Nitrate sinks and sources as controls of spatio-temporal water quality dynamics in an agricultural headwater catchment

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Abstract

Several controls are known to affect water quality of stream networks during flow recession periods such as solute leaching processes, surface water - groundwater interactions as well as biogeochemical in-stream turnover processes. Throughout the stream network combinations of specific water and solute export rates and local in-stream conditions overlay the biogeochemical signals from upstream sections. Therefore, upstream sections can be considered as functional units which could be distinguished and ordered regarding their relative contribution to nutrient dynamics at the catchment outlet. Based on snapshot sampling of flow and nitrate concentrations along the stream in an agricultural headwater during the summer flow recession period, we determined spatial and temporal patterns of water quality for the whole stream. A data-driven, in-stream-mixing-and-removal model was developed and applied for analyzing the spatio-temporal in-stream retention processes and their effect on the spatio-temporal fluxes of nitrate from sub-catchments. Thereby, we have been able to distinguish quantitatively between nitrate sinks and sources per stream reaches and sub-catchments and thus we could disentangle the overlay of nitrate sink and source signals. For nitrate sources we have determined their permanent and temporally impact on stream water quality and for nitrate sinks we have found increasing nitrate removal efficiencies from up- to downstream. Our results highlight the importance of distinct nitrate source locations within the watershed for in-stream concentrations and in-stream removal processes, respectively. Thus, our findings contribute to the development of a more dynamic perception of water quality in streams and rivers concerning ecological and sustainable water resources management.

1. Introduction

Dissolved nutrients such as nitrate and soluble reactive phosphorus control surface water trophic status (e.g. Likens and Bormann, 1974). Therefore, increasing concentrations of nitrate in streams and rivers of agricultural landscapes pose a severe risk for their ecological status and downstream for drinking water resources. Local nitrate concentrations in streams and rivers depend largely on two antagonistic controls: nitrate export processes from landscapes to the stream network (e.g. Carpenter et al., 1998; Lam et al., 2012; Schilling and Zhang, 2004; Tesoriero et al., 2013) and in-stream removal processes (e.g. Bowes et al., 2014; Burgin and Hamilton, 2007; Covino et al., 2012; Hill, 1996; Montreuil et al., 2010; Mulholland et al., 2008). The stream network itself can be treated as an interface that connects the different landscape components and determine the dynamics of the water quality (Hunsaker and Levine, 1995). Moreover, the convolution of water and matter fluxes from up- to downstream can be dominated by hydrological turnover processes (i.e. the sum of stream – groundwater exchange fluxes) throughout the stream network (Mallard et al., 2014).

Nitrate export processes comprise various interacting processes and drivers. Depending on present landuse (Mulholland et al., 2008) and land management (Basu et al., 2010; Marwick et al., 2014; McCarty et al., 2014), the balance between N inputs (fertilizers, N deposition, N fixation) and N uptake by plants is the main driver, especially in agricultural landscapes. Organic nitrogen mineralization in soils plays also a major part, in relation with biological activity (Bormann and Likens, 1967), climate (Mitchell et al., 1996), hydrology (Montreuil et al., 2010) and landscapes hydrogeological and pedological characteristics (Schilling and Zhang, 2004). Another important source for in-stream nitrate is direct nitrification of ammonium in the water column (Bernhardt et al., 2002). Denitrification in anoxic zones, and particularly the riparian zone, acts as an important sink of nitrate (Aquilina et al., 2012; Wriedt et al., 2007). During recession periods (e.g. in summer) the connectivity between groundwater (GW) and surface waters plays a key role (Molenat et al., 2008; Smethurst et al., 2014). In agricultural landscapes this is important due to dense artificial surface and sub-surface drainage networks (Buchanan et al., 2013; Guan et al., 2011; Lam et al., 2012), because they drain superficial GW which is well known to store N excess from many years.

In-stream removal summarizes various processes contributing to a decrease of apparent nitrate concentrations within the stream channel and the adjacent hyporheic zone or stream sediments (Ranalli and Macalady, 2010). The intensity of in-stream removal processes is variable and depends on local conditions and the combination of occurring removal processes. Local streambed morphology determines available mineral and vegetation surfaces for the development of microbial biofilms, which can decrease nitrate concentrations by denitrification processes (Triska et al., 1989). For example microbial biofilm thickness is an important control for in-stream respiration processes (Haggerty et al., 2014) and thus for denitrification (Burgin and Hamilton, 2007). The impact of photoautotrophic nitrate assimilation depends on incoming solar radiation and occurs mainly during the hours of highest ecosystem productivity (e.g. Fellows et al., 2006; Hall and Tank, 2003). Streambed permeability and the hydraulic conductivity of underlying sediments govern hyporheic exchange fluxes in dependence of local hydraulic gradients (Krause et al., 2012) and thus largely control denitrification processes (by controlling available nitrate loads) in the anaerobic compartments of the hyporheic zone. There is a large body of literature studying denitrification processes in the hyporheic zone (e.g. Briggs et al., 2013; Harvey et al., 2013; Lewandowski and Nützmann, 2010; Zarnetske et al., 2011, 2012). Without additional information, such as isotopic data, dissolved oxygen concentration dynamics or dissolved organic carbon concentration changes, it is difficult to distinguish biotic and abiotic processes properly. Hence, these processes are summarized as in-stream removal processes, which are either estimated using land use /-scale (e.g. Covino et al., 2012), water temperatures (e.g. Lomas and Glibert, 1999), water levels (e.g. Basu et al., 2011; Hensley et al., 2015; Thompson et al., 2011) or discharge (e.g. Flewelling et al., 2014). Compared to hydrological export processes (concentration and dilution processes) in-stream removal processes have a smaller impact on total in-stream nitrate concentrations, but they can be responsible for nitrate removal (apparent decrease of nitrate concentrations, excluding dilution processes) in the range of 2 % - 10 % at the reach scale (i.e. 100 m - 200 m) (Harvey et al., 2013; Hensley et al., 2015), 10 % - 30 % for entire river networks (Dupas et al., 2013; Windolf et al., 2011) and up to around 70 % of total exported nitrate-nitrogen at larger scales (i.e. total retention, including retention processes e.g. in the riparian zone or in wetlands) (Dupas et al., 2013; Howarth et al., 1996).

In agricultural landscapes, nitrate export is a diffuse pollution even if nitrate fluxes can have distinct locations of inflow into the stream network according to sub-catchments and related drainage network outlets. Groundwater might enter streams and rivers at spatially distinct locations, due to topography, local heterogeneity of streambeds and hydrogeological settings (Binley et al., 2013; Krause et al., 2012). Hence, changes in total water and nitrate fluxes occur frequently all along the stream network. This is mainly true for first-order stream networks. Considering, that a major part of the regional stream and river network consists of first-order streams (e.g. 48 % for the contiguous United States (Poff et al., 2006)) nitrate export and turnover processes in first-order stream networks can have a large impact on total catchment nitrate export even on larger scales.

In this study we define the different sub-catchments and stream reaches where nitrate fluxes can vary as nitrate sinks or sources: nitrate sources are tributaries which cause an increase in stream nitrate loads; nitrate sinks are stream sections where nitrate load is decreasing. A nitrate source does not necessarily result in an increase of in stream nitrate concentration, but does always increase the total nitrate load.

The temporal variations of hydrological and nitrate export processes along different spatial scales have been reproduced by varying modeling approaches (e.g. Donner et al., 2002; Huang et al., 2014; Johnes, 1996; Smethurst et al., 2014; Wagenschein and Rode, 2008; Wriedt and Rode, 2006). Nevertheless, there is still a lack of knowledge on how the spatial patterns of in-stream nitrate concentrations evolve throughout stream networks and whether these patterns are constant over time or vary in time. We analyze this complex interplay of different processes by investigating two main research questions:

1) Can we quantify the spatio-temporal impact of distinct nitrate sinks and sources on nitrate dynamics in a first-order stream network?

2) Can we determine underlying processes and drivers?

Answering these questions is relevant for a future improvement of water quality threshold compliances in agricultural landscapes, ecological water quality management e.g. planning of river restoration and the implementation of environmental guidelines, such as the European Water Framework Directive.

In this study we use a set of discharge and water quality data gathered during 10 snapshot sampling campaigns along the main stream of a small agricultural headwater catchment. A dense artificial drainage network and a predominantly impervious streambed allowed for detecting distinct groundwater inflow locations. This unique setting allowed us to quantify and model the dynamics of nitrate sinks and sources in a first-order stream network during the summer period. Thus we can distinguish and quantify the interaction of conservative mixing and dilution processes and biogeochemical in-stream processes on the (first-order) network scale.

