Groundwater

Modeling the Impact of Stream Discharge Events on Riparian Solute Dynamics

by Muhammad Nasir Mahmood[1], Christian Schmidt[1], Jan H. Fleckenstein[1], and Nico Trauth[1]

Abstract

The biogeochemical composition of stream water and the surrounding riparian water is mainly defined by the exchange of water and solutes between the stream and the riparian zone. Short-term fluctuations in near stream hydraulic head gradients (e.g., during stream flow events) can significantly influence the extent and rate of exchange processes. In this study, we simulate exchanges between streams and their riparian zone driven by stream stage fluctuations during single stream discharge events of varying peak height and duration. Simulated results show that strong stream flow events can trigger solute mobilization in riparian soils and subsequent export to the stream. The timing and amount of solute export is linked to the shape of the discharge event. Higher peaks and increased durations significantly enhance solute export, however, peak height is found to be the dominant control for overall mass export. Mobilized solutes are transported to the stream in two stages (1) by return flow of stream water that was stored in the riparian zone during the event and (2) by vertical movement to the groundwater under gravity drainage from the unsaturated parts of the riparian zone, which lasts for significantly longer time (> 400 days) resulting in long tailing of bank outflows and solute mass outfluxes. We conclude that strong stream discharge events can mobilize and transport solutes from near stream riparian soils into the stream. The impact of short-term stream discharge variations on solute exchange may last for long times after the flow event.

Introduction

Water fluxes in riparian zones often vary strongly in time and space, altering solute transport across the river-groundwater interface. Fluctuations in the direction and magnitude of hydraulic gradients between the stream and the connected groundwater lead to complex water exchange patterns enhancing mixing of groundwater and stream water (Vidon and Hill 2004; Boutt and Fleming 2009; Welch et al. 2015). These hydraulic gradients are induced by morphological features at various scales such as river bed dunes (Cardenas and Wilson 2007), gravel bars (e.g., Trauth et al. 2015), meander bends (e.g., Boano et al. 2006).

Besides flow driven by morphological features, transient stream stage variations drive varying hydraulic head gradients which in turn control water and matter exchanges between streams and riparian zones (Cooper and Rorabaugh 1963; Sandén et al. 1997; Rassam et al. 2006). Stream stage fluctuations can occur at different time scales caused by dam regulation (Gerecht et al. 2011; Sawyer et al. 2014), rain events (McCallum et al. 2010; Vidon et al. 2017), and seasonal variations (Bartsch et al. 2014). These variations in stream stage induce the well-studied bank storage effect where water is temporarily stored in the riparian zone during high stream stage and subsequently released back to the stream when stream stage recedes to pre-event conditions (Squillace et al. 1993; Chen and Chen 2003; McCallum et al. 2010; Doble et al. 2012; Grabs et al. 2012; McCallum and Shanafield 2016). Along with the infiltration of river water into the riparian zone, river water constituents are transported into the riparian aquifer (Boutt and Fleming 2009; Sawyer et al. 2014), where they potentially undergo transformations (Gu et al. 2012; Diem et al. 2013). For instance, riparian zones are known to be capable of removing elevated nutrient concentrations, like nitrogen species (Hill 1996). In contrast, riparian zones can act as net source of solutes for the receiving streams such as for organic carbon or nitrate carried by groundwater (Bishop et al. 1994; Inamdar et al. 2004; Pellerin et al. 2012).

Hornberger et al. (1994) proposed that DOC flushing from the unsaturated riparian soils to the stream occurs during high flow events. Wondzell and Swanson (1996) demonstrated in a field study that flood events facilitated nitrogen fluxes from riparian zones to the stream. Sawyer et al. (2014) observed increase in solute concentration in both riparian water and stream during a strong stream the discharge event.

[1]Corresponding author: Helmholtz Centre for Environmental Research – UFZ, Permoserstraße 15, 04318 Leipzig, Germany; nasir.m@daad-alumni.de

Article impact statement: Short-term stream stage fluctuations trigger long-term solute mobilization within riparian zone and consequent transport to the stream.

