How Important is Denitrification in Riparian Zones? Combining End-Member Mixing and Isotope Modeling to Quantify Nitrate Removal from Riparian Groundwater

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Abstract Riparian zones are important buffer zones for streams as they are hotspots of nitrate transformation and removal in agricultural catchments. However, mixing of water from different sources and various transformation processes can complicate the quantification of nitrate turnover in riparian zones. In this study, we analyzed nitrate concentration and isotope data in riparian groundwater along a 2-km stream section in central Germany. We developed a mathematical model combining end-member mixing and isotope modeling to account for mixing of river water and groundwater and quantify nitrate transformation in riparian groundwater. This enabled us to explicitly determine the extent of denitrification (as process leading to permanent nitrate removal from riparian groundwater) and transient nitrate removal by additional processes associated with negligible isotope fractionation (e.g., plant uptake and microbial assimilation) and to perform an extensive uncertainty analysis. Based on the nitrogen isotope data of nitrate, the simulations suggest a mean removal of up to 28% by additional processes and only about 9% by denitrification. Nitrate removal from riparian groundwater by additional processes exceeded denitrification particularly in winter and at larger distance from the river, underlining the role of the river as organic carbon source. This highlights that nitrate consumption by additional processes predominates at the field site, implying that a substantial fraction of agricultural nitrogen input is not permanently removed but rather retained in the riparian zone. Overall, our model represents a useful tool to better compare nitrogen retention to permanent nitrogen removal in riparian zones at various temporal and spatial scales.

Plain Language Summary Nitrogen is an important nutrient for agricultural crops. However, excessive nitrogen input into surface water in the form of nitrate can lead to algae blooms and lack of oxygen. The riparian zones of rivers are important buffer zones where groundwater is connected to soils, which are rich in soil organisms and organic matter pools fueling reaction processes. Hence, plants and bacteria can remove nitrate from riparian groundwater before it reaches the river. Bacterial consumption of nitrate (denitrification) leads to complete removal of nitrogen via release of nitrogen gas into the atmosphere. In contrast, other biogeochemical processes such as nitrate uptake by plants merely result in nitrogen retention within riparian zones. To quantify the role of denitrification relative to other processes, we developed a novel model combining concentration and isotope data of nitrate and applied it to a groundwater study site in Central Germany. We found that nitrate removal from riparian groundwater by additional processes largely exceeded denitrification. Hence, a major fraction of nitrogen inputs was retained in the riparian zone and may eventually end up in the river. Such information is highly relevant for many river ecosystems at risk of eutrophication because of high nitrogen inputs from agriculture.

1. Introduction

Despite efforts to reduce nutrient inputs, the contamination of freshwater resources with nitrate (NO₃⁻) poses a continuing problem in many European countries (European Union, 2010). For example, Germany has been taken to court by the European Commission due to insufficient measures to combat increasing...
NO$_3^−$ pollution of its freshwater resources (European Commission, 2016). Nitrogen (N) fertilizers and organic nitrogen in manure are major sources of nitrogen pollution, as crops assimilate part of the applied N only. The excessive N can be transformed to NO$_2^−$ and leach to groundwater or enter rivers via direct run-off. In this context, riparian zones can act as buffers against NO$_2^−$ pollution, as they are hydrologically and biogeochemically active zones where uptake and transformation of nutrients occur (Anderson et al., 2014; Dhondt et al., 2003; Hill, 1996; Mayer et al., 2007; Osborne & Kovacic, 1993; Vidon & Hill, 2004; Vought et al., 1994).

Nitrate removal from riparian groundwater can occur via various processes including denitrification of NO$_3^−$ to N$_2$ or N$_2$O gas, plant uptake, microbial assimilation, dissimilatory NO$_3^−$ reduction to ammonium (DNRA), and anaerobic ammonium oxidation (anammox) consuming nitrite (NO$_2^−$) derived from NO$_3^−$ or NH$_4^+$ (Matheson et al., 2002; McPhillips et al., 2015; Naheer et al., 2015; Rivett et al., 2008). While all these processes reduce the risk of immediate NO$_3^−$ pollution, denitrification is the only process that directly results in permanent N removal from riparian ecosystems via emission of N$_2$ and N$_2$O gas. In contrast, DNRA, microbial assimilation, and plant uptake lead to N retention in the riparian ecosystem, and anammox requires reduction from NO$_3^−$ to NO$_2^−$ by, for example, denitrifying bacteria before NO$_2^−$ and ammonium (NH$_4^+$) are converted to N$_2$ (Burgin & Hamilton, 2007; Jahangir et al., 2017; Matheson et al., 2002). As the retained N might eventually be nitrified to NO$_3^−$ and leach to riparian groundwater, the additional processes might result in transient NO$_3^−$ removal only and are thus in contrast to permanent NO$_3^−$ removal from riparian groundwater by denitrification. In order to accurately describe the fate of NO$_3^−$ in riparian ecosystems, it is therefore vital to distinguish between denitrification and other biogeochemical processes acting on NO$_3^−$ in riparian groundwater and to determine their relative contribution to overall (transient or permanent) removal of NO$_3^−$ from riparian groundwater. Such information is, in turn, pertinent to the management of NO$_3^−$ pollution in catchments, as understanding how, where and when denitrification efficiently removes NO$_3^−$ from groundwater can support a targeted design of riparian buffer zones.

Quantification of denitrification rates is challenging as the end product of the transformation (i.e., N$_2$) is not easy to measure due to high background concentrations and spatial and temporal variability in denitrification rates (Groffman et al., 2006). The magnitude of in situ denitrification in riparian zones has typically been assessed using the acetylene block method (Bragan et al., 1997; Clément et al., 2003; McCarty et al., 2007), $^{15}$N-labelled NO$_3^−$ in “push-pull” experiments (Anderson et al., 2014; McPhillips et al., 2015), the N$_2$:Ar method (Blicher-Mathiesen et al., 1998; Böhlke et al., 2002), and NO$_3^−$ concentration gradients in conjunction with chloride as a conservative natural tracer to account for dilution (Hill et al., 2014; Schilling et al., 2017; Trauth et al., 2018). However, field-scale quantification of denitrification in riparian groundwater remains challenging (Rivett et al., 2008) as these methods work at a local scale and can become impractical and expensive under in situ conditions (Groffman et al., 2006). Moreover, denitrification rates are controlled by local factors including NO$_3^−$ and oxygen concentrations, temperature, and availability of electron donors such as organic carbon (Anderson et al., 2014; Burgin & Hamilton, 2007; Rivett et al., 2008). These factors can vary substantially both in time and space such that a limited number of in situ experiments might fail to accurately describe seasonal and spatial variations of denitrification in riparian groundwater.

Previous field studies distinguishing denitrification from other NO$_3^−$ removal processes in riparian groundwater have mostly employed isotopically labelled NO$_3^−$. They have reported significantly differing contributions of denitrification to overall NO$_3^−$ removal, depending on the analyzed system and field conditions. For example, using push-pull experiments in a riparian aquifer next to a third-order stream in central New York, McPhillips et al. (2015) attributed 5%–12% of total NO$_3^−$ consumption to riparian denitrification and a similar contribution to DNRA, in contrast to 29%–69% that might have been removed by plant uptake, abiotic immobilization, and microbial assimilation. Using the same method, Jahangir et al. (2017) assessed removal contributions of around 15% by denitrification and 40%–63% by DNRA in groundwater beneath constructed wetlands in southeastern Ireland. These somewhat deviating results highlight the need for more research into methods quantifying denitrification relative to other processes in freshwater systems (Burgin & Hamilton, 2007; McPhillips et al., 2015). Considering the spatial and temporal limitations of experiments with isotopically labelled NO$_3^−$, analyzing field isotope data of NO$_3^−$ might be a viable alternative tool for quantification of NO$_3^−$ removal from riparian groundwater over longer periods and under varying field conditions.
Removal processes of $\text{NO}_3^-$ occurring in riparian groundwater can entail changes in the isotopic composition of the residual $\text{NO}_3^-$ (i.e., kinetic isotope fractionation). Among all removal processes, denitrification entails the most significant isotope fractionation effects in both nitrogen and oxygen (N and O) isotopes, whereas other removal processes occurring in riparian zones such as plant uptake or assimilation by cyanobacteria are usually associated with considerably smaller or no isotope fractionation effects (Bauersachs et al., 2009; Dhondt et al., 2003; Granger et al., 2008; Kendall, 1998; Mariotti et al., 1982; Yoneyama et al., 2001). Hence, changes in the environmental isotopic composition of $\text{NO}_3^-$ have been used as qualitative evidence for denitrification in groundwater (Clément et al., 2003; Mengis et al., 1999; Wexler et al., 2014).

However, the environmental isotopic composition of $\text{NO}_3^-$ has been rarely used to quantify the extent of denitrification in riparian zones. One exception is a study conducted in the riparian zone of a second-order river in Belgium (Dhondt et al., 2003), which reports seasonally varying contributions of denitrification (between 49% and 75%) and plant uptake (between 25% and 51%) to overall $\text{NO}_3^-$ removal under the assumption of limited isotope fractionation for plant uptake compared to denitrification. However, this approach did not account for reduction in $\text{NO}_3^-$ concentrations due to mixing or transformation processes additional to plant uptake, which might distort the estimates of denitrification and plant uptake under typical field conditions in riparian zones (i.e., mixing of groundwater and river water and simultaneous occurrence of different biogeochemical processes).

The combined analysis of N and O isotopes of $\text{NO}_3^-$ (i.e., the dual-isotope approach) has proven beneficial for deciphering $\text{NO}_3^-$ sources and distinguishing between isotopic changes due to denitrification versus mixing of several sources (Kendall, 1998; Xue et al., 2009). Dual-isotope mixing models for $\text{NO}_3^-$ have been applied to distinguish major natural and anthropogenic $\text{NO}_3^-$ sources in rivers and groundwater, mostly by assuming negligible denitrification or including denitrification in uncertainty terms (Deutsch et al., 2006; Kim et al., 2015; Matiatos, 2016; Wang et al., 2016). However, there is a lack of methods utilizing the strength of the dual-isotope approach to distinguish changes in the isotopic composition of $\text{NO}_3^-$ caused by denitrification from those caused by mixing (e.g., between groundwater and river water), which is needed to accurately quantify denitrification in riparian zones.

In view of the importance of denitrification for reducing $\text{NO}_3^-$ inputs to freshwater, the general potential of isotopic methods as well as their limitations in denitrification quantification, the aim of this study was to develop and test a model able to quantify both denitrification and additional removal processes in riparian zones in the presence of two mixing $\text{NO}_3^-$ sources. We summarize under the term additional processes all uptake and transformation processes other than denitrification that lead to $\text{NO}_3^-$ removal from riparian groundwater and subsequent N retention in the riparian zone. To distinguish between denitrification, additional removal processes and dilution due to mixing, we adapted the recently developed stable isotope and permanent removal and thus requires the extension of the original SISS model. In the following, we illustrate the derivation and application of the SISS model to nitrate isotope data (SISS-N) using the example of a groundwater study area along a 2-km stream section in central Germany.

2. Field Site and Data

2.1. Field Site Description

We examined a 2-km stretch along the Selke River in Central Germany (Figure 1) located in the Harz/Central German Lowland Observatory of the TERrestrial ENviromental Observatories network (Wollschläger et al., 2016; Zacharias et al., 2011). The Selke Catchment has a total size of 456 km², of which 200 km² are upstream of the field site. The catchment can be broadly divided into the more forested upstream part in the Harz Mountains and the agricultural downstream part in the lowland area (Figure 1a). Fertilizer application on agricultural fields is the main N source in the catchment (Rode et al., 2016). Previous studies
in the field site area have analyzed hyporheic exchange (Trauth et al., 2015; Trauth & Fleckenstein, 2017), hydrochemical gradients between the unsaturated zone and groundwater (Gassen et al., 2017), riparian travel times (Nixdorf & Trauth, 2018), and NO$_3^-$ removal in the riparian zone (Trauth et al., 2018). The field site has been extensively described in Trauth et al. (2018). In brief, annual mean air temperature was 8.8 °C and monthly mean air temperatures ranged from 0.4 °C in January to 18.0 °C in July between 1981 and 2010 (average of three meteorological stations at a distance of below 15 km from the field site; Deutscher Wetterdienst (DWD) Climate Data Center, 2018). Mean annual rainfall was 582 mm and mean monthly rainfall ranged from 36 mm in February to 63 mm in July between 1981 and 2010 (average of four stations at a distance of <15 km; DWD Climate Data Center, 2018). The Selke River at the field site meanders and flows through distinct pool-riffle sequences including in-stream gravel bars with an annual mean discharge of 1.5 m$^3$ s$^{-1}$. It is buffered from the surrounding agricultural fields by riparian vegetation (mainly willow, beech, and pasture) with a maximum width of 50 m at both sides. Groundwater generally flows parallel to the river toward the northeast, while mixing between groundwater and river water occurs in the

Figure 1. Land use in the Selke Catchment and location of the field site (a); overview of the field site (b) with distant groundwater wells (red dots, distance of >100 m from the river), groundwater wells in the riparian zone (blue dots, distance of <25 m from the river, and orange dots, distance of 25–55 m from the river) and river sampling point (dark blue diamond); schematic cross section of the field site indicating hydrogeological setup and location of the riparian zone (c); and plan view of the field site delimited by the dotted rectangle in (b) with interpolated groundwater levels in blue (m a.s.l.) (d). The location of the cross section in (c) is indicated in (d) by the line from P to Q. Letters A–C in (b) represent different well transects, with N and S indicating the location north and south of the Selke River, respectively.
proximity of the Selke River due to the meandering river channel depending on hydrologic conditions and channel morphology (Nixdorf & Trauth, 2018). Chloride concentrations in riparian groundwater and the river suggest that the A and B-N transects are less impacted by infiltrating river water compared to the other well clusters (Figure 1b; Trauth et al., 2018). The aquifer is mainly composed of alluvial sand and gravel deposits transported by the river from the Harz Mountains to the alluvial plains. At the field site, the aquifer has a maximum thickness of 8 m, is covered by up to 1.2 m of alluvial loam, and overlies an aquitard consisting of silty clay. Hydraulic conductivity in the aquifer of the riparian zone determined from salt tracer tests ranges from 1.7 × 10⁻³ to 1.2 × 10⁻² m s⁻¹. Depth to groundwater in the riparian zone ranges from 2 m during summer to 0.5 m during winter.