2. Study area

The study area is in the Löchernbach catchment, a 1.7 km² agricultural headwater catchment. It is located in southwestern Germany within the wine-growing area of the Kaiserstuhl (Fig. 1), with a temperate climate characterized by warm summers and evenly distributed precipitation (Koeppen-classification: Cfb). Mean annual precipitation was 765 mm between 2008 and 2013 with a mean air temperature of 10.9 °C. Event runoff coefficients vary between 6 and 20% (e.g. Gassmann et al., 2011; Luft et al., 1985). The dominant soil is a silty calcaric regosol with gleizations in the colluvium (10% sand, 80% silt and 10% clay). The underlying geology is a deep layer of aeolian loess (> several 10s of m) over tertiary volcanic basalts. Due to agricultural landscape management in the 1970s the catchment is divided into an upper area with large artificial terraces covered with vineyards (63.2 % of the area) and the main valley where arable crops (e.g. cabbage, corn, beetroots) are dominating (18.3 %). Other surfaces are paved roads (4.6 %), steep terrace slopes (10.3 %) and beech forest (3.5 %) in the uppermost part of the catchment. The catchment's elevation spans from 213 m a.s.l. to 378 m a.s.l.. The stream length of the main stream is 1330 m from the spring (256 m a.s.l.) to the catchment outlet; the main tributary has a length of 600 m (Fig. 1). The mean streambed slope is 3.2 %. A dense sub-surface pipe network (about 9 km total length) drains the terraces and the fields in the open valley down to the stream. The road drainage system connects to these pipes as well. Considering non-turbulent in-stream conditions during low flow, active drainpipes and mixing lengths in the stream for optimal sampling positions have been determined using handheld thermal imaging (Schuetz and Weiler, 2011). Since the 1970s we observe an increase of the unsaturated zone area (>30 m) in some parts of the catchment and the disconnection of the saturated zone from the stream during summer; that is why during summer months base flow is only generated through the artificial drainage system. Clogging effects and artificially fixed streambanks and -beds cause a predominantly impervious streambed, which causes little stream bed infiltration during summer low flows.

3. Methods

3.1 Sampling methods & water quality data

Sampling campaigns were carried out during base flow periods from June to August 2012. Two types of campaigns were conducted (Table 1): we sampled: a) a 100 m stream reach (Reach 1, Fig. 1) at 5 positions during 5 campaigns for water temperatures (T), electrical conductivity (EC) and major anion concentrations (chloride, nitrate, sulfate) and b) the main stream upstream, downstream and inside all active drainpipes/tributaries (Fig. 1) during 10 campaigns for T, EC and during 2 campaigns (No. 1, No. 10) for major anion concentrations (chloride, nitrate, sulfate). During each campaign discharge was determined with salt dilution gauging (slug injection) at the catchment outlet and at several locations (0-4) throughout the stream network (Fig. 1).

For T absolute measurement uncertainty was 0.2 K and the relative accuracy for EC was 0.5 % of the measurement (WTW LF92). Water samples were taken with 100 ml brown glass bottles, which were stored in a refrigerator and analyzed for major anions (chloride, nitrate, sulfate) within two to four weeks after sampling with ion chromatography (*Dionex* DX-500). Measurement uncertainty was 0.1 mg/l for major anions. Climate data (Air temperatures (T_{air}), rel. humidity, global radiation, wind speed) were taken from a nearby climate station (1.3 km distance to the south).

Channel geomorphology and streambed structural characteristics such as channel widths and depths, rock outcrops and vegetation at the stream banks and in the stream bed were mapped once at 23 random locations distributed throughout the stream network.

3.2 Stream network discharge patterns

Patterns of relative stream network discharges are determined by the successive application of mixing equations on EC data (and *T,* chloride or sulfate data at reaches where two active drain pipes were found) obtained upstream, downstream and inside all active drain pipes from the catchment outlet up to the main spring. Fractions *f* of reach drain water discharge f_{di} relative to downstream stream discharge (Q_i) are calculated after Genereux et al. (1998) based on the conservative mixing equations for two or three endmembers (*EC* and *T,* alternatively chloride and sulfate, when available (the majority (66%) of the reaches have only one active drain pipe, thus the equations are reduced to two end-members which can be solved using one parameter only (*EC*))):

$$Q_i = Q_{di_1} + Q_{di_2} + Q_{i-1}, \tag{1}$$

$$1 = f_{di_1} + f_{di_2} + f_{i-1} \tag{2}$$

$$EC_i = f_{di_1} EC_{i_1} + f_{di_2} EC_{di_2} + f_{i-1} EC_{i-1} \tag{3}$$

and

$$T_i = f_{di_1} T_{i_1} + f_{di_2} T_{di_2} + f_{i-1} T_{i-1} \quad (4)$$

where the subscript i represent the total number of upstream stream reaches (i.e. the number of the actual reach of interest) with i=0 at the stream network main source and the subsubscripts $_1$ and $_2$ stands for the drain pipes leading to the stream at the upstream end of reach i. Resulting fractional drain pipe water contributions are then used to calculate relative discharge patterns throughout the stream network for all sampling campaigns with following equations

$$f_{net,di} = f_{net,i} \cdot f_{di} \quad (5)$$

and

$$f_{net,i-1} = f_{net,i} - f_{net,di_1} - f_{net,di_2}, \quad (6)$$

where the subscript $_{net}$ stands for fractional water fluxes of all stream reaches (and drain pipes) relative to the discharges at the catchment outlet. This simple conceptual stream-source-model was possible due to the disconnection of the saturated zone to the stream, the visual exclusion (thermal imaging (e.g. Schuetz and Weiler, 2011)) of other groundwater sources and the assumption of negligible water losses to the (anthropogenically restructured) colluvium. Absolute stream network discharge patterns and drain pipe discharges are then derived by combining absolute discharge measurements from the catchment outlet ($Q_{i=9,obs}$) with the fractional results of the stream-source-model (Eq. 7) for each stream reach (Q_i) and each drainpipe, respectively in following form

$$Q_{di} = f_{net,di} \cdot Q_{i=9,obs} \quad . \quad (7)$$

Measurement errors and associated uncertainties of calculated stream network discharges and drain pipe discharges are propagated applying the equations given in *Genereux* (1998) for mixing equations with two and three components, respectively. Stream network discharges ($Q_{i,obs}$) observed with salt dilution gauging (with an approximated error of 10 % (e.g. Moore, 2005)) are then used to validate derived stream network discharge patterns.

3.3 Nitrate source concentrations

Nitrate concentrations measured inside all active drainpipes ($C_{di,obs}$) during sampling campaigns No. 1 and No. 10 are used to assess nitrate source concentrations for the whole study period: Assuming a groundwater system with slow seasonal nitrate dynamics drain pipe nitrate concentrations for all sampling campaigns (campaigns No. 2 to No. 9) are derived by linearly interpolating between the observed nitrate concentrations from the first and the last sampling campaign (sampling campaigns No.1 and No. 10). This assumption is in line with observations made in the following summer (results not shown).

3.4 In-stream nitrate removal

The sum of all nitrate removal processes in surface waters (i.e. in-stream removal) under stationary conditions regarding discharge input and conservation (i.e. change in concentration equals change in load) is commonly simulated with a kinetic first-order removal model following an exponential function (e.g. Stream Solute Workshop, 1990)

$$C_{i,obs}(\tau_i) = C_{i,obs}(0) \cdot \exp(-k_i \tau_i), \tag{8}$$

where $C_{i,obs}(0)$ stands for the nitrate concentration observed at the beginning of a stream reach *i and* $C_{i,obs}(\tau_i)$ stands for the nitrate concentration observed at the end of stream reach *i*. k stands for the removal rate (T^{-1}) and τ stands for the stream reach residence time (T). τ is determined by

$$\tau = \frac{l}{v}, \tag{9}$$

where l stands for the reach length (L) and v for the mean flow velocity (L T^{-1}). v can be approximated with the ratio of discharge to the wetted stream cross section A (L^2)

$$v = \frac{Q}{A}. \tag{10}$$

For a trapezoidal stream bed with a known stream bank angle α *(°),* stream bed width b (L) and mean water depth h (L), A can be estimated with

$$A = b \cdot h + h^2 \cdot \tan\alpha. \tag{11}$$

Combining the Manning-Strickler equation

$$v = n^{-1} \cdot R_{hy}^{2/3} \cdot s^{1/2} \tag{12}$$

where n stands for Mannings' n (T1/3/L), R_{hy} (L) for the hydraulic radius, s stands for the hydraulic gradient (approximated with stream bed slope (L L^{-1})) with following assumption after *Moore and Foster* (1990)

$$R_{hy} = \xi \cdot A^{1/2}, \quad (13)$$

where the constant ξ (-) depends on the side slope ratio of the stream bank and stream bed width to depth ratio (Moore and Foster, 1990) Eq. (10) to (13) can be transformed into

$$h = \frac{b + \left(b^2 + 4 \cdot \tan\alpha \left(\frac{Q \cdot n}{s^{1/2} \cdot \xi^{2/3}} \right)^{3/4} \right)^{1/2}}{2 \cdot \tan\alpha}. \quad (14)$$

Applying Eq. (9), (10) and (14) with actual stream reach discharges (Q_i), τ can be determined individually for each stream reach and discharge.

