Effects of Heterogeneous Stream-Groundwater Exchange on the Source Composition of Stream Discharge and Solute Load

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Abstract  The exchange of water and solutes between the stream and groundwater along a stream network affects the source composition of discharge and solute load in the stream. To date, this hydrologic turnover has only been analyzed with respect to the exchange of water. In this study, we extend the concept of hydrologic turnover to solutes and analyze the effects of different hydrologic conditions on the spatial patterns and magnitude of exchange fluxes. Based on a coupled stream-groundwater model built in MODFLOW using the Streamflow-routing package, we simulated stream-groundwater exchange along a stream of 30 km in length and evaluated the evolution of stream water source composition under different precipitation and streamflow conditions. Results show that even for highly variable hydrologic conditions, the direction of stream-groundwater exchange (loss/gain) remained unchanged in consistently gaining or losing reaches, but changed in interspersed transitional reaches. The comparison between the source composition of discharge and nitrate load in stream water revealed a decoupling of discharge and solute load contribution from groundwater to the stream, as zones of high water gains do not necessarily coincide with zones of high solute concentrations. Overall, nearly 80% of total groundwater contributions to the outflow of water from the catchment were generated over only 20% of the total stream length. Our research highlights the importance of distinguishing water and solute load contributions to streams. This in turn implies that to reduce groundwater-borne nutrient loads to streams, measures need to focus on the specific reaches with highest load contributions.

Plain Language Summary  Streams and groundwater are connected and continuously exchange water and solutes. For example, the inflow of groundwater into streams not only increases streamflow, but also influences the chemical composition of stream water if the groundwater contains different solutes than the stream. Therefore understanding the spatial patterns of water and solute contributions from groundwater to the stream is important for the management of stream water quality. Taking the lower Selke River in central Germany as an example, we investigated the influence of stream gains and losses on the source composition of discharge and solute loads along the stream network as well as the influence of different precipitation and streamflow conditions. We found that higher precipitation and the associated elevated groundwater recharge or lower stream flows can increase the total length of gaining reaches, decreasing the relative importance of the source water from the upper stream. Due to the heterogeneous distribution of groundwater and solute gains, the magnitude of solute contribution from groundwater to stream can be quite different from the associated discharge contribution. However, both water and solute contributions are typically dominated by focused groundwater gains along only a few key reaches.

1. Introduction

Stream networks integrate the lateral influx of water and solutes generated throughout the catchment. Observations and analysis of discharge and concentration at the catchment outlet can provide information on
Both solute and hydrological signals are influenced by exchange and transformation processes which occur along transport in the stream network (e.g., Battin et al., 2008; Mineau et al., 2015).

During base flow conditions, groundwater discharge is the key source of stream water and also delivers solutes to the stream network (Neal et al., 2012; Winter et al., 1998). Across scales from reaches (Conant, 2004; Kalbus et al., 2009) to stream networks (Batlle-Aguilar et al., 2014), groundwater discharge to streams is spatially heterogeneous. Thus, not all parts of a catchment contribute equally to stream flow. Concentrations of solutes in the discharging groundwater are also spatially heterogeneous reflecting the effects of the land use at the recharge locations and mixing along the transport flow paths (Batlle-Aguilar et al., 2014; Lee et al., 2020; Wang et al., 2015). The patterns of solute source contributions along a stream network are thus controlled by the combined effect of the magnitude of groundwater discharge and the patterns of solute concentration in the discharging groundwater. The term “source” refers to the location where water and solutes enter the stream.

Stream networks are biogeochemically active systems and loads of reactive solutes are modified during downstream transport. For example, denitrification and biotic uptake of nitrate in stream networks are considered to significantly reduce nitrate export from catchments (Alexander et al., 2000; Botter et al., 2010). As a result, reactive solutes entering the stream network at upstream locations have a higher probability of being removed before reaching the catchment outlet than solutes from sources closer to the catchment outlet (Battin et al., 2008; Dehaspe et al., 2021). Thus, biogeochemical processes influence the solute source composition of stream water.

Stream networks not only integrate and process solutes but can also lose water and solutes into the subsurface. An analysis of water levels in 4.2 million wells and stream stages in the nearby streams across the contiguous USA indicated the potential for stream water losses to the adjoining aquifers in the vicinity of 64 percent of all wells (Jasechko et al., 2021). Hydrologic losses influence the stream water source composition by reducing the relative contribution of upstream sources and increase those from further downstream (Covino et al., 2011; Mallard et al., 2014). This process was termed hydrologic turnover by Covino et al. (2011). When the chemical signatures of stream water lost and those of groundwater gained are distinct, hydrologic turnover modifies both the water source and the solute source composition.

The effects of hydrologic turnover have so far only been studied in smaller catchments by empirical upscaling of stream tracer based mass balances (Covino et al., 2011; Mallard et al., 2014). The largest catchment analyzed using this methodology has been 64 km$^2$ in size (Mallard et al., 2014). These studies have focused on the effects of hydrologic turnover on the source composition of stream water where “source” means the most recent point of entry into the stream and have not explicitly accounted for solutes. As locations with high groundwater discharge do not necessarily coincide with high groundwater concentrations, the evolution of the source composition of stream water may be substantially different from that of solute loads. As the magnitude and direction of stream-groundwater exchange could change under different hydrologic conditions (Conant, 2004; Dwivedi et al., 2018; Schmidt et al., 2006; Zimmer & McGlynn, 2017), the source composition could also be affected by hydrologic conditions.

In this study, we evaluated the effects of heterogeneous stream-groundwater exchange along a 30-km-long river in a 468 km$^2$ catchment on the source composition of stream water and solute loads by applying a coupled, catchment-scale stream-groundwater flow and transport model. We further tested the influence of different precipitation and streamflow conditions on gaining and losing patterns as well as on the evolution of source compositions. Moreover, we addressed the question how varying hydrologic conditions influence the spatial patterns of gaining and losing reaches. Under overall dryer condition, we expect an increasing share of losing reaches, which in turn can influence the water source composition at the catchment outlet. Solute and water sources upstream of losing reaches might then contribute less to the source composition at the catchment outlet.
2. Methods

2.1. Study Area

The Selke catchment (Figure 1a) located in central Germany can be roughly divided into an upper forest-dominated part and a lower agriculturally dominated part, due to significant differences in topography and land use (Dupas et al., 2017; Yang et al., 2018). Accordingly, the main stem of the Selke River can be divided into the upper Selke River and the lower Selke River with the Meisdorf gauging station marking the transition between the two land use types (Figure 1a). The total area of the Selke catchment is 468 km². To

Figure 1. Geographic data and conceptual model of the study area. (a) Topography; (b) boundary conditions; (c) geological model with profiles. The number of segments and control points in (b) are used for Streamflow-routing (STR) Package. Legend in (c): Mi-Mining layer, LT-Lower terrace, MT-Middle terrace, E-Elster basic moraine, HT-High terrace, Q-Quaternary, T-Tertiary, PT-Pretertiary.
avoid the error caused by the inconsistency between Selke catchment divide and groundwater divide, the
groundwater model boundaries are extended from the topographic divide to perennial rivers such as the
Bode River, the Eine River, and the Wipper River (Figure 1a).