Received October 2017, accepted March 2018.

doi: 10.1111/gwat.12664

The changes in stream stage induce variations in near stream water table and therefore in the vertical extent of unsaturated zone. Consequently, the solutes stored in the unsaturated zone (e.g., nitrogen species and organic carbon) are tapped by the rise in groundwater level (Creed et al. 1996; Biron et al. 1999; Hill et al. 2000) leading to their dissolution and mobilization as well as potential transport into the groundwater and adjacent stream (Creed and Band 1998). As a result, the increased solute concentration leads to a changing hydrochemical system which may fuel biogeochemical processes, for example, an increased denitrification activity, which has strong implications on the status of the entire aquatic ecosystem (Simmons et al. 1992; Burt et al. 2002; Hefting et al. 2004; Gift et al. 2010).

Despite such an important interplay between transient stream conditions and the availability of solutes in riparian zone, only a few studies have systematically investigated the implications of stream stage variation on solute dynamics in variable saturated riparian zone. Boutt and Fleming (2009) found that diurnal stream stage oscillations caused by dam regulations, enhance mass transport into the banks compared to the base flow conditions. McCallum et al. (2010) focused on the influence of bank inflows on the chemical base flow separation method. They found that bank flows during stream discharge events significantly alter the chemical signature of groundwater discharge which in turn leads to incorrect estimations of the baseflow. Gu et al. (2012) found that biogeochemical activity in the near stream riparian zone is enhanced by the bank storage process. However, the impact of different types of stream stage variations on riparian solute export to the stream has not yet been explored.

This paper aims at evaluating the effect of stream stage variations on the mobilization of solutes residing in the unsaturated part of the riparian zone and the resulting solute mass export to the stream. We use a generic setup with a conservative solute initially stored in the unsaturated part of the riparian zone as we focus on the hydraulic effects of solute dynamics in the riparian zone. The processes are elucidated by means of numerical simulations of flow and conservative solute transport scenarios. The effects are evaluated by investigating the time scales of bank inflow, outflow and the resulting solute mass outfluxes into the stream during and after stream flow events. To differentiate the influence of magnitude and timing of stream stage on exchange processes, the flow scenarios were systematically varied in terms of peak streamflow height and event duration.

Methods

Concept and Modeling Setup

In natural systems, riparian bank storage processes are controlled by various factors like changing hydraulic gradients, heterogeneity of the subsurface sediments, groundwater recharge, and evapotranspiration (Vidon and Hill 2004; Duval and Hill 2006; Grabs et al. 2012). Accounting for all existing factors in a model would lead to a very complex setup and model parameterization, where the role of a single factor is difficult to identify. Therefore, in our modeling setup only the effect of changing stream stages is considered, whereas all other parameters are kept constant for the range of the scenarios. By using such kind of a simplified model, we can evaluate the effect of stream stage fluctuations on solute mobilization in the riparian zone. The simplification of the natural processes allows us to investigate the sensitivity of solute mobilization to discharge events. This type of "explorative numerical modeling" has been very common recently (Cardenas and Wilson 2007; McCallum et al. 2010; Frei et al. 2012; Trauth et al. 2014) because it enables the evaluation of individual effects of multiple factors of a processes, which are hard to disentangle otherwise in the field and fully representative modeling studies.

The conceptual model consisted of three major components: (1) a variably saturated riparian zone (unconfined aquifer) which is hydraulically connected to (2) a gaining stream, and (3) a layer of a conservative solute residing in the upper, unsaturated part of the riparian zone.

The domain geometry is similar to the one described for the analytical solution of bank storage flow by Cooper and Rorabaugh (1963). The domain extends 50 m in horizontal (x) and 1.26 m in vertical (z) direction (Figure 1). The domain length was selected after performing test-simulations considering various domain lengths for stream stage event scenario of the highest peak height and the longest duration. Based on these model runs, we found that at a distance of more than 50 m from the stream the effect of stream stage variations on groundwater level was negligible. Increasing the length of the model domain would not affect the overall results, but would increase computational effort. The model geometry is a generic representation of a typical riparian zone observable at river corridors of third to fourth order streams in humid regions (perennial rivers) (Bishop et al. 1990; Castelle et al. 1994; Mayer et al. 2005).