Empirical nitrate removal rates k_i for the five data sets observed at Reach 1 and for the two data sets (campaign No. 1 and No. 10) observed throughout the stream network can then be determined by rearranging Eq. (8) to

$$k_i = -\frac{\ln \frac{C_i(\tau_i)}{C_i(0)}}{\tau_i} \quad . \quad (15)$$

In order to calculate k_i for all the sampling campaigns we try to relate observed k_i (for campaigns No. 1 and No. 10 and the five detailed sampling campaigns in Reach 1) with parameters measured systematically. For this, we developed the conceptual transfer T_{AWET} (°C/L; *A*ir-*W*ater-*E*nergy-*T*ransfer)

$$T_{AWET,i} = T_{air} \frac{\Delta T_i}{(T_{air} - T_i)} \quad (16)$$

which is based on observed mean daytime air temperatures T_{air} (°C) on the day of each sampling campaign (8 a.m. to 8 p.m.), reach scale stream water heating ΔT (°C L^{-1}) and the temperature gradient between T_{air} and stream water temperatures T_i (°C). We try to consider the spatial variability of energy inputs into the stream system as a control of biological activity by accounting for the effect of shading (slows down the increase of ΔT) and the effect of local groundwater contributions at the upstream end of a stream reach, which cools down T_i and thus increases the gradient between air and water temperatures.

Uncertainties for empirical in-stream nitrate removal rates k_i and removal rates estimated with the empirical relationship for T_{AWET} are done by propagating (Gaussian error propagation) measurement errors and associated uncertainties of observed water and air temperatures and nitrate concentrations.

Standardized comparison of in-stream nitrate removal processes with stream/catchment specific properties is commonly done following the recommendations of the *Stream Solute Workshop* (1990) by calculating (amongst others) in-stream uptake rates k_C, which equals k_i introduced above, and areal nitrate uptake U_i (M L^{-2} T^{-1}), which is defined by

$$U_i = C_i(0) \cdot h_i \cdot k_i . \tag{17}$$

3.5 Implementation of the in-stream-mixing-and-removal-model

Accounting for lateral drain pipe discharges (chapter 3.2) and stream network discharge patterns, lateral source/ drain pipe nitrate concentrations (chapter 3.3) and in-stream nitrate removal processes (section 3.4) we define a conceptual data-driven in-stream-mixing-and-removal model by combining previous equations as follows:

$$C_{i+1} = \frac{C_i(0) \cdot \exp(-k_i \tau_i) \cdot Q_i + C_{di+1_1} \cdot Q_{di+1_1} + C_{di+1_2} \cdot Q_{di+1_2}}{Q_{i+1}} . \tag{18}$$

Model application is done by using the measured/estimated *C(0)* of the uppermost reach, the measured/estimated C_{di} of the drain pipes, the Q_i / Q_{di} calculated from the endmember mixing and k_i estimated with T_{AWET} as input variables for the successive calculation of stream network nitrate concentrations from up- to downstream. All parameters, nitrate concentrations and discharges integrated into eq. 18 are estimated without any calibration. Taking into account that modelling uncertainties will be influenced not only by the uncertainties of Q_i (successively estimated from down- to up-stream) and k_i estimated with T_{AWET}, but as well by the uncertainties implied through the assumptions which were made for the estimations of τ_i and drain pipe nitrate concentrations, the uncertainties in our modelling results will be larger than the differences within our simulations. Hence, we will refrain from an uncertainty analysis of stream network modelling results. However, observed versus predicted comparisons of various parameters quantified the overall error.

4. Results

4.1 Nitrate spatio-temporal patterns on the reach and stream network

Besides the main spring, we detected in total 11 active drainpipes (plus one tributary, Fig. 1) of which six were intermittent. At three locations two pipes drain at one point into the stream. Stream network nitrate concentrations sampled during campaign No. 1 and No. 10 upstream, downstream and inside all active drainpipes revealed a spatial concentration patterns with increasing concentrations from up- to downstream (Fig. 2) and with different concentration changes among the stream reaches. Nitrate concentrations in the drainpipes differed clearly from in-stream concentrations. In most of the stream reaches nitrate concentrations decreased, particularly within stream reach No.1 (Fig. 2, inset), where nitrate was additionally sampled during 5 snapshot campaigns with a higher spatial resolution.

4.2 Stream network discharge patterns

We determined all drain pipe discharges for each sampling campaign applying Eq. (1) to (7) using the obtained *EC* data (and *T*, chloride or sulfate data, where two drain pipes are located at one position) and the discharges observed at the catchment outlet. Discharge varied among all drainpipes and between all campaigns between 0.05 l/s and 1.7 l/s with a mean error of 0.21 l/s. While the main spring and drain pipes D1 - D6 never contributed more than 0.5 l/s, drain pipes D7.1, D7.2 and D8 delivered most of the time either distinctly more than 0.5 l/s or were dry. Using the individual discharge contribution of all drainpipes we determined distinct stream network discharge patterns for each campaign (Fig. 3A and 3B) with a mean absolute discharge increase of 0.2±0.06 l/s/100 m and a mean relative discharge increase of 8±7 %/100m. Comparing observed discharges with calculated discharges we find a good agreement with an R^2 of 0.51 ($p < 0.0001$; $n = 24$) and a mean absolute error of 0.83 l/s (Fig. 3A inset). The patterns of relative longitudinal discharge evolution show a clear change between the different sampling campaigns.

Based on a digital elevation model with a spatial resolution of 1 m² and a vertical resolution of 0.1 m we determined the mean slopes of the streambed per reach. Mean channel roughness was estimated with a Manning's *n* of 0.0585 ($s^{1/3/m}$) for the total stream network following the procedure described in *Arcement and Schneider* (1989). Stream bank angles were uniformly approximated with 30° and mean streambed width was set to 0.38 m based on the observed mean streambed width obtained during a random sampling of stream morphology (the channel was restructured in the 1970s, and is very homogenously shaped). Applying Eq. (9) to (14) the residence times of each stream reach was derived, which varied between 234 und 1583 s. Variations of residence times between the reaches and the different campaigns depend only on the differences of reach lengths, streambed slopes and actual discharge (Table 2).

4.3 Nitrate dynamics along the stream network

Nitrate concentrations in the drainpipes ranged between 8.7 mg/l and 48 mg/l with a mean increase of 1.3 mg/l /100m from up- to downstream ($R^2 = 0.21$; $p < 0.05$; $n = 24$). Between campaign No.1 and No. 10 eight drainpipes showed decreasing concentrations with a mean decrease of 5.2 +/- 2.7 mg/l and four drainpipes showed increasing concentrations with a mean increase of 2.3 +/- 0.9 mg/l.

Applying Eq. (15) to the observed in-stream nitrate concentration changes within the reaches, the empirical in-stream nitrate removal rate k_i was calculated, which varies between $3.5*10^{-6}$ s^{-1} and $5*10^{-4}$ s^{-1}. Relating the empirical nitrate removal rate k_i to the conceptual transfer coefficient T_{AWET} shows a significant linear correlation ($R^2 = 0.82$; $p < 0.0001$; $n = 21$). In order to avoid the prediction of negative removal rates the log-transform of k_i is tested against T_{AWET}. This yields a linear correlation with lower statistical power ($R^2 = 0.63$; $p = 0.0002$; $n = 16$). Comparing the resulting regression model with empirical in-stream nitrate removal rates we find a good approximation with a mean relative error of 40%, which seems to be appropriate, though deviations between empirical and estimated removal rates increase only when the observed removal rates become very small (Fig. 4A).