2.2. Monitoring Setup, Hydrochemical, and Isotopic Analyses

Groundwater was monitored in 30 wells (inner diameter of 2.54 to 5.05 cm), among which 24 were located within the riparian zone (Figure 1b). The length of the well screens ranged between 1 and 3 m, giving a maximum screening depth of 4- to 5-m below ground in the wells close to the river and up to 8-m below ground in the more distant wells. The groundwater wells were classified according to their distance from the Selke River into a near groundwater (distance of <25 m), intermediate groundwater (distance of 25–55 m) and distant groundwater zone (distance of >100 m). The wells in the riparian zone were all assigned to the near or intermediate groundwater zones. Moreover, river water was sampled close to the most downstream riparian wells (Figure 1b).

Monthly time series for hydrochemical and NO₃⁻ isotope data for the well and river samples were taken from Trauth et al. (2018), including dissolved oxygen, cations (Ca²⁺, Fe²⁺, K⁺, Mg²⁺, Na⁺, and NH₄⁺), anions (Cl⁻, NO₃⁻, NO₂⁻, PO₄³⁻, SO₄²⁻), dissolved organic carbon (DOC), alkalinity (HCO₃⁻), redox potential (Eₜ), electrical conductivity (EC), pH, temperature, groundwater level as well as N and O isotope data of NO₃⁻, and hydrogen and oxygen isotope data of water. Moreover, discharge at the river sampling point was measured on the same sampling dates. Sampling mostly occurred during average to low-flow conditions in the river. Detailed information on analytical methods and their uncertainties can be found in Trauth et al. (2018).

Nitrate isotope analyses were performed using a GasBench II connected to an Isotope Ratio Mass Spectrometer (DELTA V plus; Thermo Scientific) following conversion of NO₃⁻ to N₂O using the bacterial denitrifier method (Casciotti et al., 2002; Sigman et al., 2001). The isotope values express the relative abundance of heavy versus light isotopes of N and O, respectively (i.e., the isotope ratio); they are reported in per mille as δ¹⁵N and δ¹⁸O values with respect to the international standards of atmospheric N (isotope ratio of AIR N₂ = 3.667 × 10⁻³) for N and Vienna standard mean ocean water (isotope ratio of VSMOW = 2.0052 × 10⁻³) for O:

\[ \delta_S = \frac{IR_S}{IR_{ref}} - 1 \]  

(1)

where δ_S is the isotope value of the sample (i.e., δ¹⁵N or δ¹⁸O), IR_S is the isotope ratio of the sample, and IR_ref is the isotope ratio of the international reference (i.e., AIR N₂ or VSMOW). The analytical uncertainties of the isotope analyses in this study were ±0.4‰ for δ¹⁵N and ±1.6‰ for δ¹⁸O. In addition, stable water isotope values (i.e., δ²H-H₂O relative to VSMOW = 1.5576 × 10⁻⁴ and δ¹⁸O-H₂O relative to VSMOW = 2.0052 × 10⁻³) were determined for riparian groundwater and river samples as well as for rainfall close to the field site using cavity ring-down spectroscopy (L2130-i, Picarro Inc.) with analytical uncertainties of 1.0‰ for δ²H-H₂O and 0.3‰ for δ¹⁸O-H₂O.

2.3. Hydrochemical Characterization

In the following, we briefly present the chloride (Cl⁻) concentrations, NO₃⁻ concentrations and NO₃⁻ isotope data, which are required for the application of the SISS-N model. We consider the river sampling point close to the well transect C (Figure 1b) as river end-member. For the groundwater end-member, we chose two different wells in the distant groundwater as separate end-members for the southern and the northern part of the field site (Figure 1b), as the agricultural fields in the north of the river differ from the fields in the south in terms of area, agricultural practices and groundwater NO₃⁻ concentrations (Figure 2c). This agrees
with the assumptions in Trauth et al. (2018) for the calculation of the fraction of river water in the riparian groundwater samples (\(F_{\text{river}}\) scaling from 0 to 1) and total \(\text{NO}_3^-\) removal. Trauth et al. (2018) assessed \(F_{\text{river}}\) using an end-member mixing model with \(\text{Cl}^-\) concentrations (equation (2) below). They computed larger mean \(F_{\text{river}}\) values in the near than in the intermediate groundwater (mean of 0.8 ± 0.24 vs. 0.34 ± 0.23; Figure 2a and Table S1 in the supporting information).
Mean Cl$^-$ concentrations in the distant groundwater were twice as high as river concentrations (67.2 ± 24.4 and 33.2 ± 6.7 mg L$^{-1}$, respectively), with the intermediate and near groundwater concentrations (49.1 ± 13.5 and 35.7 ± 9.0 mg L$^{-1}$, respectively) lying in between (Table S1). For the southern groundwater end-member, Cl$^-$ concentrations show a slightly decreasing trend (Figure 2b) from 109.0 to 91.7 mg L$^{-1}$ over the study period, while there was no obvious temporal trend for the northern groundwater end-member. Chloride concentrations of the river end-member ranged between 18.6 and 48.4 mg L$^{-1}$ and were mostly below Cl$^-$ concentrations in riparian groundwater (Figure 2b).

Similar to Cl$^-$ concentrations, mean NO$_3^-$ concentrations in the distant groundwater (65.3 ± 36.5 mg L$^{-1}$) exceeded by far those in the intermediate groundwater (15.5 ± 10.4 mg L$^{-1}$), near groundwater (8.5 ± 4.9 mg L$^{-1}$), and river (7.6 ± 4.6 mg L$^{-1}$; Table S1). Nitrate concentrations of the northern groundwater end-member (Figure 2c) show no clear trend during the study period. In contrast, concentrations of the southern groundwater end-member decreased from high concentrations of up to 117.2 to 75.1 mg L$^{-1}$ at the end of the study period, possibly as a result of decreasing fertilizer application and thus N surplus from agriculture in the region (Bach & Frede, 1998). Nitrate concentrations in riparian groundwater (Figure 2c) generally exceeded those in the river, peaked in spring, and decreased in summer.

Mean δ$^{15}$N values were lowest in the river (7.2‰ ± 2.9‰) and highest in the near groundwater (9.9‰ ± 6.8‰), with the values of the intermediate (8.3‰ ± 3.4‰) and distant groundwater (7.6‰ ± 2‰) lying in between (Table S1). River δ$^{15}$N values ranged between 2.2‰ and 20.8‰ over the study period (Figure 2d). The δ$^{15}$N values at the river sampling point were similar to those measured 1.5-km upstream in the Selke River and in a small tributary discharging into the Selke River just upstream of the field site (data not shown). Moreover, the δ$^{15}$N values of the two groundwater end-members covered a smaller range than those of the river (Figure 2d), while the δ$^{15}$N values in the riparian zone largely exceeded the end-member signatures.

In line with the δ$^{15}$N values, the δ$^{18}$O values of NO$_3^-$ where higher in the near and intermediate groundwater (means of 6.2‰ ± 6.5‰ and 4.0‰ ± 3.6‰, respectively; Table S1) compared to the distant groundwater and the river (means of 3.0‰ ± 1.9‰ and 3.1‰ ± 2.3‰, respectively). The temporal dynamics of δ$^{18}$O values were generally similar to the dynamics of δ$^{15}$N values, with a large enrichment (i.e., increase in isotope values) in the riparian zone compared to the river and the two groundwater end-members (Figure 2e). The location of the riparian groundwater samples in the dual-isotope space points toward soil N, manure, and sewage as main NO$_3^-$ sources and shows considerable isotopic enrichment in both δ$^{15}$N and δ$^{18}$O outside of the typical source ranges for some samples (Trauth et al., 2018).

### 3. Mixing and Transformation Models

#### 3.1. Model Assumptions

We combined two different models in the assessment of mixing between river water and groundwater and NO$_3^-$ removal: a linear mixing model using Cl$^-$ and NO$_3^-$ concentrations and the SISS model (Lutz & Van Breukelen, 2014a) using the δ$^{15}$N and δ$^{18}$O values of NO$_3^-$. The SISS model applied to nitrate isotope data (SISS-N; derived below) provided the extent of denitrification, whereas the linear mixing model was used to calculate the fraction of river water in each sample (F$_{river}$) from Cl$^-$ concentrations and, subsequently, derive total NO$_3^-$ removal from riparian groundwater using F$_{river}$ and NO$_3^-$ concentrations. In the original SISS model, Cl$^-$ and NO$_3^-$ concentrations would not be needed, as the model would determine the extent of transformation (here: denitrification) only. In the SISS-N model, however, we used the end-member contributions from the Cl$^-$ mixing model to allow a direct comparison between overall NO$_3^-$ removal (known from the Cl$^-$ mixing model) and extent of denitrification. Moreover, unlike the dual-element isotope data, Cl$^-$ concentrations generally differ between the distant groundwater and the river, which permits a clear distinction between the two end-members (Figure 2b; see also section 3.3).

For simplicity and as temporal changes in groundwater flow paths are not known, we considered each sampling date separately and assumed that (i) the isotope signatures of the wells in the riparian zone result from mixing between the two end-members (i.e., river end-member and northern or southern groundwater end-member) and (ii) mixing occurs prior to any significant removal processes in the riparian zone. We restricted the model to the two end-members as we consider lateral flow in shallow soil and associated Cl$^-$ and NO$_3^-$
fluxes as secondary due to the fact that samples were mostly taken during average to low-flow conditions and because the aquifer at the field site is highly conductive, as opposed to the overlying loamy sediments. This model assumption thus agrees with the finding that riparian groundwater at the field site is mainly governed by infiltrating river water at shallow depths and by regional groundwater at greater depth (Gassen et al., 2017). Regarding assumption (ii), we postulate that the end-member signatures are not subject to significant isotope fractionation before mixing, in agreement with end-member mixing models that assume conservative end-member concentrations. This yields a conservative (i.e., smaller) estimate of the extent of denitrification with the SISS-N model in comparison to scenarios of prior denitrification before mixing (Lutz & Van Breukelen, 2014a).

We assumed that denitrification is the only process occurring at the field site that entails significant isotope fractionation in both N and O isotopes. Isotope fractionation effects during other NO3\(^-\) removal processes in groundwater and riparian zones are generally unknown (e.g., DNRA; Nikolenko et al., 2018) and, when reported, refer only to the nitrogen isotopic composition of NO3\(^-\). There is evidence of limited isotope fractionation in nitrogen isotopes during plant uptake (Dhondt et al., 2003; Mariotti et al., 1982), and most studies have associated plant uptake with negligible isotope fractionation compared to denitrification (Högberg et al., 1999; Lund et al., 1999). Moreover, we do not distinguish between heterotrophic and autotrophic denitrification (i.e., oxidation of organic carbon vs. inorganic compounds), as the extent of isotope fractionation associated with autotrophic denitrification is assumed similar to that of heterotrophic denitrification (Torrentó et al., 2010; Torrentó et al., 2011).

The SISS-N model only considers isotope fractionation in NO3\(^-\) isotopes. Hence, it does not indicate whether N\(_2\) has been produced by denitrifying or anammox bacteria, as the first reaction step of both complete denitrification and anammox is the conversion of NO3\(^-\) to NO2\(^-\) by denitrifying bacteria. It follows that the SISS-N model assessment of NO3\(^-\) removal from groundwater is not affected by the potential occurrence of anammox, unless there is a significant fraction of NO2\(^-\) in riparian groundwater that is produced by other processes than denitrification and subsequently reduced to N\(_2\) by anammox bacteria. The latter is not likely for our field site, as riparian groundwater is highly influenced by infiltration of river water, which does not favor the slowly growing anammox bacteria requiring stable conditions with little water exchange rates (Wang et al., 2020). Similarly, river water infiltration provides organic carbon to riparian groundwater, whereas anammox is assumed to occur primarily when organic carbon supply is low (e.g., Burgin & Hamilton, 2007; Du et al., 2019). Third, the low NO2\(^-\) and NH4\(^+\) concentrations do not suggest a substantial role of anammox at our field site. Hence, while we cannot fully rule out the occurrence of anammox at the field site, we will focus on the comparison between denitrification and additional nonfractionating processes in the following.

### 3.2. River Water Fractions and Total Nitrate Removal

Chloride was considered as conservative tracer for the mixing processes between distant groundwater and river water that result in mixed samples in the riparian groundwater wells. The fraction of river water in these samples was determined as

\[
F_{\text{river}} = \frac{[\text{Cl}^-_{\text{rip}}] - [\text{Cl}^-_{\text{dist}}]}{[\text{Cl}^-_{\text{river}}] - [\text{Cl}^-_{\text{dist}}]}
\]  

(2)

where [Cl\(^-\)\(_{\text{rip}}\)], [Cl\(^-\)\(_{\text{dist}}\)], and [Cl\(^-\)\(_{\text{river}}\)] denote the chloride concentrations of the riparian groundwater sample, distant groundwater end-member, and river water end-member, respectively, on each sampling day. The \(F_{\text{river}}\) values in this study deviate from those in Trauth et al. (2018) due to the incorporation of analytical uncertainties in the model (see section 3.5).

