

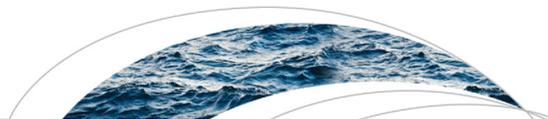
## ***Original***

Kunz, V.; Hensley, R.; Brase, L.; Borchardt, D.; Rode, M.:  
**High frequency measurements of reach scale nitrogen uptake in a fourth  
order river with contrasting hydromorphology and variable water  
chemistry (Weiße Elster, Germany).**

In: Water Resources Research. Vol. 53 (2017) 1, 328 - 343.

First published online by AGU: 22.12.2016

<https://dx.doi.org/10.1002/2016WR019355>



## RESEARCH ARTICLE

10.1002/2016WR019355

### Key Points:

- Quantitative measurements of NO<sub>3</sub> uptake using high-frequency sensors in higher order rivers
- Way-paving concept for future use of sensors in nutrient research and water quality monitoring
- Main restrictions: Quantify dynamics of additional N sources other than NO<sub>3</sub>

### Supporting Information:

- Supporting Information S1
- Data Set S1
- Data Set S2

### Correspondence to:

J. V. Kunz,  
vanessa.kunz@ufz.de

### Citation:

Kunz, J. V., R. Hensley, L. Brase, D. Borchardt, and M. Rode (2017), High frequency measurements of reach scale nitrogen uptake in a fourth order river with contrasting hydromorphology and variable water chemistry (Weiße Elster, Germany), *Water Resour. Res.*, 53, 328–343, doi:10.1002/2016WR019355.

Received 16 JUN 2016

Accepted 9 DEC 2016

Accepted article online 22 DEC 2016

Published online 13 JAN 2017

# High frequency measurements of reach scale nitrogen uptake in a fourth order river with contrasting hydromorphology and variable water chemistry (Weiße Elster, Germany)

Julia Vanessa Kunz <sup>1</sup>, Robert Hensley <sup>2</sup>, Lisa Brase <sup>3</sup>, Dietrich Borchardt <sup>1</sup>, and Michael Rode <sup>1</sup>

<sup>1</sup>Helmholtz Centre for Environmental Research UFZ, Magdeburg, Germany, <sup>2</sup>University of Florida, School of Forest Resources and Conservation, Gainesville, Florida, USA, <sup>3</sup>Helmholtz Centre Geesthacht HZG, Geesthacht, Germany

**Abstract** River networks exhibit a globally important capacity to retain and process nitrogen. However direct measurement of in-stream removal in higher order streams and rivers has been extremely limited. The recent advent of automated sensors has allowed high frequency measurements, and the development of new passive methods of quantifying nitrogen uptake which are scalable across river size. Here we extend these methods to higher order streams with anthropogenically elevated nitrogen levels, substantial tributaries, complex input signals, and multiple N species. We use a combination of two station time-series and longitudinal profiling of nitrate to assess differences in nitrogen processing dynamics in a natural versus a channelized impounded reach with WWTP effluent impacted water chemistry. Our results suggest that net mass removal rates of nitrate were markedly higher in the unmodified reach. Additionally, seasonal variations in temperature and insolation affected the relative contribution of assimilatory versus dissimilatory uptake processes, with the latter exhibiting a stronger positive dependence on temperature. From a methodological perspective, we demonstrate that a mass balance approach based on high frequency data can be useful in deriving quantitative uptake estimates, even under dynamic inputs and lateral tributary inflow. However, uncertainty in diffuse groundwater inputs and more importantly the effects of alternative nitrogen species, in this case ammonium, pose considerable challenges to this method.

## 1. Introduction

Nearly 200 Tg-N (200 billion kg) of reactive nitrogen (N) is added worldwide to the land surface every year for agricultural purposes, with only a small fraction being assimilated by crops [Böhlke *et al.*, 2009; Galloway *et al.*, 2003]. While the majority returns to the atmosphere via soil denitrification, a substantial fraction of terrestrial N loads, roughly 25%, ultimately enter into river drainage networks [Galloway *et al.*, 2003; Gruber and Galloway, 2008], resulting in widespread cultural eutrophication of downstream water bodies [Böhlke *et al.*, 2009; Smith *et al.*, 2006]. However, far from being nonreactive conduits, river networks exhibit a remarkable capacity to process and remove N in-transit [Galloway *et al.*, 2003]. Models suggest that up to 70% of N inputs may be removed during transport through river networks [Garcia-Ruiz *et al.*, 1998; Seitzinger, 1988; Seitzinger *et al.*, 2002; Wollheim *et al.*, 2008].

Despite their importance in global N cycling, direct methods of quantifying in-stream removal in defined reaches have largely been limited to small streams [Ensign and Doyle, 2006; Hall *et al.*, 2013; Tank *et al.*, 2008; Wollheim *et al.*, 2006]. For rivers, active methods such as isotope addition [Dodds *et al.*, 2000; Ruehl *et al.*, 2007], plateau enrichment [Mulholland *et al.*, 2002; Wollheim *et al.*, 2008] or even pulse enrichment [Tank *et al.*, 2008; Covino *et al.*, 2010] are commonly impracticable due to the large masses needed to achieve detectable signals. Prior to the advent of high-resolution, high frequency sensors, inferring reliable uptake rates from a passive mass balance approach was typically not feasible because analytical precision was too low and effects of errors in discrete samples too high [Rode and Suhr, 2007]. Other passive methods, like naturally abundant isotope fractionation may identify presence of removal processes, but not quantitative estimates of uptake rates [Bartoli *et al.*, 2012; Cohen *et al.*, 2012]. Thus, until recently, uptake rates in larger rivers have largely been estimated using models which scale up observations from smaller streams

[Wollheim *et al.*, 2006]. The resulting high degree of uncertainties represented a substantial knowledge gap on real uptake quantities in higher order streams [Böhlke *et al.*, 2009].

The expanding availability of high-frequency, high-resolution stream solute signals from automated sensors [Kirchner *et al.*, 2004; Pellerin *et al.*, 2009; Saraceno *et al.*, 2009; Rode *et al.*, 2016b], has allowed development of new passive methods of inferring uptake rates which scale across river size. Heffernan and Cohen [2010] demonstrated how uptake rates could be calculated from high temporal resolution time-series profiles. This method allows partitioning of N removal into assimilatory and dissimilatory pathways. Hensley *et al.* [2014] demonstrated an alternative approach using highly temporally and spatially resolved longitudinal profiling which allows for the detection of uptake “hotspots.” This method also enables the identification of potential sources of dilution or enrichment from lateral inputs which might be misinterpreted as biogeochemical uptake or release when taking a black box approach to reach-scale processing. However, these initial studies took place within very specific study sites, spring-fed rivers, which are fundamentally different from most other river reaches in several ways. The goal of this study was to extend existing methods to higher order streams with anthropogenically elevated N levels, substantial tributaries, complex input signals, and multiple N species.

Springs integrate catchment dynamics over long time scales, producing temporal stability in stream hydraulic parameters such as discharge, stage and residence time, as well as water chemistry [Heffernan *et al.*, 2010]. Adaptations to the methodology [Hensley *et al.*, 2015] allowed its application to tidal-spring run, where these properties varied over a well-defined frequency. However in most river systems hydraulics and stream water chemistry, two primary drivers of N retention rates [Dodds *et al.*, 2002; Hall *et al.*, 2009; Mulholland *et al.*, 2002], are much more dynamic. Another major challenge, new in the application presented here was the presence of multiple N-species. In rivers where these methods have previously been applied, ammonium ( $\text{NH}_4^+$ ) was below detection limits [Heffernan *et al.*, 2010], such that N uptake estimates could be derived from measurement of a single species: nitrate ( $\text{NO}_3^-$ ). Furthermore because rates of denitrification and assimilatory uptake exceeded rates of nitrification by several orders of magnitude [Cohen *et al.*, 2012], assumptions made about the time-varying nature of nitrification [Grimm and Petrone, 1997; Gücker and Pusch, 2006; Strauss *et al.*, 2004] were not as critical. We expected that additional  $\text{NH}_4^+$  loading might confound quantification of N uptake using  $\text{NO}_3^-$  alone, and that production of  $\text{NO}_3^-$  through nitrification might bias estimates of denitrification rates. In this study we evaluated how far  $\text{NO}_3^-$  sensor signals can be used to interpret overall N dynamics when other N species are also present. We hypothesized that a combination of above mentioned methods and concurrent assessment of autotrophic primary production, ecosystem respiration and estimation of autotrophic N demand from concurrent dissolved oxygen time series would enable differentiation between different N processing pathways.

The morphology and vegetative characteristics of rivers where the method has previously been applied were also relatively constant [Hensley and Cohen, 2012], and spatial variability in processing rates relatively small [Hensley *et al.*, 2014]. In other river systems, particularly those subject to anthropogenic modifications, these properties are expected to vary substantially. One extreme example of anthropogenic modifications is river channelization, which may substantially impact nutrient processing dynamics [Laub and Palmer, 2009; O'Connor and Hondzo, 2008]. Natural rivers are assumed to have a higher  $\text{NO}_3^-$  removal capacity than modified systems [Kemp and Dodds, 2002; Opdyke *et al.*, 2006; Boyacioglu *et al.* 2012] and restoration efforts can have a positive effect on nitrogen uptake [Bukaveckas, 2007; Stanley and Doyle, 2002]. Channelization shortens water residence time, one of the primary predictors of N retention [Seitzinger *et al.*, 2002; Wollheim *et al.*, 2006]. Concrete filling of river beds inhibits the rooting of vegetation. In addition to direct assimilation, vegetation promotes sediments favorable for denitrification [Pinaridi *et al.*, 2009] as do other natural structures such as gravel bars or downed trees [Groffman *et al.*, 2005]. The limitation or absence of hyporheic flow in channelized rivers excludes the main compartment of denitrification [Alexander *et al.*, 2009; Fischer *et al.*, 2005; Rode *et al.*, 2015; Ward *et al.*, 2016; Zarnetske *et al.*, 2011]. Choosing two reaches contrasting in morphology and  $\text{NH}_4^+$  as study sites guarantees the presence of differences in N cycling dynamics and is therefore an effective way of testing if a combination of longitudinal profiling and two-station time-series is sensitive enough to quantify N cycling rates and inter-reach differences on the reach scale. We expected that a natural study reach would exhibit higher rates of both assimilatory and dissimilatory N uptake than a channelized one. Finally, as seasonal variation in day length and its effect on photic and temperature conditions strongly control rates of nutrient removal and prevalence of different uptake processes



**Figure 1.** Study reaches in July 2015. (left) NATURE was un-altered, and featured a meandering pattern with pools and riffles. (right) CHANNEL was straightened and concrete lined.

[Worrall *et al.*, 2015], we evaluated the method under different temperature and light conditions. While Hefernan and Cohen [2010] did note light driven seasonal variation in processing rates, the proximity of their study sites to the tropics means that their study sites experience less seasonal variation in insolation than streams at higher latitudes. Additionally, as spring-fed rivers there was negligible seasonal variation in temperature.