Based on the 25 m resolution DEM from the State Office for Surveying and Geoinformation of Saxony-An-
halt, the elevation in this 1,132 km² study area falls overall from 593 m in the southwest to the 59 m in the
northeast. Note that the vertical datum for all elevations in the current study is sea level. Originating from
the Harz mountain range, the Selke River discharges into the Bode River, which leaves the study area at
the Stassfurt gauging station. Inside the study area, three gauging stations (Silberhütte, Meisdorf, and
Hausneindorf) exist along the Selke River and six gauging stations exist along the Bode River and the Eine
River (Figure 1a).

Groundwater levels in the catchment have been influenced by former open cast lignite mines which had
been converted into lakes (Concordia Lake, Koenigsauer Lake, and Wilslebener Lake). The water levels
of the Concordia Lake and the Koenigsauer Lake were continuously elevated by groundwater seepage
and direct pumping recharge from the Selke River between November 1998 and December 2004 (Jiang
et al., 2014). To maintain the lake levels at a specified elevation, an artificial channel (Hauptseegraben) con-
necting the three lakes is used to discharge pumped lake water into the Selke River. The confluence of the
Selke River with the Hauptseegraben channel is ~0.3 km upstream of the Hausneindorf gauging station.
Since 2011, the water levels in the lakes have remained constant.

Nearly 65% of the study area is dominated by arable land, based on the data from Corine Land Cover 2018
of Germany (https://land.copernicus.eu/pan-european/corine-land-cover). More details such as land use,
soil type, and the geological map of Selke catchment could be obtained from Jiang et al. (2014) and Yang
et al. (2018).

2.2. Flow Model

The coupled stream-groundwater model is built in MODFLOW (Harbaugh, 2005) using the Stream-
flow-routing (STR) Package (Prudic, 1989).

2.2.1. Model Geometry/Domain

The model domain is the same as the study area. The elevation of the land surface is interpolated from a
25 m DEM and the bottom of the model is assumed to be ~200 m. The model is divided into eight layers
with equal thickness while the horizontal grid spacing is 200 m. Around the lower Selke River, the grid is
refined by a factor of two in x and y directions, leading to a 100 m grid spacing.

2.2.2. Boundary Conditions

To investigate the influence of stream-groundwater exchange on the evolution of source composition of
discharge and solute load along the stream, a steady-state groundwater model was built to identify the long-
term, steady-state exchange patterns. Since lake levels have been constant since 2011, the simulation period
in the current steady-flow model is set from 2011 to 2018.

Figure 1b shows the main settings of boundary conditions in the conceptual model. The divide in the south-
western boundary, which coincides with the topographic boundary of Selke catchment, is assumed to be a
no-flow boundary. The remaining river boundary is treated as the specified-head boundary where the head
is interpolated by the multi-year average river level at several gauging stations, which are provided by the
State Agency for Flood Protection and Water Management of Saxony-Anhalt (LHW). The three lakes are
treated as the constant head boundaries where the lake levels are 84.5, 102.2, and 106.25 m for Concordia
Lake, Koenigsauer Lake, and Wilslebener Lake, respectively.

Groundwater recharge is calculated by using the rainfall flux computed by the recharge (RCH) package
minus the evaporation flux computed by the evapotranspiration (EVT) package. Three parameters are re-
quired in EVT package: evapotranspiration (ET) surface, extinction depth, and maximum ET rate. We set
ET surface to be the same as the land surface and assume the extinction depth, which is the maximum
depth to evaporate water, to 3 m, according to the type of land covers in Selke catchment (Shah et al., 2007).
Maximum ET rate is obtained in the form of gridded data sets from the German Weather Service (DWD) in a monthly temporal and 1 km² spatial resolution from 2011 to 2018.

### 2.2.3. Hydrogeological Structure

The hydraulic conductivity depends on the geological structure and associated material properties. The study area has a complex stratigraphic distribution, in which most strata are thin and discontinuous with pinching out at many places (Figure 1c). Thus, there was a need for a simplified representation of the geological structure. We used the Hydrogeologic-Unit Flow (HUF) package (Anderman & Hill, 2000) by viewing every geological layer as a hydrogeologic unit and then calculated the effective hydraulic property of numerical layers based on the thickness and hydraulic properties of the hydrogeologic units, which were defined in the geological model and materials (Table S1). To avoid the uncertainty induced by the insufficient geological information in the upper Selke catchment, and to focus on stream-groundwater interactions in the lower Selke catchment, the average of the observed discharge at the Meisdorf gauging station from 2011 to 2018 is used as the inflow rate of the lower Selke River. Meanwhile, the lower Selke River and its main tributaries are treated with STR package (Prudic, 1989) while the upper Selke River and the other rivers are treated with Drain package by setting a high conductance value of 0.115 m²/s and setting the drain elevation equal to the elevation of the land surface, which is a common approach used by previous studies (Goderniaux et al., 2013; Wang et al., 2016). The vadose zone is not considered in the current study.

### 2.3. Stream Simulation

#### 2.3.1. Calculating Stream-Groundwater Exchange Using the STR Package

In the STR package, the stream network is conceptualized as lines with coordinate and direction. Each stream can be divided into several segments, and each segment contains one or several stream grid cells (reaches). Streams are parameterized per segment, thus, stream width, slope, Manning’s roughness, and hydraulic conductivity are equal for all reaches in the same segment. Streambed elevations are assigned to the bottom and top ends of each segment, the streambed elevations of the reaches are then obtained by interpolation. The length of the stream reach in every stream grid cell is calculated based on its real geometry. Surface sources can be added at the beginning of a segment or subtracted at the end of a segment.

