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Benthic nitrite exchanges in the Seine River (France): An early diagenetic modeling analysis

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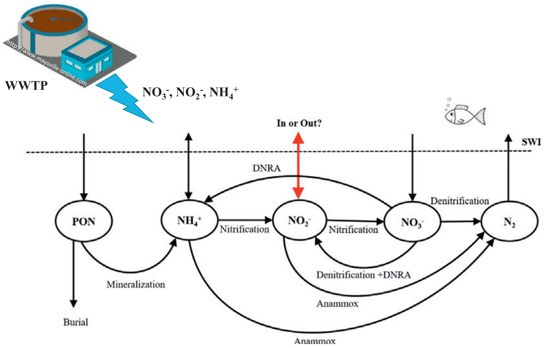
HIGHLIGHTS

- Elevated concentrations of nitrite (NO_2^-) are observed in the Seine River.
- Sediment cores were collected upstream and downstream of Paris's largest WWTP.
- Benthic fluxes of NO_2^-, NO_3^- and NH_4^+ were measured in core incubations.
- Pore water data and benthic fluxes were analyzed with a reactive transport model.
- Sediments act as source or sink of nitrite, depending on sampling location and time.

GRAPHICAL ABSTRACT



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ABSTRACT

Nitrite is a toxic intermediate compound in the nitrogen (N) cycle. Elevated concentrations of nitrite have been observed in the Seine River, raising questions about its sources and fate. Here, we assess the role of bottom sediments as potential sources or sinks of nitrite along the river continuum. Sediment cores were collected from two depocenters, one located upstream, the other downstream, from the largest wastewater treatment plant (WWTP) servicing the conurbation of Paris. Pore water profiles of oxygen, nitrate, nitrite and ammonium were measured. Ammonium, nitrate and nitrite fluxes across the sediment-water interface (SWI) were determined in separate core incubation experiments. The data were interpreted with a one-dimensional, multi-component reactive transport model, which accounts for the production and consumption of nitrite through nitrification, denitrification, anammox and dissimilatory nitrate reduction to ammonium (DNRA). In all core incubation experiments, nitrate uptake by the sediments was observed, indicative of high rates of denitrification. In contrast, for both sampling locations, the sediments in cores collected in August 2012 acted as sinks for nitrite, but those collected in October 2013 released nitrite to the overlying water. The model results suggest that the first step of nitrification generated most pore water nitrite at the two locations. While nitrification was also the main pathway consuming nitrite in the sediments upstream of the WWTP, anammox dominated nitrite removal at the downstream site. Sensitivity analyses indicated that the magnitude and direction of the benthic nitrite fluxes most strongly depend on bottom water oxygenation and the deposition flux of labile organic matter.

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1. Introduction

Humans have greatly modified the nitrogen (N) cycle, nearly doubling the inputs of bioavailable nitrogen to the environment (Gruber and Galloway, 2008). Excess nitrogen negatively impacts human and ecosystem health, causing eutrophication of aquatic ecosystems, decreasing air quality and contaminating drinking water supplies (Driscoll et al., 2003; Erisman et al., 2013; Ndegwa et al., 2008). The application of N-containing fertilizers and human wastewater release have been linked to the expansion of hypoxic and anoxic conditions in aquatic systems (Diaz and Rosenberg, 2008; Rabalais et al., 2010), while enhanced microbial nitrification and denitrification causes emission of nitrous oxide (N_2O), an important greenhouse gas (Crutzen et al., 2007).

Nitrate (NO_3^-) and nitrous oxide (N_2O) have received most attention as N contaminants. Strict nitrate water quality standards are in place in most developed countries (Oenema et al., 2011), while interest in N_2O emissions stems from concerns about accelerating climate change (e.g. Clough et al., 2006; Beaulieu et al., 2007; Rosamond et al., 2012). In comparison, relatively little research has been done on the intermediate species nitrite (NO_2^-). High nitrite concentrations in drinking water can cause serious illness in infants; shortness of breath and blue baby syndrome are some of the associated symptoms (Knobeloch et al., 2000). The maximum level of nitrite for drinking water set by the US Environmental Protection Agency is 1 ppm. Nitrite is also toxic to aquatic life (Cowling et al., 1998; Philips et al., 2002): according to the EU Water Framework Directive, the nitrite limit for good environmental status is 0.09 mg $N\text{-}NO_2^-\ L^{-1}$.

Nitrite is a reactive intermediate produced and consumed in several redox pathways of the N cycle (Kelso et al., 1997; Mordy et al., 2010). It is produced during the first steps of nitrification and denitrification from ammonium (NH_4^+) and nitrate (NO_3^-), respectively. Under oxic conditions, nitrite oxidizers consume NO_2^- producing nitrate as part of the overall nitrification process. Under reducing conditions, nitrite can be transformed to N_2 gas during denitrification or anammox, or to ammonium via dissimilatory nitrate reduction to ammonium (DNRA). In addition to biotic transformations, nitrite is chemically reactive (Udert et al., 2005). Thus, in general, nitrite concentrations in the environment are expected to be negligible. Nonetheless, accumulation of nitrite has been observed in rivers and streams. In particular, relatively high nitrite concentrations have been reported in various urbanized rivers, for instance the Lahn River in Germany (von der Wiesche and Wetzel, 1998), rivers of Northern Ireland (Kelso et al., 1997), and the Seine River in France (Garnier et al., 2006; Raimonet et al., 2015; Raimonet et al., 2017).