This study presents the extension of existing methods for deriving N uptake parameters from time series under new conditions. We developed conceptual and methodological supplements and adaptations based on the expected challenges connected to tributary inflow, diurnal variations and additional  $\text{NH}_4^+$  loading. We hypothesize that a combination of existing methods allows quantifying N-uptake on the reach scale and distinguishing different removal processes. This hypothesis was tested under contrasting conditions to identify prospects and limitations in the application of presented methods.

## 2. Methods and Materials

### 2.1. Study Site

The Weiße Elster is a 250 km long river, originating in the northern Czech Republic and discharging into the Saale River near Halle, Germany. The 4<sup>th</sup> order river drains a watershed of 5300 km<sup>2</sup>. Land use within the basin varies along a longitudinal gradient, with the headwaters dominated by forests while the lower reaches are dominated by agriculture. Because of agricultural runoff as well as waste water treatment plant effluent, the water quality in the middle to lower reaches is marked by high N concentrations [Wagenschein and Rode, 2008]. For our study sites we selected two morphologically contrasting reaches (Figure 1), later referred to as “NATURE” and “CHANNEL,” within a previously studied [Wagenschein and Rode, 2008; Boyacioglu *et al.*, 2012] section of the middle Weiße Elster. We performed two deployments on each reach, in July and September 2015. Parameters for each reach are provided in Table 1.

The NATURE reach was 7.1 km long (starting point 51°06'11.6"N 12°12'19.0"E), and retains an un-altered, meandering pattern, with varying widths and depths, debris islands, pools and riffles. Riparian vegetation is

expansive, and large parts of the reach may be shaded when leaves are present. Allochthonous inputs from litterfall are likely extensive. Due to mining activity in the surrounding area, the groundwater table in the area is unnaturally low. The responsible mining company MIBRAG is continuously monitoring the groundwater level in the Weiße Elster basin. The 6 h time step readings from 16 groundwater wells in the area of the NATURE reach showed that groundwater table was at

**Table 1.** Main Features of the Two Study Reaches<sup>a</sup>

Parameter	NATURE	CHANNEL	Units
L	7100	7600	M
T	2.5	1.4	
Q	6.2–9.3	6.3–8.3	m <sup>3</sup> s <sup>-1</sup>
D	1.7	0.7	M
W	23	23	M
T	7	3.5	H

<sup>a</sup>L, reach length; T, tortuosity; Q, discharge; d, mean depth; w, width; τ, mean travel time.

minimum 1.5 meters below water level in the Weiße Elster during summer and autumn 2015. Groundwater inflow to the reach is therefore not expected. The only inflow is a mining drainage, consisting of groundwater that is collected in the close by mine, pumped to the surface and flows then via gravity in an open ditch until it discharges into the main stem in the last fifth of the NATURE reach. The discharge of this artificial tributary is continuously measured by the mining company MIBRAG and the assumedly stable (*Peter Jolas*, personal communication, 2016) water chemistry is analyzed once per week.

The CHANNEL reach started 12 km downstream of the end of NATURE (51°12'27.8"N 12°18'02.4"E). It was 7.6 km long, straightened and completely sealed within a concrete channel. In 1971, a 10 km long stretch of the Weisse Elster was relocated and transferred into a concrete bed in order to prevent it from draining into open pit lignite mines in the area or refilling the artificially lowered groundwater body. These conditions remain valid today [*Sächsisches Landesamt für Umwelt, Referat 46 – Bergbaufolgen*, 2013]. The cross-sectional profile of the CHANNEL reach is trapezoidal with uniform width and depths. Both banks are unvegetated; shading and litterfall are essentially zero. Because of the concrete lining, there is no groundwater exchange. The only inflow is the Elstermühlgraben, a mill ditch which was extracted from the Weiße Elster just upstream and reenters within the first 0.5 km of the study reach. Its water chemistry is nearly identical to the main stem of the Weiße Elster. There is a waste water treatment plant upstream of the study reach. While  $\text{NH}_4^+$  concentrations in NATURE were small and negligible relative to  $\text{NO}_3^-$ , within CHANNEL  $\text{NH}_4^+$  contributed between 10 and 15% to the total N load.

## 2.2. Two Stations Time Series

We installed water chemistry sensor stations at the upstream and downstream ends of each reach. Each deployment lasted 3–4 days. All sensors were synchronized before the start of the experiment by running them simultaneously in a bucket filled with Weiße Elster water. Discrete samples from the same bucket, which were analyzed in the laboratory as stated below, were used as benchmark samples. At each station we installed automated ultra-violet spectrophotometers (ProPS WW, TriOS) to measure  $\text{NO}_3^-$ . In long time monitoring, these sensors have shown high stability and concordance to frequent routine laboratory analysis [e.g., *Jiang et al.*, 2015; *Rode et al.*, 2016b]. The sensors used in this study utilized a pathlength of 10 mm and measured adsorption over wavelengths from 190 to 360 nm. Manufacturer stated precision was  $0.03 \text{ mg NO}_3^- \text{-N L}^{-1}$  and accuracy was  $\pm 2\%$ . Measurement frequency was set to 10 min.

Additionally each station was equipped with a multi-parameter probe YSI 6600 V2/4 (YSI Environmental, Yellow Springs, Ohio) recording the following parameters, accuracy and precision as stated by the manufacturer: pH (precision 0.01 units, accuracy  $\pm 0.2$  units), specific conductivity (precision  $0.001 \text{ mS cm}^{-1}$ , accuracy  $\pm 0.5\%$ ), dissolved oxygen (precision  $0.01 \text{ mg L}^{-1}$ , accuracy  $\pm 1\%$ ), temperature (precision  $0.01^\circ\text{C}$ , accuracy  $\pm 0.15^\circ\text{C}$ ), turbidity (precision 0.1 NTU, accuracy  $\pm 2\%$ ) and chlorophyll-a (precision  $0.1 \mu\text{g L}^{-1}$ , linearity:  $R^2 > 0.9999$  relative to dilution of rhodamine WT solution of 0–400  $\mu\text{g L}^{-1}$ ). Measurement frequency was set to 5 min.

Discharge ( $Q$ ) measurements were obtained at 15 min intervals from gauging stations operated by the local authorities. For NATURE we used the gauging station at Zeitz which is run by the Federal State Authority for Flood Protection and Water Management of Saxony-Anhalt (Landesamt für Hochwasserschutz und Wasserwirtschaft Sachsen-Anhalt) and located 10 km upstream. For CHANNEL we used the gauge at Kleindalzig, situated in the first 300 m of the study reach. This station is managed by the Saxony Federal state authority (Sächsisches Landesamt für Umwelt). Discharge of the mining drainage into NATURE was obtained from the mining company MIBRAG, which provided 20 min time step records from the company run gauging station. The Elstermühlgraben has a constant discharge of  $0.5 \text{ m}^3 \text{ s}^{-1}$ , we assumed that its water chemistry did not differ from the main channel as it was fed from Weisse Elster water, subtracted 1 km further upstream.

Stream widths ( $w$ ), depths ( $d$ ) and bed slopes ( $s$ ) were obtained from the hydraulic model DYNHYD [*Wagenschein*, 2006] which is based on 876 cross-sectional profiles on a 70 km long stretch of the Weiße Elster during low flow conditions (calibrated  $Q$  ranging from  $5.6$  to  $7.0 \text{ m}^3 \text{ s}^{-1}$ ), including both study reaches. The conductivity signal between upstream and downstream stations was used as a natural tracer to estimate mean velocity ( $u$ ) and mean travel time ( $\tau$ ). Mean travel time for NATURE was estimated as 7 h, while mean travel time for CHANNEL was 3.5 h.

We utilized a two-station method to calculate within-reach uptake of  $\text{NO}_3^-$ . Notably *Heffernan and Cohen* [2010] used a single station, however in their case the spring vent served as a constant upstream station.

For rivers without a constant upstream boundary, a two station approach is critical for extracting the in-stream processing signal for nongaseous solutes such as  $\text{NO}_3^-$  [Hensley and Cohen, 2016]. For each time step ( $t$ ) we calculated the change in  $\text{NO}_3^-$  mass flux between upstream ( $Q_{US,t-\tau/2}[\text{NO}_3^-]_{US,t-\tau/2}$ ) and downstream stations ( $Q_{DS,t+\tau/2}[\text{NO}_3^-]_{DS,t+\tau/2}$ ). We also accounted for the lateral inflows  $Q_L[\text{NO}_3^-]_L$  from the mine drainage and the Elstermühlgraben for NATURE and CHANNEL respectively. For the mine drainage we used  $\text{NO}_3^-$  concentrations from manual grab samples and discharge records provided by the mining company, while for the Elstermühlgraben we assumed equal concentrations as in the main stem and a constant discharge of  $0.5 \text{ m}^3 \text{ s}^{-1}$ . This net change in  $\text{NO}_3^-$  load was then divided by the benthic surface area ( $w \times L$ ) of the reach to calculate total net uptake ( $U_T$ ) in units of  $\text{mg NO}_3\text{-N m}^{-2} \text{ d}^{-1}$ .

$$U_{T,t} = \frac{Q_{DS,t+\tau/2}[\text{NO}_3^-]_{DS,t+\tau/2} - (Q_{US,t-\tau/2}[\text{NO}_3^-]_{US,t-\tau/2} + Q_L[\text{NO}_3^-]_L)}{w \times L} \quad (1)$$

We initially assumed that concentrations in the mine drainage stayed constant over each 4 days of the experiment. A derivation of  $\pm 10\%$  was projected on the data to analyze the uncertainty in net uptake ( $U_T$ ) calculation deriving from variation in drainage water concentration. Though we consider groundwater inflow extremely unlikely because of the groundwater table relative to the stream bed, we similarly estimated the uncertainty in  $U_T$  arising from unaccounted inflows by generating an imaginary inflow equal to 5% the discharge of the study reaches (the maximum we reasoned could be plausible over the reach length) and  $\text{NO}_3^-$  concentrations of zero (completely denitrified groundwater) and twice the observed concentration (waste water effluent). The effect of sensor accuracy on deduced  $U_T$  was also evaluated by adding 2% to the actual  $\text{NO}_3^-$  signal at the downstream station.

Using the method of Heffernan and Cohen [2010] we then estimated the amount of  $U_T$  composed of autotrophic uptake ( $U_A$ ) by interpolating a baseline across nighttime values of  $U_T$ . Increases in uptake during the day relative to this nighttime baseline were ascribed to  $U_A$ . This makes several critical assumptions: First, that nighttime  $U_T$  values reflect no  $U_A$ . Second, it assumes that other  $\text{NO}_3^-$  processing pathways such as heterotrophic uptake of  $\text{NO}_3^-$  by bacteria and fungi, denitrification and nitrification vary linearly between nighttime values.