Stream grid cell can not only have a stream stage but also a groundwater head. The general idea to compute the water exchange between stream and groundwater is described as follows. First, calculating the water depth in the most upstream grid cell based on inflow rate and Manning’s equation. Then, calculating the water exchange between stream and groundwater based on the stream stage and the groundwater head in the same grid cell. Then, the discharge in the first stream grid cell is calculated by adding the net gains to the initial flow rate. Finally, this discharge is viewed as the inflow rate at the reach downstream and used to calculate the water depth in the grid cell. If the computed groundwater head is lower than the bottom of streambed, it is assumed to be equal to the bottom elevation of streambed in the calculation of stream-groundwater exchange amount. For more details, see Prudic (1989).

#### 2.3.2. Parameter Setting for Stream Simulation

In the current study, we divided the lower Selke River and its tributaries into 14 segments by 15 streambed control points including two gauging stations and 13 “virtual gauging stations” (Figure 1b). At the Meisdorf and Hausneindorf gauging stations, the measured elevation of the streambed surface are 189.13 and 104.54 m, respectively, while their corresponding ground elevations are 196.07 and 105.8 m, respectively. This indicates a substantial difference between the elevation of streambed surface and the ground elevation obtained from the current 25 m resolution DEM. Due to the lack of precise streambed elevations along the stream, linear relationship between streambed’s top elevation and ground elevation determined by values at the Meisdorf and Hausneindorf gauging stations was applied to the lower Selke catchment to obtain the top elevation of streambed at 13 “virtual gauging stations”. Streambed elevations within a segment are interpolated between the elevations of the two end points.

The other parameters are set based on previous studies. According to the calibration results of Selke River parameters in Munz et al. (2017), the Manning’s roughness coefficient is set to 0.022 and the hydraulic conductivity of the streambed is set to $1.16 \times 10^{-5} – 1.16 \times 10^{-4}$ m/s with a decreasing trend toward the outlet.
According to the model setup in Nixdorf and Trauth (2018) and values measured in the field, the width of the Hauptseegraben channel is set to 3 m and the width of the Selke River is 1–10 m. The streambed thickness is assumed to be 1 m. Because the Hauptseegraben channel connects all the three lakes, for simplification, this stream is simulated starting from the discharge point connecting Concordia Lake with a specified inflow rate of 0.1 m$^3$/s, which is the average abstraction rate from the Concordia Lake from 2014 to 2017. More details about the stream parameter could be found in Table S2.

2.4. Solute Transport Simulation

To evaluate the evolution of the source composition of solute load, nitrate has been selected as an example substance. A steady-state transport model was built where we assumed that nitrate infiltrates into groundwater uniformly from the arable land (Figure 1b). The mass input of nitrate leaching into groundwater, which is denoted as $M_{\text{input}}$, is assumed to be 5 kg/ha/yr based on the range of nitrate loads previously simulated for the Selke catchment (Jiang et al., 2019).

In this simple model, the reactions of nitrate in the vadose zone are not considered. Similar to previous work (Almasri & Kaluarachchi, 2007; Lee et al., 2020), nitrate transport inside the groundwater is simulated using MT3DMS (Zheng & Wang, 1999). Denitrification in groundwater has been considered as first order decay (Almasri & Kaluarachchi, 2007; Frind et al., 1990; Liu & Koenig, 2002) with a decay coefficient ($\lambda$) of 0.693/$\tau$ (Almasri & Kaluarachchi, 2007), where $\tau$ is the half-life time [d]. The half-life time of nitrate is assumed to be 693 d, which is in the range of 365–840 days as reported in previous studies (Frind et al., 1990), corresponding to a decay coefficient of 0.001/d. The longitudinal dispersivity and transverse dispersivities are set to 50 and 5 m, respectively. The effective diffusion coefficient is set to $5.79 \times 10^{-10}$ m$^2$/s (Frind et al., 1990).

Based on the groundwater nitrate concentration computed by MT3DMS, the nitrate concentration of stream water is calculated under the assumption of instantaneous mixing of all water sources. We assume the stream losses do not influence the nitrate concentration of groundwater. The stream water and solute mass balance is detailed in Section 2.5. Further biogeochemical reactions of nitrate after it has entered the stream are not considered.

By using the above parameterization, we aimed at implementing a simplified representation of reactive nitrate transport at catchment scale, which results in heterogeneous patterns of groundwater nitrate concentration and nitrate load in streams. We deemed this appropriate, because our main focus is on the effects of hydrologic turnover on the source composition of solute load in the stream water.

2.5. Calculation of Source Composition of Discharge and Solute Load of Stream Water

In the current study, the stream water and solute load in a reach can be composed of three types of sources: upstream contributions, tributaries, and groundwater. The groundwater source can be further subdivided into groundwater discharge across numerous reaches at different locations. Note that the process that water lost from one segment returns to stream through a subsequent segment (hyporheic exchange) is not considered in this concept.

Different from the tracer mass balance approach where gross losses and gains can occur in a single reach, in the numerical model a reach cannot be concurrently gaining and losing water. The changing source water composition is represented by the fraction of water from upstream reaches that remains in the stream during downstream transport. If the stream gains water through a reach, all water from upstream reaches is kept, if the stream loses water, only a fraction of the upstream water will remain in the channel, that is,

\[
R_i = \begin{cases} 
1, & \text{if } Q_{\text{gain}} \geq 0 \\
\frac{Q_i}{Q_{i-1}}, & \text{if } Q_{\text{gain}} < 0
\end{cases}
\]

(1)

where $R_i [-]$ is the fraction of water from the upstream reach $i-1$ remaining in the reach $i$, $Q_i$ [L$^3$T$^{-1}$] and $Q_{i-1}$ [L$^3$T$^{-1}$] are the stream discharge at the end of the reach $i$ and the reach immediately upstream, respectively. $Q_{\text{gain}}$ [L$^3$T$^{-1}$] is the water gains from groundwater to stream through the reach $i$, which contains all kinds of sources such as groundwater and tributary, and it represents water losses for a negative value.
The discharge contribution from upstream \( j \) to reach \( i \), \( Q_{i,j} \, [L^3/T] \), can be calculated based on the initial water gains through the reach \( j \) and the product of all \( R \) between upstream \( j \) and the current reach \( i \):

\[
Q_{i,j} = \begin{cases} 
0, & \text{if } Q_{j,\text{gain}} \leq 0 \\
Q_{j,\text{gain}} \times \prod_{k=j}^{i} R_k, & \text{if } Q_{j,\text{gain}} > 0, j = 1, 2, 3, \ldots, i
\end{cases}
\]  
(2)