Knowing \(F_{\text{river}}\) allows calculation of the theoretical NO3\(^-\) concentration in the riparian groundwater sample that would occur under the same mixing conditions between distant groundwater and river water in the absence of any NO3\(^-\) removal processes:

\[
[\text{NO}_3^-_{\text{mix}}] = ([\text{NO}_3^-_{\text{river}}] - [\text{NO}_3^-_{\text{dist}}]) \times F_{\text{river}} + [\text{NO}_3^-_{\text{dist}}]
\]

(3)

where [NO3\(^-\)\(_{\text{mix}}\)] is the theoretical concentration following mixing in riparian groundwater and [NO3\(^-\)\(_{\text{river}}\)] and [NO3\(^-\)\(_{\text{dist}}\)] are the NO3\(^-\) concentrations of the river and groundwater end-member, respectively.
Comparing $[\text{NO}_3^- \text{mix}]$ to the actual $\text{NO}_3^-$ concentration of the riparian groundwater sample $[\text{NO}_3^- \text{rip}]$ yields the total extent of removal from groundwater:

$$R_{\text{tot}}[\%] = \frac{[\text{NO}_3^- \text{mix}] - [\text{NO}_3^- \text{rip}]}{[\text{NO}_3^- \text{mix}]} \times 100\%$$  \hspace{1cm} (4)

where $R_{\text{tot}}$ (in %) describes the net $\text{NO}_3^-$ removal from riparian groundwater comprising $\text{NO}_3^-$ production and removal processes (e.g., nitrification, denitrification, and assimilation into biomass).

Equation (2) can only be applied if $[\text{Cl}^- \text{rip}]$ lies within the range delimited by the end-member concentrations $[\text{Cl}^- \text{dist}]$ and $[\text{Cl}^- \text{river}]$. Similarly, equation (4) is valid only for samples with $[\text{NO}_3^- \text{mix}] \geq [\text{NO}_3^- \text{rip}]$.

### 3.3. Denitrification and Additional Fractionating Processes

Denitrification and additional fractionating processes were assessed with a simplified version of the SISS model, which has been developed to quantify mixing and degradation of a pollutant in a scenario of two mixing sources and degradation using compound-specific isotope data. Lutz and Van Breukelen (2014a) provided a detailed derivation and description of the SISS model. In brief, while simultaneous occurrence of mixing and degradation processes complicates the use of isotope mixing models, the SISS model disentangles the effects of these processes on the isotope data and thus allows quantification of both mixing and degradation.

For this study, the original SISS model was simplified by assuming that the trajectory in the dual-isotope plot for ongoing transformation (here: denitrification trajectory as black line in Fig. 3) can be approximated by a straight line, which deviates from the exact non-linear equation only for pronounced isotope fractionation effects (Lutz and Van Breukelen, 2014a). The theoretical isotope value of the riparian groundwater sample following mixing between river water and groundwater in the absence of denitrification, i.e., the mixing signature, is defined by the point of intersection between the mixing line and the denitrification trajectory (Fig. 3). The slope and intercept of the mixing line are calculated via equations (5) and (6), respectively, and plugged into equations (7) and (8) to determine the mixing signature ($\delta^{15}\text{N}_{\text{mix}}$ and $\delta^{18}\text{O}_{\text{mix}}$):

\[
a = \frac{\delta^{18}\text{O}_{\text{river}} - \delta^{18}\text{O}_{\text{dist}}}{\delta^{15}\text{N}_{\text{river}} - \delta^{15}\text{N}_{\text{dist}}} \quad \text{ (5)}
\]

\[
b = \delta^{18}\text{O}_{\text{river}} - a \cdot \delta^{15}\text{N}_{\text{river}} \quad \text{ (6)}
\]

\[
\delta^{15}\text{N}_{\text{mix}} = \left(\frac{\delta^{18}\text{O}_{\text{rip}} - \frac{\varepsilon_\text{N}}{\varepsilon_\text{O}} \cdot \delta^{15}\text{N}_{\text{rip}} - b}{a - \frac{\varepsilon_\text{N}}{\varepsilon_\text{O}}}\right) \quad \text{ (7)}
\]

\[
\delta^{18}\text{O}_{\text{mix}} = a \cdot \delta^{15}\text{N}_{\text{mix}} + b \quad \text{ (8)}
\]

where $a$ and $b$ are the slope and intercept of the mixing line equation, respectively, $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ are the N and O isotope values of $\text{NO}_3^-$ for the river water end-member (subscript river), distant groundwater end-member (subscript dist), and riparian groundwater sample (subscript rip), and $\varepsilon_\text{N}$ and $\varepsilon_\text{O}$ are the isotopic enrichment factors of nitrogen and oxygen associated with denitrification. It follows for the proportional contribution of the river endmember to nitrate in riparian groundwater in terms of the number of nitrate molecules, $s_{\text{river}}$:

\[
s_{\text{river}} = \frac{\delta^{15}\text{N}_{\text{mix}} - \delta^{15}\text{N}_{\text{dist}}}{\delta^{15}\text{N}_{\text{river}} - \delta^{15}\text{N}_{\text{dist}}} \quad \text{ (9)}
\]

The fraction $s_{\text{river}}$ is not used for further model calculations, but serves as a criterion for valid mixing model results (i.e., $0 \leq s_{\text{river}} \leq 1$).
The change in the isotope ratio (i.e., isotope fractionation) associated with denitrification can be described using the Rayleigh equation (Mariotti et al., 1981):

\[ \frac{IR_t}{IR_0} = f_{\text{den}}^{(\alpha-1)} \]  

(10)

where \( IR_0 \) and \( IR_t \) are the isotope ratios of NO\(_3^-\) at time 0 and time \( t \), respectively, \( f_{\text{den}} \) is the nondenitrified fraction of NO\(_3^-\) at time \( t \), and \( \alpha \) is the isotope fractionation factor describing the strength of isotope fractionation during denitrification. The \( \alpha \) value is typically expressed in per mille as isotopic enrichment factor \( \varepsilon = (\alpha - 1) \) (Coplen, 2011). In the dual-element isotope plot, the ratio of the two enrichment factors (e.g., \( \varepsilon_O/\varepsilon_N \)) is approximately equal to the slope of the degradation trajectory (Figure 3).

According to equations (1) and (10), the remaining NO\(_3^-\) fraction in the riparian groundwater sample after denitrification of the theoretical mixture is given by

\[ f_{\text{den}} = \left( \frac{\delta^{15}N_{\text{rip}} + 1000}{\delta^{15}N_{\text{mix}} + 1000} \right)^{\text{app}} \]  

(11)

where \( \delta^{15}N_{\text{mix}} \) and \( \delta^{15}N_{\text{rip}} \) are the nitrogen isotope values of the theoretical mixture and riparian groundwater sample, respectively, and \( \varepsilon_{\text{app}} \) is the enrichment factor assumed representative of denitrification-induced isotope fractionation. Application of Equation (11) using the O isotope values (\( \delta^{18}O_{\text{mix}} \) and \( \delta^{18}O_{\text{rip}} \)) instead of the \( \delta^{15}N \) values should give the same \( f_{\text{den}} \) estimates.

As we assumed that denitrification is the only NO\(_3^-\) removal process associated with significant isotope fractionation at the field site, the dual-element isotope data were not used to distinguish between different transformation pathways, unlike in Lutz and Van Breukelen (2014b).

Quantification of removal by denitrification follows from equation (11):

\[ R_{\text{den}}[\%] = (1-f_{\text{den}}) \times 100\% \]  

(12)

Nitrate removal by processes other than denitrification (\( R_{\text{add}} \)) can be determined as the difference between total removal (\( R_{\text{tot}} \), equation (4)) and removal by denitrification (\( R_{\text{den}} \), equation (12)):

\[ R_{\text{add}}[\%] = R_{\text{tot}} - R_{\text{den}} \]  

(13)

\( R_{\text{den}} \) and \( R_{\text{add}} \) were calculated analogously using O isotope data and \( \varepsilon_O \). Negative \( R_{\text{add}} \) values (i.e., \( R_{\text{den}} > R_{\text{tot}} \)) were set to zero unless mentioned otherwise.

The percentages given by equations (4), (12) and (13) are not to be understood as relative contributions to overall NO\(_3^-\) removal but as removal percentages relative to the theoretical NO\(_3^-\) concentration that would occur without any transformation or retention processes.

### 3.4. Specification of Isotopic Enrichment Factors

According to equation (11), NO\(_3^-\) concentrations and isotope values before and after denitrification at our field site are related via the apparent isotopic enrichment factor \( \varepsilon_{\text{app}} \):

\[ \Delta = 1,000 \ln \left( \frac{[NO_3^-]_{\text{rip}} + 1}{[NO_3^-]_{\text{mix}} + 1} \right) = \ln(f_{\text{den}}) \times \varepsilon_{\text{app}} = \ln \left( \frac{\delta^{15}N_{\text{rip}}}{\delta^{15}N_{\text{mix}}} \right) \times \varepsilon_{\text{app}} \]  

(14)

where \( \Delta \) is the isotopic shift, \( [NO_3^-]_{\text{mix}} \) is the theoretical NO\(_3^-\) concentration of the mixture (equation (3)), \( [NO_3^-]_{\text{rip}} \) is the actual NO\(_3^-\) concentration in riparian groundwater, \( \delta_{\text{mix}} \) is the theoretical isotope value (i.e., \( \delta^{15}N_{\text{mix}} \) or \( \delta^{18}O_{\text{mix}} \)) of the mixture known from equations (5) to (8), and \( \delta_{\text{rip}} \) is the isotope value measured in riparian groundwater. Equation (14) thus accounts for concentration decreases due to dilution and, when applied to field data, incorporates the combined effect of fractionating (i.e., denitrification) and nonfractionating processes (i.e., additional processes) on NO\(_3^-\) isotope values via \( \varepsilon_{\text{app}} \). Provided the presence of additional NO\(_3^-\) removal processes at our field site, isotopic enrichment factors derived from our field data are bulk \( \varepsilon \)-values resulting from denitrification-induced isotope fractionation.
and decreasing concentrations due to additional nonfractionating processes. Hence, they are likely to be smaller in absolute terms (i.e., less negative) than laboratory-derived enrichment factors using isolated bacterial cultures (Dhondt et al., 2003; Knöller et al., 2011). In order to delimit \( \varepsilon \) values representative of pure denitrification at the field site, we calculated the apparent enrichment factors for N and O (i.e., \( \varepsilon_{N,app} \) and \( \varepsilon_{O,app} \)) for each season using the isotopic shift and the right-hand side of equation (14) and compared them to laboratory-derived values of \( \varepsilon_N \) and \( \varepsilon_O \) from literature (see section 4.1). Given the impact of additional removal processes on apparent isotope fractionation measured in the field, we refrained from a direct use of the field-derived \( \varepsilon_{N,app} \) and \( \varepsilon_{O,app} \) values in the calculation of \( R_{\text{den}} \). Instead, we assumed that apparent enrichment factors close to laboratory-derived values are representative of denitrification-induced isotope fractionation occurring at the field site under conditions of little interference by additional removal processes.

**3.5. Uncertainty Calculations**

In order to include the analytical uncertainties of concentration and isotope data, we conducted 10,000 Monte Carlo simulations of the SISS-N model, assuming the concentrations and isotope values of the end-members and riparian groundwater samples \( \left( n = 482 \right) \) to be normally distributed around their measured values with the following standard deviations: 3% for \( \text{Cl}^- \) (equation (2)) and \( \text{NO}_3^- \) (equations (3) and (4)) concentrations (i.e., maximum measurement error of ion-chromatography), 0.4% for \( ^{15}\text{N} \) and 1.6% for \( ^{18}\text{O} \) (i.e., standard errors of the isotope analyses; equations (5) to (8), (11) and (14)). This yielded valid SISS-N model results for substantially more samples \( \left( n = 283 \right) \) than without consideration of analytical uncertainties in concentration and isotope data \( \left( n = 66 \right) \). The SISS-N model results for a riparian groundwater sample were considered valid if \( 0 \leq F_{\text{river}} \leq 1 \) (equation 2), \( 0 \leq s_{\text{river}} \leq 1 \) (equation 9) and \( 0 \leq f_{\text{den}} \leq 1 \) (equation 11) in at least 100 Monte Carlo simulations (i.e., 1% of all simulations). Increasing this threshold to 10% of all simulations had little effect on the SISS-N model results (not shown). Analytical uncertainties in concentration and isotope data were incorporated accordingly into equation (14) to account for their impact on apparent isotopic enrichment factors. Uncertainties in \( R_{\text{den}} \) and \( R_{\text{add}} \) associated with the choice of \( \varepsilon_N \) and \( \varepsilon_O \) are discussed in section 5.3.

In addition to considering analytical uncertainties, we also analyzed how our results were affected by the assumption of instantaneous mixing prior to denitrification (i.e., the base scenario). Given the proximity of the riparian groundwater wells to the river, this assumption seems less critical for the river end-member compared to the distant groundwater end-members: The northern and southern end-members are located at distances of 167 and 503 m, respectively, from the river and might thus undergo significant denitrification before mixing with the river water in the riparian zone. To assess the effect of prior denitrification of the groundwater end-members, we determined the total extent of denitrification \( \left( R_{\text{den,ext}} \right) \) of the riparian groundwater sample in an extreme scenario assuming maximum denitrification before mixing for the groundwater end-members and no denitrification before mixing for the river end-member. This scenario implies that denitrification occurs prior to mixing and in groundwater only and that any removal following mixing between groundwater and river water occurs via additional processes. To simulate this, we set \( R_{\text{den}} \) of the river end-member to zero and \( R_{\text{den}} \) of the respective groundwater end-member to the maximum value possible considering \( s_{\text{river}} \) and the mixing line between the source signature of the river end-member and the riparian groundwater sample (Figure S2). It follows that \( R_{\text{den,ext}} \) is defined solely by \( s_{\text{river}} \) and the isotope value of the groundwater end-member undergoing maximum denitrification (equation (S1)). We calculated the deviation of \( R_{\text{den}} \) and \( R_{\text{add}} \) in the extreme scenario from the base-scenario values (i.e., \( R_{\text{den,ext}} \) vs. \( R_{\text{den}} \) and \( R_{\text{add,ext}} \) vs. \( R_{\text{add}} \), respectively) in 10,000 Monte Carlo simulations, using the same probability distributions for the concentration and isotope values of end-members and riparian groundwater as in the base scenario. We considered only those simulations with \( 0 \leq R_{\text{den}} \leq 100\% \) and \( 0 \leq R_{\text{den,ext}} \leq 100\% \). Moreover, as in the base scenario, we set all negative \( R_{\text{add,ext}} \) values to zero.