Net ecosystem production (NEP) was calculated for each time step from the DO profiles using a two station method similar to  $\text{NO}_3^-$  but also including a reaeration term. Whereas the single station metabolism method integrates over a limited upstream area, roughly  $3u/k$  where  $u$  is velocity ( $\text{m s}^{-1}$ ) and  $k$  ( $\text{s}^{-1}$ ) is the reaeration coefficient [Chapra and Toro, 1991], the two station method integrates over the entire reach, making direct comparisons with nongaseous  $\text{NO}_3^-$  processing more tenable [Hensley and Cohen, 2016].

$$NEP_t = \frac{Q_{DS,t+\tau/2}[\text{DO}]_{DS,t+\tau/2} - (Q_{US,t-\tau/2}[\text{DO}]_{US,t-\tau/2} + Q_L[\text{DO}]_L)}{w \times L} + k[\text{DO}]_{\text{def},t} \times d \quad (2)$$

The value of  $k$  was estimated from the energy dissipation model [Bott, 2006; Zappa et al., 2007] and was  $2.5 \times 10^{-5} \text{ s}^{-1}$  for NATURE and  $2.13 \times 10^{-4} \text{ s}^{-1}$  for CHANNEL. The DO saturation deficit  $[\text{DO}]_{\text{def}}$  for each time step was calculated as the mean difference between the saturation DO concentration based on measured water temperature and barometric pressure (German Weather Service), and observed DO over the reach over that time step (i.e., average of US at  $t-\tau/2$  and DS at  $t+\tau/2$ ). We assumed no primary production occurred at night, and that nighttime NEP values were equal to ecosystem respiration (ER) [Bott, 2006]. We then assumed that ER was constant over 24 h, and ascribed daytime increases in NEP to gross primary production (GPP) in units of  $\text{g-O}_2 \text{ m}^{-2} \text{ d}^{-1}$  [Roberts et al., 2007]. We assumed that primary productivity (NPP) was equal to half of GPP [Hall and Tank, 2003; Hall and Beaulieu, 2013; Rode et al., 2016a]. We then estimated the assimilatory demand for nitrogen ( $D_A$ ) by converting NPP to molar units, assuming 1 mol C fixed per mol  $\text{O}_2$  produced, and multiplying by the ecosystem autotrophic C/N ratio. The molar C/N ratio used was 7 for July and 9 for September, corresponding to data collected during a previous study in the Weisse Elster middle reach [Junge et al., 2005]. These estimates of  $D_A$  were then compared to  $U_A$  calculated from the observed  $\text{NO}_3^-$  signals. A  $U_A$  value substantially less than  $D_A$  demand may indicate that  $D_A$  is being partially met by an additional source of assimilatory N, potentially  $\text{NH}_4^+$ , or that autotrophic uptake of  $\text{NO}_3^-$  from the water column is being partially compensated by  $\text{NO}_3^-$  production through nitrification (underestimating actual  $U_A$ ).

### 2.3. Longitudinal Profiling

A third set of sensors was used for longitudinal profiling. The longitudinal profiling was conducted in an inflatable rubber dinghy, drifting with the thalweg water velocity with sensors suspended over the side, submersed 15–20 cm. Drifting took 3.5 h in NATURE and 2.25 h in CHANNEL. While *Hensley et al.* [2014] showed that sampling speed can be critical to accurately estimating reaction kinetics (i.e., linear versus exponential decline), estimates of reaction rates (overall profile slope) in reaches of this length are typically much less influenced by sampling speed (in this case  $\sim 2u$ ) because biogeochemical processes generally vary over the time scale of hours. Measurement frequency was set to 5 min. Sensor clocks were synchronized with a handheld GPS unit, providing a location of each measurement. Rates of  $U_{T-prof}$  were calculated based on the slopes ( $\delta C/\delta x$ ) of the longitudinal profiles (equation (3)). For NATURE this was done over two subreaches separated by the mine drainage input, while in CHANNEL the profile was fit in its entirety. Similar to the time series analysis, a negative value (negative slope or decreasing concentration with downstream distance) indicates net removal.

$$U_{T-prof} = \frac{Q}{W} \frac{\partial C}{\partial X} \quad (3)$$

Statistical uncertainty in the line slope was used to estimate uncertainty in inferred uptake rate. During each deployment we performed both a day time profile and night time profile, typically on the second or third day of the deployment. Day profiles started at noon, night profiling 1–2 h after sunset. By assuming that  $U_A$  is negligible at night, we estimated the magnitude of  $U_{A-prof}$  by subtracting night profile  $U_{T-prof}$  from day profile  $U_{T-prof}$ .

Additionally, manual samples for  $\text{NO}_3^-$ , nitrite ( $\text{NO}_2^-$ ),  $\text{NH}_4^+$ , total nitrogen (TN), soluble reactive phosphorus (SRP), total phosphorus (TP), and naturally abundant  $\delta^{15}\text{N}_{\text{NO}_3}$  and  $\delta^{18}\text{O}_{\text{NO}_3}$  isotopes were taken every 20–30 min. Grab samples for  $\text{NO}_3^-$  served as benchmark samples for calibration of the sensors as described above. Estimates of  $\text{NH}_4^+$  uptake were derived using equation (3) for NATURE upstream of the mine drainage input and the entirety of CHANNEL. Downstream of the mine drainage in NATURE there were too few grab samples to fit a slope.

Nutrient species were analyzed in the analytical laboratory of the UFZ on a Segmented Flow Analyser Photometer (DR 5000, Hach Lange):  $\text{NO}_3\text{-N}$  and  $\text{NO}_2\text{-N}$  at 540 nm (precision of  $0.042 \text{ mg L}^{-1}$  and  $0.012 \text{ mg L}^{-1}$  respectively),  $\text{NH}_4\text{-N}$  at 660 nm (precision  $0.011 \text{ mg L}^{-1}$ ), SRP at 880 nm (precision  $0.003 \text{ mg L}^{-1}$ ). TP was oxidatively decomposed and then photometrically measured as SRP following colorant reaction. Stable isotopes of  $\text{NO}_3^-$  were determined using the denitrifier method at the Helmholtz-Centre Geesthacht [*Sigman et al.*, 2001]. Measurements were performed with an isotope ratio mass spectrometer (Delta V Advantage, Software Isodat 3.0, Thermo Scientific) with an analytical precision of  $< 0.2 \text{ ‰}$  for  $\delta^{15}\text{N}_{\text{NO}_3}$  and  $< 0.5 \text{ ‰}$  for  $\delta^{18}\text{O}_{\text{NO}_3}$ . The isotopic ratios were calculated as delta notations, referring to the ratio of the heavier to the lighter isotopes.

## 3. Results

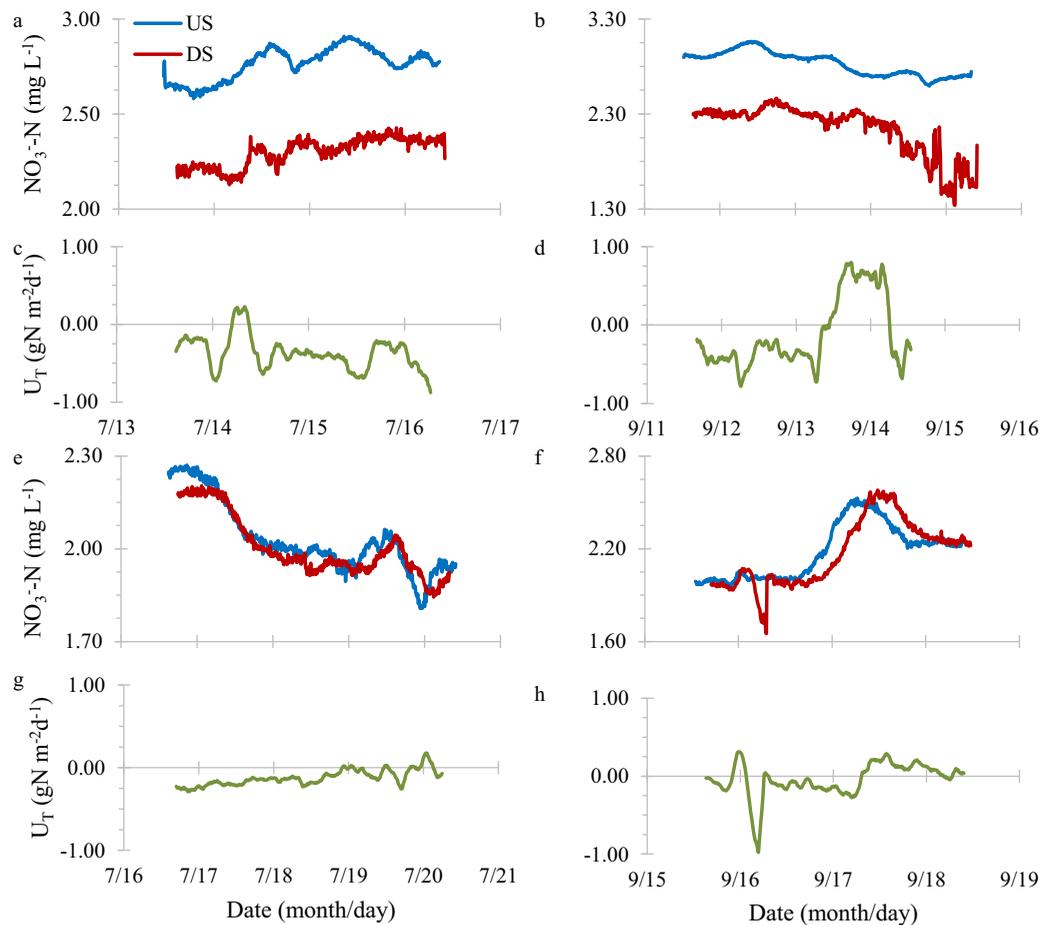
### 3.1. Two Stations Time Series

Average  $\text{NO}_3^-$  concentration during the deployments were 30% lower in CHANNEL versus NATURE, due to the inflow of low  $\text{NO}_3^-$  mining water at the end of NATURE (Table 2). After accounting for dilution, rates of net  $\text{NO}_3^-$  removal ( $U_T$ ) inferred from the flux balance between station signals (Figure 2) were nearly always negative in NATURE, indicating net removal. In CHANNEL,  $U_T$  was frequently positive portending net enrichment (Table 3). The resulting uncertainty in  $U_T$  arising from potential 10% variation in  $\text{NO}_3^-$  concentration of lateral inflows was only 1% in July and 0.4% in September. A 5% unaccounted inflow with twice the  $\text{NO}_3^-$  than the stream could result in a very large (3–10 times) underestimation of real  $U_T$ . However, we find this scenario extremely unlikely for two reasons: First, such a high concentration would likely only be found in point-source sewage. Second, the groundwater gradient is out of the stream, and in the case of CHANNEL the stream bed is completely impervious. Errors related to 2% instrumental derivation of sensors were 35% of  $U_T$  in NATURE and 400% of  $U_T$  in CHANNEL. This difference arises from the lower actual values in CHANNEL.