Correspondingly, the solute load contribution of stream gains from reach \( j \) to reach \( i \), \( L_{i,j} \, [MT^{-1}] \), is the product of initial solute gains through the reach \( j \) and fractions from reach \( j \) to \( i \):

\[
L_{i,j} = \begin{cases} 
0, & \text{if } Q_{j,\text{gain}} \leq 0 \\
c_{j,\text{gain}} \times Q_{j,\text{gain}} \times \prod_{k=j}^{i} R_k, & \text{if } Q_{j,\text{gain}} > 0, j = 1, 2, 3, \ldots, i
\end{cases}
\]  
(3)

where \( c_{j,\text{gain}} \, [ML^{-3}] \) is the concentration of gaining water through the reach \( j \). It is a pure groundwater concentration when there is no tributary inflow, or a mixed concentration when tributary inflows occur. When stream loss occurs, there is no solute load gains, therefore the solute load contribution to downstream reaches is set to 0. The mixed concentration of stream water is then calculated as the ratio of total solute load to total discharge.

### 2.6. Model Calibration

To calibrate the model parameters, we used observed heads in wells and observed discharge at the Hausneindorf gauging station as calibration targets. As the simulations are steady-state for both the discharge and the groundwater levels, averages between 2011 and 2018 were used for the calibration. Time series data were available from 20 wells but only three of them are located close to the stream (Wells_A in Figure 1b). As a supplement, we also used 131 groundwater heads which were observed as a snapshot in time in wells around the stream (Wells_B in Figure 1b). The long-term observational records from 2011 to 2018 show that around the lower Selke River the maximum water table fluctuation in wells is 2.16 m, while in other places it can be as high as 6 m (Figure S1). Therefore, the difference between the computed head and the observed head is believed acceptable when it is within 1 m in the vicinity of the Selke River and less than 3 m in other areas of the domain.

### 2.7. Scenarios

Stream-groundwater exchange fluxes are variable over time due to the fluctuating stream stages or groundwater levels. To evaluate the effects of such varying hydrologic conditions on hydrologic turnover, we selected two variables: precipitation and streamflow. Different combinations of both variables have been applied in multiple steady-state scenarios. First, we defined a baseline case and then generated another eight primary scenarios for water flow simulation by changing precipitation and discharge at the Meisdorf gauging station (Table 1). Then, the evolution of source composition of nitrate load were also evaluated in these nine primary scenarios. Since the evaporation parameters remain unchanged in all simulations, the impact of precipitation implies the influence of groundwater recharge.

For the baseline case, the precipitation in form of gridded data sets, which is denoted as \( P_{\text{mean}} \), is calculated as the average of precipitation data sets from 2011 to 2018 that are obtained from the German Weather Service (DWD) in a yearly temporal and 1 km\(^2\) spatial resolution. For reference, the average of \( P_{\text{mean}} \) in all grid cells is 534 mm/yr. The average of the discharge at the Meisdorf gauging station from 2011 to 2018, which is denoted as \( Q_{0,\text{mean}} \) and equals to 1.15 m\(^3\)/s, is used as the inflow rate of the lower Selke River in the STR package. Nitrate concentration of stream water at the Meisdorf gauging station is set to 6.9 mg/L, which was observed on April 19, 2018.

The other scenarios which are used for sensitivity analysis are setup based on the climate and hydrology data from 2011 to 2018 (Table 1). Specifically, the precipitation (\( P \)) is varied from 0.5\( P_{\text{mean}} \) to 2\( P_{\text{mean}} \), which covers the range of all observations. The discharge at Meisdorf (\( Q_0 \)) is varied from 0.087 m\(^3\)/s to 2.3 m\(^3\)/s, covering 88% of the observed discharge range over the period from 2011 to 2018. Note that the real discharge at Meisdorf ranges from 0.087 m\(^3\)/s to 34.1 m\(^3\)/s and their average value is 1.15 m\(^3\)/s. The reason why \( Q_0 \) in
the high streamflow scenario is selected as twice as the $Q_{0\text{mean}}$ rather than the real maximum discharge is to clearly show the water amount from the lowland in the source composition figures. To explore the full range of streamflow values that might exist and push the system to more extreme drought or flood condition, some extended scenarios are also simulated with the parameter listed in Table 1. All other parameters such as the hydraulic conductivities, stream and streambed properties are kept constant in all the scenarios.

### 3. Results

#### 3.1. Hydrological Model Performance

The simulation results show that the computed heads reasonably match the observed heads (Figure 2a). The deviation of computed heads from observed heads in nearly 80% of wells are less than 1 m (Figure 2b). Observation wells are mainly located in the lower catchment (Figure 2c), to focus on the calibration of interactions between groundwater and the lower Selke River. Due to the insufficient geologic information on the mountainous area of the investigated catchment, the groundwater heads in this region could not be further constrained by calibration, but were found to be reasonable with respect to elevation of land surface. Moreover, the simulated discharge at the Hausneindorf gauging station is 1.53 m$^3$/s, which is only 0.65% off the mean observed discharge (1.54 m$^3$/s) between 2011 and 2018.

#### 3.2. Evolution of the Source Composition of Discharge

##### 3.2.1. Stream-Groundwater Exchange and Source Composition (Baseline Case)

The modeled magnitude of water exchange between stream and groundwater in each stream grid cell, $\Delta Q_{gw}^{s}$, is shown in Figure 3a and the corresponding spatial distribution of gaining and losing reaches is shown in Figure 3c. Water losses from the stream into groundwater mainly occur in the vicinity of Concordia Lake. Gaining reaches are mainly located downstream of the Meisdorf gauging station and near the catchment outlet (Figure 3a). Overall, the cumulative gross gains (0.66 m$^3$/s) are higher than cumulative gross losses (0.22 m$^3$/s), but the total length of losing reaches (14.35 km) almost accounts for half of the total stream length.

