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Atmospheric nitrate export in streams along a montane to urban gradient

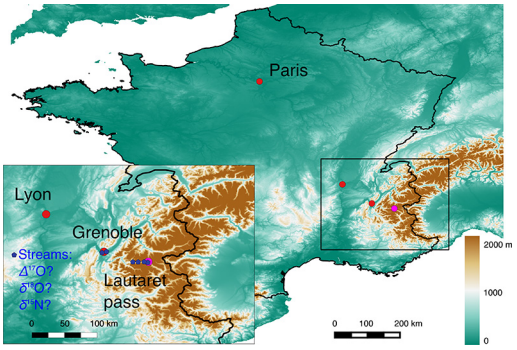
Ilann Bourgeois [a,b,*], Joel Savarino [a], Julien Némery [a], Nicolas Caillon [a], Sarah Albertin [a], Franck Delbart [c], Didier Voisin [a], Jean-Christophe Clément [b,d]

[a] Université Grenoble Alpes, CNRS, IRD, Grenoble INP [1], IGE, F-38000 Grenoble, France
[b] Université Grenoble Alpes, CNRS, LECA, F-38000 Grenoble, France
[c] Université Grenoble Alpes, CNRS, SAJF, F-38000 Grenoble, France
[d] Université Savoie Mont Blanc, INRA, CARRTEL, F-74200 Thonon-Les Bains, France

HIGHLIGHTS

- How is nitrogen deposition reflected in streams NO_3^- exports in the French Alps?
- NO_3^- exports in 7 streams along an altitude gradient were monitored for two years.
- NO_3^- isotopic composition ($\Delta^{17}O$, $\delta^{15}N$, $\delta^{18}O$) was analyzed to apportion the sources.
- ≤21% of NO_3^- in montane streams and 5% in urban streams was unprocessed $NO_3^-{}_{atm}$.
- Nitrification of atmospheric and microbial NH_4^+ was the main NO_3^- source in streams.

GRAPHICAL ABSTRACT



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ABSTRACT

Nitrogen (N) emissions associated with urbanization exacerbate the atmospheric N influx to remote ecosystems – like mountains –, leading to well-documented detrimental effects on ecosystems (*e.g.*, soil acidification, pollution of freshwaters). Here, the importance and fate of N deposition in a watershed was evaluated along a montane to urban gradient, using a multi-isotopic tracers approach ($\Delta^{17}O$, $\delta^{15}N$, $\delta^{18}O$ of nitrate, $\delta^{2}H$ and $\delta^{18}O$ of water). In this setting, the montane streams had higher proportions of atmospheric nitrate compared to urban streams, and exported more atmospheric nitrate on a yearly basis (0.35 *vs* 0.10 kg-N ha^{-1} yr^{-1}). In urban areas, nitrate exports were driven by groundwater, whereas in the catchment head nitrate exports were dominated by surface runoff. The main sources of nitrate to the montane streams were microbial nitrification and atmospheric deposition, whereas microbial nitrification and sewage leakage contributed most to urban streams. Based on the measurement of $\delta^{15}N$ and $\delta^{18}O$-NO_3^-, biological processes such as denitrification or N assimilation were not predominant in any streams in this study. The observed low $\delta^{15}N$ and $\delta^{18}O$ range of terrestrial nitrate (*i.e.*, nitrate not coming from atmospheric deposition) in surface water compared to literature suggests that atmospheric deposition may be underestimated as a direct source of N.

* Corresponding author now at: Cooperative Institute for Research in Environmental Sciences, University of Colorado at Boulder, Boulder, Colorado, USA. Earth System Research Laboratory, NOAA, Boulder, Colorado, USA.
E-mail address: ilann.bourgeois@noaa.gov (I. Bourgeois).
[1] Institute of Engineering Univ. Grenoble Alpes.