**Table 2.** Average, Minimal (min), and Maximal (max)  $\text{NO}_3^-$  Concentration (in  $\text{mgNO}_3^- \cdot \text{N L}^{-1}$ ) in the Study Reaches and the Mine Drainage Inflow to NATURE During the Two Measurement Phases

$\text{NO}_3^- \cdot \text{N}$	NATURE		CHANNEL		Mining Water	
	July	September	July	September	July	September
average	2.76	2.84	2.05	2.18	0.047	0.054
min	2.58	2.59	1.81	1.95		
max	2.90	3.06	2.27	2.53		

The upstream station of CHANNEL consistently exhibited a diel signal in the raw  $\text{NO}_3^-$  signal, suggesting assimilatory processing further upstream. Using a two-station approach within the study reaches themselves, however we did not observe a coherent diel  $U_T$  signal during any of the deployments. Without true nighttime minima to interpolate across, the *Heffernan and Cohen* [2010] method could not be used to make justifiable estimates of  $U_A$ . Instead we compared averaged  $U_T$  values for daytime versus nighttime measurement intervals (Figure 3). Despite the autocorrelation inherent to time-series data and the high variance in these averaged values, general trends are clearly visible: In NATURE average uptake during day was only slightly (9%) higher than during night in July, whereas in September average uptake was 12 times higher at day than at night. In CHANNEL,  $U_T$  during night was even slightly (4%) higher than during day in July, in September nighttime uptake was negative, signifying net  $\text{NO}_3^-$  production. In both study reaches, we observed strong diel signals in DO at both the upstream and downstream stations in July and September (Figure 4 and supporting information Appendix A). Calculated rates of GPP were generally an order of



**Figure 2.** Time series  $\text{NO}_3^-$  profiles for (a and b) NATURE and (e and f) CHANNEL during the measurements in (left) July and (right) September 2015. The decline in  $\text{NO}_3^-$  in NATURE is largely the result of dilution by the inflow of low  $\text{NO}_3^-$  mine drainage water.  $U_T$  in (c and d) NATURE typically exhibits more negative values, (g and h) indicative of greater net removal relative to CHANNEL.

**Table 3.** Summary of Time Series Means<sup>a</sup>

Parameter	NATURE		CHANNEL		Units
	July	September	July	September	
$U_T$	-331	-147	-193	-47	$\text{mgNO}_3^- \text{-N m}^{-2} \text{d}^{-1}$
$U_{T\text{day}}$	-346	-325	-188	-125	$\text{mgNO}_3^- \text{-N m}^{-2} \text{d}^{-1}$
$U_{T\text{night}}$	-316	-27	-197	+4	$\text{mgNO}_3^- \text{-N m}^{-2} \text{d}^{-1}$
GPP	1.7	1.6	12.8	7.2	$\text{gO}_2 \text{ m}^{-2} \text{d}^{-1}$
ER	-1.7	-2.1	-8.5	-5.2	$\text{gO}_2 \text{ m}^{-2} \text{d}^{-1}$
P/R	1.0	0.8	1.6	1.4	
C/N	7	9	7	9	mol-C/mol-N
$D_A$	-51	-39	-399	-176	$\text{mg-N m}^{-2} \text{d}^{-1}$

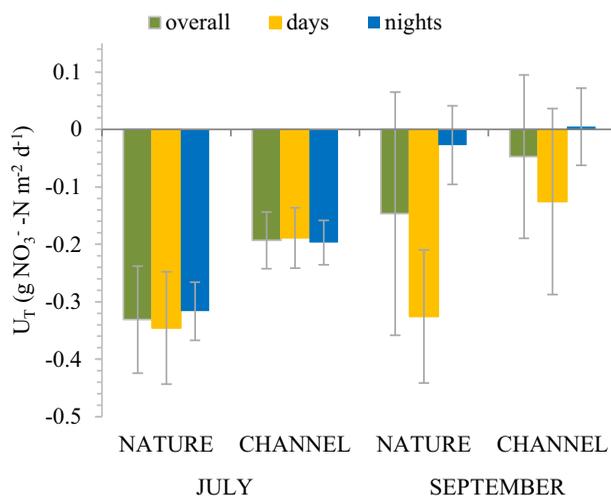
<sup>a</sup> $U_T$ , net  $\text{NO}_3^-$  uptake (negative values) or release (positive values);  $U_{T\text{day}}$ , averaged daytime  $\text{NO}_3^-$  uptake/release;  $U_{T\text{night}}$ , averaged nighttime  $\text{NO}_3^-$  uptake/release; GPP, gross primary production; ER, ecosystem respiration; P/R, ratio of GPP to ER;  $D_A$ , assimilatory N demand inferred from NPP and C/N.

magnitude larger in CHANNEL versus NATURE, consistent with greater solar forcing due to less riparian shading. We note in NATURE P/R was close to 1 or even slightly net heterotrophic ( $\text{GPP} < \text{ER}$ ), while CHANNEL was consistently net autotrophic ( $\text{GPP} > \text{ER}$ ) (Table 3). A lower P/R is consistent with greater shading and more allochthonous carbon from litterfall in NATURE. With higher rates of GPP, inferred rates of  $D_A$  were also higher in CHANNEL (Table 3).

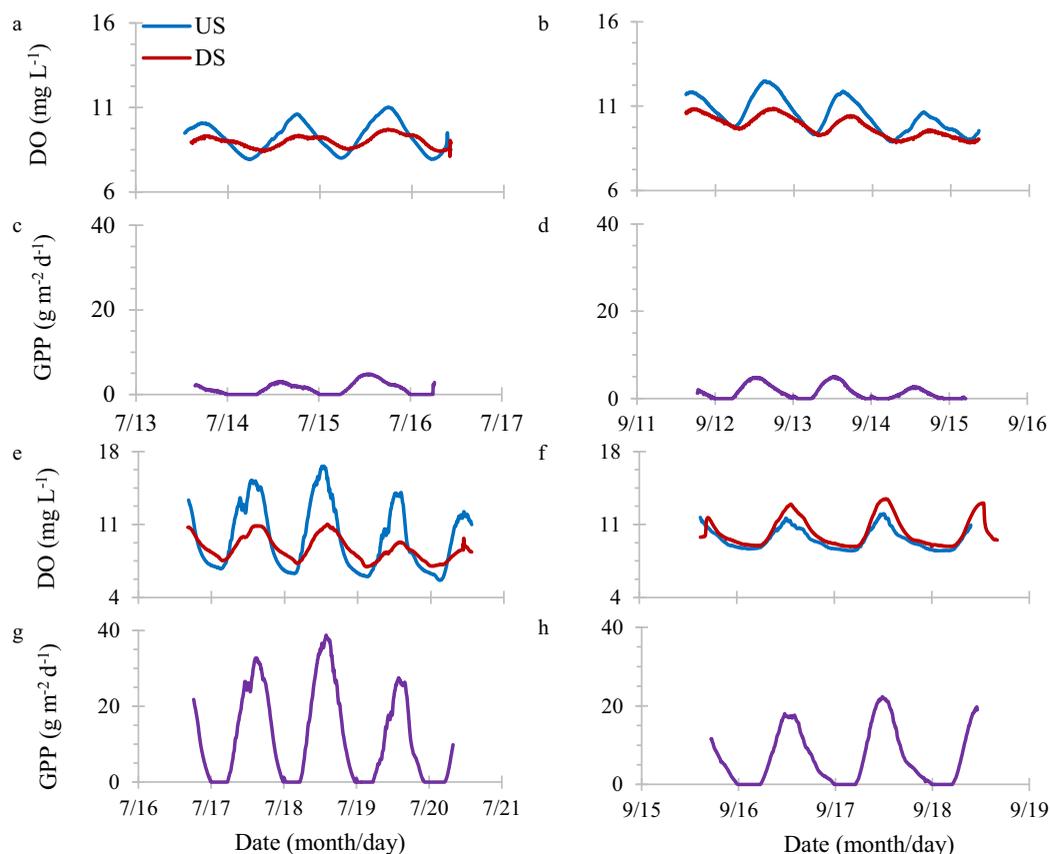
### 3.2. Longitudinal Profiling

Longitudinal profiling revealed several consistent spatial trends. Most apparent was the dilution effect of the mining water inflow in NATURE (Figure 5). The majority of the July daytime and both September profiles in the NATURE reach exhibited longitudinal declines, indicating net  $\text{NO}_3^-$  removal. The July nighttime profile from NATURE and all profiles from CHANNEL slope upward, indicating net  $\text{NO}_3^-$  production. In most cases, slopes of daytime profiles (Table 4) were steeper than nighttime profile slopes, suggesting greater removal (or less enrichment) during the day. The slopes of all profiles were relatively uniform, showing a lack of local  $\text{NO}_3^-$  processing hotspots with one major exception: In NATURE profiles generally sloped downward along the entire reach length (net removal), until the mine drainage, at which point the slopes flipped to sloping upward (net production). The inflow of mining water with 4–5 times higher  $\text{NH}_4^+$  concentrations than the main stem at the end of NATURE constitutes a major point source of  $\text{NH}_4^+$  so that at this point the change in water chemistry may cause a shift in the balance of processing pathways. Overall,  $\text{NH}_4^+$  exhibited longitudinal declines in both NATURE and CHANNEL.

We believe that this decline was predominantly the result of assimilatory uptake and nitrification rather than volatilization, as the pH never rises above 9 ( $\text{pK}_a = 9.24$ ).  $\text{NH}_4^+$  was mainly higher at night than during the day (Figure 6). Additional to the effect of the mine drainage inflow, concentrations of  $\text{NH}_4^+$  become even more elevated in the downstream CHANNEL versus NATURE due to the WWTP situated between the two study reaches so that initial  $\text{NH}_4^+$  concentrations are nearly an order of magnitude larger in CHANNEL.  $\text{NH}_4^+$  uptake was greater in CHANNEL than in NATURE, day and night behaved conversely in September than July (Table 5).  $\text{NO}_2^-$  decreased with downstream distance in NATURE by 70% (range  $0.012\text{--}0.007 \text{ mg NO}_2^- \text{-N L}^{-1}$ ) in July and by 44% (range  $0.013\text{--}0.009 \text{ mg NO}_2^- \text{-N L}^{-1}$ ) in September. In



**Figure 3.** Average  $\text{NO}_3^-$  uptake (negative values) or release (positive values) rates  $U_T$  for the two sampling periods, and differentiated between day and night hours for both reaches in July (left) and September (right), error bars indicate standard deviation between averaged 15 min-interval measurements.



**Figure 4.** Time series DO profiles for (a and b) NATURE and (e and f) CHANNEL during the measurements in (left) July and (right) September. GPP in (c and d) NATURE is roughly an order of magnitude lower than in (g and h) CHANNEL, consistent with the degree of riparian shading.

contrast,  $\text{NO}_2^-$  in CHANNEL increased with distance, by 80% (range 0.010–0.017  $\text{mg NO}_2^- \text{-N L}^{-1}$ ) in July and by 60% (range 0.011–0.018  $\text{mg NO}_2^- \text{-N L}^{-1}$ ) in September. Day and night dynamics were very similar.