As a result of sequential water gains and losses, the source composition of stream discharge evolves along the stream (Figure 3b). As water moving downstream, both the absolute amount and the relative proportion of source water from upstream reaches in stream water decreases. When the stream gains water, the amount of water components in previous reach remains unchanged but their proportion decreases; when the stream loses water, their amount decreases while their proportion stay unchanged. This is exactly the mechanism of how sequential stream-groundwater exchange modifies the source composition of discharge.

| Scenario | $Q_0$ (m$^3$/s) | $P/P_{\text{mean}}$ | Scenario | $Q_0$ (m$^3$/s) | $P/P_{\text{mean}}$ |
|----------|-----------------|---------------------|----------|-----------------|---------------------|
| 1        | 0.087           | 0.5                 | 10       | 11.5            | 1                   |
| 2        | 1.15            | 0.5                 | 11       | 20              | 1                   |
| 3        | 2.3             | 0.5                 | 12       | 34.1            | 1                   |
| 4        | 0.087           | 1                   | 13       | 1.15            | 0.1                 |
| 5 (baseline) | 1.15       | 1                   | 14       | 1.15            | 1.5                 |
| 6        | 2.3             | 1                   | 15       | 1.15            | 3                   |
| 7        | 0.087           | 2                   |          |                 |                     |
| 8        | 1.15            | 2                   |          |                 |                     |
| 9        | 2.3             | 2                   |          |                 |                     |

**Note:** $P$ is the gridded precipitation, $Q_0$ is the discharge at the Meisdorf gauging station.
The water gains from two tributaries, which are not included in $\Delta Q_{gw-s}$, cause an abrupt rise of stream flow and a significant change of stream water source composition (Figure 2b).

3.2.2. The Effect of Precipitation and Streamflow on Stream-Groundwater Exchange Patterns

Consistent with previous studies (Zimmer & McGlynn, 2017), the change of hydrologic conditions could result in a change of the exchange pattern between streams and groundwater. As precipitation increases (Figure 4 columns left-to-right) or streamflow decreases (Figure 4 rows bottom-to-top), not only the flux from groundwater in gaining reaches rises, but also the total length of gaining reaches increases, leading to higher overall gains from groundwater. For example, compared with the baseline case, the gaining flux in the reach downstream of Meisdorf gauging station increases from about 13 to 20 L/s and the total length of gaining reaches increases from about 15.4 to 19 km as $P$ increases to $2P_{mean}$ (Figures 4e and 4h), while the corresponding values increase to 13.1 L/s and 16.7 km as $Q_0$ decreases to 0.087 m$^3$/s (Figures 4d and 4e).

Additionally, extended scenario simulations show that there is a positive relationship between the fraction of gaining reaches $l_{gain}/l_{total}$ and $P/P_{mean}$, and a negative relationship between $l_{gain}/l_{total}$ and $Q_0$ (Figure 5a). The total length of gaining reaches increases with precipitation and decreases with streamflow. Reaches can be classified into consistently gaining or losing and transitional reaches. The hydrologic conditions at the different scenarios influence the magnitude of water flux in the consistently gaining or losing reaches but do not result in a reverse of hydraulic gradients. Transitional reaches are characterized by a reversal of hydraulic gradients in different scenarios. Across all nine scenarios, the consistently gaining and losing reaches account for 37% and 34% of the total stream length, respectively (Figure 5b). Correspondingly, the transitional reaches account for 29%.

3.2.3. The Effect of Precipitation and Streamflow on the Source Composition of Discharge

The spatial evolution of stream water source composition is influenced by varying hydrologic conditions both in terms of absolute and relative source contributions. As $P$ increases (Figure 6 columns left-to-right)
or \( Q_0 \) decreases (Figure 6 rows bottom-to-top), stream discharge increases faster as water moving downstream, in which the amount contributed by source water from the upper catchment decreases more slowly but the relative contribution decreases faster, due to increasing gaining length and magnitude of water gains from the lowland.

As for the stream water source composition at a specified location such as the catchment outlet, Figure 7 shows the absolute amount and relative contributions of water from four types of sources: the upper Selke River, the tributary of the Getel River, the tributary of the Hauptseegraben channel, and groundwater discharge. For the component of source water from the upper Selke River, the contributed amount increases while the proportion decreases as \( P \) increases (Figure 7). As for water from groundwater, the contributed amount increases as \( P \) or \( Q_0 \) increases, while the contributed proportion decreases as \( Q_0 \) increases and increases for an increase in \( P \). For example, when \( Q_0 \) equals 1.15 m\(^3\)/s and \( P \) increases from 0.5 to 2, the amount contributed by groundwater increases from 0.24 to 0.7 m\(^3\)/s, while the proportion increases from 19% to 35%. If groundwater recharge to the tributaries is also considered, the corresponding amount and proportion will be even higher.

The magnitudes of groundwater discharge are heterogeneously distributed across the reaches. About 80% of groundwater discharge is contributed only along 20% of the stream lengths (Figure 8c). These patterns vary with the hydrologic scenarios. For example, compared with 82% of the total groundwater contributions provided by 20% of the total stream length in the baseline case, the proportion is 90% (0.5\( P_{\text{mean}} \)) and 75% (2\( P_{\text{mean}} \)) when \( Q_0 \) equals \( Q_0_{\text{mean}} \). In all these nine scenarios, the highest value is 92% (\( P/P_{\text{mean}} = 0.5 \) and \( Q_0 = 2.23 \) m\(^3\)/s), the lowest value is 74% (\( P/P_{\text{mean}} = 2 \) and \( Q_0 = 0.087 \) m\(^3\)/s), and the average of values in all scenarios is 82%.
3.3. Evolution of the Source Composition of Nitrate Load

3.3.1. Nitrate Concentration in Stream Water Along the Stream (Baseline Case)

Along the downstream direction, instream nitrate concentrations increase from 6 to 14 mg/L. Simulated nitrate concentrations in the adjacent groundwater range from almost 0 to 120 mg/L (Figure 8a). The

![Figure 4](image)

Figure 4. Magnitude of stream-groundwater exchange in each stream grid cell along the Selke River under different precipitation ($P$) and streamflow conditions. $Q_0$ means the discharge at Meisdorf and the unit is m$^3$/s.

3.3. Evolution of the Source Composition of Nitrate Load

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![Figure 5](image)

Figure 5. (a) The effect of precipitation ($P$) and discharge at Meisdorf ($Q_0$) on the proportion of total gaining length in total stream length, $l_{gain}/l_{total}$, based on all primary scenarios and extended scenarios listed in Table 1. (b) The distribution of three types of stream reaches across all nine primary scenarios: consistently gaining reaches, transitional reaches, and consistently losing reaches.
concentrations in the stream change as a result of nitrate loading. High gaining loads result from the combination of the magnitude of groundwater discharge and groundwater nitrate concentration (Figure 8). Instream concentrations depend on both the magnitude of stream-groundwater exchange and the spatially heterogeneous solute concentration of groundwater.

Figure 6. Evolution of the source composition of discharge moving Selke downstream under different precipitation ($P$) and streamflow conditions. $Q_0$ means the discharge at Meisdorf gauging station, with the unit of m$^3$/s.