Further model uncertainties might be associated with evaporation effects in the riparian zone that increase \( \text{Cl}^- \) and \( \text{NO}_3^- \) concentrations (i.e., evapoconcentration; Ong et al., 1995) of riparian groundwater samples and thus affect the Cl mixing model (equations (2)–(4)). While the concentration increase associated with evapoconcentration is difficult to quantify, we assessed its impact on the SISS-N model results indirectly.
by identifying riparian groundwater samples that show evaporation effects in their $\delta^{2}H$–$\delta^{18}O$ values. To this end, we determined the line-conditioned excess using the stable water isotope data of precipitation and riparian groundwater samples (lc-excess, equation (S2); Landwehr & Coplen, 2006), which is negative for samples affected by evaporation-induced isotope fractionation effects (see Text S3).

Using lc-excess < 0 as indicator of evapoconcentration following mixing between river water and groundwater, we reran the model for the subset of riparian groundwater samples with nonnegative lc-excess values ($n = 271$) and compared the model results to the base scenario.

4. Results

4.1. Isotopic Enrichment Factors

The NO$_3^-$ isotope data indicate that apparent isotopic enrichment was generally smaller during winter and spring than during summer and autumn (Figure 4). The isotopic shifts (i.e., $\Delta^{15}N$ and $\Delta^{18}O$) were in the range of a few per mille or even negative (mainly during winter and spring). Linear regression through the origin (i.e., assuming that $\Delta = 0$ if $\ln(f) = 0$) using equation (14) and all riparian samples with positive isotopic shifts yielded the largest isotopic enrichment factors (in terms of absolute values) in summer ($\epsilon_{N,app} = -10.4^{\circ}$ and $\epsilon_{O,app} = -8.6^{\circ}$) and the smallest enrichment factors in winter and spring (i.e., $\epsilon_{N,app} = -3.1^{\circ}$ and $\epsilon_{O,app} = -2.6^{\circ}$ in winter, and $\epsilon_{N,app} = -3.6^{\circ}$ and $\epsilon_{O,app} = -3.0^{\circ}$ in spring; Table 1). The $\epsilon_{N,app}$ and $\epsilon_{O,app}$ values for winter and spring, in particular, are smaller than $\epsilon_{N}$ and $\epsilon_{O}$ values determined from denitrification experiments with pure bacterial cultures (see shaded areas in Figure 4).

![Figure 4. Apparent enrichment factors derived from $\delta^{15}N$ values (a) and $\delta^{18}O$ values (b) for all riparian groundwater samples and different seasons using equation (14) with an intercept of zero and accounting for analytical uncertainties in concentrations and NO$_3^-$ isotope data. $\Delta^{15}N$ and $\Delta^{18}O$ denote the isotopic shifts defined by the left-hand side of equation (14) and $\ln(f)$ is the fraction remaining relative to the theoretical NO$_3^-$ concentration that would result from hydrological mixing only. Samples with negative isotopic shifts were not included in the linear regression. Literature ranges refer to experiments with pure cultures (Barford et al., 1999, Mariotti et al., 1981, Sutka et al., 2006, and Wellman et al., 1968 for $\epsilon_N$ and Granger et al., 2008, Hosono et al., 2015, Knöller et al., 2011, Torrentó et al., 2010, and Wunderlich et al., 2012 for $\epsilon_N$ and $\epsilon_O$) and are shown as shaded areas between the slopes of minimum and maximum values of $\epsilon_N$ and $\epsilon_O$, respectively. The directions of changes in $\ln(f)$ and isotopic shifts associated with denitrification, nitrification, and additional processes are indicated by black arrows.](https://www.agu.org/journals/wr/)

![Table 1. Apparent Isotopic Enrichment Factors From Linear Regression Using Equation (14) and N ($\epsilon_N$) and O Isotope Data ($\epsilon_O$), Respectively, and Literature Values of Laboratory-Derived Enrichment Factors](https://www.agu.org/journals/wr/)

| Source | $\epsilon_N$ (%) (R$^2$) | $\epsilon_O$ (%) (R$^2$) |
|--------|-----------------|-----------------|
| This Study | | |
| Winter | $-3.1^{\circ}$ (0.7) | $-2.6^{\circ}$ (0.7) |
| Spring | $-3.6^{\circ}$ (0.5) | $-3.0^{\circ}$ (0.5) |
| Summer | $-10.4^{\circ}$ (0.5) | $-8.6^{\circ}$ (0.5) |
| Autumn | $-7.0^{\circ}$ (0.6) | $-5.7^{\circ}$ (0.6) |
| Literature | | |
| Barford et al. (1999) | $-28.6^{\circ}$ ± 1.9 | - |
| Mariotti et al. (1981) | $-29.4^{\circ}$ ± 2.4 | - |
| Torrentó et al. (2011) | $-26.3^{\circ}$ ± 1.8 | $-20.4^{\circ}$ ± 1.3 |
| Granger et al. (2008)$^a$ | $-26.6^{\circ}$ ± 0.5 | $-22.6^{\circ}$ ± 0.4 |
| Wunderlich et al. (2012)$^b$ | $-23.5^{\circ}$ ± 1.9 | $-23.7^{\circ}$ ± 1.8 |

Note. For the $\epsilon_N$ and $\epsilon_O$ derived in this study, the coefficients of determination ($R^2$) are provided in parentheses. $^a$Maximum values among freshwater bacterial strains. $^b$Maximum values with acetate as carbon source.
We suggest that the samples in Figure 4 indicating significant isotopic enrichment comparable to that found in laboratory studies represent denitrification-induced isotope fractionation with minor impact of additional processes and nitrification. In contrast, samples with ln(f) < 0 plotting close to the horizontal lines of Δ^{15}N = 0 or Δ^{18}O = 0 suggest NO$_3^-$ removal without isotope fractionation effects in the remaining NO$_3^-$ pool. This applies, in particular, to the samples taken during winter or spring. Hence, for the following calculations, we adopted ε values at the more negative end of the ranges of laboratory-derived values (Table 1) to describe “pure” denitrification-induced isotope fractionation, that is, ε$_N$ = −28.0‰ and ε$_O$ = −23.0‰. These choices of ε$_N$ and ε$_O$ yield an ε$_O$/ε$_N$ ratio of about 0.82, which is in agreement with Torrentó et al. (2010) and Wunderlich et al. (2012).

### 4.2. Temporal Dynamics of Nitrate Removal

In the following, we refer to the SISS-N model using ε$_N$ = −28.0‰ and δ$^{15}$N-NO$_3^-$ data as the δ$^{15}$N model and to the SISS-N model using ε$_O$ = −23.0‰ and δ$^{18}$O-NO$_3^-$ data as the δ$^{18}$O model. Based on the δ$^{15}$N model and applying a threshold of 100 simulations with 0 ≤ R$_{den}$ ≤ 100, the model calculated R$_{den}$ and R$_{add}$ for 78% of the riparian well samples for which F$_{river}$ was successfully determined (n = 364; i.e., 77% of the entire data set). For the remaining samples, the model gave more than 100 simulations with R$_{den}$ < 0 because of the theoretical mixture being more enriched in $^{15}$N than the riparian groundwater sample (see equation (11)). Using the δ$^{18}$O model, R$_{den}$ and R$_{add}$ could be determined for the same number of samples because of the interdependency between δ$^{15}$N and δ$^{18}$O values via ε$_N$ and ε$_O$ (see equations (5) to (8)).

We present the temporal dynamics of NO$_3^-$ removal separately for the near and the intermediate groundwater zones (wells with a distance of <25 and 25–55 m, respectively, from the river; see Figure 1). In the near groundwater, mean NO$_3^-$ removal via denitrification (R$_{den}$) was 10.4±12.5% and mean NO$_3^-$ removal by additional processes (R$_{add}$) was 27.8±18.5%, resulting in a mean total removal (R$_{tot}$) of 37.8±21.1% using the δ$^{15}$N model (Table 2). In the near groundwater, the mean R$_{add}$ was thus nearly three times as large as the mean R$_{den}$ during the study period. In terms of temporal variations, denitrification showed a clear relationship with groundwater temperature, with larger values during summer and autumn than during winter and spring (Figure 5a). Considering the median value of all wells per sampling date using the δ$^{15}$N model, R$_{den}$ ranged between 1.6% in April 2014 and 36.7% in July 2015, while the median R$_{add}$ ranged between 7.8% in March 2016 and 59.1% in April 2014.

**Table 2** Overall NO$_3^-$ Removal (R$_{tot}$), Denitrification (R$_{den}$), and Removal by Additional Processes (R$_{add}$) in the Base Scenario, the Extreme Scenario With Maximum Denitrification in Groundwater (R$_{tot,ext}$, R$_{den,ext}$, and R$_{add,ext}$) and for the Sample Subset With Nonnegative lc-Excess (R$_{tot,lc}$, R$_{den,lc}$, and R$_{add,lc}$).

|                         | near groundwater | intermediate groundwater |
|-------------------------|------------------|-------------------------|
| **δ$^{15}$N**           | **δ$^{18}$O**    | **δ$^{15}$N**           | **δ$^{18}$O**           |
| R$_{den}$ [%]           | 10.4±12.5        | 10.4±12.5               | 5.8±8.9                 | 5.8±8.9                 |
| R$_{add}$ [%]           | 27.8±18.5        | 27.8±18.5               | 27.9±14.1               | 27.9±14.1               |
| R$_{tot}$ [%]           | 37.8±21.1        | 37.8±21.1               | 33.5±15.2               | 33.5±15.2               |
| **max. denitrification in groundwater** |                   |                         |                         |                         |
| R$_{den,ext}$ [%]       | 15.0±18.0        | 15.1±18.1               | 8.0±13.0                | 8.1±13.0                |
| R$_{add,ext}$ [%]       | 24.3±18.6        | 24.3±18.6               | 26.0±14.3               | 25.9±14.3               |
| R$_{tot,ext}$ [%]       | 37.8±21.1        | 37.8±21.1               | 33.5±15.2               | 33.5±15.2               |
| **samples with lc-excess≥0** |                   |                         |                         |                         |
| R$_{den,lc}$ [%]        | 10.7±12.9        | 10.7±13.0               | 6.1±9.4                 | 6.1±9.4                 |
| R$_{add,lc}$ [%]        | 27.1±18.2        | 27.1±18.2               | 27.8±14.6               | 27.7±14.6               |
| R$_{tot,lc}$ [%]        | 37.3±20.9        | 37.3±20.9               | 33.7±15.9               | 33.7±15.9               |

**Note.** Values are given as mean ± standard deviation of the sample subset with R$_{den}$ ≥ 0, R$_{den,ext}$ ≥ 0, or R$_{den,lc}$ ≥ 0, respectively, after setting negative R$_{add}$ values to zero. Samples with less than 100 successful Monte Carlo simulations were discarded. R$_{tot}$ differs between the model scenarios as the statistics refer to different sample subsets.
With a mean value of $R_{\text{tot}} = 33.5\% \pm 15.2\%$ using the $\delta^{15}\text{N}$ model, total $\text{NO}_3^−$ removal was smaller in the intermediate than in the near groundwater (Table 2). The model attributed most of $\text{NO}_3^−$ removal in the intermediate groundwater to $R_{\text{add}}$ (mean of $27.9\% \pm 14.1\%$), while $R_{\text{den}}$ was, on average, by a factor of five smaller than $R_{\text{add}}$ (mean of $5.8\% \pm 8.9\%$) and less pronounced than in the near groundwater. In terms of temporal variations, there was no pronounced increase in denitrification during summer and autumn, as opposed to the dynamics in the near groundwater. The median $R_{\text{den}}$ of all wells per sampling date ranged between $1.3\%$ in May 2015 and $8.1\%$ in November 2015 using the $\delta^{15}\text{N}$ model (Figure 5b). In contrast, the median $R_{\text{add}}$ of all wells ranged between $0\%$ in July 2015 and $50.8\%$ in March 2016 and was mostly above $15\%$.

The $\delta^{18}\text{O}$ model essentially gives the same temporal patterns as the $\delta^{15}\text{N}$ model in both the near and intermediate groundwater (Fig. 5c and d).

In summary, using the median values per sampling date from the $\delta^{15}\text{N}$ model, the relative contribution by $R_{\text{den}}$ to overall $\text{NO}_3^−$ removal (i.e., sum of $R_{\text{den}}$ and $R_{\text{add}}$) ranged over time from $4.2\%$ to $61.3\%$ (mean of $23.8\% \pm 16.2\%$) in the near groundwater and from $4.9\%$ to $100.0\%$ (mean of $16.2\% \pm 19.9\%$) in the intermediate groundwater. Moreover, the base scenario suggests that average $\text{NO}_3^−$ removal by additional processes exceeded denitrification, at least, by a factor of 2.7 in the near groundwater and by a factor of 4.8 in the intermediate groundwater (Table 2).