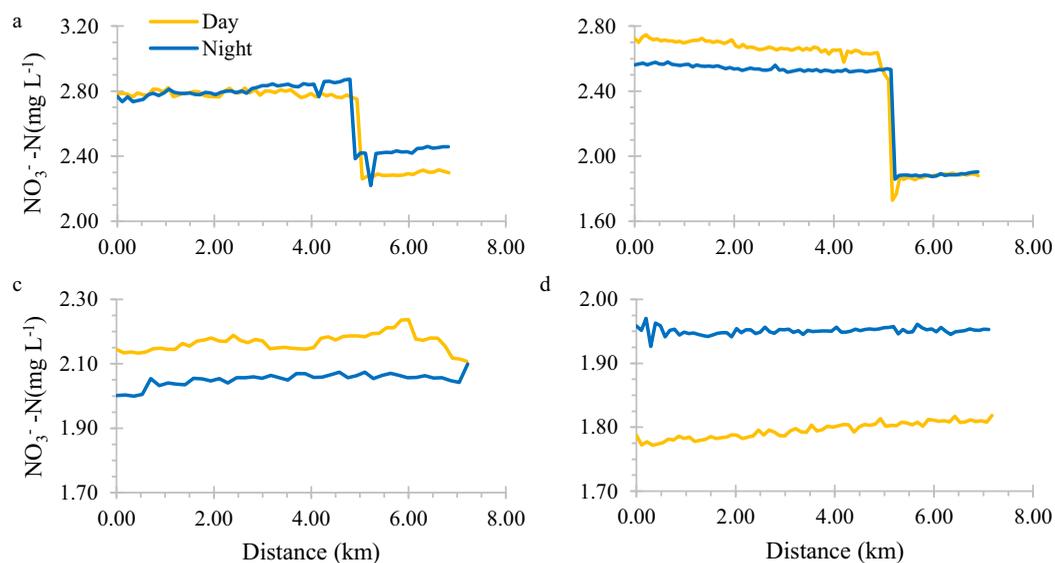
Discrete longitudinal sampling did not reveal any longitudinal trends in TP, which in both reaches averaged 0.15  $\text{mg L}^{-1}$  in July and 0.12  $\text{mg L}^{-1}$  in September (supporting information Appendix B).

All deltas in  $\text{NO}_3^-$  isotopes were smaller than the range of instrumental accuracy (0.2 ‰), so that reliable conclusions could not be made based on these measurements. Still, different trends between the two reaches and between July and September were visible. In July  $\delta^{15}\text{N}_{\text{NO}_3^-}$  values of  $\text{NO}_3^-$  were heavier during day in NATURE and indicated a trend of a slight enrichment downstream. In contrast to July, isotope measurements from September showed a relative depletion of  $\delta^{15}\text{N}_{\text{NO}_3^-}$  at day compared to night, with a higher concentration of  $\text{NO}_3^-$ . In CHANNEL, lighter values of  $\delta^{15}\text{N}_{\text{NO}_3^-}$  were measured in July during day compared to night sampling, whereas in September no differences could be estimated in  $\delta^{15}\text{N}_{\text{NO}_3^-}$ . Isotopic fractionation was only detected during day time profiling (supporting information Appendix B).

## 4. Discussion

### 4.1. Diel Variation

While average values of  $U_T$  were generally greater during the day (and longitudinal profiles also suggested more removal during the day), diel variation in  $U_T$  was not nearly as coherent as in the systems where this method has been used before [Heffernan and Cohen, 2010; Rode et al., 2016a]. In NATURE in September a consistent pattern seemed to appear, however the timing was asynchronous with solar forcing and the GPP signal, with maximum apparent uptake occurring around 6:00 rather than the expected 12:00. Furthermore, there were no consistent nighttime minima in any of the data sets and therefore no clear baseline for partitioning pathways. In NATURE, assumedly due to heavy shading, GPP was low indicating that assimilatory

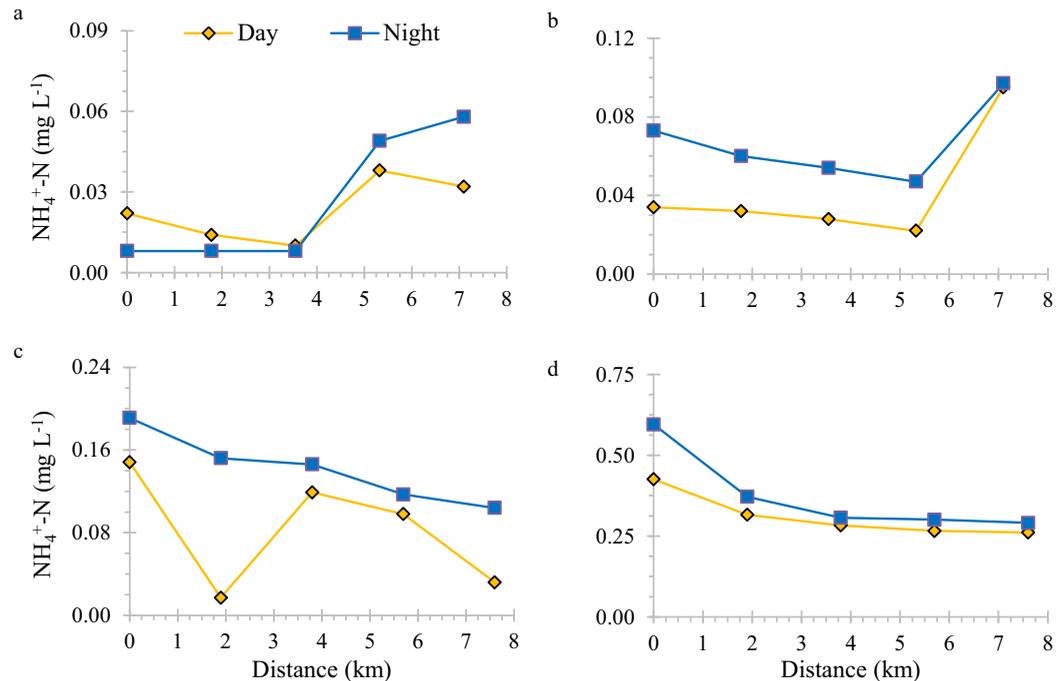


**Figure 5.** Longitudinal  $\text{NO}_3^-$ -N profiles for (top) NATURE and (bottom) CHANNEL in (left) July and (right) September. Note the large dilution effect of low  $\text{NO}_3^-$  mine drainage entering NATURE at 5.2 km.

demand may have been small enough that  $U_A$  induced variation in  $\text{NO}_3^-$  was beyond the sampling precision of the sensors. However, this is not likely. Also the effect of uncertainty introduced by measurement accuracy of the temporally varying influx from the lateral inflows on  $\text{NO}_3^-$  uptake was below 1% in NATURE as well as in CHANNEL. We suggest that the lack of a diel  $\text{NO}_3^-$  uptake signal in both reaches was occurring for two reasons: First, the autotrophic demand for N might have been met by a different N species. CHANNEL in particular was enriched in  $\text{NH}_4^+$ , which energetically represents a preferential source of metabolic N [Martí and Sabater, 1996; Stanley and Hobbie, 1981]. Second,  $\text{NO}_3^-$  uptake might have been confounded by temporally varying production of  $\text{NO}_3^-$  through nitrification. Rates of nitrification are generally expected to be greater during day because of its dependence on temperature, pH and oxygen saturation [Bernot and Dodds, 2005; Christensen and Sorensen, 1986; Laursen and Seitzinger, 2004; Strauss et al., 2004]. Applying the equations derived by Warwick [1986] to the maximal diurnal variation in pH and temperature observed in CHANNEL, these factors might explain a change of 20 (September) to 30 (July) % in stream nitrification rates, with higher values occurring under higher temperatures and higher pH during day. The modified Arrhenius equation suggested by Shammass [1986] for calculating temperature dependent nitrification rates yields slightly lower (10–20%) variation in nitrification related to temperature. However, the same studies found that an increase of  $\text{NH}_4^+$  concentration by 5% already resulted in 40% higher nitrification rates. In the

**Table 4.** Summary of Total ( $U_T$ ) and Assimilatory ( $U_A$ ) Uptake (Negative Values) or Release (Positive Values) Inferred From  $\text{NO}_3^-$  Longitudinal Profiling

	Slope ( $\text{mg L}^{-1} \text{m}^{-1}$ )	$U_T$ ( $\text{mg-N m}^{-2} \text{d}^{-1}$ )	$U_A$ ( $\text{mg-N m}^{-2} \text{d}^{-1}$ )
<b>NATURE</b>			
<i>Upstream of Mine Drainage Inflow</i>			
7/14 Day	$-3.17 \pm 1.74 \times 10^{-6}$	$-102 \pm 56$	$-825$
7/14 Night	$2.25 \pm 0.19 \times 10^{-5}$	$723 \pm 60$	
9/14 Day	$-2.09 \pm 0.12 \times 10^{-5}$	$-533 \pm 30$	$-275$
9/14 Night	$-1.01 \pm 0.08 \times 10^{-5}$	$-258 \pm 19$	
<i>Downstream of Mine Drainage Inflow</i>			
7/14 Day	$2.39 \pm 0.35 \times 10^{-5}$	$735 \pm 111$	
7/14 Night	$3.09 \pm 0.41 \times 10^{-5}$	$995 \pm 133$	$-260$
9/14 Day	$2.84 \pm 0.33 \times 10^{-5}$	$467 \pm 84$	
9/14 Night	$-1.22 \pm 0.26 \times 10^{-5}$	$311 \pm 66$	$157$
<b>CHANNEL</b>			
7/17 Day	$4.06 \pm 1.77 \times 10^{-6}$	$104 \pm 45$	$-56$
7/17 Night	$6.23 \pm 1.09 \times 10^{-6}$	$159 \pm 28$	
9/16 Day	$5.44 \pm 0.24 \times 10^{-6}$	$139 \pm 6$	$126$
9/16 Night	$5.13 \pm 3.09 \times 10^{-7}$	$13 \pm 8$	



**Figure 6.** Longitudinal  $\text{NH}_4^+$  profiles for (top) NATURE and (bottom) CHANNEL in (left) July and (right) September. While diluting  $\text{NO}_3^-$  concentrations, the mine drainage entering NATURE at 5.2 km is a major point source of  $\text{NH}_4^+$ .