Figure 7. The source composition of discharge at the catchment outlet under different precipitation ($P$) and streamflow conditions. (a) Absolute source composition of discharge with unit of m$^3$/s; (b) Relative source composition of discharge; (c) relationship between cumulative $l_{\text{gain}}/l_{\text{total}}$ and cumulative $Q_{\text{gain}}/Q_{\text{gw}}$ after sorting the velocity of water gains in all reaches from high to low. Parameter setting in all scenarios see Table 1.
3.3.2. The Effect of Hydrologic Conditions on the Source Composition of Nitrate Load

Affected by the combination of heterogeneous water gains and solute gains, the overall nitrate load in the stream increases as water moving downstream, with a decreasing amount and proportion of source water from upstream reaches. As $P$ increases (Figure 9 columns left-to-right) or $Q_0$ decreases (Figure 9 rows bottom-to-top), the stream receives more nitrate loads from the lower catchment, leading to a lower proportion of source loads from the upper catchment.

Similar to the influence pattern of varying hydrologic conditions on the source composition of discharge, a lower streamflow condition or a higher precipitation condition will lead to a higher relative solute contribution of groundwater source in stream water at the catchment outlet (Figure 10a). However, inconsistencies between the discharge contribution and solute load contribution from groundwater are widely found in all scenarios. Taking the baseline case for instance, the relative contribution of groundwater source in nitrate load and discharge are 43% and 28%, respectively (Figure 10a).

After sorting the unit velocity of load gains from high to low, top 20% of the stream length were found to provide about 80% of the total solute load contributed by groundwater to stream water at the outlet (Figure 10b). Specifically, compared with 85% of total groundwater contribution provided by top 20% of total stream length in the baseline case, the proportion decreases from 99% to 73% when $P$ increases from 0.5$P_{\text{mean}}$ to 2$P_{\text{mean}}$, while it increases from 84% to 87% when $Q_0$ increases from 0.087 to 2.3 m$^3$/s (Figure 10b). This is because the increase of streamflow and decrease of precipitation would decrease the length of gaining reaches, resulting in a higher proportion contributed by the rest gaining reaches.

4. Discussion

4.1. Hydrologic Turnover and Losing Conditions

Patterns of streamflow, solute concentration, and loads observed at the outlet of a catchment can be interpreted as a signal, which reflects characteristics of the catchment and processes within the catchment. The stream signal is influenced by external factors such as the hydrologic regime and the spatial distribution of solute sources in the catchment. If streams would only act as conservative conduits for water and solutes (only water gains from the catchment and no biogeochemical reactions that reduce solute loads), the source composition of stream water and its solute loads would simply reflect the proportional contribution from different parts of the catchment. Losses of stream water into the subsurface are thus a prerequisite for the evolution of water source and solute source composition along the course of a stream.

In our analysis, losing conditions occur over at least 34% of the total stream length. As our study is based on a numerical groundwater model, reaches can only be net losing or gaining. In the previous tracer-based studies of Payn et al. (2009) and Covino et al. (2011), the mass balance analysis focused on gross losses. In Covino et al. (2011), all reaches indicated gross losses and 33% are net losing conditions. While the original concept of hydrologic turnover has been developed in the light of gross gains and losses, the same effects on the source composition of water and solutes occur for sequentially gaining and losing reaches. Overall, streams must be net gaining but net losing reaches occur frequently. In an analysis of 4.2 million wells across the contiguous USA, 64% of them indicated a losing hydraulic gradient with respect to the nearest stream. Losing conditions typically occur under dryer conditions, flat topography and if groundwater heads are influenced by pumping (Jasechko et al., 2021). This observation is in line with our results where losing reaches occur predominantly in the downstream sections of the river with flat topography and partial artificially lowered groundwater due to former open cast lignite mining.
Different hydrologic conditions can alter magnitude and direction of stream groundwater exchange along the course of a stream (Dwivedi et al., 2018; Zimmer & McGlynn, 2017). Hence also the source composition of stream water is modified by changes of water and solute fluxes and by the reversal of hydraulic gradients. In our study, across the 9 hydrologic scenarios, 34% of the reaches are consistently losing, 37% are consistently gaining and 29% are transitional.

![Figure 9](image)

**Figure 9.** Evolution of the source composition of nitrate load moving Selke downstream under different precipitation ($P$) and streamflow conditions. $Q_o$ means the discharge at Meisdorf, with the unit of m$^3$/s.

![Figure 10](image)

**Figure 10.** (a) The source composition of nitrate load in the stream water at the outlet in different scenarios. (b) Relationship between cumulative $l_{gam}/l_{total}$ and cumulative $M_{gam}/M_{gw}$ after sorting the velocity of load gains in all reaches from high to low. For comparison, the corresponding source compositions of discharge are also shown in the figure. $M_{gam}/M_{gw}$ is the ratio of load gains from groundwater through a certain reach to the total loads contributed by groundwater in the stream water at the catchment outlet.
The prevalence of losing streams has implications for the design of studies which focus on the in-stream processing of reactive solutes. Not considering the loss of stream water and solute load and its replacement with groundwater with a different solute load may lead to the overestimation or underestimation of the reactive potential of streams. Instream solute concentrations can change considerably as a result of stream-groundwater exchange and the evolution of source composition.

4.2. Decoupling of Water Source Composition From the Source Composition of Solute Load

By taking nitrate as an indicator, we extended the concept of hydrologic turnover from discharge to solutes. We not only show the evolution of the source composition of solute loads along the stream network, but also reveal the difference between discharge contribution and nitrate load contribution from groundwater to the stream. Compared with the numerous studies about discharge contributions from groundwater to streams (Birtles, 1978; Cey et al., 1998; Gonzales et al., 2009; Lee, 1977; Paulsen et al., 2001), the load contribution from groundwater has rarely been investigated quantitatively, especially at larger scales. A few related studies have addressed nutrient inputs into lakes or coastal systems (Adyasari et al., 2018; Einarsdotir et al., 2017; Oberdorfer et al., 1990). If solute concentration in groundwater is homogeneous there is no difference between water and solute source composition. Homogeneous groundwater concentrations are typically assumed or are implicitly derived if instream concentrations under base-flow conditions are used as a surrogate for groundwater concentrations (e.g., Pinder & Jones., 1969; Zhi & Li., 2020).