The main enhancement compared to previous studies, is the addition of an unsaturated zone containing a solute layer, which has been observed during many riparian zone field studies (Bishop et al. 1990, 1994; Wondzell and Swanson 1996; Grabs et al. 2012; Gassen et al. 2017). During groundwater level rise induced by stream flow events, solutes can be mobilized and consequently and can be potentially exported to the stream (Bishop et al. 1994). These observations are represented in our model concept by implementing a 0.66 m thick and 33 m long (75% of the total domain length) layer of a conservative solute source of uniform concentration in the unsaturated zone ranging from $z = 0.6$ to $z = 1.26$ m and $x = 0$ to $x = 33$ m.

The solute layer was not extended over the entire length of the domain in order to observe the movement of solute within the bank as well as to avoid loss of solute mass across the left boundary. In all scenarios,

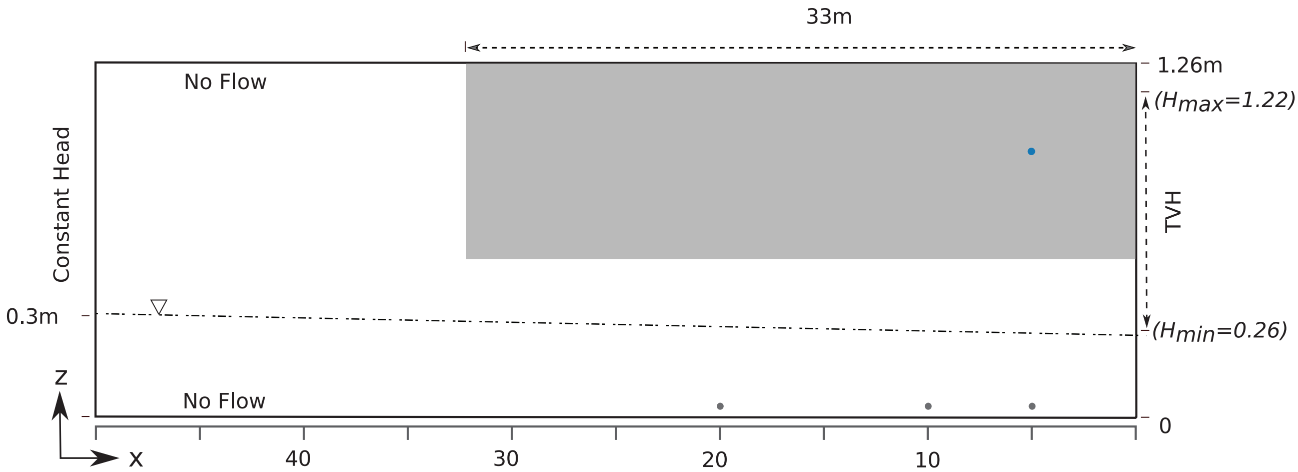

Figure 1. Cross sectional view of the model setup (not to scale). Filled area represents the extent of the solute layer. The stream is represented by the time varying head (TVH) boundary (from $z = 0.26$ to 1.26 m) at the right boundary. At the left boundary of the domain a fixed head boundary is assigned, representing the ambient groundwater level ($z = 0.3$) at the outer bound of the riparian zone. The dots represent observation points referred to in the subsequent figures where changes in groundwater head (black dots) and detailed solute mobilization process in unsaturated zone (blue dot) are observed.

Table 1
Hydrologic Properties of the Porous Medium

Parameter	Unit	Value
Saturated hydraulic conductivity ($K_s x = K_s y = K_s z$)	m/s	1 E-03
Specific storage	m^{-1}	10^{-4}
Effective porosity (n)	—	0.3
Residual saturation (θr)	—	0.01
Van Genuchten—n	—	3.5
Van Genuchten—α	m^{-1}	8.5
Longitudinal dispersivity	m	0.01
Transversal vertical dispersivity	m	0.0001

bank overflows were not considered ($h_o < h < z$). The porous medium was assumed to be homogenous and isotropic, whereas dispersivity in horizontal direction was assumed to be one order of magnitude higher than in the transversal vertical direction. Hydraulic properties of the porous medium represent sand (Table 1).