### 4.3. Spatial Patterns of Nitrate Removal

Given the consistency in temporal patterns of the two models, we present only the results of the $\delta^{15}\text{N}$ model in the following. To analyze spatial patterns of seasonal dynamics in $\text{NO}_3^−$ removal, we calculated $R_{\text{den}}$ and $R_{\text{add}}$ of each well separately for the summer and winter months. Averaged over the summer months in 2014 and 2015, $R_{\text{den}}$ at individual wells ranged between $1.0\%$ and $54.0\%$ (mean of $19.3\% \pm 15.8\%$; Fig. 6a). Denitrification was most pronounced at C-N and C-S and smallest at A and B-N. In contrast, $\text{NO}_3^−$ removal by additional processes during summer was largest at B-N and smallest at C-S (Figure 6b). The model yielded a mean (maximum) $R_{\text{add}}$ of $23.9\% \pm 16.5\%$ (50.5%) and $R_{\text{add}} = 0$ for two C-S wells and one B-S well during summer.
The extent of denitrification during winter months (Figure 6c) was substantially smaller than during summer months and never exceeded R<sub>tot</sub>, as opposed to the three wells in summer. The mean R<sub>den</sub> at all wells was 4.4% ± 3.0% (range from 1.5% to 14.2%; Fig. 6c) and, in contrast to the summer months, R<sub>den</sub> was below 8% in all transects apart from one well at C-N with R<sub>den</sub> = 14.2%. Mean removal by additional processes during winter was R<sub>add</sub> = 29.7% ± 10.1% (range from 11.2% to 52.2%; Fig. 6d). In contrast to denitrification, additional processes accounted for pronounced removal in the A and B transects and some of the C transect wells. In summary, R<sub>add</sub> during winter was high at most B transect wells, while the smallest R<sub>add</sub> values occurred in the C transect.

Overall, R<sub>den</sub> was substantially larger during summer than winter, whereas R<sub>add</sub> values were comparable during both seasons (Figure 6). During summer, R<sub>den</sub> was at a similar level as R<sub>add</sub>, whereas it was largely exceeded by R<sub>add</sub> during winter. Considering the mean values with the δ<sup>15</sup>N model over the entire study period (not shown), R<sub>den</sub> was largest in the C transect (above 75th percentile of 14.9%) and smallest in the A and B-N transects (below 25th percentile of 5.3%). In contrast, R<sub>add</sub> was largest at B-N (above 75th percentile of 31.8%) and smallest at B-S and C (below 25th percentile of 25.3%). These spatial patterns of R<sub>den</sub> and R<sub>add</sub> were identical using the δ<sup>18</sup>O model, thereby highlighting some wells of clusters C and B as hotspots of denitrification and additional NO<sub>3</sub><sup>-</sup> sinks, respectively.

### 4.4. Additional Model Scenarios
The occurrence of denitrification for the groundwater end-member prior to mixing was assessed by the scenario assuming maximum R<sub>den</sub> for the groundwater end-member (Figure S2). The percentage of samples for
which \( R_{\text{den,ext}} \) exceeded \( R_{\text{tot,ext}} \) increased from 4.2% in the base scenario to 9.9% in the extreme scenario using the \( \delta^{15}N \) model. Correspondingly, the extreme scenario yielded larger denitrification estimates (especially in the near groundwater) and somewhat smaller estimates of \( \text{NO}_3^- \) removal by additional processes compared to the base scenario (i.e., \( R_{\text{den,ext}} > R_{\text{den}} \) and \( R_{\text{add}} > R_{\text{add,ext}} \), Table 2). In the near groundwater, mean denitrification increased from \( R_{\text{den}} = 10.4\% \pm 12.5\% \) in the base scenario to \( R_{\text{den,ext}} = 15.0\% \pm 18.0\% \), whereas removal by additional processes decreased from \( R_{\text{add}} = 27.8\% \pm 18.5\% \) in the base scenario to \( R_{\text{add,ext}} = 24.3\% \pm 18.6\% \) (Table 2). In the intermediate groundwater, the extent of denitrification slightly increased from \( R_{\text{den}} = 5.8\% \pm 8.9\% \) to \( R_{\text{den,ext}} = 8.0\% \pm 13.0\% \), while \( \text{NO}_3^- \) removal by additional processes marginally decreased from \( R_{\text{add}} = 27.9\% \pm 14.1\% \) to \( R_{\text{add,ext}} = 26.0\% \pm 14.3\% \). The same tendency of increasing \( R_{\text{den,ext}} \) and decreasing \( R_{\text{add,ext}} \) compared to the base scenario became also apparent using the \( \delta^{18}O \) model (especially in the near groundwater).

In the second additional scenario, we applied the SISS-N model to those riparian groundwater samples with \( lc\)-excess \( \geq 0 \) in order to exclude samples that might have been significantly affected by evaporation (Text S3 and Figure S3). Using negative \( lc\)-excess values as indicator of enhanced evaporation, potential evapoconcentration effects in riparian groundwater might have particularly occurred during April and June 2014 and April 2015 (not shown). Nonnegative \( lc\)-excess values for riparian groundwater samples occurred for 85.7% of all valid SISS-N model runs. For this subset, \( F_{\text{river}} \) was equal to that in the base scenario (i.e., mean of 0.61 \pm 0.34) and overall \( \text{NO}_3^- \) removal was nearly identical to that in the base scenario (i.e., using the \( \delta^{15}N \) model, \( R_{\text{tot,lc}} = 37.3\% \pm 20.9\% \) vs. \( R_{\text{tot}} = 37.8\% \pm 21.1\% \) in the near groundwater, and \( R_{\text{tot,lc}} = 33.7\% \pm 15.9\% \) vs. \( R_{\text{tot}} = 33.5\% \pm 15.2\% \) in the intermediate groundwater; Table 2). Moreover, the scenario yielded overall slightly larger denitrification estimates and slightly smaller estimates of removal by additional processes in both groundwater zones (Table 2), with maximum deviations of below 1% (in absolute values) between mean \( R_{\text{den,lc}} \) and mean \( R_{\text{den}} \) and between mean \( R_{\text{add,lc}} \) and mean \( R_{\text{add}} \), respectively.

### 5. Discussion

#### 5.1. Isotope Fractionation and Enrichment Factors

The isotopic enrichment factors of \( \epsilon_N = -28.0\%c \) and \( \epsilon_O = -23.0\%c \) chosen in this study lie at the more negative end of the range reported previously (i.e., indicating larger isotope effects; Table 1). This implies that the model results represent conservative estimates of denitrification at the field site. In other words, assuming less pronounced isotope fractionation (i.e., less negative values of \( \epsilon_N \) and \( \epsilon_O \)) would result in larger \( R_{\text{den}} \) values and thus smaller \( R_{\text{add}} \) values. As this would have given more instances of \( R_{\text{add}} < 0 \) even in the conservative base scenario (assuming accurate \( R_{\text{tot}} \) estimates), we suggest that \( \epsilon_N = -28.0\% \) and \( \epsilon_O = -23.0\% \) accurately describe denitrification-induced isotopic fractionation that is not diluted by the occurrence of nonfractionating processes, in contrast to apparent isotopic enrichment factors derived from field isotope data. Hence, in addition to quantifying the contribution of denitrification to overall \( \text{NO}_3^- \) removal, combining concentration and isotopic data such as in the SISS-N model can help delimit a plausible range for isotopic enrichment factors under field conditions.

In addition to the Rayleigh plot (Figure 4), the \( \epsilon_O/\epsilon_N \) slope in the dual-isotope plot can provide more insights into the magnitude of \( \epsilon_N \) and \( \epsilon_O \) at our field site. In contrast to Rayleigh plots, dual-isotope plots have the advantage of being unaffected by concentration decreases due to nonfractionating processes. While matching the upper quartile of the literature range (i.e., 0.33 to 0.99; Granger et al., 2008; Hosono et al., 2015; Knöller et al., 2011; Torrentó et al., 2010; Wunderlich et al., 2012), the comparably large \( \epsilon_O/\epsilon_N \) slope might result from underestimation of the actual \( \epsilon_O \) or overestimation of the actual \( \epsilon_N \) (in terms of absolute values). Moreover, deviations of the \( \epsilon_O/\epsilon_N \) slope from literature values might also indicate addition of newly nitrified \( \text{NO}_3^- \) or \( \text{NO}_2^- \) produced by anammox (Granger & Wankel, 2016). The fact that we cannot conclusively determine what processes in addition to denitrification might affect the field isotope data is another reason why we employed \( \epsilon \) values in agreement with studies using isolated bacterial cultures instead of apparent \( \epsilon \) values derived from our field data.

The concurrent isotopic enrichment in \( \delta^{15}N \) and \( \delta^{18}O \), associated with decreasing \( \text{NO}_3^- \) concentrations between spring and summer (Figures 2c–2e), suggests the occurrence of denitrification in the riparian
cates the importance of the river as organic carbon source, either directly via in-stream denitrification or as a result of exchange between distant groundwater and river water governing the hydrochemistry in riparian groundwater, this indicates systematic isotopic enrichment associated with denitrification along the 2 km reach at our field site. Hence, while in-stream denitrification can be significant at the river-network scale (Seitzinger et al., 2002), we focused here on the analysis of NO$_3^-$ removal from riparian groundwater and neglected potential in-stream removal processes.

5.2. Quantification of Denitrification

The SISS-N model results highlight pronounced temporal changes in the importance of different NO$_3^-$ removal processes, which complicates a comparison of our estimates to those from previous studies that have assessed denitrification over the course of a few months only (Dhondt et al., 2003; Jahangir et al., 2017; McPhillips et al., 2015). Nonetheless, our results underline substantial differences in the extent of denitrification between near and intermediate groundwater, and suggest that additional processes other than denitrification govern NO$_3^-$ removal at our field site. This is in line with previous studies such as McPhillips et al. (2015), who calculated a contribution of 29%–69% to overall NO$_3^-$ removal by plant uptake, abiotic immobilization, and microbial assimilation, and Jahangir et al. (2017), who assessed a relative contribution of 40%–63% by DNRA. Note that while $R_{\text{den}}$ in the near groundwater is generally larger than $R_{\text{den}}$ in the intermediate groundwater, this does not necessarily apply to absolute values of NO$_3^-$ removal via denitrification, as these depend on the NO$_3^-$ fluxes through the respective groundwater zones.

Denitrification in the near groundwater increased with rising groundwater temperatures in summer (Figures 5a and 5c), which agrees with the strong temperature dependency of denitrification reported previously (Pfenning & McMahon, 1997; Saunders & Kalff, 2001; Stanford et al., 1975). However, denitrification in the intermediate groundwater was limited despite similar temperatures as in the near groundwater, which corroborates the relevance of additional factors for denitrification such as the presence of organic carbon provided by infiltrating river water (Trauth et al., 2018). Dissolved organic carbon concentrations in the river were indeed more than twice as high as in distant groundwater (Table S1). Provided that mixing between distant groundwater and river water governs the hydrochemistry in riparian groundwater, this indicates the importance of the river as organic carbon source, either directly via in-stream primary production (Dupas et al., 2017) or indirectly via hydrological connectivity between rivers and wetland soils rich in organic carbon (Lambert et al., 2011; Shang et al., 2018). The importance of DOC provided by the river becomes apparent in the spatial analysis, which yielded the largest summer $R_{\text{den}}$ at the B-S and C transects (Figure 6a). Those are the well clusters for which $F_{\text{river}}$ indicates significant inflow of river water (Figure 1b), as opposed to the A and B-N transects, for which our model calculated smaller $R_{\text{den}}$ values. This suggests that denitrification depends to a greater extent on the exchange with surface water than on subsurface properties such as the varying thickness of the alluvial aquifers (see Vidon & Hill, 2004) north and south of the river (Figure 1c). In addition to hydraulic conditions, northern and southern wells differed in their NO$_3^-$ concentration levels, with concentrations of the southern groundwater end-member being, on average, 4.5 times as high as those of the northern groundwater end-member (Figure 2c). As denitrification potential is generally positively correlated with NO$_3^-$ concentrations (Ahn & Peralta, 2012; Seitzinger, 1994), this might further explain the larger $R_{\text{den}}$ values south of the river (Figures 6a and 6c).

The variability in $\delta^{15}N$ and $\delta^{18}O$ values in the more distant groundwater wells south of the river do not indicate systematic isotopic enrichment associated with denitrification (Text S6 and Figure S7). Nonetheless, using the extreme scenario of maximum denitrification for the groundwater end-member, we were able to assess how denitrification during flow from the groundwater end-member to the riparian zone might affect the estimates of total denitrification. The $R_{\text{den, ext}}$ estimates in valid simulations of this scenario were larger than $R_{\text{den}}$ (Table 2), which demonstrates that the base scenario gives a conservative estimate of the extent of denitrification and, hence, of permanent NO$_3^-$ removal from riparian groundwater. Nonetheless, before setting them to zero, $R_{\text{add, ext}}$ values were in the double-digit negative range in a few cases, which highlights that this scenario likely overestimates $R_{\text{den, ext}}$ especially in the near groundwater where isotope fractionation was more pronounced. In reality, considering the role of organic carbon from river water, the denitrification potential in groundwater flowing from the distant groundwater to the river is likely smaller than that in the riparian zone. Moreover, even in this extreme scenario, $R_{\text{add, ext}}$ substantially contributed to overall...
NO\textsubscript{3}\textsuperscript{−} removal (i.e., amounting to around 62% and 74% of R\textsubscript{tot,ext} in the near and intermediate groundwater, respectively, using the δ\textsuperscript{15}N model).