The Seine River receives large N inputs from diffuse agricultural and urban sources, as well as point sources, primarily waste water treatment plant (WWTP) discharges (Cébron and Garnier, 2005; Naeher et al., 2015; Raimonet et al., 2015; Raimonet et al., 2017). Downstream of the metropolitan area of Paris, the effluents from a very large WWTP, known by its acronym SAV (daily capacity of 1.7 M m^3), greatly impact the river water quality (Vilmin et al., 2014). Nitrogen pollution in the past was dominated by ammonium, resulting in nitrification and even anoxia in the water column (Cébron and Garnier, 2005; Chesterikoff et al., 1992; Garban et al., 1995). Upgrades to the SAV WWTP, with the introduction of treatment by nitrification and denitrification in 2007 and 2011, respectively, considerably decreased N loading to the river: ammonium discharges dropped from 58 ± 22 to 12 ± 17 t N d^{-1} (Aissa-Grouz et al., 2015). Nitrate concentrations in the river have remained elevated, however, mainly because of agricultural activity in the surrounding area. In addition, even after the improvements, nitrite concentrations in the outflow of the WWTP have remained above European water quality standards (Raimonet et al., 2017).

With an estimated daily loading of around 2.4 ± 2 tonnes NO_2-N (Aissa-Grouz et al., 2015), the WWTP is a major source of nitrite to the Seine River (Garnier et al., 2006; Raimonet et al., 2015). Surprisingly, elevated concentrations of nitrite persist for over 300 km downstream of Paris, despite fully oxic conditions along the river channel (Aissa-Grouz et al., 2015). Possible explanations include the sustained production of nitrite in the water column (Raimonet et al., 2015), or a continuous efflux of nitrite from streambed sediments. Benthic processes are known to have a significant impact on the water quality of aquatic systems in general (Han et al., 2014; Paraska et al., 2014; Thouvenot et al., 2007), and on the cycling of nitrogen in particular (Han et al., 2014). Fixed nitrogen is removed by sediments via permanent burial of organic nitrogen and clay-bound ammonium, as well as through denitrification or anammox, which return dinitrogen gas to the atmosphere. Alternatively, dissolved inorganic nitrogen species can be recycled to the water column following mineralization of deposited organic matter (Thamdrup and Dalsgaard, 2008).

Here, we present a preliminary assessment of the potential role of benthic nitrite exchanges in the Seine River: pore water and benthic flux measurements on sediments collected upstream and downstream of the SAV WWTP are analyzed quantitatively by developing and applying an early diagenetic model that includes a comprehensive representation of the benthic N cycle. Early diagenetic models simulate the coupled transport and transformation processes that affect the chemical species of interest below the sediment-water interface (SWI) (Boudreau, 1996). While these reactive transport models have been frequently used to interpret multicomponent data sets collected in marine and lacustrine sediments, applications to riverbed sediments remain limited. Paraska et al. (2014), who reviewed 83 early diagenetic modeling studies published since 1996, only report four studies on river sediments (Devallois et al., 2008; Massoudieh et al., 2010; Trinh et al., 2012; Van Den Berg et al., 2000).

Moreover, existing early diagenetic models representing N transformations rarely account for reactive intermediates in general, and nitrite in particular. A limited number of studies have analyzed nitrite pore water profiles using modeling. Stief et al. (2002) and Meyer et al. (2008), for example, measured nitrite pore water profiles in a freshwater mesocosm experiment and an estuarine sediment, respectively. In both studies, an inverse reaction-transport model was used to extract the depth distributions of nitrite production and consumption rates. Inverse modeling, however, is unable to predict how the rate distributions change under varying boundary conditions and transport regimes, in contrast to the forward reactive transport modeling used here. Box modeling approaches have also been used to estimate nitrite exchanges between streambed sediments and the overlying river (e.g., Aissa-Grouz et al., 2015; Raimonet et al., 2015; Vilmin et al., 2014), or to simulate nitrite production and consumption in sediments incubation experiments (e.g., Babbin and Ward, 2013). However, because box models do not predict spatial distributions they are not appropriate to analyze pore water profiles. Closest to our modeling approach is that of Dale et al. (2011) who developed a diagenetic model that includes nitrite as a reactive species and represents nitrification, denitrification, DNRA and anammox. This model was applied to a data set from a coastal marine site in the Baltic Sea.

In the present paper, we expand the reaction network for benthic N cycling in an existing early diagenetic computer code in order to explicitly include the reaction pathways producing and consuming nitrite. Reactive transport calculations are then used to interpret a data set