Numerical Model

Flow and transport simulations for the variably saturated media were performed with the multicomponent reactive transport modeling code MIN3P. It solves the Richards equation for water flow simulation and the advection-dispersion equation for solute transport. The van Genuchten-Mualem approach is utilized for the estimation of the unsaturated hydraulic conductivity (Mualem 1976; van Genuchten 1980) whereas tortuosity is calculated by Millington formula (Millington 1959). The MIN3P code has been used for simulating a variety of problems in contaminant transport and stream-groundwater interaction studies (Mayer et al. 2002; Trauth et al. 2014, 2015; Trauth and Fleckenstein 2017). Although MIN3P is fully capable of simulating reactive transport, in this study we are focusing on non-reactive solute transport because the objective of this study is to investigate how conservative solute transport is affected by changing hydraulic conditions.

At the interface between the stream and the riparian zone (right boundary), a time varying head boundary was applied (along z direction) that enables a simulation of changes in hydraulic head caused by the stream stage fluctuations. The head at inflow boundary (stream end) was varied between base flow condition ($h_o = 0.26$ m) and the peak stage height (h), to represent the stream flow event. A constant head boundary condition (Dirichlet boundary), representing ambient groundwater level of 0.3 m, was assigned at the landside of the riparian zone (left boundary) to obtain the gaining conditions (groundwater is feeding the stream) under base flow. No flow boundaries were assigned at top and bottom of the model domain. A uniform grid size of 0.04 m was used both along z (perpendicular to stream section) and x direction in all simulation runs. Third-order boundary conditions were applied for solute exchange at inflow and outflow boundaries, enabling the transport of solutes in both directions. A relatively high solute concentration of 100 mg/L was assigned to the solute source layer. In the remaining model domain the concentration was set to zero. Similarly zero concentration was assigned to both groundwater (right) and stream water (left) boundaries, leaving the solute source layer as the only source of solute concentration.

A long simulation time of 1000 days was selected to account for expected long tailing of solute breakthrough curves. In the transient scenarios, flow events were introduced after 41.6 days (1000 h) of simulation time when the outflux of water and solute from the riparian zone had reached a constant value.

Stream Discharge Events

Stream stage fluctuations during flow events were represented by applying a stream hydrograph at the right boundary (stream-aquifer interface) of the model (Figure 1). The flow event is characterized by (1) the peak of the hydrograph representing the maximum stream stage, (2) the time length of the hydrograph corresponding to the duration of the event. These two parameters determine the magnitude, height and the timing of water entering into the riparian zone.

A typical single peak hydrograph derived from a real flow event of a third order stream was adjusted to a set of flow scenarios where variants of changing maximum peak and event duration were applied. Discharge for each hypothetical event scenario is calculated by the rating curve equation:

$$Q(t) = (G(t) - a)^b \tag{1}$$

Where G is the stream stage and a is the gauge reading against zero discharge while b is the rating curve constant. In our hypothetical case $a = 0$ and $b = 0.11$.

A total of 160 input hydrograph scenarios were developed, organized in a matrix of combinations of 16 peak heights and 10 event durations. Peak heights ranging between 0.06 and 0.96 m above base flow level were equally spaced at 0.06 m interval. Similarly event durations were also equally spaced at 10 h intervals between 10 and 100 h.

Model Results Evaluation

The influence of stream stage variation on riparian solutes is evaluated in terms of the mass balance of solutes and the temporal behavior of solute outfluxes with respect to stream discharge.