Applying the in-stream-mixing-and-removal model (eq. 18) to all stream network data sets (spatially discretized drain pipe discharges and nitrate loads) we find distinct patterns of nitrate concentrations along the stream network (Fig. 4B). Stream nitrate concentration patterns show that the impact of nitrate sources regarding the downstream changes of in-stream nitrate concentrations is directly connected with interaction between local source fluxes and in-stream nitrate and water fluxes. The temporal variability of removal processes simulated for different stream reaches is clearly changing the picture. Some of the nitrate sources and some of the stream reaches show a distinctly stronger impact on the temporal and spatial evolution of in-stream nitrate concentrations than others. The simulation results were tested against in-stream nitrate concentrations observed during sampling campaigns No. 1 and No. 10 (Fig. 4B (blue and red lines/symbols)) and 4C). With an R^2 of 0.91 for sampling campaign No. 1 and an R^2 of 0.97 for sampling campaign No. 10 (Fig. 4C) the observations are reproduced quite well. This includes the temporal changes of in-stream nitrate concentrations: at the beginning of the study (sampling campaign No. 1) in-stream nitrate concentrations were generally less variable throughout the stream network than at the end of the study (sampling campaign No. 10), when very low concentrations occurred as well.

4.4 Hierarchy of nitrate sinks and sources

The effects of nitrate sinks and sources on in-stream nitrate dynamics are visualized considering the spatial and temporal distribution of nitrate loads throughout the stream network (Fig. 5A). For each sampling campaign distinct nitrate load distributions and contributions were found. The detailed spatial representation of nitrate sinks and sources in Fig. 5 shows that absolute and relative impacts of distinct sinks and sources on total nitrate load at the catchment outlet are more pronounced than the variations of nitrate concentration (Fig. 4B) and discharge dynamics (Fig. 3A). Median relative nitrate removal per source (i.e. the magnitude of in-stream removal per source at the catchment outlet (Fig. 5B)) clearly depends on the position of a source in the stream network ($R^2 = 0.95$; $p < 0.0001$; $n = 12$). Nitrate loads emitted at the catchment spring are removed between 20 and 50%, while loads emitted in the lower sections of the stream network show a much lower relative removal. In contrary, the differences of relative nitrate load removal per source between adjacent nitrate sources are not related to the specific reach lengths.

Nitrate sources show a distinct hierarchy among the different sources (Fig. 6A), which is more controlled by drainpipe discharge (median nitrate load vs drainpipe discharge: $R^2 = 0.85$; $p < 0.0001$; $n = 120$) than by nitrate concentrations (no significant correlation between median nitrate loads and drainpipe nitrate concentrations). Some sources contribute during most of the days the major part of total nitrate loads (D8, D6, D4.1) while other sources are varying between major nitrate load contributions and no contributions at all (i.e. intermittent drain pipes, e.g. D7.1, D7.2). Positioning along the stream shows no correlation with the rank of the source contribution.

When comparing the rankings of median in-stream nitrate removal k_i (Fig. 6B) and median areal nitrate uptake rates U_i (Fig. 6C) we find a different order of stream reaches: while in-stream nitrate removal rates decrease from upstream to downstream ($R^2 = 0.74$; $p = 0.0029$; $n = 9$), the areal nitrate uptake rates U_i do not show such a clear pattern. In the downstream reaches (Reach 7, 9, and 8) areal uptake rates are the highest but there is no significant relation within the ranking of areal nitrate uptake U_i and the spatial location along the stream network.

5. Discussion

We have quantified nitrate sinks and sources, which contribute to the spatial patterns of in-stream nitrate concentrations along a first-order stream network and their evolution in time.

We could show how distinct nitrate sinks and sources persistently dominate these patterns over time. These findings are supported by several recent studies which show for larger scales the uniqueness of spatial water quality composition based on stream sampling campaigns (e.g. Lam et al., 2012; Vogt et al., 2015) or based on modelling approaches describing the spatial distribution of nitrate export in stream networks (e.g. Isaak et al., 2014). Both approaches show the importance of spatial "hot spots" regarding nitrate sources. The originality of our work, in comparison to these studies, is that we have studied the temporal variations of nitrate contributions with an emphasis on local flux contributions based on a data-driven modelling approach.

5.1 Nitrate sources

The unique setting in our study area (known locations of groundwater inflow and negligible stream water losses) allowed inferring water and nitrate fluxes and flux changes along the stream without neglecting important contributions. Looking at the longitudinal stream profiles of absolute and relative discharges (Fig. 3A and 3B) we find a high temporal variability within the spatial patterns of the catchment drainage system. This can be explained by specific discharge recessions for different landscape elements/hydrogeological storages during baseflow periods (Payn et al., 2012). The different sub-catchments (or rather the areas connected to the drain pipes) show differences regarding their spatial extent, elevations and land use combinations. This high variability was not expected before, though *Mallard et al.* (2014) show that for specific catchments (e.g. with a certain shape and channel network) characteristic longitudinal stream discharge profiles can be found. Our data show for the observed time period that these patterns are rather unstable. Consequently, the impact of certain sub-catchments on total nitrate export changes over time and the spatial changes can be more or less dominant.

5.2 Nitrate sinks

In this study stream network nitrate sinks are defined as the sum of all in-stream nitrate removal processes on each reach. We do not use the presented approach to distinguish between different biogeochemical processes but to empirically simulate the net effect of biogeochemical processes on downstream nitrate concentrations. For other catchments, additional nitrate mass losses along the stream channel (i.e. indirect groundwater recharge) have to be considered. *Mallard et al.* (2014) showed that cumulative gross channel discharge losses could retain large parts of the discharges generated in the headwaters (and thus large parts of the nitrate loads emitted from the headwaters). Depending on the spatial differences in groundwater nitrate concentrations the hydrological turnover could then overlay partly the processes described in this study. But the hydrological turnover will likewise influence downstream groundwater nitrate concentrations and thus the magnitude of downstream nitrate sources.

We estimated in-stream nitrate removal rates k_i using the empirical transfer coefficient T_{AWET}, which describes the energy limitation of a specific stream reach. Comparing the ranking of in-stream nitrate removal rates k_i and areal uptake rates U_i (Fig. 7A) we find an increasing uptake-efficiency (i.e. lower removal rates cause equal areal uptake) from up- to downstream. Considering that for a given reach, U_i and k_i are linked by stream reach water levels and nitrate concentrations (Eq. 17), we can conclude that the increase in uptake-efficiency can be caused by increasing water levels or nitrate concentrations, likewise. Nonetheless, observable changes in in-stream nitrate concentrations are larger in up-stream reaches than in the downstream reaches.

However, on smaller scales (such as the study area) the temporal variability of in-stream nitrate concentrations cannot be explained by land use alone (e.g. Mulholland et al., 2008; Ruiz et al., 2002). A higher spatial resolution of geomorphic or physic-chemical information is needed. Although we know that gross primary production and in-stream nitrate turnover in stream ecosystems is directly linked to water temperatures and incoming radiation (e.g. Fellows et al., 2006; Hall and Tank, 2003; Lomas and Glibert, 1999), the high spatial resolution of our study did not allow a direct comparison of observed in-stream nitrate removal to atmospheric conditions. We found a significant correlation for T_i and empirical removal rates k_i on the reach scale (Reach 1), which was not valid on the network-scale. This can be explained by the spatial variability of inflowing groundwater/nitrate sources, channel geomorphology or vegetation density. Hence, we consider explicitly the impacts of local shading, upstream stream water temperatures (which is a measure of surface travel time) and local cooling effects of inflowing groundwater for the derivation of T_{AWET}. A more physically based interpretation of the involved processes would have required deeper knowledge on the spatial distribution of stream bed geomorphology and vegetation. In many other studies (e.g. Alexander et al., 2009; Basu et al., 2011; Hensley et al., 2015) water levels alone were used for the estimation of in-stream removal processes. Though existing hydraulic information is commonly used to estimate both, stream reach residence times (Stream Solute Workshop, 1990) and areal nitrate uptake rates U_i (Eq. 14), we think that the independent estimation of k_i, by using additional measurements of stream water temperatures, groundwater temperatures and air temperatures improves the reliability of the presented non-calibrated and data-driven modelling approach. Nonetheless, one must consider that hyporheic exchange processes (and thus denitrification by heterotrophic organisms) contribute to nitrate removal processes as well (Harvey et al., 2013; Kiel and Cardenas, 2014; Zarnetske et al., 2011). Hence, the interdependency of hydraulic conditions and energy availability at the reach scale cannot be easily resolved. For the present study we could show that the change in nitrate concentrations per reach relates almost 1:1 to the change in nitrate-N/chloride ratios per reach for all our observations (Fig. 7B). This is also true for the three observations where an increase in nitrate concentrations occurred from up- to downstream. Nitrate-N to chloride mass ratios has been used before as a signature that other processes as dilution (Schilling et al., 2006) or rather denitrification processes (Tesoriero et al., 2013) are responsible for the change in nitrate concentrations. Hence, we conclude that both controls are relevant for a specific stream network and thus the decision for one or the other measurement should be made with great care.