In this study, we have considered heterogeneous groundwater concentrations which induce differences between groundwater and solute load contributions. Consequently, the source composition of stream water develops differently from the solute source composition. Heterogeneous concentrations are common in riparian groundwater and have been reported in other studies (Batlle-Aguilar et al., 2014; Lee et al., 2020; Wang et al., 2015). The heterogeneity of groundwater concentrations can be caused by specific source locations and mass loading, catchment structure and the resulting flow paths, as well as groundwater transit times, which affect the reactive turnover and removal of solutes (Mineau et al., 2015; Musolff et al., 2017; Wang et al., 2015). Since stream water at the catchment outlet is composed of discharge contributions from all gaining reaches, groundwater adjacent to the losing reaches does not contribute to the solute load in the stream. Therefore, the average of the solute concentrations from a set of monitoring wells may not adequately represent the concentration of gains from groundwater.

4.3. Implications for Solute Export From Catchments

Losing conditions and hydrologic turnover modify the solute loads exported from catchments. For a reactive solute such as nitrate, it has long been recognized that the location where the solutes enter the stream network controls the opportunity for reducing loads. Removal is maximized for upstream sources which are then subject to long travel times (Alexander et al., 2000; Mineau et al., 2015). A similar effect is induced by hydrologic turnover. A large fraction of solutes and water from upstream sources is lost from the stream network and does not reach the catchment outlet.

Another interesting finding is that regardless of discharge or nitrate load and whether the climate is dry or wet, nearly 80% of the total groundwater contributions to streamflow at the outlet were generated over only 20% of the total stream length. Similar results have also been found by Conant (2004) and Schmidt et al. (2006) that stream-groundwater exchange tends to be focused on small portions of a stream reach. If highly gaining reaches coincide with high groundwater concentrations, these reaches contribute disproportionately to the solute loading of a stream. This suggests that measures to reduce solute export ideally should be focused on the high load reaches close to the catchment outlet.

Hydrologic turnover can potentially influence temporal concentration discharge (C-Q) relationships. Archetypal C-Q relationships (dilution, enrichment, and constant) have been shown to be related to the spatial distribution of solute source where highly heterogeneous sources are associated with more variable C-Q patterns (Musolff et al., 2017). Hydrologic turnover adds an additional controlling factor as the source contributions change for different hydrologic conditions. During high streamflow condition, the stream network acts more as conduit where the solute source composition is more dominated by upstream sources. Under low flow condition, the solute source composition is controlled by downstream sources.
4.4. Limitations and Uncertainties

The current study aims at extending the concept of hydrologic turnover proposed by Covino et al. (2011) from the source composition of discharge to the source composition of solute load and investigating the effect of varying hydrologic conditions on hydrologic turnover. We applied a catchment-scale, steady-state numerical groundwater flow and transport model. The ground water flow model is well constrained and calibrated to observational data of heads and streamflow. The simulation of solute transport is more conceptual, which does not aim at representing the real conditions at the field site but should illustrate the concept of hydrologic turnover and its effects on the source composition of solutes. Thus, our analysis is based on several simplifications and assumptions, which in turn result in limitations and uncertainties.

We acknowledge that nitrate transport is a very complex process and our model does not consider all mechanistic aspects. Instead, the selected implementation and parameter setting reflect reasonable and effective parameters, which should suffice to investigate the difference between the source composition of discharge and solute load at catchment-scale.

For stream parameters, sensitivity analyses show that the streambed thickness, Manning's roughness, the hydraulic conductivity of streambed and stream width have a limited impact on model results (Figure S2). However, the top elevation of streambed does have a larger impact on the computed discharge since it fundamentally controls the elevation of stream stage. Since the current top elevation of streambed in stream grid cells is estimated based on 25 m-resolution DEM and an empirical relationship mentioned in Section 2.3.2, we acknowledge that the top elevation of streambed might be the biggest uncertainties in the current settings.

We recognize that the vadose zone could have an important effect on stream-groundwater exchange (Frei et al., 2009; Hong et al., 2020) and solute composition of stream water (Neal et al., 2012; Zhi et al., 2019). However, limited by the capacity of MT3DMS, we used the STR package to simulate the stream, which does not consider the unsaturated zone. For nitrate simulation, we assume that nitrate uniformly percolates into groundwater through the soil and vadose zone of the arable land, which could be a major source of uncertainty since it controls the spatial heterogeneity of groundwater concentrations. The nitrate removal processes such as denitrification rate in the stream, which are not considered in the current study, could also induce uncertainty as water entering the upper stream would have more time to react and be removed.

Previous studies show that the net gains in a reach result from simultaneous water gains and losses at smaller scales (Covino et al., 2011; Mallard et al., 2014; Schmidt et al., 2006), which, for example, could be caused by abrupt changes in streambed slope or by meanders (Winter et al., 1998). From the perspective of the numerical model, a stream grid cell can only be gaining or losing, and the net gains in one stream grid cell could contain hydrologic loss at the smaller sub-grid scale. Therefore, because additional losses at the sub-grid scale could increase the loss of source water from upstream reaches, the current results of source compositions may underestimate the degree of hydrologic turnover, that is, overestimate the water contribution from upstream sources and underestimate the water contribution from the low reaches.

Although the current simplified simulations may not reproduce the exact conditions at the test site in every detail, they can serve to generally illustrate the effects of hydrologic turnover and the decoupling of solute load and water source composition at catchment-scale.

5. Conclusions

Inspired by the work on the source composition of discharge in Covino et al. (2011) and Mallard et al. (2014), we extended the original concept of hydrologic turnover to an assessment of the source composition of solute loads in the stream water using nitrate as an example of substance. Furthermore, we systematically evaluated the effects of changing hydrologic conditions (defined by varying precipitation and streamflow) on stream-groundwater exchange patterns, hydrologic turnover and the resulting source composition of water and solute load in the stream water at catchment scale.

It was found that stream-groundwater exchange could significantly modify the source composition of both discharge and solute load by decreasing the amount of initial source water when the stream loses water and
by decreasing the relative proportion of initial source water when the stream gains water. As precipitation increases or streamflow decreases, the magnitude of water gains increases, while the magnitude of water losses decreases. Results further show that even hydrologic conditions change extremely, the direction of stream-groundwater exchange (loss/gain) would remain unchanged in consistently gaining/losing reaches while switch in transitional reaches. In our case, consistently losing reaches could account for 34% of the total stream length.

