Science of the Total Environment 615 (2018) 773–783

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

# Tomography of anthropogenic nitrate contribution along a mesoscale river

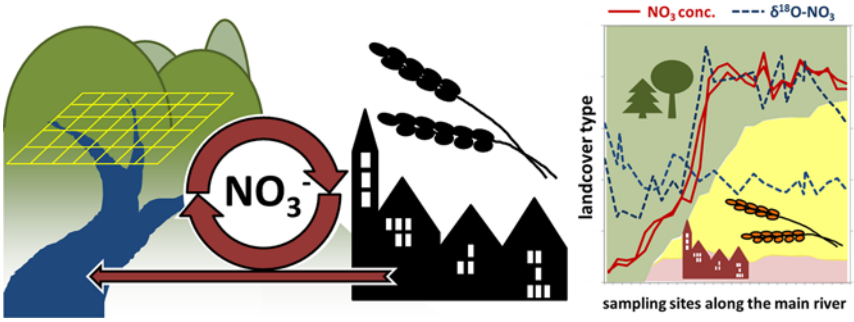
Christin Müller [a,*], Andreas Musolff [b], Ulrike Strachauer [c], Mario Brauns [c], Larisa Tarasova [a], Ralf Merz [a], Kay Knöller [a]

[a] *Helmholtz Centre for Environmental Research – UFZ, Department Catchment Hydrology, Theodor-Lieser-Straße 4, 06120 Halle, Germany*
[b] *Helmholtz Centre for Environmental Research – UFZ, Department of Hydrogeology, Permoserstr. 15, 04318 Leipzig, Germany*
[c] *Helmholtz Centre for Environmental Research – UFZ, Department of Aquatic Ecosystem Analysis, Brückstr. 3a, 39114 Magdeburg, Germany*

## HIGHLIGHTS

- Spatially highly resolved water quality was evaluated along a meso-scale river.
- Systematic changes in $NO_3^-$ concentrations and isotope signature were observed along the river.
- Agricultural land use and treated wastewater were the main sources of $NO_3^-$.
- Isotope signature and concentration of agricultural $NO_3^-$ hardly varied over time.
- Wastewater sources spatiotemporally changed isotope signature in the river.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

*Article history:*
Received 19 May 2017
Received in revised form 7 September 2017
Accepted 27 September 2017
Available online xxxx

Editor: Ouyang Wei

*Keywords:*
Nitrogen isotope of nitrate
Meso-scale isotope pattern
Nitrate pollution
Surface water
Water quality

## ABSTRACT

Elevated nitrate concentrations are a thread for water supply and ecological integrity in surface water. Nitrate fluxes obtained by standard monitoring protocols at the catchment outlet strongly integrate spatially and temporally variable processes such as mobilization and turnover. Consequently, inference of dominant nitrate sources is often problematic and challenging in terms of effective river management and prioritization of measures. Here, we combine a spatially highly resolved assessment of nitrate concentration and fluxes along a mesoscale catchment with four years of monitoring data at two representative sites. The catchment is characterized by a strong land use gradient from pristine headwaters to lowland sub-catchments with intense agricultural land use and wastewater sources. We use nitrate concentrations in combination with hydrograph separation and isotopic fingerprinting methods to characterize and quantify nitrate source contribution.

The hydrological analysis revealed a clear dominance of base flow during both campaigns. However, the absolute amounts of discharge differed considerably from one another (outlet: 1.42 $m^3 s^{-1}$ in 2014, 0.43 $m^3 s^{-1}$ in 2015). Nitrate concentrations are generally low in the pristine headwaters (<3 $mg L^{-1}$) and increase downstream (15 to 16 $mg L^{-1}$) due to the contribution of agricultural and wastewater sources. While the agricultural contribution did not vary in terms of nitrate concentration and isotopic signature between the years, the wastewater contribution strongly increased with decreasing discharge. Wastewater-borne nitrate load in the entire catchment ranged between 19% (2014) and 39% (2015). Long-term monitoring of nitrate concentration and isotopic composition in two sub-catchments exhibits a good agreement with findings from spatially monitoring. In both datasets, isotopic composition indicates that denitrification plays only a minor role. The spatially highly resolved

---

* Corresponding author.
*E-mail address:* christin.mueller@ufz.de (C. Müller).

https://doi.org/10.1016/j.scitotenv.2017.09.297

monitoring approach helped to pinpoint hot spots of nitrate inputs into the stream while the long-term information allowed to place results into the context of intra-annual variability.