Weisse Elster  $\text{NH}_4^+$  concentrations were lower during the day than during the night during all longitudinal profilings. The correlation provided by *Zhu and Chen* [2002] indicates that  $\text{NH}_4^+$  concentrations could have caused 50% higher nitrification rates during night in September and 20% higher in July. Differences in  $\text{NH}_4^+$  concentration between September and July could thereafter result in 4 times higher nitrification rates in September than July. Accordingly, the slopes in  $\text{NH}_4^+$  during the profile suggest that  $\text{NH}_4^+$  uptake was greater during night than during day and that it was overall higher in September than July. Conclusively,  $\text{NH}_4^+$  uptake rates in the Weiße Elster were determined more by input concentration than by temperature or pH. Assuming that all the decline of  $\text{NH}_4^+$  was due to nitrification (which is unlikely, but allows estimating dimensions) instream  $\text{NO}_3^-$  production could certainly have counterbalanced denitrification in CHANNEL. This implies, that assuming constant dissimilatory uptake rates might be problematic and that inferring  $U_A$  from  $\text{NO}_3^-$  alone likely underestimates actual uptake of N in reaches like CHANNEL which are enriched in  $\text{NH}_4^+$ . The importance of considering the effects of  $\text{NH}_4^+$  on inferred processing rates is further illustrated by the longitudinal profiles of NATURE. In most cases, the majority of the  $\text{NO}_3^-$  profiles sloped downward indicating net removal. The inflow of the mine drainage in the last 1.5 km changed the water chemistry dramatically, diluting the  $\text{NO}_3^-$  concentration by about 20%, but enriching the  $\text{NH}_4^+$  concentration by a factor of 2–3. The  $\text{NO}_3^-$  profiles instantaneously switched to sloping upward, suggesting the balance of N processing

**Table 5.** Summary of  $\text{NH}_4^+$  Uptake (Negative Values) and Release (Positive Values) Derived From Manual Samples Taken During the Longitudinal Profilings

	Slope ( $\text{mg L}^{-1} \text{m}^{-1}$ )	$U_{T-\text{NH}_4}$ ( $\text{mg-N m}^{-2} \text{d}^{-1}$ )	$U_{A-\text{NH}_4}$ ( $\text{mg-N m}^{-2} \text{d}^{-1}$ )
<b>NATURE</b>			
<i>Upstream of Mine Drainage Inflow</i>			
7/14 Day	$-3.43 \pm 0.66 \times 10^{-6}$	$-110 \pm 21$	-110
7/14 Night	0.00	0	
9/14 Day	$-2.29 \pm 0.36 \times 10^{-6}$	$-58 \pm 9$	64
9/14 Night	$-4.80 \pm 0.63 \times 10^{-6}$	$-122 \pm 16$	
<b>CHANNEL</b>			
7/17 Day	$-1.52 \pm 0.45 \times 10^{-6}$	$-389 \pm 114$	-84
7/17 Night	$-1.19 \pm 0.15 \times 10^{-5}$	$-305 \pm 39$	
9/16 Day	$-2.13 \pm 0.70 \times 10^{-5}$	$-545 \pm 178$	450
9/16 Night	$-3.89 \pm 1.46 \times 10^{-5}$	$-995 \pm 373$	

pathways has shifted to net production of  $\text{NO}_3^-$ . This supports the assumption that  $\text{NH}_4^+$  concentration dominantly influenced nitrification rates.

There were several assumptions inherent to the *Heffernan and Cohen* [2010] method for estimating  $U_A$ , which may make it unsuitable in the Weisse Elster and other systems. For one, the method assumes that nighttime maxima reflects no assimilatory uptake, an assumption which is likely for CHANNEL ( $\tau = 3.5$  h), however not in NATURE ( $\tau = 7$  h) in July, where darkness at this latitude lasts for only 8 h. Second, the method assumes nonassimilatory pathways (heterotrophic uptake, nitrification and denitrification) are constant, or vary linearly between observed nighttime values. As discussed in detail above, we strongly suggest that this might not be the case. Particularly if  $\text{NH}_4^+$  nitrification rates follow  $\text{NH}_4^+$  concentration which vary on an irregular basis due to WWTP operation, this assumption might not be tenable. Distinguishing averaged night- and daytime intervals of  $U_T$  as presented in the present study can be used to detect general trends in net  $\text{NO}_3^-$  removal. Still, it likewise failed to distinguish denitrification from nitrification for the same reasons mentioned above: time varying  $\text{NH}_4^+$  transformation to  $\text{NO}_3^-$  could not be quantified and stoichiometric calculations did not allow distinguishing assimilatory  $\text{NO}_3^-$  uptake from assimilatory  $\text{NH}_4^+$  uptake.

#### 4.2. Comparison Between Sampling Periods

We recognize that it is speculative to draw broad seasonal inferences from our limited data set. However, time-series and longitudinal profiling both indicate higher net  $\text{NO}_3^-$  retention in July versus September for both study reaches. We assume that differences between the two periods would mainly relate to irradiation and temperature. In addition to sunlight driven variation in assimilatory uptake, other processing pathways which positively (denitrification) or negatively (nitrification) contribute to net uptake vary in response to temperature [*Heffernan and Cohen*, 2010; *Gücker and Pusch*, 2006; *Pribyl et al.*, 2005]

*Wagenschein and Rode* [2008] concluded from their model assessment of  $\text{NO}_3^-$  uptake in the Weiße Elster that denitrification exceeded assimilation by more than three times during summer, whereas in autumn the amount of uptake allocated to denitrification declined to less than half of total uptake. Similarly, we measured in July in both reaches only slightly lower uptake during night than during day. In September night time uptake declined to one tenths of the July rates in NATURE and was not measurable anymore in CHANNEL. Likewise, inferred demand for assimilatory N decreased from July to September as a result of decreased GPP and increased C/N. However, this decline was not as large as the measured decrease in net uptake. As a result, in both reaches  $D_A$  represented a larger fraction of  $U_T$  in September than in July. While we cannot exclude that in CHANNEL this effect might have been induced by higher nitrification rates in September, it must have been attributed to changes in denitrification in NATURE, because  $\text{NH}_4^+$  was of minor importance there. For NATURE this shift between prevalent uptake processes can also be seen in the different  $\delta^{15}\text{N}_{\text{NO}_3}$  pattern in July versus September. In July, isotopic data indicated a predomination of  $\text{NO}_3^-$  uptake, presumably due to assimilation, whereas in September  $\text{NO}_3^-$  production seems to be more dominant during day time. Contrary in CHANNEL, in July  $\text{NO}_3^-$  uptake was of minor importance and a predomination of nitrification could be estimated during the day. In September, no differences could be measured in  $\delta^{15}\text{N}_{\text{NO}_3}$  between day and night making an interpretation of microbial processes based on isotopes impossible.

#### 4.3. Inter-Reach Comparison

Net removal of  $\text{NO}_3^-$  was substantially (on average 1.8 times in July and 3 times in September) higher in NATURE than in CHANNEL. In fact, at many times during the deployments CHANNEL was a net source of  $\text{NO}_3^-$ , suggesting nitrification exceeded denitrification and assimilation.

The higher net uptake rates measured in NATURE can be attributed to several factors: First, assuming denitrification follows efficiency-loss kinetics [*Mulholland et al.*, 2009], higher concentrations in NATURE would have caused slightly higher denitrification rates. Alternatively, the second reactant in the denitrification equation, labile carbon, might also have influenced denitrification rates [*Heffernan and Cohen*, 2010]. The lack of allochthonous carbon due to the absence of riparian vegetation, likely contributed to low denitrification rates in CHANNEL [*Cooke and White*, 1987; *Knowles*, 1982]. Thirdly, the bulk part of denitrification is generally attributed to microbial activity in the hyporheic zone and thus dependent on advective solute exchange between surface and subsurface water [*Alexander et al.*, 2009; *Fellows et al.*, 2001; *Harvey et al.*, 2013]. In CHANNEL the sealing of river bed and walls with concrete restricted water exchange with the

subsurface in CHANNEL and reduced denitrification. Previous model based studies estimated that denitrification in a natural reach of the Weiße Elster was 1.2 [Birgand *et al.*, 2007] to 2.4 [Rode *et al.*, 2008] times higher than in a channelized one, due to those factors.

However, even though river morphology may contribute to the differences between the reaches, results suggest that  $\text{NH}_4^+$  concentrations may be the determinant factor for the reaches examined here.  $\text{NH}_4^+$  was much higher in CHANNEL than in NATURE and  $\text{NH}_4^+$  mass balances from the profiling suggest that nitrification rates might have counterbalanced  $\text{NO}_3^-$  removal through denitrification, resulting in lower net removal of  $\text{NO}_3^-$  in this reach. Additionally, the higher dissolved oxygen and temperature observed in CHANNEL may also result in greater nitrification. It is worth noting that net uptake of total N (sum of  $\text{NO}_3^-$  and  $\text{NH}_4^+$  uptake) was much more similar across the reaches. Based on the longitudinal profiles, net uptake of  $\text{NO}_3^-$  in CHANNEL was lower (Table 4), but uptake of  $\text{NH}_4^+$  was higher (Table 5). In conclusion, it was not possible to definitively determine whether the inter-reach differences are related to morphology or water chemistry.

#### 4.4. Comparison of the Weiße Elster and Other Rivers

Net  $\text{NO}_3^-$  uptake rates measured in the Weiße Elster (mean 239 and 120  $\text{mg-N m}^{-2} \text{d}^{-1}$  in NATURE and CHANNEL respectively) are comparable to those measured in other studies in rivers of similar size. For example, Hensley *et al.* [2014] reported a median of 292  $\text{mg-N m}^{-2} \text{d}^{-1}$  across 6 subtropical streams of similar discharge, and Ensign and Doyle [2006] found a mean uptake rate of 249  $\text{mg-N m}^{-2} \text{d}^{-1}$  across 14 4<sup>th</sup> order streams. The two reaches fall neatly along the regression between  $\text{NO}_3^-$  concentration and uptake rate for the 72 streams in the LINXII data set [Hall *et al.*, 2009]. For  $\text{NH}_4^+$ , Ensign and Doyle [2006] report a mean uptake rate of only 28  $\text{mg-N m}^{-2} \text{d}^{-1}$  for fourth order streams, but 59  $\text{mg-N m}^{-2} \text{d}^{-1}$  across all stream orders. This is comparable to rates estimated for NATURE but substantially lower than CHANNEL (mean 73 and 559  $\text{mg-N m}^{-2} \text{d}^{-1}$  respectively). This may be because CHANNEL is heavily enriched in  $\text{NH}_4^+$ . As uptake is influenced by a multitude of factors, for instance  $\text{NO}_3^-$  and  $\text{NH}_4^+$  concentration, primary production, other water chemistry parameters and river morphology, direct comparison across systems is quite difficult. Additionally, different studies utilize distinct measures (e.g., gross versus net uptake) and methods which account for these factors to varying degrees. Thus, the methodology used would also determine the comparability of results to a certain degree, highlighting the need for the establishment of a universally applicable methodology.