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1. Introduction

Atmospheric nitrogen (N) deposition has increased 10-fold over the past century, increasingly contributing to the global N availability (Galloway et al., 2004). Anthropogenic activities such as fossil-fuel combustion, agriculture, and fertilizers use are responsible for this increase (Fowler et al., 2015; Galloway et al., 2008; Vitousek et al., 1997), with impacts observed in remote ecosystems (Hastings et al., 2009; Holtgrieve et al., 2011; Preunkert, 2003). High N loading to the environment has been documented for many ecosystems (Aber et al., 1989; Clark et al., 2017; Elser et al., 2009; Matson et al., 2002). To address this issue, global efforts are underway to alleviate N inputs into ecosystems, aiming at "minimizing the consequent harm to humans and the environment" (International Nitrogen Initiative, http://www.initrogen.org). Nitrate (NO_3^-) concentrations, and fluxes in soils and streams, have often been used to assess the N saturation status in watersheds (Aber et al., 1989; Baron and Campbell, 1997; Lovett and Goodale, 2011). However, N exports in streams depend on multiple parameters such as basin topography (Balestrini et al., 2013; Clow and Sueker, 2000), land-cover (Barnes et al., 2014; Williams et al., 2016) and land-management (Barnes and Raymond, 2010; Burns et al., 2009; Lefebvre et al., 2007). As streams integrate many processes at the watershed scale, understanding the specific sources of NO_3^- is necessary to (1) evaluate the respective contribution of natural and anthropogenic sources, (2) clarify the fate of deposited N in the environment, and (3) understand the origin and the development of N saturation.

Mountainous ecosystems are particularly sensitive to increased N inputs by atmospheric deposition (Baron et al., 2000, 2005, 2011), as they are historically N-limited (Kaye and Hart, 1997). Critical N loads for these ecosystems are among the lowest for pristine environments (Baron et al., 2011; Bowman et al., 2006; Nanus et al., 2017), making them vulnerable to long-range transport of atmospheric N emitted from distant sources (Mast et al., 2014; Wasiuta et al., 2015). Atmospheric deposition of N has been shown to contribute significantly, either directly or indirectly, to year-round NO_3^- exports from mountainous catchments (Hundey et al., 2016; Nanus et al., 2008), typically showing a pulse at spring as soils subsurface NO_3^- reservoirs are flushed by snowmelt water (Kendall et al., 1995; Williams et al., 2009; Williams and Melack, 1991).

Atmospheric deposition is also a major source of N to urban areas, which receive much higher loads than adjacent environments (Bettez and Groffman, 2013; Fang et al., 2011; Hall et al., 2014; Rao et al., 2014; Templer et al., 2015). Local and regional emissions and subsequent deposition of fuel-combustion derived NO_x and ammonia (NH_3) are responsible for this pattern (Galloway et al., 2004; Kean et al., 2000). NO_x compounds are oxidized into NO_3^- within hours (Beirle et al., 2011), then scavenged from the atmosphere by wet and dry deposition (Hertel et al., 2012). In the atmosphere, NH_3 is in equilibrium with ammonium (NH_4^+), the other primary component of bulk N deposition. Because of the particular topography of urban basins (extended impervious surface, rapid precipitation runoff), urbanization can lead to high NO_3^- exports in freshwater bodies (Groffman et al., 2004; Riha et al., 2014), with major ecological, economic and health consequences (Dodds et al., 2009).