### 5.3. Nitrate Removal by Additional Processes

Among the biotic NO\textsubscript{3}− consumption processes, DNRA is a process that might lead to a similar extent of NO\textsubscript{3}− removal as denitrification (Jahangir et al., 2017; McPhillips et al., 2015). Microbial transformation via DNRA occurs (such as denitrification) under anaerobic and reduced conditions and is favored over denitrification when C:N ratios are large (Dhondt et al., 2003; Jahangir et al., 2017; Matheson et al., 2002). However, in our study, the mean C:N ratio using the molar concentrations of DOC and N-NO\textsubscript{3}− of the six wells with the largest R\textsubscript{add} (i.e., above the 75th percentile) was smaller than that of the six wells with the largest R\textsubscript{den} (i.e., 1.1 vs. 1.5 using the δ\textsuperscript{15}N model). Moreover, wells with large R\textsubscript{add} values generally showed elevated E\textsubscript{h} values, unlike the wells with large R\textsubscript{den} values (i.e., means of 61.6 mV and 176.9 mV for the six wells with the largest R\textsubscript{den} and largest R\textsubscript{add}, respectively, and 132.1 mV for all riparian wells). Third, concentrations of NH\textsubscript{4}+ (i.e., the reaction product of DNRA) did not exceed 0.55 mg L\textsuperscript{−1} and were mostly below detection limit (0.02 mg L\textsuperscript{−1}) in riparian groundwater. Overall, a substantial contribution of DNRA to NO\textsubscript{3}− consumption during the study period at our field site is thus unlikely.

In contrast to R\textsubscript{den}, R\textsubscript{add} is of similar magnitude in the near and intermediate groundwater zones (Figure 5). A potential NO\textsubscript{3}− sink that does not show a significant gradient with distance from the river is riparian vegetation. In general, although Clément et al. (2003) suggested that plants primarily use riparian groundwater during high flow conditions, the common assumption is that NO\textsubscript{3}− uptake by plants mainly occurs from late spring to autumn during the growing season (Li et al., 2016; Muñoz et al., 1993). This is consistent with the positive relationship of R\textsubscript{add} with temperature in the intermediate groundwater (Figures 5b and 5d) and the slightly larger R\textsubscript{add} in summer compared to winter (Figures 5 and 6). However, these relationships might as well indicate increased microbial NO\textsubscript{3}− removal under warm conditions. In addition, as the additional processes were also active during the dormant season, plant uptake cannot be the only major NO\textsubscript{3}− sink besides denitrification at our field site.

A mechanism that is potentially active during winter is the abiotic immobilization of NO\textsubscript{3}− into soil organic matter following reaction with Fe\textsuperscript{2+} species (Davidson et al., 2003; McPhillips et al., 2015). Although challenged by Colman et al. (2007), this pathway has been assumed to be a major NO\textsubscript{3}− sink in forest soils (Judd et al., 2007; Providoli et al., 2006). Ferrous iron at our field site was detectable only in a few cases in groundwater, making it impossible to assess whether this process might also play a role in the riparian zone. In addition to abiotic immobilization, microbial assimilation of NO\textsubscript{3}− might be an important additional NO\textsubscript{3}− sink, particularly during winter time (Dhondt et al., 2003). Nitrate uptake has, for example, been reported by cyanobacteria in groundwater (Hu et al., 2000) and benthic algae in a mountainous stream (Baker et al., 2009). A detailed study on microbial NO\textsubscript{3}− uptake would be necessary in order to assess the role of this pathway relative to other NO\textsubscript{3}− sinks. This is not feasible based on our data and goes beyond the scope of this study.

Provided that the overall assessment of R\textsubscript{add} is adequate, our results indicate that NO\textsubscript{3}− removal by processes other than denitrification might play a significant role in riparian zones (Clément et al., 2003; Davis et al., 2008; Dhondt et al., 2003; McPhillips et al., 2015), particularly if enrichment factors associated with denitrification are comparably large under field as under laboratory conditions. As additional removal processes result in nitrogen retention in riparian zones rather than in permanent nitrogen loss to the atmosphere, attributing NO\textsubscript{3}− consumption to denitrification exclusively might greatly overestimate the capacity of riparian ecosystems for permanent NO\textsubscript{3}− removal in similar systems. Hence, we assume that our results might be, in particular, transferable to river sections where groundwater flow similarly dominates streamflow generation and organic carbon supply to groundwater relies on the interaction between stream water and groundwater. Our data do not allow unequivocally identifying individual NO\textsubscript{3}− consumption processes or inferring their relative contribution to total NO\textsubscript{3}− removal from groundwater. We suggest that microbial and abiotic immobilization and plant uptake are the potential main contributors to NO\textsubscript{3}− removal at our field site, while DNRA presumably plays a minor role. This information is also relevant for future studies as it highlights what processes and parameters have to be investigated in more detail with regard to isotope analyses and
5.4. Uncertainties and Limitations

During times of hydrological connectivity between soil and riparian groundwater, soil NO$_3^-$ carrying the isotopically depleted imprint of nitrification can leach to shallow riparian groundwater (Clément et al., 2003; Hall et al., 2016). Consequently, as indicated in Figure 4, vertical mixing with freshly nitrified NO$_3^-$ might shift isotopic signatures toward larger ln($f$) values and smaller $\Delta^{15}$N and $\Delta^{18}$O than would occur for denitrification only. The isotopic signature of nitrified NO$_3^-$ depends on the isotopic signatures of NH$_4^+$ and O from water and atmosphere as well as varying isotope fractionation effects during nitrification (Granger & Wankel, 2016; Kendall et al., 2007). Hence, we cannot readily quantify the isotopic shift associated with nitrification and, accordingly, neither its effect on the assessment of isotopic enrichment factors in this study. However, for our field site, we consider it safe to assume that NO$_3^-$ stems from the most part from surrounding arable land and the contribution of freshly nitrified NO$_3^-$ from riparian soils to groundwater NO$_3^-$ is minor. Provided that nitrification in the riparian zone plays a significant role, the SISS-N model yields conservative estimates of denitrification as nitrification can partially mask denitrification-induced isotope fractionation (Hall et al., 2016; Wexler et al., 2014). Moreover, data points plotting to the right and top of the shaded area in Figures 4a and 4b (i.e., larger ln($f$) and $\Delta$ values) might be affected by addition of manure or NO$_3^-$ fertilizers, which are generally more enriched in $^{15}$N and $^{18}$O, respectively, than NO$_3^-$ originating from NH$_4^+$ fertilizers. Similar to nitrification, the effect of additional sources cannot readily be assessed without detailed information on source signatures and associated NO$_3^-$ loads.

A crucial model assumption is that denitrification is the only NO$_3^-$ sink entailing significant isotope fractionation at the field site. Data on potential isotope fractionation effects associated with additional processes are scarce or not available, in contrast to the extensively studied fractionation effects accompanying denitrification. In the case of DNRA, for example, the occurrence or extent of isotope fractionation is unknown to date (Nikolenko et al., 2018). However, given it is a microbially mediated NO$_3^-$ reduction process such as denitrification, DNRA might also cause significant isotopic enrichment in the remaining NO$_3^-$.

Similarly, in agreement with Dhondt et al. (2003) who measured enrichment factors of $\varepsilon_N = -4.4\%o \pm 0.3\%o$ in hydroponics, plant uptake has been generally associated with minor isotope fractionation compared to denitrification (Denk et al., 2017; Högberg et al., 1991; Lund et al., 1999). In contrast, recent enzymatic assays using eukaryotic NO$_3^-$ assimilatory reductases (Karsh et al., 2012; Treibergs & Granger, 2017) have reported $\varepsilon_N$ and $\varepsilon_O$ values as large as $\approx 30\%o$. Nonetheless, we are not able to assess either the transferability of such enzyme-level isotope effects to field conditions or the role of the associated eukaryotes for NO$_3^-$ removal at the field site.

The accuracy of $R_{tot}$ is, in part, affected by the temporal resolution of our data, considering that monthly data do not allow capturing short-term variations in NO$_3^-$ production and transformation (and potential associated fractionation processes) in the riparian zone. Second, uncertainties in $R_{tot}$ result from the assumption of instantaneous end-member mixing and are thus inherited from the concentration-based mixing model via the calculation of $F_{river}$ (equation (2)) and $[NO_3^{-\text{mix}}]$ (equation (3)). The assumption of instantaneous mixing is valid as long as travel times from the end-members to the riparian zone are short or end-member concentrations and isotope values remain stable over time. Considering that the distant groundwater has to travel a longer distance to the riparian zone than river water, these restrictions might be more problematic for the groundwater end-member than for the river end-member. The uncertainties related to the assumption of instantaneous mixing are particularly critical for the southern groundwater end-member, which shows a downward NO$_3^-$ concentration trend (but no distinct trend in isotope values) over the study period (Figure 2c). If we were to account for a certain travel time from the distant groundwater to the riparian zone, we would have to increase the concentration of the southern groundwater end-member in the SISS-N model according to the decreasing concentration trend. This would lead to larger NO$_3^{-\text{mix}}$ values in equation (4) and thus to larger $R_{tot}$ and $R_{add}$ values. However, estimates of flow velocities in the southern groundwater using the Darcy equation (assuming similar hydraulic properties as reported in Gassen et al., 2017 for the riparian zone) suggest flow velocities of around 5 m day$^{-1}$ and thus comparably short travel times to the
A riparian zone. We, therefore, consider the uncertainties associated with the assumption of instantaneous mixing to be small compared to model applications for systems with less permeable aquifers.

Evapoconcentration of Cl\(^-\) in Riparian groundwater samples might lead to a bias in Friver toward the groundwater end-members, as the Cl\(^-\) concentrations of the groundwater end-members (especially south of the river) were higher than those of the river end-member (Figure 2b). Similarly, evapoconcentration might result in larger NO\(_3^-\) concentrations measured in riparian groundwater and thus smaller R\(_{tot}\) and R\(_{add}\) estimates. Using le-excess < 0 as indicator of increased evaporation, the fraction of riparian groundwater samples for which the SISS-N model might be affected by evaporation-induced isotope fractionation was around 14%. However, F\(_{river}\) for the subset of samples with le-excess ≥ 0 was nearly identical to F\(_{river}\) in the base scenario, indicating a minor impact of potential evapoconcentration effects on the results of the Cl\(^-\) mixing model. Correspondingly, application of the SISS-N model to this subset yielded deviations of below 1% between the means of R\(_{tot,lc}\) and R\(_{tot}\), R\(_{den,lc}\) and R\(_{den}\), and R\(_{add,lc}\) and R\(_{add}\), respectively (Table 2). Hence, although evapoconcentration effects might have played a role for some samples, we can assume that the SISS-N model results remained largely unaffected by these.

While evapoconcentration appears to play a minor role, there might be other factors leading to the considerable amount of invalid F\(_{river}\) values (i.e., 23% of all samples) and thus to failure of the chloride mixing model. For example, addition of Cl\(^-\) from potassium chloride fertilizers during flow from the distant groundwater to the riparian zone might increase Cl\(^-\) concentrations above the end-member concentrations and thus lead to negative F\(_{river}\) values (see equation (2)). Moreover, F\(_{river}\) < 0 mostly occurs in the northern groundwater zone, for which we chose a groundwater well on the western fringe of the field site as distant groundwater end-member, which might not fully represent all wells north of the river. The opposite effect of F\(_{river}\) > 1 is mainly associated with sample concentrations below the end-member concentrations and might result from dilution in the riparian zone via an additional source with low Cl\(^-\) concentrations such as rapid infiltration of rainwater in the riparian zone. The latter scenario would also imply dilution of NO\(_3^-\) concentrations in the riparian zone. While we cannot exclude the presence of an unknown third end-member, the requirement of 0 ≤ F\(_{river}\) ≤ 1 enables us to restrict the analysis to samples for which such uncertainties do not majorly affect the model results.

### 5.5. Recommendations for Future Model Applications

We restricted our model to two mixing end-members as the study site is dominated by groundwater flow, and runoff generation via shallow soil flow paths is not significant. In more “flashy” systems where shallow flow paths become active during rainfall events, it might be required to add a third end-member to represent a hydrochemically disparate soil layer that temporally plays a substantial role for stream water chemistry (e.g., in steep headwater catchments; Seibert et al., 2009; Zhi et al., 2019), provided that this soil end-member significantly differs from the other two in its Cl\(^-\) or NO\(_3^-\) concentrations or NO\(_3^-\) isotope values. In such cases, river water during high-flow conditions represents a mixture of deeper groundwater and more shallow soil flow paths. Hence, unlike in our model application, it might be necessary to characterize the hydrochemistry of shallow riparian soil and amend the mixing equations such that river water results from mixing between the soil and groundwater signatures for ion concentrations and isotope values.

The minimum data requirements for application of the SISS-N model to assess NO\(_3^-\) removal from riparian groundwater are concentration data of chloride (or another conservative tracer), and concentration and N (or O) isotope data of NO\(_3^-\). These data should be measured in the stream, distant groundwater, and one or several riparian groundwater wells, ideally at least at monthly resolution during one year to assess seasonal dynamics. If the dual-element isotope values of the end-members do not sufficiently differ from each other, it is also possible to calculate the isotopic mixing signature from F\(_{river}\), weighted by the endmember concentrations. Regardless of the approach used to determine the mixing signature, the isotope data alone do not provide R\(_{tot}\)-estimates and, therefore, do not obviate the use of a mixing model using tracer and NO\(_3^-\) concentrations to quantify overall NO\(_3^-\) removal from riparian groundwater.

The SISS-N model cannot provide any information additional to conventional end-member mixing models in the absence of significant isotope fractionation at the field site. However, it is not straightforward to
specify a threshold above which apparent isotope fractionation can actually be considered significant, as the extent of denitrification associated with a certain isotopic shift depends on the underlying isotopic enrichment factor. Fortunately, the SISS-N model allows testing the plausibility of different enrichment factors with little computational effort. Hence, it is not necessary to decide a priori whether isotope fractionation at a field site should be considered as significant, as long as there is some reasonable estimate of the “true” enrichment factor associated with pure denitrification at the field site.