## 5. Conclusions

Methodologies based on high-frequency data from sensors have great potentials to deliver the long needed quantitative data for instream nutrient cycling studies. The presented work is the first application of this methodology in higher order streams with complex input signals, tributaries and anthropogenically impacted water chemistry. The intricacy of natural systems, in this case primarily the composition of the N pool and the presence of inflowing tributaries pose mayor challenges which we assessed in our study. Uncertainty analysis showed that unaccounted inflows can bias the inferred results. While the longitudinal profiling is effective in identifying point sources, it is less suitable for detecting diffuse inflows from groundwater seepage. Due to the special conditions in the Weisse Elster basin related to the mining activity in the region (artificially lowered groundwater table and routine control of groundwater flow by the mining company and an impervious channel bottom in CHANNEL), we could confidently exclude groundwater inflow in this study. When transferring the concept to other systems however, groundwater might be a challenge to the method.

The lack of contemporary high frequency measurements of  $\text{NH}_4^+$  and the resulting failure to quantify nitrification, presents the greatest uncertainty on  $\text{NO}_3^-$  and total N processing rates in this and likely other future studies. Potential nitrification rates derived from  $\text{NH}_4^+$  mass balances during the longitudinal profiling deliver rough dimensions of potential nitrification rates in the reaches. They are limited in number (though statistical uncertainty in profile slope in most cases is relatively small) and only represent conditions at the specific sampling time. To our knowledge no portable and fully automated  $\text{NH}_4^+$  sensor currently exists. In the future collection of contemporaneous, high-frequency time series of other N species, specifically  $\text{NH}_4^+$  but potentially also  $\text{NO}_2^-$ , and organic nitrogen will substantially improve the ability to quantify the multitude of N cycling pathways.

We did not observe the strong diel variation in assimilatory uptake observed in many other sites, which we believe was due to the overlapping of several time varying processes, some of them natural (temperature related oscillation in denitrification and nitrification) but others potentially artificial and irregular (variation in WWTP inflow). Commonly used assumptions on constancy in dissimilatory processes proved to be invalid under the conditions examined in this study. Thus, the *Heffernan and Cohen* [2010] method of partitioning N-removal processes based on diurnal variations in  $\text{NO}_3^-$  concentration, fail in systems where nonassimilatory processes are time varying, or where other N species are of importance.

Our results highlight some of the important controls of temporal and spatial variation in processing rates. Temporally, sunlight and temperature can influence N processing rates over diel as well as seasonal time scales. We only assessed short periods, with the primary goal to pave the way for the future use of high frequency measurements in instream nutrient studies or monitoring. However, continuous application of the presented method will finally allow to quantitatively describe seasonal patterns in  $\text{NO}_3^-$  cycling and at best to identify hot moments in in-stream N retention.

Despite the limitations, the current study extends previous techniques to higher order fluvial systems with anthropogenically elevated N-level, substantial tributaries, complex input signals, and multiple species of N. We believe that the permanent implementation of automated sensors will become more common in the coming years. The long term observation of variation in nutrient behavior will provide valuable insights into in-stream nutrient dynamics of all rivers. A better understanding of the drivers of variability will allow for better predictions of system dynamics under future conditions such as increased loading, channel modification and climate change. This knowledge will permit better long-term management strategies for mitigating the effects of anthropogenic N loading and cultural eutrophication of aquatic ecosystems.

#### Acknowledgments

We thank Uwe Kewel for his technical support during the field work. We are also grateful for the cooperation of the Saxon State Office for Environment, Agriculture and Geology, the Federal State Authority for Flood Protection and Water Management Saxony-Anhalt and the Central German Brown Coal Company MIBRAG in providing discharge data. Supporting information are included in two Appendixes (A and B) as excel files; any additional data may be obtained from the corresponding author (email: vanessa.kunz@ufz.de)

#### References

- Alexander, R. B., J. K. Böhlke, E. W. Boyer, M. B. David, J. W. Harvey, P. J. Mulholland, S. P. Seitzinger, C. R. Tobias, C. Tonitto, and W. M. Wollheim (2009), Dynamic modeling of nitrogen losses in river networks unravels the coupled effects of hydrological and biogeochemical processes, *Biogeochemistry*, *93*, 91–116.
- Bartoli, M., E. Racchetti, C. A. Delconte, E. Sacchi, E. Soana, A. Laini, D. Longhi, and P. Viaroli (2012), Nitrogen balance and fate in a heavily impacted watershed (Oglio River, Northern Italy): In quest of the missing sources and sinks, *Biogeosciences*, *9*, 361–373.
- Bernot, M. J., and W. K. Dodds (2005), Nitrogen retention, removal, and saturation in lotic ecosystems, *Ecosystems*, *8*, 442–453.
- Birgand, F., R. W. Skaggs, G. M. Chescheir, and J. W. Gilliam (2007), Nitrogen removal in streams of agricultural catchments—A literature review, *Crit. Rev. Environ. Sci. Technol.*, *37*, 381–487.
- Böhlke, J. K., R. C. Antweiler, J. W. Harvey, A. E. S. Larsen, L.K., R. L. Smith, and M. A. Voytek (2009), Multi-scale measurements and modeling of denitrification in streams with varying flow and nitrate concentration in the upper Mississippi River basin, USA, *Biochemistry*, *93*, 117–141.
- Bott, T. L. (2006), Primary productivity and community respiration, in *Methods in Stream Ecology*, chap. 28, pp. 663–690.
- Boyacioglu, H., T. Vetter, V. Krysanova, and M. Rode (2012), Modeling the impacts of climate change on nitrogen retention in a 4th order stream, *Clim. Change*, *113*, 981–999.
- Bukaveckas, P. A. (2007), Effects of channel restoration on water velocity, transient storage, and nutrient uptake in a channelized stream, *Environ. Sci. Technol.*, *41*, 1570–1576.
- Chapra, S. C., and D. M. D. Toro (1991), Delta method for estimating primary production, respiration, and reaeration in streams, *J. Environ. Eng.*, *17*, 640–655.
- Christensen, P. B., and J. Sorensen (1986), Temporal variation of denitrification activity in plant-covered, littoral sediment from Lake Hampen, Denmark, *Appl. Environ. Microbiol.*, *51*, 1174–1179.
- Cohen, M. J., J. B. Heffernan, A. Albertin, and J. B. Martin (2012), Inference of riverine nitrogen processing from longitudinal and diel variation in dual nitrate isotopes, *J. Geophys. Res.*, *117*, G01021, doi:10.1029/2011JG001715.
- Cooke, J. G., and R. E. White (1987), Spatial distribution of denitrifying activity in a stream draining an agricultural catchment, *Freshwater Biol.*, *18*, 509–519.
- Covino, T. P., B. L. McGlynn, and R. A. McNamara (2010), Tracer Additions for Spiraling Curve Characterization (TASCC): Quantifying stream nutrient uptake kinetics from ambient to saturation, *Limnol. Oceanogr. Methods*, *8*, 484–498.
- Dodds, W. K., et al. (2000), Quantification of the nitrogen cycle in a prairie stream, *Ecosystems*, *3*, 574–589.
- Dodds, W. K., et al. (2002), N uptake as a function of concentration in streams, *J. North Am. Benthol. Soc.*, *21*, 206–220.
- Ensign, S. H., and M. W. Doyle (2006), Nutrient spiraling in streams and river networks, *J. Geophys. Res.*, *111*, G04009, doi:10.1029/2005JG000114.
- Fellows, C. S., H. M. Valett, and C. N. Dahm (2001), Whole-stream metabolism in two mountain streams: Contribution of the hyporheic zone, *Limnol. Oceanogr.*, *46*, 523–531.
- Fischer, H., F. Kloep, S. Wilzcek, and M. T. Pusch (2005), A river's liver - microbial processes within the hyporheic zone of a large lowland river, *Biogeochemistry*, *76*, 349–371.
- Galloway, J. N., J. D. Aber, J. W. Erisman, S. P. Seitzinger, R. W. Howarth, E. B. Cowling, and B. J. Cosby (2003), The nitrogen cascade, *BioScience*, *53*, 341–356.
- García-Ruiz, R., S. N. Pattinson, and B. A. Whitton (1998), Kinetic parameters of denitrification in a river continuum, *Appl. Environ. Microbiol.*, *64*, 2533–2538.
- Grimm, N. B., and K. C. Petrone (1997), Nitrogen fixation in a desert stream ecosystem, *Biogeochemistry*, *37*, 33–61.