5.3 Hierarchy of nitrate sinks and sources

Considering the relationship of in-stream water fluxes and nitrate concentrations with water and nitrate flux contributions from landscape units along the stream network, in-stream nitrate concentrations can change clearly from upstream to downstream through enrichment and dilution processes. The effect of the spatial arrangement of nitrate source areas and stream reaches along the stream network with high or low retention potential is manifested in the longitudinal nitrate concentration patterns observable along a stream or river (e.g. Fig. 2 and Fig. 4A). It becomes clear that there is a direct impact of the location of a tributary or a groundwater source of nitrate and stream reaches with high nitrate turnover rates on downstream nitrate concentrations. Nitrate loads emitted by specific upstream sources can be removed to a large extent on their way through a stream network (Fig. 5).

The seasonal variations of in-stream nitrate concentrations could be larger than the variations of nitrate concentrations presented within this study. Nevertheless, these variations occur during relatively short time periods (summer low flows) when ecological in-stream conditions are crucial for in-stream habitat conditions: e.g. a nutrient surplus in combination with warm temperatures and high solar radiation input can cause eutrophic conditions in the stream ecosystem. Hence, a better understanding of the evolution of apparent in-stream nitrate concentrations is relevant for e.g. water quality threshold exceedances. Due to the stationary or slowly changing conditions during low flow periods, spatial water quality patterns are little affected by hydrodynamic and geomorphic dispersion of point source /sub-catchment nitrate emissions (Botter and Rinaldo, 2003). Hence, observed step changes of in-stream concentrations can be expected as a frequently occurring phenomenon. In many studies published on nitrate export the focus is on nitrate concentrations observed at a single location in the stream (i.e. catchment outlet). Our results (specifically Fig. 2B and 4B) illustrate that there is a clear need to better understand the spatio-temporal hydrological connectivity (and thus water and matter fluxes) of landscapes to the fluvial systems. For the in-stream-mixing-and-removal model applied to the Löchernbach catchment distinct boundary conditions could be defined. In other systems where export processes to the stream occur more diffusely and where non-negligible stream water losses occur (i. e. groundwater - surface water interaction) an improved understanding of nitrate sinks and sources is even more important. For these systems we have to additionally consider the variable interplay of local gradients between groundwater and surface water (Krause et al., 2012) and their influence on water and matter turnover processes in the stream network and the reverse effect of in-stream-mixing-and-removal processes on local groundwater quality dynamics. The study of *Mallard et al.* (2014) provided a first step into a longitudinally more dynamic system understanding of water flux dynamics (and thus water quality dynamics) in stream and river networks. We could show that for biogeochemically active substances, such as nutrients, their approach should be supplemented by the consideration of in-stream cycling and retention processes and their masking effects from up- to downstream.

Our results apply mostly to first-order stream networks. However, due to the large effects on first-order catchment nitrate export and the dominance of first-order catchments in the regional river network (Poff et al., 2006) they are relevant even on larger scales: Our findings imply that a more complex understanding of the hydro-ecological functioning of a specific stream or river system regarding the origin of water and of matter fluxes has to be applied for the planning of ecological measures or sustainable water resources management. This concerns the distribution of different types of land use within the catchment (e.g. intensive agriculture) as well as their hydrological connectivity to the stream network. For example, when planning river restorations, we have to recognize that e.g. the combination of high soil nitrate concentrations and a shallow tile drain system may lead to increased export rates for a specific sub-catchment. For such a case the downstream implementation of a restored river corridor could then have an enhanced impact as a nitrate sink (compare e.g.: Bukaveckas, 2007). Contrarily, in densely populated countries, as in the mid-western part of Europe, the implementation of e.g. river restoration measures is usually done at places where property rights (and legal terms) allow the implementation of the measure. Furthermore, the integral impact of local ecological in-stream measures on downstream nitrate concentration patterns, which are more relevant for water quality threshold compliances than nitrate loads, should be considered as well. This might be even economically useful in river systems with downstream drinking water production plants and occurring stream bank filtration processes. Moreover, the planning and operation of water quality monitoring networks could be improved by regarding the spatial and temporal covering of important nutrient sinks and sources.

6. Conclusions

Summarizing the findings of this study we can show that the effect of nitrate sinks and sources on stream network water quality and its dynamics and total catchment nitrate export can be quantified and ordered regarding their impact along the stream. On the scale of a first-order stream network we could directly derive the impact of specific nitrate sinks and sources on downstream water quality variations. In accordance with other studies, we find that spatially distinct nitrate sources can dominate catchment nitrate export and that "hot spots" of in-stream nitrate removal can be found at the reach scale. Moreover, the specific boundary conditions of the study area allowed to fully distinguish between mixing and dilution processes and biogeochemical in-stream removal processes along the first-order stream network. Simulating in-stream nitrate removal by applying a novel transfer coefficient based on energy availability, we show that N-cycling in agricultural headwater streams can be predicted by other than hydraulic information as well. Contributing to the actual discussion in stream-ecohydrology our findings highlight the relevance of first-order stream networks even for larger scales and they imply that a more dynamic anticipation of water quality from up- to downstream has to be considered for the setup of ecohydrological studies but as well for the implementation of ecological measures and stream or river restoration.

Acknowledgements We would like to thank Manuel Saroos for his efforts during the sampling campaigns, Till Volkmann for the climate data and Barbara Herbstritt for her help in the lab. The article processing charge was funded by the German Research Foundation (DFG) and the Albert Ludwigs University Freiburg in the funding programme Open Access Publishing.

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Tables

Table 1. Overview on the measurements and samples obtained/taken during June and August 2012. The number of samples taken at a specific location is given in Arabic numbers. The number of sampling locations is given in Roman numbers.

		Snapshot sampling campaings	
Parameter	**Catchment outlet**	**Stream network (1330 m)**	**Reach No. 1 (100 m)**
Discharge (salt dilution gauging)	10	10 x 0-IV Locations	
Physical water parameters	10	10 x XXXVI Locations	5 x V Locations
Major ions	2	2 x XXXVI Locations	5 x V Locations
Meteorolgical observations	10 (Dist. 1.3Km)		
Channel geomorphology		XXIII locations	II locations

Table 2. Overview on stream reach residence times τ and stream reach specific parameters applied in equations (9) to (12).

Reach No.	Reach length [m]	Stream bed slope [m/m]	Mean discharge [l/s]	Max. discharge [l/s]	Min. discharge [l/s]	Mean residence time [s]	Min. residence time [s]	Max. residence time [s]
1	100	0.075	0.2	0.5	0.02	642	441	1092
2	150	0.052	0.5	1.1	0.1	836	640	1184
3	195	0.039	0.8	1.5	0.2	1068	854	1517
4	185	0.022	1.1	1.9	0.2	1133	937	1583
5	140	0.019	1.5	2.4	0.4	820	704	1138
6	50	0.023	1.6	2.4	0.4	267	234	358
7	145	0.014	2.0	3.0	0.6	877	772	1178
8	235	0.019	2.4	5.2	1.1	1211	969	1428
9	35	0.021	3.1	5.2	1.7	163	140	188