Assuming that all of the solute outflux (J) from the riparian zone is entering the stream, the total solute mass outflux (J_{tot}) from riparian zone caused by the stream stage fluctuations over the entire simulation period (τ) can be estimated as:

$$J_{\text{tot}} = \int_0^{\tau} J(t)\, dt \tag{2}$$

An addition of solute mass into the stream results in increased stream concentration. Considering the initial solute concentration in the stream is zero, the resulting stream concentration of the solute in the stream water (C_{str}) can be calculated as:

$$C_{\text{str}}(t) = \frac{J(t)}{Q(t)} \tag{3}$$

Where J (M/T) is the solute outflux into the stream, from the unit cross sectional area of the domain perpendicular to the river. Q (L^3/T) is the stream discharge and C_{str} (M/L^3) is the solute concentration in the stream at time (t). Solute mass export was evaluated in terms of peak height and duration of the corresponding flow event.

Results and Discussion

Response of Water and Solute Exchange to Stream Discharge Events

Water Exchange Time Scales

The time scales of water infiltration and exfiltration to and from the riparian zone induced by a stream flow event are presented in Figure 2. In our model setup the 100 h stream event starts at 41.66 days (1000 h) of the simulation in order to account for the effect of initial conditions (Figure 2a). The flow event reaches peak flow height above base flow level at about 9 h, then slowly recedes, terminating at about 100 h (at 45.83 days) after the beginning of the flow event. Groundwater hydraulic heads (Figure 2b) respond to the stream discharge variation with delay depending upon the distance from stream-riparian interface (black dots in Figures 1 and 3 indicate the location of observation points). The effect of the stream stage fluctuation is most pronounced in the near stream riparian zone. This effect is the result of the spatial and temporal variation of the hydraulic gradients in the domain (Figure 2c). Prior to the event, the stream is slightly gaining (positive i) due to lower stream stage compared to the ambient groundwater head. With the beginning of the flow event, the direction of the hydraulic gradient is changing towards losing conditions, indicating that stream water flows into the riparian zone (negative i). The shift in the near stream hydraulic gradient i_5 is earlier and higher than the respective changes in the hydraulic gradient over the entire modeling domain (i_{50}). In turn, the change in the hydraulic head difference between the stream and the near stream groundwater during the flow event controls the timing and magnitude of Q_{in} and Q_{out} (Figure 2d). The time of peak Q_{in} coincides with the time of the strongest negative value of i_5. After the peak of the event, both i_5 and Q_{in} start declining towards pre-event value. The i_5 switches to positive on the falling limb of the stream flow event, causing a reversal in the direction of the exchange flow, marking the termination of net Q_{in} and the beginning of a net Q_{out}. In contrast, the negative value of i_{50} slowly declines reaching the pre-event value at the end of flow event. The peak value for positive i_5 is only 0.23 times that of the peak negative i_5, however a positive i_5 is maintained for more than 6-times the duration of the negative hydraulic gradient forcing substantially lower Q_{out} rates for long duration compared with Q_{in}. The peak Q_{out} in this case is 0.16 of peak Q_{in}. After the end of the flow event a rapid decline in Q_{out} is observed which is driven by a decrease in i_5. During Q_{in} the total water saturation within the domain increases, reaching the peak value of 1.6 times higher at the end of Q_{in} than its pre-event value (Figure 2e). Q_{out} starts before the end of the event at the falling limb, which leads to an overall decline in saturation within the domain. At the end of the flow event about 60% of Q_{in} is already released back to the stream. After 12 days ($T = 53$ h), Q_{out} rate as well as saturation drops to a very small value, however they do not reach their pre-event value. After