## 1. Introduction

Nitrate concentrations in surface and groundwater ecosystems have increased in recent decades due to land use change and accompanying application of fertilizer in agriculture as well as from fossil fuel combustion and subsequent atmospheric deposition (Galloway et al., 2003; Pattinson et al., 1998; Zweimüller et al., 2008). Although since the 1980s, nitrogen oxide and ammonia emissions in Europe declined by 49% and 18%, respectively (Hettelingh et al., 2014), inputs especially from agricultural fertilizers are still high (Federal Ministry for the Environment and Federal Ministry of Food, 2012) resulting in water quality deterioration in groundwater and surface water (Altman and Parizek, 1995; Sebilo et al., 2003; Wassenaar, 1995) and are a major control of eutrophication, especially for coastal environments (Decrem et al., 2007; Prasuhn and Sieber, 2005). Moreover, nitrate increases primary production and has the ability to change food web structures of riverine and coastal ecosystems (Howarth et al., 1996; Turner and Rabalais, 1991). Similarly, elevated nitrate concentrations are the cause for the bad chemical status of 26% of all groundwater bodies in Germany (Völker et al., 2016). In 2016, the European Commission filed a law suit against the German Federal Government related to constantly elevated nitrate concentrations in groundwater (ZEIT-ONLINE, 2016). Existing and partly legally binding targets failed for river and lake protection, air quality control and natural conservation. In a report from the German Advisory Council on the Environment (SfU, 2015) 40 proposed measures coping with nitrate as an environmental pollutant were listed. To draft an amendment for a fertilization ordinance regulating the application of manure and fermentation waste products and to implement a pollution tax for nitrate surplus from agricultural practice are two of the highest priorities. To make effective use of these measures, it is important to characterize and quantify potential nitrate sources and in-stream nitrate processing and its controls in individual catchments. Different sources of nitrate are often characterized by individual isotopic signatures that can be used as fingerprints for source delineation or process mapping in hydrological systems (Rock and Mayer, 2004; Xue et al., 2009). For instance, atmospheric $NO_3^-$, nitrified soil nitrogen can be distinguished from synthetic fertilizer by its distinct nitrate isotopic signatures (Aravena et al., 1993; Kendall and McDonnell, 1998; Wassenaar, 1995). However, a clear isotope-based distinction between different sources is not always possible. Sometimes N and O isotope signatures overlap as observed for $NO_3^-$ from animal manure and wastewater effluents (Aravena et al., 1993). Therefore, a combination of stable isotope information with other environmental tracers (i.e. chloride, bromide, manganese, ammonium and iron) (Altman and Parizek, 1995; Mengis et al., 1999) as well as a land use analysis (Mueller et al., 2016; Nestler et al., 2011) can enhance the ability to describe the origin of nitrate. To characterize the mobilization of different nitrate pools, it is also important to investigate discharge and corresponding nutrient loads during different seasonal discharge scenarios. High seasonal and interannual variations in discharge and nutrient flows are associated with changing landuse patterns (Klose et al., 2012). Fairbairn et al. (2016) investigated micropollutants in a small watershed under different seasonal and hydrological conditions. They found out that agricultural herbicides showed the highest loadings during increased flows. In agriculturally-influenced prairie streams, Kemp and Dodds (2001) found out that nitrate concentrations are negatively correlated with discharge. Therefore, hydrological effects can have various impacts on the water quality of the gaining stream.

The objective of this study is to apply a fingerprint monitoring method to assess spatial and temporal variability of nitrogen sources within a mesoscale river catchment. The studied Holtemme catchment represents a blueprint example of pristine mountainous headwaters and agricultural as well as urban impacts in the downstream parts. The novelty of this study is the combination of spatially highly resolved assessments along the river with a longer-term monitoring in typical land use types: More specifically, two spatially highly resolved snapshot monitoring campaigns were conducted in October 2014 and 2015 during comparable hydrological base flow conditions. Sampling included 27 points within the river, 12 tributaries and two wastewater treatment plants. We measured nitrate isotopic compositions in concert with major ion concentrations and discharge to differentiate the impact of different nitrate sources and to quantify nitrate loads. This data is combined with a multi-annual, monthly monitoring at two stations representing undisturbed and agricultural land use sites. With this concept, we aim at identifying critical spatial areas as well as seasonal variations of nitrate related aspects of the water quality at catchment scale.

## 2. Study area

### 2.1. General information

The Holtemme River is a major tributary of the Bode River in the Harz Mountains, Germany (Fig. 1). The stream is part of the Terrestrial Environmental Observatories' (TERENO) network and therefore one of the best equipped regions for Meteorology and Hydrology in Central Germany (Wollschläger et al., 2016; Zacharias et al., 2011). The Holtemme basin has a total size of 282 km$^2$ (Mueller et al., 2015) and a mean annual discharge (MQ) at the outlet of 1.55 m$^3$ s$^{-1}$ (1982–2013), monitored by the State Office of Flood Protection and Water Management (LHW) Saxony-Anhalt. The long-term mean precipitation between the mountainous region and the lowlands varies between 1951 and 2015 from 1262 mm to 614 mm (Rauthe et al., 2013). The length of the river is 47 km and the altitude range is from 862 m a.s.l. at the headwaters to 85 m a.s.l. at the river mouth. The Holtemme River extends from the Harz Mountains in the south to the beginning of the Central German Lowlands and Magdeburger Börde (one of the most fertile agricultural areas in Germany) in the north (Wollschläger et al., 2016). The investigated area is dominated by Mesozoic rocks which are covered by Tertiary and Quaternary sediments (Schuberth, 2008). Intensively used agricultural land and non-irrigated arable land is the dominant land use type with a total area of 173.5 km$^2$ (61.6% of the entire Holtemme catchment area) in the middle and northern region of the river basin (Fig. 1). The mountainous southern region is mainly covered by coniferous forest with an area of 82.1 km$^2$ (29.2% of the total Holtemme catchment). Two waste water treatment plants (WWTP) are located in the catchment collecting the waste water from the major towns (Wernigerode and Halberstadt) and their surroundings; one in Silstedt (WWTP I) and one in Halberstadt (WWTP II) (observation points 16 and 29 in Fig. 1, respectively). Both WWTP's are connected to a combined and a separated collection system, respectively. During extreme rain events WWTP II has an overflow into the Holtemme River. The capacities of the WWTPs are shown in Table 1. The untreated water shows $NH_4$-N between 30 and 50 mg L$^{-1}$, $N_{ges}$-N between 60 and 80 mg L$^{-1}$. The limits for water discharged from the WWTPs to the Holtemme River are set for ammonium ($NH_4$-N) to 10 mg L$^{-1}$ and for total nitrogen ($N_{ges}$-N) to 18 mg L$^{-1}$. The WWTP II