Figures

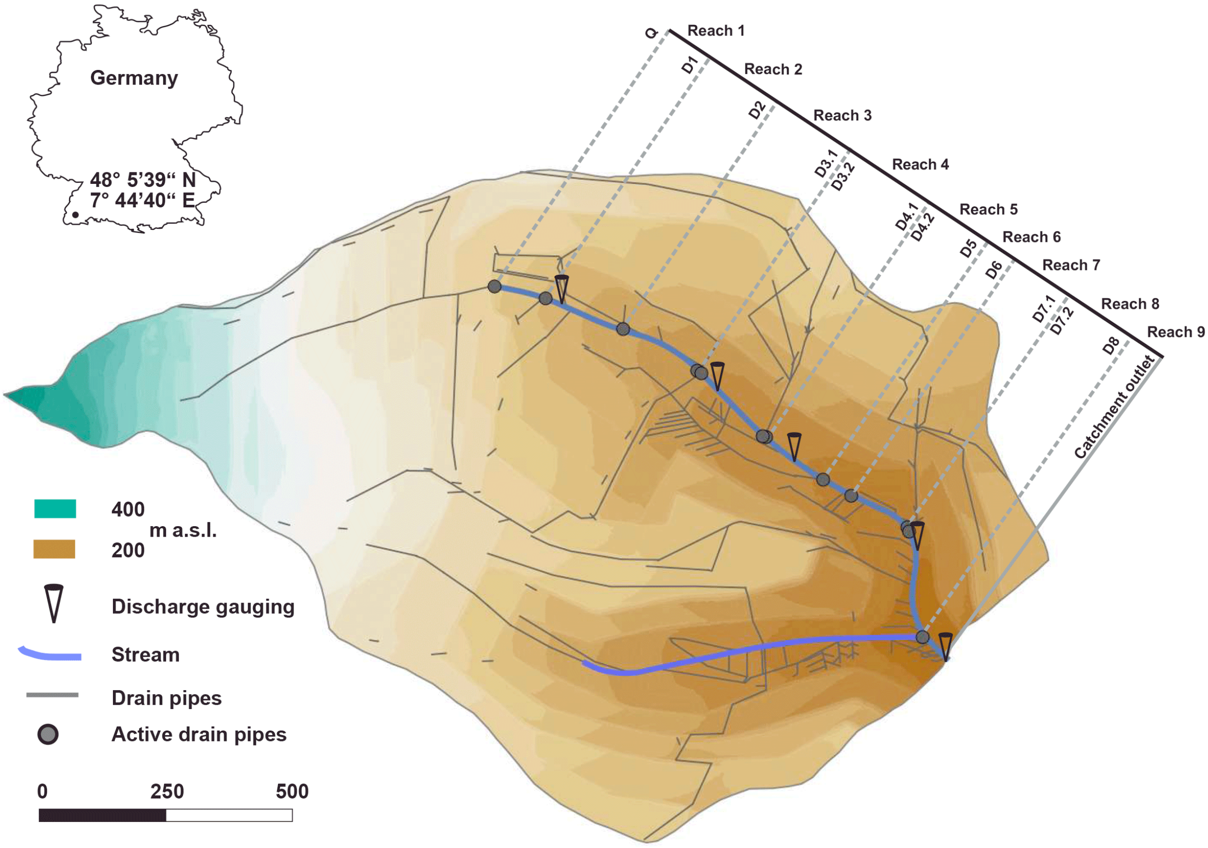

Figure 1. Topographical map of the Löchernbach catchment. The sharp elevation steps in the map represent the vineyard terraces within the catchment. Locations of active drain pipes and stream reaches are marked (dashed lines) with the names referred to throughout the manuscript.

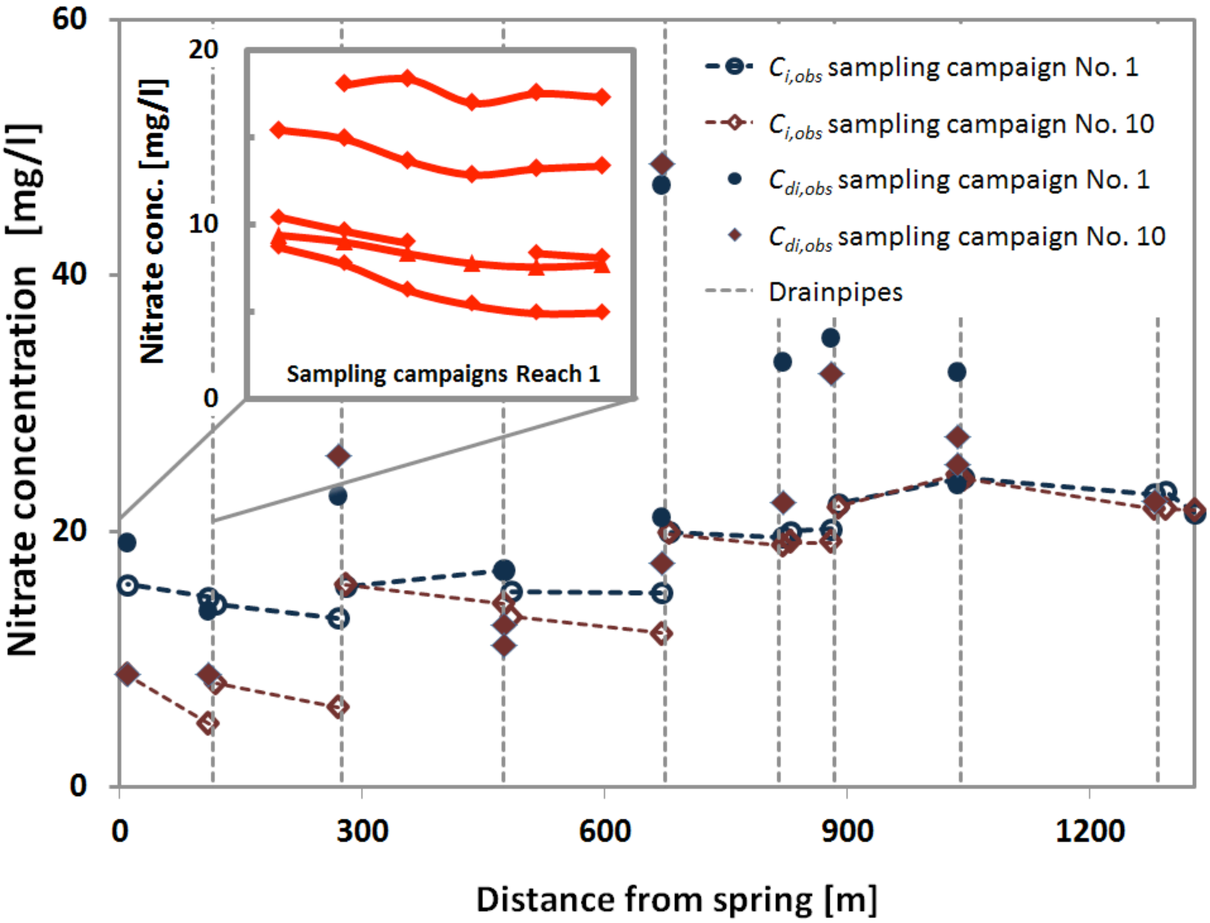

Figure 2. Observed spatio- temporal variations in in-stream and drainpipe nitrate concentrations along the stream network for sampling campaigns No. 1 (27.06.2012) and No. 10 (09.08.2012) and during 5 sampling campaigns at Reach 1 (inset).