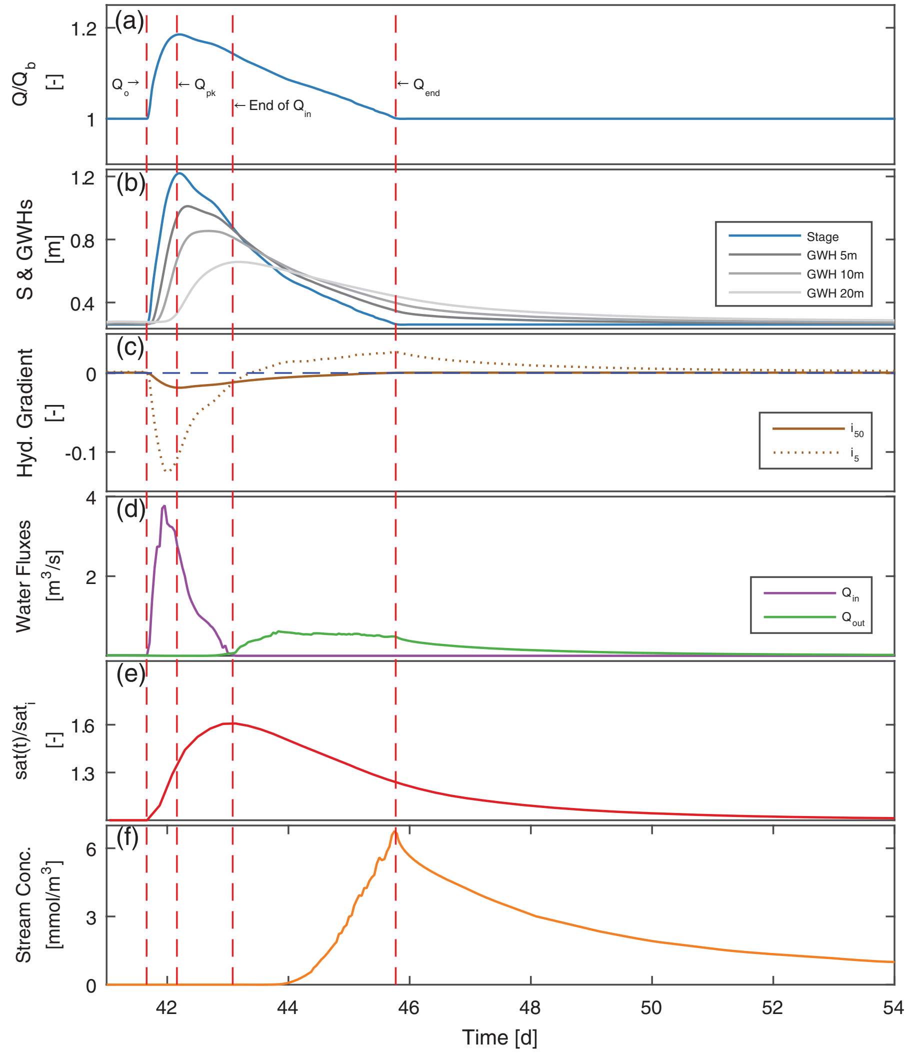

Figure 2. Time scales of water and solute fluxes during a bank flow event of 0.96 m peak height above base flow and duration of 100 h. (a) stream discharge normalized to the base flow (Q/Q_b), (b) stage and groundwater heads at 5, 10, and 20 m distance from stream boundary (black dots in Figure 1), (c) hydraulic gradient at stream-riparian interface, i_{50} is the hydraulic gradient between the stream stage and the ambient groundwater head at the left boundary, while i_5 is the local gradient between the stream stage and the groundwater head at a distance of 5 m from stream (dotted blue line represents the hydraulic gradient in absence of the flow event), (d) water fluxes into (Q_{in}) and out (Q_{out}) of the riparian zone, (e) change in saturation during the flow event, (f) concentration (C_{str}) in stream water. The red dotted vertical lines across the figures show the relative position of fluxes at these time steps.

a quick initial release of the bulk of the stored water, a relatively small amount remains in the riparian zone which is released subsequently over a long period of time due to slow unsaturated zone drainage. Even after 50 days of the start of the flow event, still 2% of Q_{in} is present in the unsaturated riparian zone (Figure S3, Supporting information), resulting in a slightly higher saturation (0.2%) than the pre-event value. These higher and shorter Q_{in}, lower but longer Q_{out} and long tailing of Q_{out} are consistent with other bank flow studies (McCallum et al. 2010; Doble et al. 2012; McCallum and Shanafield 2016).

