model input parameters can be measured in the field or derived, mainly for large scale applications, from available data through artificial intelligence techniques such as Machine Learning [18], [20].

Model outputs underline the importance of both surface and subsurface riverine environments in controlling the fate of dissolved inorganic nitrogen species and on the production of  $N_2O$ . Results of the proposed model will be

socially relevant to policy makers addressing elevated nitrogen concentrations in surface waters with potential applicability to land use, non-point source management, and river restoration projects. Furthermore, the obtained results will provide useful information to policy makers attempting to address global greenhouse gas emissions.

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