- Groffman, P. M., A. M. Dorsey, and P. M. Mayer (2005), N processing within geomorphic structures in urban streams, *J. North Am. Benthol. Soc.*, *24*, 613–625.
- Gruber, N., and J. N. Galloway (2008), An Earth-system perspective of the global nitrogen cycle, *Nature*, *451*, 293–296.
- Gücker, B., and M. T. Pusch (2006), Regulation of nutrient uptake in eutrophic lowland streams, *Limnol. Oceanogr. Methods*, *51*, 1443–1453.
- Hall, R. O., and J. J. Beaulieu (2013), Estimating autotrophic respiration in streams using daily metabolism data, *Freshwater Sci.*, *32*, 507–516.
- Hall, R. O., and J. L. Tank (2003), Ecosystem metabolism controls nitrogen uptake in streams in Grand Teton National Park, Wyoming, *Limnol. Oceanogr. Methods*, *48*, 1120–1128.
- Hall, R. O., et al. (2009), Nitrate removal in stream ecosystems measured by N-15 addition experiments: Total uptake, *Limnol. Oceanogr. Methods*, *54*, 653–665.
- Hall, R. O., Jr., M. A. Baker, E. J. Rosi-Marshall, J. L. Tank, and J. D. Newbold (2013), Solute-specific scaling of inorganic nitrogen and phosphorus uptake in streams, *Biogeosciences*, *10*, 7323–7331.
- Harvey, J. W., J. K. Böhlke, M. A. Voytek, D. Scott, and C. R. Tobias (2013), Hyporheic zone denitrification: Controls on effective reaction depth and contribution to whole-stream mass balance, *Water Resour. Res.*, *49*, 6298–6316, doi:10.1002/wrcr.20492.
- Heffernan, J. B., and M. J. Cohen (2010), Direct and indirect coupling of primary production and diel nitrate dynamics in a subtropical spring-fed river, *Limnol. Oceanogr. Methods*, *55*, 677–688.
- Heffernan, J. B., M. J. Cohen, T. K. Frazer, R. G. Thomas, T. J. Rayfield, J. Gully, J. B. Martin, J. J. Delfino, and W. D. Graham (2010), Hydrologic and biotic influences on nitrate removal in a subtropical spring-fed river, *Limnol. Oceanogr. Methods*, *55*, 249–263.
- Hensley, R. T., and M. J. Cohen (2012), Controls on solute transport in large spring-fed karst rivers, *Limnol. Oceanogr. Methods*, *57*, 912–924.
- Hensley, R. T., and M. J. Cohen (2016), On the emergence of diel solute signals in flowing waters, *Water Resources Research*, *52*, 759–772.
- Hensley, R. T., M. J. Cohen, and L. V. Korhnak (2014), Inferring nitrogen removal in large rivers from high-resolution longitudinal profiling, *Limnol. Oceanogr. Methods*, *59*, 1152–1170.
- Hensley, R. T., M. J. Cohen, and L. V. Korhnak (2015), Hydraulic effects on nitrogen removal in a tidal spring-fed river, *Water Resour. Res.*, *51*, 1443–1456, doi:10.1002/2014WR016178.
- Jiang, S., S. Jomaa, O. Buttner, G. Meon, and M. Rode (2015), Multi-site identification of a distributed hydrological nitrogen model using Bayesian uncertainty analysis, *J. Hydrol.*, *529*, 940–950.
- Junge, F. W., C. Hanisch, L. Zerling, and M. Gehre (2005), Geochemical signatures (C, N,  $\delta^{13}\text{C}$ ,  $\delta^{15}\text{N}$ , metals) of suspended matter in the river Weiße Elster (central Germany): Their seasonal and flow-related distribution 1997–2001, *Isotopes Environ. Health Stud.*, *41*, 141–159.
- Kemp, M. J., and W. K. Dodds (2002), Comparison of nitrification and denitrification in prairie and agriculturally influenced streams, *Ecol. Appl.*, *12*, 998–1009.
- Kirchner, J. W., X. Feng, C. Neal, and A. J. Robson (2004), The fine structure of water-quality dynamics: The (high-frequency) wave of the future, *Hydrol. Processes*, *18*(7), 1353–1359.
- Knowles, R. (1982), Denitrification, *Microbiol. Rev.*, *43*–70.
- Laub, B. G., and M. A. Palmer (2009), Restoration ecology of rivers A2, in *Encyclopedia of Inland Waters*, edited by Gene E. Likens, pp. 332–341, Academic, Oxford, U. K.
- Laursen, A. E., and S. P. Seitzinger (2004), Diurnal patterns of denitrification, oxygen consumption and nitrous oxide production in rivers measured at the whole-reach scale, *Freshwater Biol.*, *49*, 1448–1458.
- Marti, E., and F. Sabater (1996), High variability in temporal and spatial nutrient retention in Mediterranean streams, *Ecology*, *77*, 854–869.
- Mulholland, P. J., et al. (2002), Can uptake length in streams be determined by nutrient addition experiments? Results from an interbiome comparison study, *J. North Am. Benthol. Soc.*, *21*, 544–560.
- Mulholland, P. J., et al. (2009), Nitrate removal in stream ecosystems measured by N-15 addition experiments: Denitrification, *Limnol. Oceanogr. Methods*, *54*, 666–680.
- O'Connor, B., and M. Hondzo (2008), Enhancement and inhibition of denitrification by fluid-flow and dissolved oxygen flux to stream sediments, *Environ. Sci. Technol.*, *42*, 566–578.
- Opdyke, M. R., M. B. David, and B. L. Rhoads (2006), Influence of geomorphological variability in channel characteristics on sediment denitrification in agricultural streams, *J. Environ. Qual.*, *35*, 2103–2112.
- Pellerin, B. A., B. D. Downing, C. Kendall, R. A. Dahlgren, T. E. C. Kraus, J. Saraceno, R. G. M. Spencer, and B. A. Bergamaschi (2009), Assessing the sources and magnitude of diurnal nitrate variability in the San Joaquin River (California) with an in situ optical nitrate sensor and dual nitrate isotopes, *Freshwater Biol.*, *54*, 376–387.
- Pinardi, M., M. Bartoli, D. Longhi, U. Marzocchi, A. Laini, C. Ribaudo, and P. Viaroli (2009), Benthic metabolism and denitrification in a river reach: A comparison between vegetated and bare sediments, *J. Limnol.*, *68*, 133–145.
- Pribyl, A. L., J. H. McCutchan, W. M. Lewis, and J. F. Saunders (2005), Whole-system estimation of denitrification in a plains river: A comparison of two methods, *Biogeochemistry*, *73*, 439–455.
- Roberts, B. J., P. J. Mulholland, and W. R. Hill (2007), Multiple scales of temporal variability in ecosystem metabolism rates: Results from 2 years of continuous monitoring in a forested headwater stream, *Ecosystems*, *10*, 588–606.
- Rode, M., and U. Suhr (2007), Uncertainties in selected river water quality data, *Hydrol. Earth Syst. Sci.*, *11*, 863–874.
- Rode, M., B. Klauer, D. Petry, M. Volk, G. Wenk, and D. Wagenschein (2008), Integrated nutrient transport modelling with respect to the implementation of the European WFD: The Weisse Elster Case Study, Germany, *Water SA*, *34*, 490–496.
- Rode, M., M. Hartwig, D. Wagenschein, T. Kebede, and D. Borchardt (2015), The importance of hyporheic zone processes on ecological functioning and solute transport of streams and rivers, in edited by L. Chicharo, F. Müller, and N. Fohrer, *Ecosyst. Serv. River Basin Ecohydrol.*, Springer, Dordrecht, 57–82.
- Rode, M., S. Halbedel, M. R. Anis, D. Borchardt, and M. Weitere (2016a), Continuous in-stream assimilatory nitrate uptake from high frequency sensor measurements, *Environ. Sci. Technol.*, *50*, 5685–5694.
- Rode, M., et al. (2016b), Sensors in the stream: The high-frequency wave of the present, *Environ. Sci. Technol.*, *50*, 10297–10307, doi:10.1021/acs.est.6b02155.
- Ruehl, C. R., A. T. Fisher, M. Los Huertos, S. D. Wankel, C. G. Wheat, C. Kendall, C. E. Hatch, and C. Shennan (2007), Nitrate dynamics within the Pajaro River, a nutrient-rich, losing stream, *J. North Am. Benthol. Soc.*, *26*, 191–206.
- Sächsisches Landesamt für Umwelt, Referat 46 - Bergbaufolgen (2013), Erweiterte Grundlagenermittlung mit Alternativuntersuchungen für das bergbaulich beeinflusste Fließgewässer Weiße Elster im Südraum von Leipzig Rep., LfULG, Leipzig, P114017GB.0220.DD1.
- Saraceno, J. F., B. A. Pellerin, B. D. Downing, E. Boss, P. A. M. Bachand, and B. A. Bergamaschi (2009), High-frequency in situ optical measurements during a storm event: Assessing relationships between dissolved organic matter, sediment concentrations, and hydrologic processes, *J. Geophys. Res.*, *114*, G00F09, doi:10.1029/2009JG000989.

- Seitzinger, S. (1988), Denitrification in freshwater and coastal marine ecosystems: Ecological and geochemical significance, *Limnol. Oceanogr.*, *33*, 702–724.
- Seitzinger, S. P., R. V. Styles, E. W. Boyer, R. B. Alexander, G. Billen, R. W. Howarth, B. Mayer, and N. Van Breemen (2002), Nitrogen retention in rivers: Model development and application to watersheds in the northeastern USA, *Biogeochemistry*, *57*, 199–237.
- Shammas, N. K. (1986), Interactions of temperature, pH, and biomass on the nitrification process, *J. Water Pollut. Control Fed.*, *58*, 52–59.
- Sigman, D., K. Casciotti, M. Andreani, C. Barford, M. Galanter, and J. Böhlke (2001), A bacterial method for the nitrogen isotopic analysis of nitrate in seawater and freshwater, *Anal. Chem.*, *73*, 4145–4153.
- Smith, V. H., S. B. Joye, and R. W. Howarth (2006), Eutrophication of freshwater and marine ecosystems, *Limnol. Oceanogr. Methods*, *51*, 351–355.
- Stanley, D. W., and J. E. Hobbie (1981), Nitrogen recycling in a North-Carolina coastal river, *Limnol. Oceanogr.*, *26*, 30–42.
- Stanley, E. H., and M. W. Doyle (2002), A Geomorphic perspective on nutrient retention following dam removal: Geomorphic models provide a means of predicting ecosystem responses to dam removal, *BioScience*, *52*, 693–701.
- Strauss, E. A., W. B. Richardson, L. A. Bartsch, J. C. Cavanaugh, D. A. Bruesewitz, H. Imker, J. A. Heinz, and D. M. Soballe (2004), Nitrification in the Upper Mississippi River: Patterns, controls, and contribution to the NO<sub>3</sub><sup>-</sup> budget, *J. North Am. Benthol. Soc.*, *23*, 1–14.
- Tank, J. L., E. J. Rosi-Marshall, M. A. Baker, and R. O. Hall Jr. (2008), Are rivers just big streams? A pulse method to quantify nitrogen demand in a large river, *Ecology*, *89*, 2935–2945.
- Wagenschein, D. (2006), Einfluss der Gewässermorphologie auf die Nährstoffretention - Modellstudie am Beispiel der mittleren Weißen Elster, dissertation thesis, Brandenburgische Tech. Univ., Leipzig, Germany.
- Wagenschein, D., and M. Rode (2008), Modelling the impact of river morphology on nitrogen retention—A case study of the Weisse Elster River (Germany), *Ecol. Modell.*, *211*, 224–232.
- Ward, A. S., N. M. Schmadel, S. M. Wondzell, C. Harman, M. N. Gooseff, and K. Singha (2016), Hydrogeomorphic controls on hyporheic and riparian transport in two headwater mountain streams during base flow recession, *Water Resour. Res.*, *52*, 1479–1497, doi:10.1002/2015WR018225.
- Warwick, J. J. (1986), Diel variation of in-stream nitrification, *Water Res.*, *20*, 1325–1332.
- Wollheim, W. M., C. J. Voosmarty, B. J. Peterson, S. P. Seitzinger, and C. S. Hopkinson (2006), Relationship between river size and nutrient removal, *Geophys. Res. Lett.*, *33*, L06410, doi:10.1029/2006GL025845.
- Wollheim, W. M., C. J. Vorosmarty, A. F. Bouwman, P. Green, J. Harrison, E. Linder, B. J. Peterson, S. P. Seitzinger, and J. P. M. Syvitski (2008), Global N removal by freshwater aquatic systems using a spatially distributed, within-basin approach, *Global Biogeochem. Cycles*, *22*, GB2026, doi:10.1029/2007GB002963.
- Worrall, F., N. J. K. Howden, and T. P. Burt (2015), Understanding the diurnal cycle in fluvial dissolved organic carbon—The interplay of in-stream residence time, day length and organic matter turnover, *J. Hydrol.*, *523*, 830–838.
- Zappa, C. J., W. R. McGillis, P. A. Raymond, J. B. Edson, E. J. Hints, H. J. Zemelink, J. W. H. Dacey, and D. T. Ho (2007), Environmental turbulent mixing controls on air-water gas exchange in marine and aquatic systems, *Geophys. Res. Lett.*, *34*, L10601, doi:10.1029/2006GL028790.
- Zarnetske, J. P., R. Haggerty, S. M. Wondzell, and M. A. Baker (2011), Dynamics of nitrate production and removal as a function of residence time in the hyporheic zone, *J. Geophys. Res.*, *116*, G01025, doi:10.1029/2010JG001356.
- Zhu, S., and S. Chen (2002), The impact of temperature on nitrification rate in fixed film biofilters, *Aquacult. Eng.*, *26*, 221–237.