A number of previous studies have used the dual isotope approach ($\delta^{18}O$ and $\delta^{15}N$ of NO_3^-) to track the spatio-temporal variability of sources contribution to NO_3^- pools in a large variety of environmental matrixes (Campbell et al., 2002; Durka et al., 1994; Elliott et al., 2009; Yang and Toor, 2016). Biochemical processes such as denitrification or assimilation have also been shown in laboratory experiments to distinguishably enrich residual NO_3^- in heavier isotopes, here ^{15}N and ^{18}O (Granger et al., 2004, 2010; Treibergs and Granger, 2017), although this enrichment can be diluted by newly nitrified NO_3^- with low N and O isotopic values (Granger and Wankel, 2016; Mayer et al., 2002). Environmental studies also reported characteristic NO_3^- isotopic enrichment for denitrification (Clément et al., 2003; Fang et al., 2015; Wexler et al., 2014), assimilation (Emmerton et al., 2001; Estrada et al., 2017; Liu et al., 2013b) or photolysis (Frey et al., 2009; Shi et al., 2015; Ye et al., 2016). However, the isotopic fingerprint of biological processes can lead to inaccurate NO_3^- source apportionment in some cases, especially in delineating the respective contribution of the microbial and the atmospheric sources (Michalski et al., 2004; Riha et al., 2014; Rose et al., 2015b). In the past few years, a growing number of studies have used an isotopic particularity of $NO_3^-{}_{atm}$ to quantify the contribution of atmospheric deposition to terrestrial N pools (Costa et al., 2011; Hundey et al., 2016; Tsunogai et al., 2014). $NO_3^-{}_{atm}$ is enriched in ^{17}O due to its production pathways (*i.e.*, oxidation of NO_x by O_3), showing a deviation from the Terrestrial Fractionation Line (Thiemens, 2006). $\Delta^{17}O$ is a quantification of this deviation, calculated as $\Delta^{17}O = \delta^{17}O - 0.52 * \delta^{18}O$ in the present work. $\Delta^{17}O$ value of $NO_3^-{}_{atm}$ generally ranges between 20 and 35‰ in temperate latitudes (Morin et al., 2009; Savarino et al., 2007), whereas $\Delta^{17}O$ value of NO_3^- from all other sources (industrial fertilizers, nitrification) or of biologically processed $NO_3^-{}_{atm}$, is 0‰ (Michalski et al., 2004, 2015). Because NO_3^- loss processes (*i.e.*, denitrification, assimilation or photolysis) obey the mass-dependent fractionation law, $\Delta^{17}O$-NO_3^- can be used as a conservative tracer of $NO_3^-{}_{atm}$ in the environment and help to better estimate $NO_3^-{}_{atm}$ contribution to streams NO_3^- pool (Michalski et al., 2004).

This study evaluates how atmospheric deposition of N contributes to NO_3^- exports in several streams along a montane to urban gradient in the French Alps. Isotopic ($\Delta^{17}O$, $\delta^{15}N$, $\delta^{18}O$ of nitrate, δ^2H and $\delta^{18}O$ of water) and *in situ* hydro-chemical techniques were combined to evaluate the drivers of NO_3^- inputs and removal in all streams. The first hypothesis was that due to a higher contribution from other sources (*e.g.*, sewage, fertilizers) in urban areas compared to the mountains, coupled with higher local atmospheric N inputs, total NO_3^- and atmospheric nitrate ($NO_3^-{}_{atm}$) exports should increase along the gradient. The second hypothesis was that different $NO_3^-{}_{atm}$ export dynamics should be observed in urban streams compare to montane streams, due to different hydrological drivers that need to be determined. To test these hypotheses, (1) NO_3^- concentration and its isotopic composition were determined in six streams and one reservoir, ranging from 2000 m above sea level (a.s.l.) to 200 m (a.s.l.) in the French Alps, and the annual export fluxes of $NO_3^-{}_{atm}$ and total NO_3^- were compared across sites along the gradient, (2) the drivers of the seasonal variability in $NO_3^-{}_{atm}$ proportion were identified and (3) the additional sources of NO_3^- in each watershed were determined.

2. Methods

2.1. Study site and selected streams

The Romanche Valley, located in the central French Alps, spreads from the Lautaret pass (2058 m a.s.l.) down to Grenoble (250 m a.s.l.) (Fig. S1). The Grenoble conurbation counts around 500,000 inhabitants, and is the biggest alpine metropolis in France.

Six streams and one reservoir were sampled from the Lautaret pass to Grenoble, draining watersheds with distinct geomorphic and biogeographic characteristics (Table 1). Two alpine streams were sampled at ~2000 m a.s.l.. These drain the South exposed side of the Lautaret pass (S-upper montane) and the North exposed side (N-upper montane), where for the latter the stream is mainly fed by glacier melt (Fig. S1d). The mid montane stream was sampled at ~1600 m a.s.l., 6 km down from the Lautaret pass (Fig. S1d). All three streams are tributaries of Romanche (lower montane stream) that was sampled 15 km down from the Lautaret pass at ~1000 m a.s.l., before ending in the Chambon Reservoir (Fig. S1c). The reservoir (~900 m a.s.l.) is artificial and it is managed by the French national electricity company (EDF), 21 km down from the Lautaret pass. The two urban streams (~210 m a.s.l.) were located, for one, upstream from Grenoble main urbanized area (upper urban stream) and, for the other, downstream (lower urban stream), and were separated by 8 km (Fig. S1c). The lower urban stream