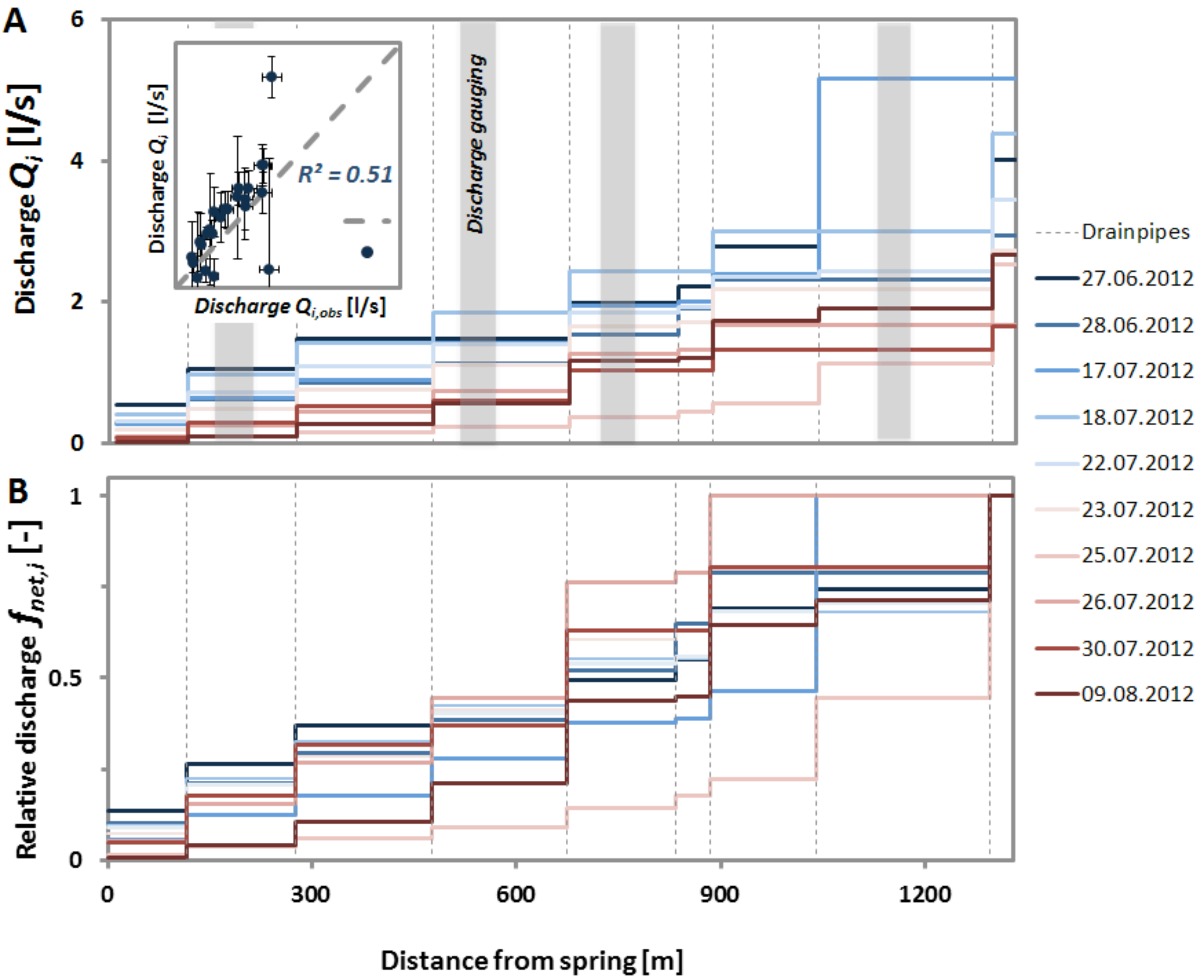

Figure 3. A) Simulated stream network discharge patterns Q_i for all days. A-inset: Comparison of calculated (Q_i) and measured discharges ($Q_{i,obs}$). B) Calculated patterns of relative discharges $f_{net,i}$ for all days. Sampling Campaigns No. 1 – No. 10 are color-coded from blue to red. Dashed lines (A, B) symbolize the positions of the drainpipes. Shaded bars (A) represent the locations of salt dilution gauging.

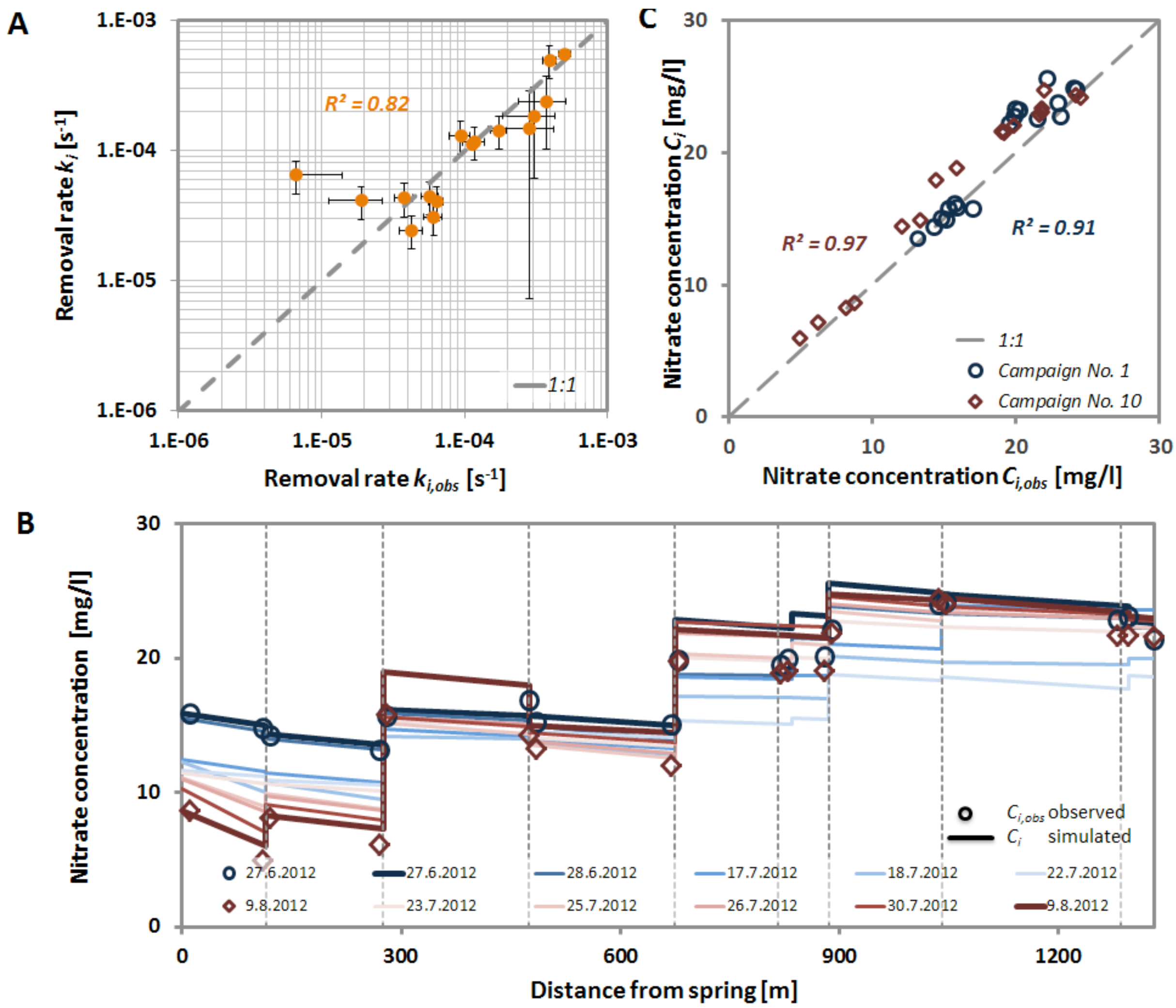

Figure 4. A) Estimated (k_i) and empirical ($k_{i,obs}$) in-stream nitrate removal rates. B) Observed ($C_{i,obs}$ symbols) and calculated (C_i lines) in-stream nitrate concentration patterns for all days. Sampling Campaigns No. 1 – No. 10 are color-coded from blue to red. Dashed lines symbolize the positions of the drain pipes. C) Comparison of modelled and observed in-stream nitrate concentrations for campaigns No. 1 (blue circles) and No. 10 (red diamonds).