Stream Water Solute Concentration

Figure 2f represents theoretical changes in stream water solute concentrations (C_{str}) derived from solute mass outflux simulations (J) (see method section). Stream water is assumed to be free of solute concentration prior to the event. Therefore change in solute concentration in the stream is solely caused by the solute mass exported with Q_{out} from the riparian zone to the stream. The onset of C_{str} is approximately 15 h later than the start of Q_{out}. The delayed response of J from the riparian zone is due to the fact that Q_{in} initially mobilizes and transports solutes from the near stream riparian zone deeper into the domain, therefore the last part of Q_{in} does not come into contact with riparian solute. When Q_{out} starts, newly infiltrated water with no solute concentrations drains out of the domain during first few hours. This lag between the starting times of Q_{out} and J depends on the duration of the flow event. C_{str} increases until the end of the flow event, even though Q_{out} is discharged at a nearly constant rate. This is because of the fact that mobilization of riparian

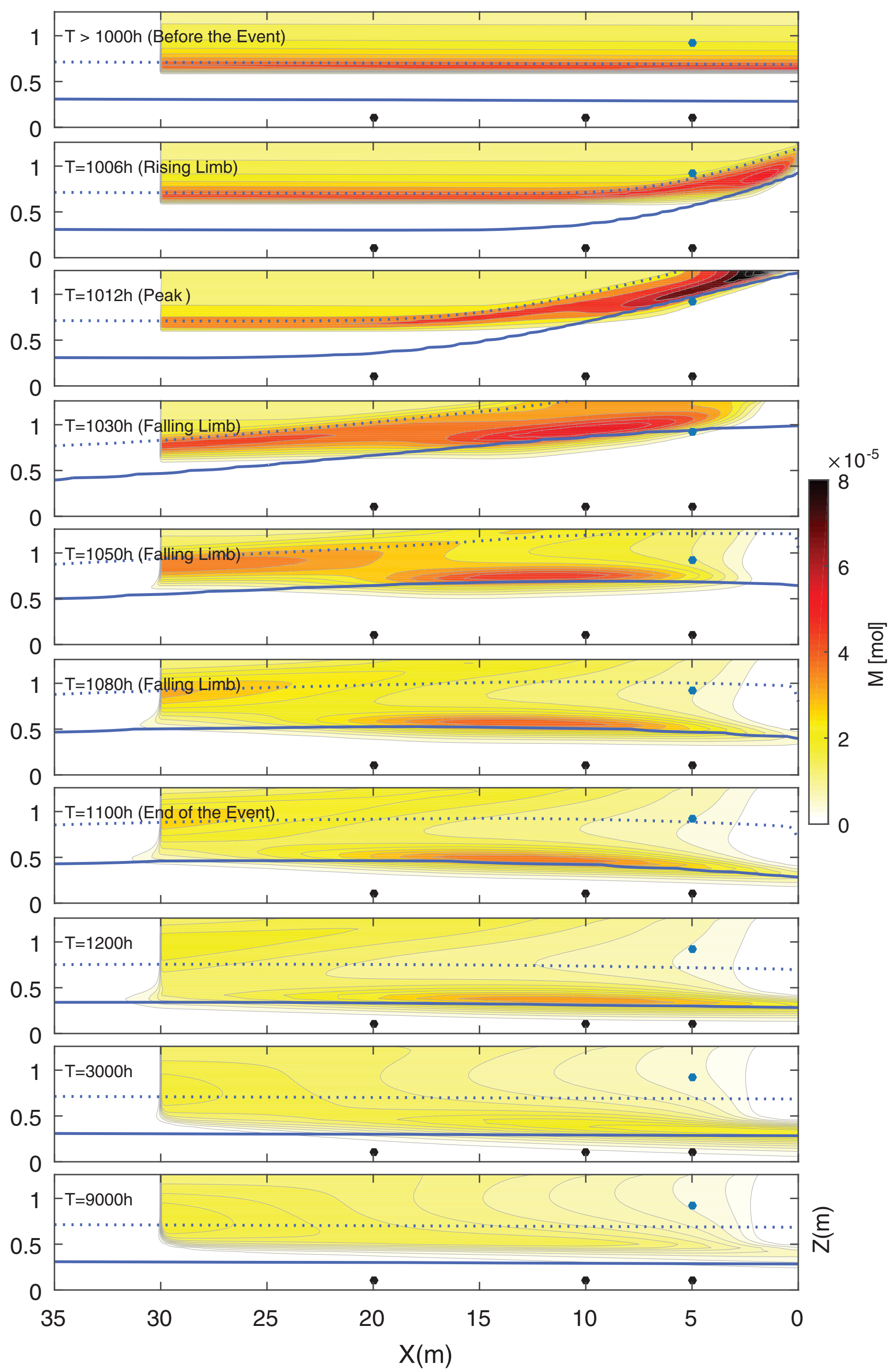

Figure 3. Solute mass (M [mol]) in the riparian zone at various time steps. The solid and dotted blue lines show the 100% (water level) and 5% water saturation, respectively. The black dots indicate the location of the observation points for groundwater heads, while the blue dot shows the location of point where a detailed description of the solute mobilization process in unsaturated zone follows in the next section.