The choice of $\varepsilon$ values has significant impact on the SISS-N model results, as well as on any other model using field isotope data to assess denitrification. Hence, based on this study, we suggest (i) a thorough comparison of field-derived maximum $\varepsilon$ values and literature values and (ii) testing of $\varepsilon$ values against the prerequisite $R_{\text{add}} \geq 0$ in order to reduce the uncertainties associated with the choice of isotopic enrichment factors. If a field site shows evidence of fractionating NO$_3^-$ removal processes besides denitrification, the SISS-N model can be driven with a bulk enrichment factor combining estimates of the isotope fractionation effects via denitrification and additional processes. Such a model would be comparable to the approach in Dhondt et al. (2003) for denitrification and plant uptake and additionally account for mixing processes in the riparian zone. Including additional fractionating processes while assuming the same $\varepsilon$-values for denitrification as before would result in a smaller contribution of denitrification to overall NO$_3^-$ removal, as the same isotopic enrichment would be attributed to fractionation effects by denitrification and other processes.

In contrast, the model estimate of NO$_3^-$ removal by nonfractionating processes ($R_{\text{add}}$) would remain unaffected by additional fractionating processes.

The uncertainty analysis indicated a minor role of evapoconcentration effects at our field site. However, under conditions of significant evapoconcentration, one would first have to correct the Cl$^-$ and NO$_3^-$ concentrations of the mixture in the riparian zone for evapoconcentration effects. This could, for example, be achieved by introducing a concentration correction factor for each sampling day proportional to potential evapotranspiration (PET) or the deviation from the local meteoric water line (LMWL). In our study, the stable water isotope data collected concurrently with the NO$_3^-$ isotope data facilitated the assessment of evaporation effects in riparian groundwater. If stable water isotope data are not available, it might be needed to measure or derive other proxies for evaporation and correct or exclude sampling dates from the modelling that fall within periods of strong evaporation. Similar to the testing of different enrichment factors, the SISS-N model is a convenient tool for running multiple simulations with subsets of the entire data set and thus allows examining the impact of site-specific factors such as evapoconcentration.

6. Conclusions

This paper presents the SISS-N model, which is a simple mathematical model combining isotope and concentration data of NO$_3^-$ to distinguish between denitrification as permanent nitrogen sink and nitrogen retention by other processes (e.g., plant uptake, microbial assimilation, and NO$_3^-$ reduction to ammonium). The model was applied to riparian groundwater wells along a 2-km river reach surrounded by intense agriculture. Based on the model, NO$_3^-$ removal from riparian groundwater via additional processes substantially surpassed denitrification (mean of 27.8% ± 17.4% vs. 9.1% ± 11.8%, respectively, using $\delta^{15}N$ values and $\varepsilon = -28.0\%$), especially at further distance from the river and in winter. The rapid decline of denitrification with increasing distance from the river underlines the role of river water as organic carbon source for denitrification. More generally, these results demonstrate that total NO$_3^-$ removal (derived from the concentration reduction relative to a conservative tracer) should not be equated with denitrification, as this might result in significant overestimation of permanent nitrogen removal in riparian zones. This questions the efficacy of relying solely on riparian denitrification to mitigate NO$_3^-$ pollution of rivers, at least for comparable agricultural river sections that are dominated by groundwater flow and dependent on stream water for organic carbon supply.

Overall, this analysis demonstrates the added value of NO$_3^-$ isotope data not only as evidence for denitrification but also for the quantification of denitrification and additional NO$_3^-$ removal processes in riparian groundwater. Moreover, in contrast to previous research on aquifer plumes under steady state conditions, this study is the first application of the SISS model to a diffuse pollutant and time-variant conditions. The extension of the original model to the SISS-N model offers the advantage of assessing apparent NO$_3^-$
removal from riparian groundwater in response not only to dilution and denitrification but also to various biogeochemical processes resulting in N retention in riparian zones. Moreover, the extensive uncertainty analysis indicated a minor impact of various sources of uncertainty, which underlines the validity of the general model outcomes. These results highlight the general capacity of the new SISS-N model to differentiate between denitrification and additional removal processes, while accounting for mixing of groundwater and river water in riparian zones. This allows identifying spatial and temporal patterns of NO$_3^-$ sinks in riparian zones. More generally, we provide a tool for the quantification of permanent NO$_3^-$ removal via denitrification in systems where several transformation and mixing processes co-occur and complicate the assessment of denitrification. The model is thus an important addition to concentration-based end-member mixing models, which provide estimates for total NO$_3^-$ removal solely, as well as to previous studies using field isotope data of NO$_3^-$, which did not account for concentration reduction due to mixing processes and additional NO$_3^-$ sinks in riparian groundwater.

While our model allows distinguishing between denitrification and additional NO$_3^-$ removal processes, we did not attempt to further quantify the potential contribution of each additional process to overall NO$_3^-$ removal. Hence, future research might combine our model with detailed measurement of field parameters that allow quantifying individual removal processes other than denitrification (e.g., by comparing vegetated and non-vegetated sites or different plant communities to elucidate the role of plant uptake). Moreover, model uncertainties can generally arise from limited knowledge of isotope fractionation under field conditions during denitrification and, possibly, additional NO$_3^-$ removal processes. While this is a challenge for every quantification method using field isotope data of NO$_3^-$, we recommend that future research should focus on the quantification of potential isotope fractionation effects associated with additional uptake and transformation processes in riparian zones such as DNRA and microbial assimilation, as well as on the potential for anammox in riparian groundwater. This would yield more robust denitrification estimates with our model at sites where such processes may be significant. Despite these uncertainties, our model provides a simple method to quantify NO$_3^-$ removal processes over long periods for which continuous measurement of field parameters and reaction products can become impractical. Hence, the SISS-N model has potential for applications at various temporal and spatial scales to obtain a more detailed picture of NO$_3^-$ mixing and transformation processes in riparian zones. This information can ultimately help assess and improve the configuration of riparian zones in order to reduce NO$_3^-$ pollution in catchments.

Acknowledgments

S. R. L. conceived the analyses, performed the computations, and wrote the manuscript; N. T., A. M., and B. M. v. B. contributed to model development and discussion of field data; S. R. L. and A. M. produced the figures, and all authors discussed the results and commented on the manuscript. We thank Toralf Keller, Helko Kotaus, Andreas Schölland, and Oliver Bednorz for carrying out the field work. We would also like to acknowledge Martina Neuber, Sibylle Mothes, Jürgen Steffen, and Kerstin Puschendorf for their laboratory work. The SISS-N model code as well as the chloride and nitrate concentration data, and the nitrate and stable water isotope data are publicly available (https://doi.org/10.4211/hs.d76491f6a4584241a7cafd868391165).

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Erratum

In the originally published manuscript, there was an error in the Method section. The errors and corrections are described in detail below. The manuscript has been updated, and this may be considered the authoritative version of record.

Equations (5) and (6) in the originally published manuscript were incorrect, as they do not consider potential concentration differences between the nitrate sources in the river and distant groundwater, which affect the isotopic signature of the mixture in riparian groundwater. More specifically, the river water fraction $F_{\text{river}}$ represents the volumetric fraction of water from the river, but not necessarily the fraction of river nitrate in the mixture. There are two ways to correct this, either by multiplying $F_{\text{river}}$ by the endmember concentrations to calculate the weighted source contributions used in the calculation of the mixing signature (see equations (7a), (8a) and (9a) below), or by applying the original (simplified) SISS model and calculating the mixing signature using $\delta^{15}$N–NO$_3$ and $\delta^{18}$O–NO$_3$ data only (see equations (5) to (8)). We opted for the second approach, i.e., application of the original SISS model, as this in line with the initial motivation of the SISS model to consistently use isotope data in the determination of mixing and transformation independently from concentration data. Moreover, using the approach with weighted $F_{\text{river}}$ values might increase the total uncertainty of the model results, as uncertainties in both $F_{\text{river}}$ and the endmember concentrations would affect the calculated mixing signature (as opposed to the calculation using isotope data only). As the correction of equations (5) and (6) affects all subsequent calculations with the SISS-N model, the specific estimates for NO$_3$ removal by denitrification and additional processes reported in the Results section change.
(including all figures from Fig. 4 on). However, the Discussion section changes only marginally (when referring to values presented in the Results) and the overall conclusion of the paper (i.e., processes other than denitrification play a significant role in this type of riparian zone) is not affected by the corrections.

This summary contains the figures and tables from the published paper that have to be updated accordingly. Moreover, it provides a summary of the paragraphs in the main text that are affected by the error in equations (5) and (6) and describes how they change in the corrected version. The corrected R script is available at http://www.hydroshare.org/resource/d76491f6a4584241a7cafd8683911f65.

Abstract

Using the corrected equations, the SISS-N model calculates a mean removal of up to 28% by additional processes and only about 9% by denitrification. This is similar to the values in the published paper (i.e., up to 27% by additional processes and about 12% by denitrification).

3. Mixing and transformation models

3.1. Model assumptions

We do no longer use the modified SISS model. We apply instead the simplified SISS model directly to the nitrate isotope data.

3.3. Denitrification and additional fractionating processes

The new manuscript gives the corrected equations and describes the direct application of the simplified SISS model (see Lutz and Van Breukelen, 2014a) to determine the theoretical mixing signature and derive the extent of denitrification. Equations (5) and (6) in the published paper are incorrect as they do not account for nitrate concentration differences in the mixing endmembers, which affect the isotopic mixing signature and, hence, all subsequent calculations with the SISS-N model. The text justifying the use of \( F_{\text{river}} \) instead of the equations from the original SISS model is, therefore, irrelevant for the revised manuscript and has been deleted from the main text.

The mixing signature in the simplified SISS model is defined by the point of intersection between the mixing line and the curve in the dual-isotope plot for ongoing transformation (here: denitrification, see Fig. 3), assuming that the latter can be well approximated by a straight line with slope \( \varepsilon_O/\varepsilon_N \). The slope and intercept of the mixing line are calculated via equations (5) and (6), and used in equations (7) and (8) to determine the mixing signature (\( \delta^{15}N_{\text{mix}} \) and \( \delta^{18}O_{\text{mix}} \)):

\[
a = \frac{\delta^{18}O_{\text{river}} - \delta^{18}O_{\text{dist}}}{\delta^{15}N_{\text{river}} - \delta^{15}N_{\text{dist}}} \tag{5}
\]

\[
b = \delta^{18}O_{\text{river}} - a \cdot \delta^{15}N_{\text{river}} \tag{6}
\]

\[
\delta^{15}N_{\text{mix}} = \frac{\left( \delta^{18}O_{\text{rip}} - \frac{\varepsilon_O}{\varepsilon_N} \delta^{15}N_{\text{rip}} - b \right)}{a - \frac{\varepsilon_O}{\varepsilon_N}} \tag{7}
\]

\[
\delta^{18}O_{\text{mix}} = a \cdot \delta^{15}N_{\text{mix}} + b \tag{8}
\]

where \( a \) and \( b \) are the slope and intercept of the mixing line equation, respectively, \( \delta^{15}N \) and \( \delta^{18}O \) are the nitrogen and oxygen isotope values of NO\(_3\) for the river water endmember (subscript \( \text{river} \)), distant groundwater endmember (subscript \( \text{dist} \)) and riparian groundwater sample (subscript \( \text{rip} \)), and \( \varepsilon_N \) and \( \varepsilon_O \) are the isotopic enrichment factors of nitrogen and oxygen associated with denitrification.

It follows for the contribution of the river endmember to the sample mixture, \( s_{\text{river}} \):

\[
s_{\text{river}} = \frac{\delta^{15}N_{\text{mix}} - \delta^{15}N_{\text{dist}}}{\delta^{15}N_{\text{river}} - \delta^{15}N_{\text{dist}}} \tag{9}
\]
Alternatively, $s_{\text{river}}$ can be calculated by weighting $F_{\text{river}}$ by the endmember concentrations $[\text{NO}_3^-_{\text{river}}]$ and $[\text{NO}_3^-_{\text{dist}}]$

\[
s_{\text{river}} = \frac{F_{\text{river}} [\text{NO}_3^-_{\text{river}}]}{F_{\text{river}} [\text{NO}_3^-_{\text{river}}] + (1-F_{\text{river}}) [\text{NO}_3^-_{\text{dist}}]}
\]  

(9a)

This yields the following corrected equations for the isotopic signature of the theoretical mixture:

\[
\delta^{15}N_{\text{mix}} = s_{\text{river}} \cdot \delta^{15}N_{\text{river}} + (1-s_{\text{river}}) \cdot \delta^{15}N_{\text{dist}}
\] 

(7a)

\[
\delta^{18}O_{\text{mix}} = s_{\text{river}} \cdot \delta^{18}O_{\text{river}} + (1-s_{\text{river}}) \cdot \delta^{18}O_{\text{dist}}
\] 

(8a)

Regardless of the correction applied, it follows for the calculation of the total extent of denitrification in the extreme scenario (equation (S1)):

\[
R_{\text{den,ext}}[\%] = \left(1-f_{\text{den,ext}}\right) \times 100\% = \left(1- \frac{1}{s_{\text{river}} + \frac{1-s_{\text{river}}}{f_{\text{max}}}}\right) \times 100\%
\] 

(S1)

In the corrected manuscript, we apply equations (5) to (9) to calculate the source contributions and isotopic signature of the theoretical mixture. The new criteria for valid results using the equations above are at least 100 simulations with $0 \leq F_{\text{river}} \leq 1$, $0 \leq s_{\text{river}} \leq 1$ and $0 \leq f_{\text{den}} \leq 1$. Using the new criterion of $0 \leq s_{\text{river}} \leq 1$ in at least 100 simulations, 15 samples (3.2%) were discarded from further calculations. Applying all three criteria resulted in a final subset of 418 samples (88.2%). Although $F_{\text{river}}$ is no longer needed to calculate the extent of denitrification, it is still used in the calculation of $R_{\text{tot}}$ and $R_{\text{add}}$ via determination of the theoretical nitrate concentration in riparian groundwater (equation (3)).

3.5. Uncertainty calculations

Due to the interdependency of $\delta^{15}N_{\text{mix}}$ and $\delta^{18}O_{\text{mix}}$ via equations (5) to (8), the results of the $\delta^{15}N$ and $\delta^{18}O$ models do no longer differ (except for rounding differences).

