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Modelling the fate of nitrite in an urbanized river using experimentally obtained nitrifier growth parameters

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ABSTRACT

Maintaining low nitrite concentrations in aquatic systems is a major issue for stakeholders due to nitrite's high toxicity for living species. This study reports on a cost-effective and realistic approach to study nitrite dynamics and improve its modelling in human-impacted river systems. The implementation of different nitrifying biomasses to model riverine communities and waste water treatment plant (WWTP)-related communities enabled us to assess the impact of a major WWTP effluent on in-river nitrification dynamics. The optimal kinetic parameters and biomasses of the different nitrifying communities were determined and validated by coupling laboratory experiments and modelling. This approach was carried out in the Seine River, as an example of a large human-impacted river with high nitrite concentrations. The simulation of nitrite fate was performed at a high spatial and temporal resolution ($\Delta t = 10$ min, $\overline{dx} = 500$ m) including water and sediment layers along a 220 km stretch of the Seine River for a 6-year period (2007–2012). The model outputs were in good agreement with the peak of nitrite downstream the WWTP as well as its slow decrease towards the estuary. Nitrite persistence between the WWTP and the estuary was mostly explained by similar production and consumption rates of nitrite in both water and sediment layers. The sediment layer constituted a significant source of nitrite, especially during high river discharges (0.1–0.4 mgN h^{-1} m^{-2}). This points out how essential it is to represent the benthic layer in river water quality models, since it can constitute a source of nitrite to the water-column. As a consequence of anthropogenic emissions and in-river processes, nitrite fluxes to the estuary were significant and varied from 4.1 to 5.5 TN d^{-1} in low and high water discharge conditions, respectively, over the 2007–2012 period. This study provides a methodology that can be applied to any anthropized river to realistically parametrize autochthonous and WWTP-related nitrifier communities and simulate nitrite dynamics. Based on simulation analysis, it is shown that high spatio-temporal resolution hydro-ecological models are efficient to 1) estimate water quality criteria and 2) forecast the effect of future

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management strategies. Process-based simulations constitute essential tools to complete our understanding of nutrient cycling, and to decrease monitoring costs in the context of water quality and eutrophication management in river ecosystems.

1. Introduction

Along with the on-going improvement of nitrogen removal efficiency in Waste Water Treatment Plants (WWTPs), total nitrogen concentrations in WWTP effluents have been reduced (García-Barcina et al., 2006; Carey and Migliaccio, 2009; Rocher et al., 2011). Even though the total nitrogen load has decreased, nitrite concentrations can still exceed the European Water Framework Directive (EU WFD) standard of good environmental status of 0.09 mgN L^{-1} in urbanized river systems (Helder and De Vries, 1983; Morris et al., 1985; von der Wiesche and Wetzel, 1998; Garnier et al., 2006; Rocher et al., 2011), as well as in agricultural ecosystems (Corriveau et al., 2010). In these anthropogenic systems, concentrations are well above 0.01 mgN L^{-1} found in pristine streams (Meybeck, 1982). Compared to nitrate, nitrite is toxic at low concentrations. A well-known consequence of nitrite toxicity is the blue baby syndrome due to direct ingestion of nitrite or to conversion of ingested nitrate to nitrite (Knobeloch et al., 2000). Maintaining low nitrite concentrations is thus a major environmental issue. However, nitrite in rivers is rarely studied independently from nitrate, due to its much lower concentration.

The presence of nitrite in aquatic systems results from its production and persistence. Nitrite is an intermediate compound produced by nitrification, denitrification and/or dissimilatory nitrate reduction to ammonium pathways in water and sediment (Wilderer et al., 1987; Kelso et al., 1997; Philips et al., 2002; Park and Bae, 2009). Nitrification is a two-step process involving two distinct microbial communities. Ammonia oxidizers (AO) transform ammonia to nitrite, and nitrite oxidizers (NO) use nitrite and generate nitrate. Ammonia oxidation is generally considered to be the limiting step (Kowalchuk and Stephen, 2001) avoiding nitrite accumulation. However nitrite has been shown to persist in oxic river waters due to low water residence time, low nitrification rates, as well as similar ammonia and nitrite oxidation rates, or non steady-state nitrification (Brion et al., 2000; Philips et al., 2002). In oxic waters of large rivers, benthic exchanges of nitrogen at the sediment-water interface are expected to be low due to low surface-to-volume ratios (Pinay et al., 2002). Based on this general knowledge, nitrification in the water column is supposed to be the main process affecting nitrite production and consumption in large oxic rivers, especially in high river discharge conditions. Anyhow, nitrite can be produced in river bed sediments and transferred to the water column by diffusion (Morris et al., 1985; Kelso et al., 1997). It is important to quantify the impact of this benthic nitrite production on nitrogen cycling and export to estuaries in the case of large human impacted river systems.

WWTPs constitute a potential source of nutrients *e.g.* nitrite as well as microorganisms (nitrifiers included) to riverine waters, depending on the processing of the influent (Servais et al., 1999; Brion et al., 2000; Cébron et al., 2003). Species and activity of microorganims (nitrifiers included) present in WWTP effluents can differ from those found in the river upstream the effluent and alter the river ecological functioning (Goñi Urriza et al., 2000; Féray and Montuelle, 2002; Cébron et al., 2003). Consequently WWTP effluents potentially modify the nitrifying community structure and biomass, and sometimes lead to an increase in nutrient concentrations in river systems, even though treatment processes were significantly improved during the last decades. As a potential consequence, nitrifying kinetics and nitrite dynamics within the aquatic system are impacted.

Models constitute efficient integrative tools to study spatio-temporal variations of nitrogen dynamics in rivers and improve our understanding of in-river biogeochemical cycling. Many hydro-ecological models of different complexity are available (Rauch et al., 1998; Reichert, 2001; Arheimer and Olsson, 2003; Cox, 2003; Kannel et al., 2011; Sharma and Kansal, 2013). They tend to simulate a large range of biogeochemical processes, requiring a large number of parameters. However, not all models represent nitrite as an intermediate between the 2-step nitrifying process, and even less models consider explicitly the involved nitrifier biomasses. These models can be used to simulate average nitrite profiles at a pluri-annual time scale (Garnier et al., 2007), or to simulate nitrite dynamics at a high resolution along small river stretches and for a short period of time (Reichert, 2001). To our knowledge, no former study focused on nitrite dynamics at a high spatio-temporal resolution, and at large spatio-temporal scales.

The aim of our study is to propose a cost-effective and realistic approach to study nitrification dynamics and improve the modelling of nitrogen species (and especially nitrite) in human-impacted river systems. The Seine River is a pertinent study case for this purpose, as this river receives effluents from the biggest European WWTP (called SAV for "Seine AVal"), and is characterized by high nitrite concentrations, exceeding the good EU WFD criteria downstream this WWTP (Rocher et al., 2011). Nitrogen removal in the SAV WWTP has significantly increased since the addition of nitrification and denitrification units in 2007, and changed the nitrogen dynamics in the Seine River (Rocher et al., 2011). These modifications most likely changed kinetic parameters of nitrifying communities in the SAV effluent, as well as the subsequent nitrite dynamics within the Seine River downstream SAV.

The originality of this study is the distinction between natural river and WWTP nitrifying communities. The biomass