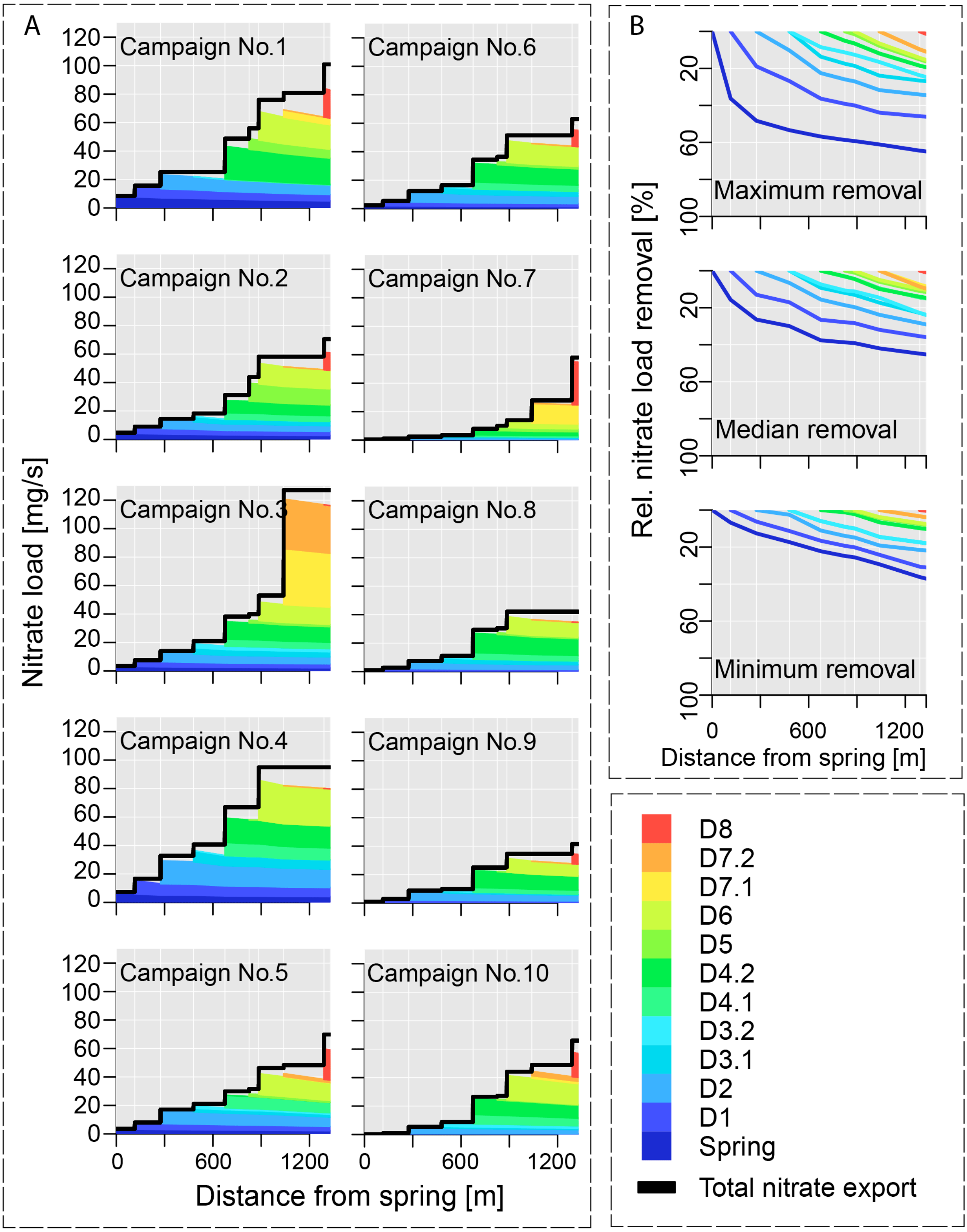

Figure 5. A) In-stream nitrate loads per source for all days (the black line presents cumulative nitrate load emissions without in-stream removal). B) Maximum, median and minimum in-stream nitrate load removal per source relative (%) to the total emitted nitrate load.

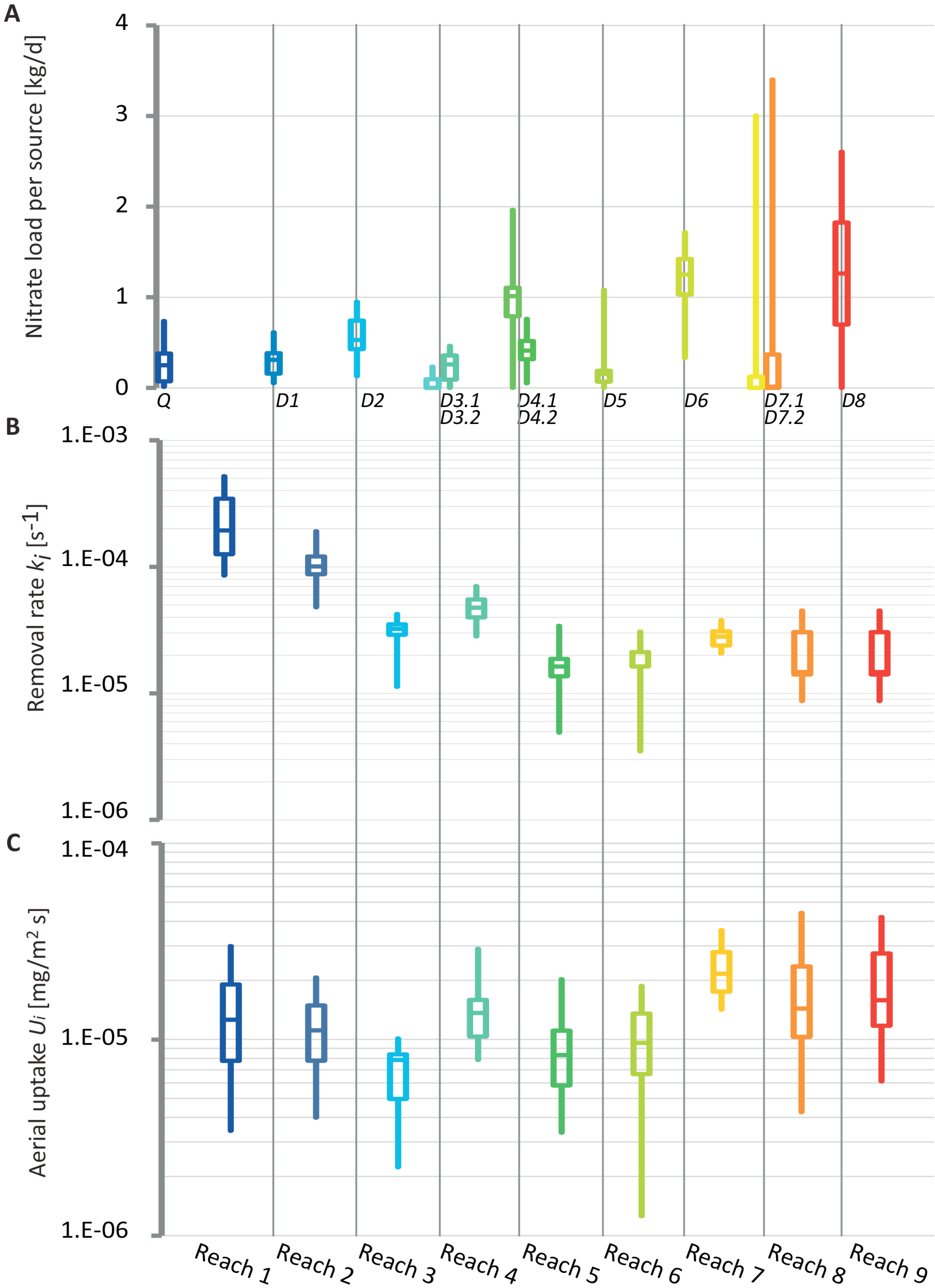

Figure 6. A) Hierarchy and range of nitrate loads per source ranked by their median nitrate load emission. B) Hierarchy and range of in-stream nitrate removal rates ki per reach sorted

from up-to downstream. C) Range of areal uptake rates Ui per reach sorted from up-to downstream. Boxplots present the 0.01, 0.25, 0.5, 0.75 and 0.99 quantiles of each measure.

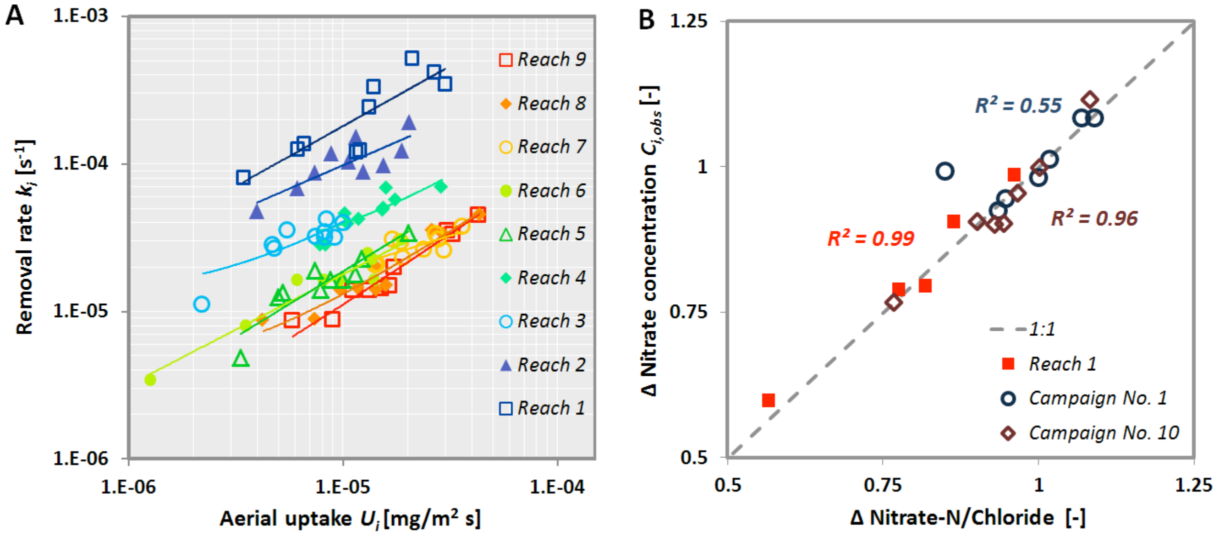

Figure 7. A) Comparison of estimated in-stream nitrate removal rates ki (s-1) and areal nitrate uptake rates Ui (mg/m2 s) per stream reach. B) Comparison of observed relative changes in nitrate concentrations with observed relative changes in the ratio of nitrate/chloride per stream reach observed during the sampling campaigns No. 1 and No. 10 and during the additional sampling campaigns at reach 1.