4. Results

4.1. Isotopic Enrichment Factors

The corrected apparent isotopic enrichment factors are slightly smaller than those reported in the published paper (see corrected Table 1). Nonetheless, the corrected equations give the same seasonal differences as in the published paper, with the largest and smallest isotopic enrichment factors for the summer and winter.

| Source              | $\varepsilon_N$ [%] ($R^2$) | $\varepsilon_O$ [%] ($R^2$) |
|---------------------|-----------------------------|-----------------------------|
| This study          |                             |                             |
| Winter              | $-3.1$ (0.7)                | $-2.6$ (0.7)                |
| Spring              | $-3.6$ (0.5)                | $-3.0$ (0.5)                |
| Summer              | $-10.4$ (0.5)               | $-8.6$ (0.5)                |
| Autumn              | $-7.0$ (0.6)                | $-5.7$ (0.6)                |
| Literature          |                             |                             |
| Barford et al. [1999]| $-28.6\pm1.9$               | $-20.4\pm1.3$               |
| Mariotti et al. [1981]| $-29.4\pm2.4$               | $-22.6\pm0.4$               |
| Torrentó et al. [2011]| $-26.3\pm1.8$               | $-23.7\pm1.8$               |
| Granger et al. [2008]$^a$ | $-26.6\pm0.5$               |                             |
| Wunderlich et al. [2012]$^b$ | $-23.5\pm1.9$               |                             |

Note. For $\varepsilon_N$ and $\varepsilon_O$ derived in this study, the coefficients of determination ($R^2$) are provided in parentheses. $^a$maximum values among freshwater bacterial strains $^b$maximum values with acetate as carbon source
months, respectively. Moreover, the $\varepsilon_N$ and $\varepsilon_O$ values are not used for further calculations such that they do not affect subsequent results in the paper.

In line with the results from the published paper, the largest and smallest isotopic enrichment factors using the corrected equations are calculated for the summer and winter, respectively. In addition, there are some samples in winter and spring with negative isotopic shifts ($\Delta^{15}N < 0$ or $\Delta^{18}O < 0$), as also shown in the published paper. Due to the direct interdependency between $\delta^{15}N$-values and $\delta^{18}O$-values using the corrected equations, the scatter of the samples plotted in the figure below does no longer differ between the panels (a) and (b), as opposed to the original version of Figure 4.

According to the corrected equations, the isotopic shifts $\Delta^{15}N$ and $\Delta^{18}O$ are now related via $\phi = \varepsilon_O / \varepsilon_N$ (see new equation (3)) and thus all plot on a straight line with slope $\phi$ in the dual-isotope plot showing the isotopic shifts. Therefore, we deem this figure to be no longer relevant to the new manuscript and discarded it from the main text.

4.2. Temporal Dynamics of Nitrate Removal

The corrected values in Table 2 do not differ substantially from those in the published paper, especially for the $\delta^{15}N$-model in the base scenario and in the scenario for samples with $lc$-excess $\geq 0$. Moreover, application of the corrected equations now gives identical estimates (apart from rounding differences) for the $\delta^{15}N$ and $\delta^{18}O$-models. This obviates the need to discuss the results of the $\delta^{18}O$-model in section 4.2. Slightly larger differences for the extreme scenario with respect to the published paper become apparent, particularly for $R_{\text{den,ext}}$. This is because the corrected equations above do no longer allow a large overestimation of isotopic enrichment and thus of $R_{\text{den,ext}}$ for this scenario. Accordingly, the number of simulations for which $R_{\text{den,ext}}$ exceeds $R_{\text{tot,ext}}$ and thus results in negative $R_{\text{add,ext}}$ values decreases from 21.7% in the published paper to 9.9%. Nonetheless, the corrections do not affect the general principal that the base scenario yields a

![Figure 4-corrected](image-url)

**Figure 4-corrected.** Apparent enrichment factors derived from $\delta^{15}N$-values (a) and $\delta^{18}O$-values (b) for all riparian groundwater samples and different seasons using equation (11) (new equation (14)) with an intercept of zero and accounting for analytical uncertainties in concentrations and NO$_3$-isotope data. $\Delta^{15}N$ and $\Delta^{18}O$ denote the isotopic shifts defined by the left-hand side of equation (11/14), and $\ln(f)$ is the fraction remaining relative to the theoretical NO$_3$ concentration. Samples with negative isotopic shifts were not included in the linear regression. Literature ranges refer to experiments with pure cultures (Barford et al. [1999]; Mariotti et al. [1981]; Sutka et al. [2006]; and Wellman et al. [1968] for $\varepsilon_N$; and Granger et al. [2008], Hosono et al. [2015], Knöller et al. [2011]; Torrentó et al. [2010]; and Wunderlich et al. [2012] for $\varepsilon_N$ and $\varepsilon_O$) and are shown as shaded areas between the slopes of minimum and maximum values of $\varepsilon_N$ and $\varepsilon_O$, respectively. The directions of changes in $\ln(f)$ and isotopic shifts associated with denitrification, nitrification and additional processes are indicated by black arrows.
conservative estimate of the possible extent of denitrification compared to scenarios for which endmember mixing does not occur instantaneously (as in the extreme scenario here). In addition, despite the corrections, the general conclusion that additional processes significantly contribute to overall NO$_3^-$ removal in the riparian zone is still valid.

![Figure 5-removed. Dual-isotope plot showing isotopic shifts ($\Delta^{18}$O-NO$_3^-$ vs. $\Delta^{15}$N-NO$_3^-$) for all riparian groundwater samples in different seasons and accounting for analytical uncertainties in concentrations and isotope data. Slopes of $\epsilon_O/\epsilon_N$ were determined by linear regression including all points with $\Delta^{15}$N$\geq$0 and $\Delta^{18}$O$\geq$0. Literature ranges refer to experiments with pure cultures [Granger et al., 2008; Hosono et al., 2015; Knöller et al., 2011; Torrentó et al., 2010; Wunderlich et al., 2012] and are shown as shaded areas between minimum and maximum literature values of $\epsilon_O/\epsilon_N$.

### Table 2 – corrected

Overall NO$_3^-$ removal ($R_{tot}$), denitrification ($R_{den}$) and removal by additional processes ($R_{add}$) in the base scenario, the extreme scenario with maximum denitrification in groundwater ($R_{tot,ext}$, $R_{den,ext}$ and $R_{add,ext}$) and for the sample subset with non-negative lc-excess ($R_{tot,lc}$, $R_{den,lc}$ and $R_{add,lc}$).

|                      | near groundwater | intermediate groundwater |
|----------------------|------------------|-------------------------|
|                      | $\delta^{15}$N   | $\delta^{18}$O          | $\delta^{15}$N   | $\delta^{18}$O          |
| base scenario        |                  |                         |              |
| $R_{den}$ [%]        | 10.4±12.5        | 10.4±12.5               | 5.8±8.9      | 5.8±8.9                  |
| $R_{add}$ [%]        | 27.8±18.5        | 27.8±18.5               | 27.9±14.1    | 27.9±14.1               |
| $R_{tot}$ [%]        | 37.8±21.1        | 37.8±21.1               | 33.5±15.2    | 33.5±15.2               |
| max denitrification in groundwater |                  |                         |              |
| $R_{den,ext}$ [%]    | 15.0±18.0        | 15.1±18.1               | 8.0±13.0     | 8.1±13.0                |
| $R_{add,ext}$ [%]    | 24.3±18.6        | 24.3±18.6               | 26.0±14.3    | 25.9±14.3               |
| $R_{tot,ext}$ [%]    | 37.8±21.1        | 37.8±21.1               | 33.5±15.2    | 33.5±15.2               |
| samples with lc-excess$\geq$0 |                  |                         |              |
| $R_{den,lc}$ [%]     | 10.7±12.9        | 10.7±13.0               | 6.1±9.4      | 6.1±9.4                 |
| $R_{add,lc}$ [%]     | 27.1±18.2        | 27.1±18.2               | 27.8±14.6    | 27.7±14.6               |
| $R_{tot,lc}$ [%]     | 37.8±20.9        | 37.8±20.9               | 33.7±15.9    | 33.7±15.9               |

Note. Values are given as mean ± standard deviation of the sample subset with $R_{den}$$\geq$0, $R_{den,ext}$$\geq$0 or $R_{den,lc}$$\geq$0, respectively, after setting negative $R_{add}$ values to zero. Samples with less than 100 successful Monte Carlo simulations were discarded. $R_{tot}$ differs between the model scenarios as the statistics refer to different sample subsets.
When applying the original SISS model, the $\delta^{15}$N and $\delta^{18}$O-models give identical estimates for $R_{\text{den}}, R_{\text{add}}$ and $R_{\text{tot}}$, which can also be seen in the corrected Figure 6 (new Fig. 5). Hence, the text discussing differences between the $\delta^{15}$N and $\delta^{18}$O-models becomes obsolete. There are no major differences in the temporal patterns of all three variables with respect to Figure 6 in the published paper. Overall, $R_{\text{add}}$ is still the dominant component of overall NO$_3^-$ removal, except for the summer of 2015. Compared to the published results, the median $R_{\text{den}}$ of all wells changes from 1.1%–42.3% to 1.6%–36.7% in the near groundwater, and slightly increases from 1.0%–8.0% to 1.3%–8.1% in the intermediate groundwater. The median $R_{\text{add}}$ increases from 2.2%–58.6% to 7.8%–59.1% in the near groundwater, and changes from 0.3%–50.0% to 0%–50.8% in the intermediate groundwater. Correspondingly, the relative contribution by $R_{\text{den}}$ to overall NO$_3^-$ removal over time decreases from 4.7%–95.1% to 4.2%–61.3% (mean of 23.8%±16.2%; was 29.0%±24.4%) in the near groundwater and increases from 2.8%–91.2% to 4.9%–100% (mean of 16.2%±19.9%; was 16.7%±18.2%) in the intermediate groundwater. Overall, the differences to the published results are secondary, as the dominance of NO$_3^-$ removal by additional processes prevails.

4.3. Spatial Patterns of Nitrate Removal

Similar to the temporal patterns in Figure 6, the spatial patterns in Figure 7 (new Fig. 6) are not majorly affected by the use of the corrected model equations. Compared to the published results, $R_{\text{den}}$ slightly decreases from 1.1%–55.8% to 1.0%–54.0% in summer (mean of 19.3±15.8%; was 21.8%±17.5%), and slightly changes from 1.3%–14.9% to 1.5%–14.2% in winter (mean of 4.4%±3.0%; was 4.5%±3.2%). $R_{\text{add}}$ marginally changes from 0%–50.4% to 0%–50.5% in summer (mean of 23.9%±16.5%; was 22.0%±15.6%), and increases from 7.8%–51.3% to 11.2%–52.2% in winter (mean of 29.7%±10.1%; was 27.3%±12.2%). The number of wells with negative $R_{\text{add}}$ during summer increases from one to three. Nonetheless, the overall spatial pattern for the entire study period does not change either for $R_{\text{den}}$ (i.e., largest mainly in the C transect and smallest in the A and B-N transects) or for $R_{\text{add}}$ (i.e., largest at B-N and smallest at B-S and C) with respect to the published results.
4.4. Additional Model Scenarios

The means and standard deviations for $R_{den}$, $R_{add}$ and $R_{tot}$ were updated in this section (see also description of new Table 2). The differences to the numbers in the published manuscript are overall minor.

5. Discussion

5.1. Isotope Fractionation and Enrichment Factors

Due to the interdependency between $\delta^{15}$N-values and $\delta^{18}$O-values in the corrected equations, there is no longer any difference in the $\varepsilon_O/\varepsilon_N$-slopes derived from apparent enrichment factors between seasons. Nonetheless, as the assumed $\varepsilon_N$ and $\varepsilon_O$ values are not affected by the corrections, the statements about the comparability to literature values remain valid.

5.2. Quantification of Denitrification

The contribution of $R_{add,ext}$ to overall NO$_3^-$ removal in the extreme scenario increases from around 55% and 77% (in the published paper) to 62% and 74% (using the corrected equations) for the near and intermediate groundwater, respectively.

5.3. Nitrate Removal by Additional Processes

Using the corrected equations, the mean C:N ratio using the molar concentrations of DOC and NO$_3^-$ of the six wells with the largest $R_{add}$ (i.e., above the 75th percentile) is still smaller than that of the six wells with the largest $R_{den}$ (i.e., 1.1 vs. 1.5 using the $\delta^{15}$N model; was 1.0 vs. 1.5). Moreover, the $E_h$ values of the six wells...
with the largest $R_{\text{den}}$ and largest $R_{\text{add}}$, respectively, slightly change from means of 58.0 and 175.0 mV in the published paper to 61.6 and 176.9 mV. Hence, in line with the published results, the corrected model calculations do not point towards the occurrence of DNRA.

5.4. Uncertainties and limitations
Using the corrected equations, the differences between the base scenario and the scenario for samples with lc-excess $\geq 0$ become even smaller compared to the published results.

5.5. Uncertainties and limitations
The comparison between the model approaches using $F_{\text{river}}$ and the original SISS model, respectively, becomes obsolete in the new version of the manuscript.

6. Conclusions
Using the corrected equations, $\text{NO}_3^-$ removal from riparian groundwater via additional processes substantially surpasses denitrification (mean of 27.8±17.4% vs. 9.1±11.8%, respectively, using $\delta^{15}N$ values and $\varepsilon_N = \sim 28.0\%$), which is similar to the results in the published paper (i.e., mean of 26.7±19.0% vs. 11.5±14.9%). The key messages in the Conclusions are not affected by the corrections of the model equations.

Acknowledgements
This study was supported by the Helmholtz Research Program (Integrated Project "Water and Matter Flux Dynamics in Catchments"), and in part by the Collaborative Research Center 1253 "CAMPOS" (Project 2, sub-catchments) funded by the German Research Foundation (DFG, Grant Agreement SFB 1253/1 2017).