The source composition of solute load is found to be significantly different from the source composition of discharge because of the heterogeneity of solute concentration in groundwater, which should be recognized especially in the prevention and treatment of water pollution. Despite having the same source location, the contribution to discharge and solute load might vary greatly, leading to a different distribution of dominant source locations contributing discharge and solute load to the catchment outflow. However, regardless of discharge or nitrate load and whether the climate is dry or wet, nearly 80% of the total groundwater contributions to streamflow at the outlet were generated over only 20% of the total stream length in our study, indicating that measures to reduce groundwater borne nutrient loadings to streams should be ideally focused on the strongly gaining reaches.

**Conflict of Interest**

The authors declare no conflicts of interest relevant to this study.

**Data Availability Statement**

The data are available via their open data portals at DWD: https://www.dwd.de/DE/leistungen/klimadaten-deutschland/klarchivtagmonat.html, LAGB: https://lagb.sachsen-anhalt.de/service/geofachinformation/landesbohrdatenbank/, and LHW: https://gld-sa.dhi-wasy.de/GLD-Portal/. The elevation data for the geological model were obtained from the TERENO (Terrestrial Environment Observatories) project coordinated by Helmholtz Centre for Environmental Research-UFZ. All other data used for building the model are available via the open-access UFZ-GitLab repository (https://git.ufz.de/zangz/selke_model).

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**References**

Adyasari, D., Oehler, T., Afiati, N., & Moosdorf, N. (2018). Groundwater nutrient inputs into an urbanized tropical estuary system in Indonesia. *The Science of the Total Environment*, 627, 1066–1079. https://doi.org/10.1016/j.scitotenv.2018.01.281

Alexander, R. B., Smith, R. A., & Schwarz, G. E. (2000). Effect of stream channel size on the delivery of nitrogen to the Gulf of Mexico. *Nature*, 403(6771), 758–761. https://doi.org/10.1038/35001562

Almasiri, M. N., & Kaluarachchi, J. J. (2007). Modeling nitrate contamination of groundwater in agricultural watersheds. *Journal of Hydrology*, 343(3), 211–229. https://doi.org/10.1016/j.jhydrol.2007.06.016

Anderman, E. R., & Hill, M. C. (2000). *MODFLOW-2000, the US Geological Survey modular ground-water model-documentation of the Hydrogeologic-Unit Flow (HUF) Package.* (U.S. Geological Survey Open-File Report 00-342). U.S. Geological Survey.

Batlle-Aguilà, J., Harrington, G. A., Leblanc, M., Welch, C., & Cook, P. G. (2014). Chemistry of groundwater discharge inferred from longitudinal river sampling. *Water Resources Research*, 50(2), 1550–1568. https://doi.org/10.1002/2013WR013591

Battin, T. J., Kaplan, L. A., Findlay, S., Hopkinson, C. S., Marti, E., Packman, A. I., et al. (2008). Biophysical controls on organic carbon fluxes in fluvial networks. *Nature Geoscience*, 1(2), 95–100. https://doi.org/10.1038/ngeo101

Birtles, A. B. (1978). Identification and separation of major base flow components from a stream hydrograph. *Water Resources Research*, 14(5), 791–803. https://doi.org/10.1029/WR014i005p00791

Bott, G., Bertuzzo, E., & Rinaldo, A. (2010). Transport in the hydrologic response: Travel time distributions, soil moisture dynamics, and the old water paradox. *Water Resources Research*, 46(3). https://doi.org/10.1029/2009WR008371

Bott, M., Burlando, P., & Fatichi, S. (2019). Anthropogenic and catchment characteristic signatures in the water quality of Swiss rivers: A quantitative assessment. *Hydrology and Earth System Sciences*, 23(4), 1885–1904. https://doi.org/10.5194/hess-23-1885-2019

Cey, E. E., Rudolph, D. L., Parkin, G. W., & Aravena, R. (1998). Quantifying groundwater discharge to a small perennial stream in southern Ontario, Canada. *Journal of Hydrology*, 210(1), 21–37. https://doi.org/10.1016/S0022-1694(98)00172-3

Conant Jr., B. (2004). Delineating and quantifying ground water discharge zones using streambed temperatures. *Ground Water*, 42(2), 243–257. https://doi.org/10.1111/j.1745-6584.2004.tb02671.x

Covino, T., McGlynn, B., & Mallard, J. (2011). Stream-groundwater exchange and hydrologic turnover at the network scale. *Water Resources Research*, 47(12). https://doi.org/10.1029/2011WR010942

Dehaspe, J., Sarrazin, F., Kumar, R., Fleckenstein, J. H., & Musolff, A. (2021). Bending of the concentration discharge relationship can inform about in-stream nitrate removal. *Hydrology and Earth System Sciences Discussions*, 2021–2022. https://doi.org/10.5194/hess-2021-16

Dupas, R., Musolff, A., Jawitz, J. W., Rao, P. S. C., Jäger, C. G., Fleckenstein, J. H., et al. (2017). Carbon and nutrient export regimes from headwater catchments to downstream reaches. *Biogeochemistry*, 14(18), 4391–4407. https://doi.org/10.5194/bg-14-4391-2017
Winter, T. C., Harvey, J. W., Franke, O. L., & Alley, W. M. (1998). *Ground water and surface water: A single resource.* (U.S. Geological survey circular 1139). U.S. Geological Survey.

Yang, X., Jomaa, S., Zink, M., Fleckenstein, J. H., Borchardt, D., & Rode, M. (2018). A new fully distributed model of nitrate transport and removal at catchment scale. *Water Resources Research,* 54(8), 5856–5877. https://doi.org/10.1029/2017wr022380

Zheng, C., & Wang, P. P. (1999). MT3DMS: A modular three-dimensional multispecies transport model for simulation of advection, dispersion, and chemical reactions of contaminants in groundwater systems; documentation and user's guide.

Zhi, W., & Li, L. (2020). The shallow and deep hypothesis: Subsurface vertical chemical contrasts shape nitrate export patterns from different land uses. *Environmental Science & Technology,* 54(19), 11915–11928. https://doi.org/10.1021/acs.est.0c01340

Zhi, W., Li, L., Dong, W., Brown, W., Kaye, J., Steefel, C., & Williams, K. H. (2019). Distinct source water chemistry shapes contrasting concentration-discharge patterns. *Water Resources Research,* 55(5), 4233–4251. https://doi.org/10.1029/2018WR024257

Zimmer, M. A., & McGlynn, B. L. (2017). Bidirectional stream–groundwater flow in response to ephemeral and intermittent streamflow and groundwater seasonality. *Hydrological Processes,* 31(22), 3871–3880. https://doi.org/10.1002/hyp.11301