solute increases with time, therefore the later part of Q_{out} carries more solute mass. At the end of the flow event, the turning point in near stream hydraulic gradient results in decreased Q_{out} as well as corresponding (J). That is why the peak concentration is observed exactly at the end of flow event (Figure 2f). Similar to Q_{out}, the pre-event conditions for C_{str} are not reached long after the flow event.

Solute Mobilization within the Riparian Zone

During the flow event, infiltrating stream water results in an increase in water saturation in the upper riparian zone leading to the mobilization of riparian solutes. In Figure 3 this solute mass within the riparian zone is shown at various time steps of the simulation period during and after the flow event. The actual mass of solute in each cell

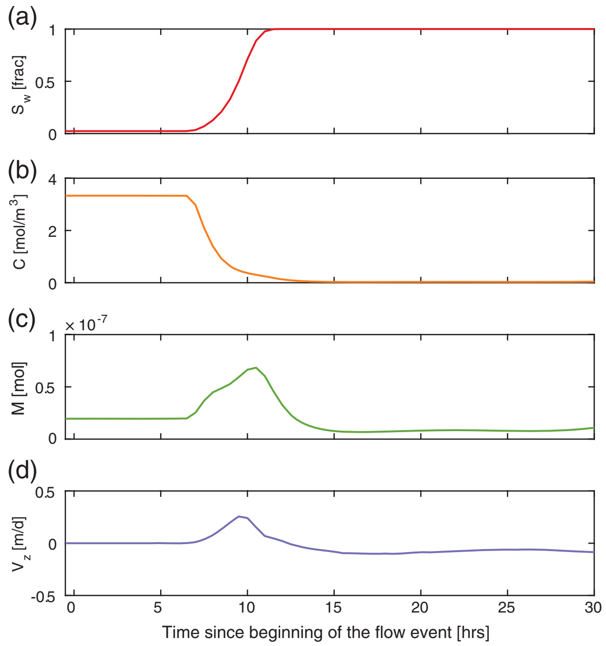

Figure 4. Water saturation (a), solute concentration (b), solute mass (c), and vertical velocity component (d) at one individual cell at location $x = 5$ m and $y = 0.9$ m (indicated by the blue dot in Figure 3).

is calculated in terms of the water content:

$$M = C \cdot S_w \cdot n \tag{4}$$

where M is the actual mass of solute, C is the concentration at the point, S_w is the water content in the mesh cell, and n is the effective porosity of the aquifer.

At pre-event conditions ($T < 1000$ h) more solute mass is concentrated in the lower part of the solute layer. The zone above water level is variably saturated. We applied a uniform solute concentration throughout the layer, resulting in a higher solute mass in the areas of higher water content (lower part). During the rising limb until the peak of the event (1006 and 1012 h) the water levels in the near stream zone rise to a maximum level while in the more distant domain it remains nearly unaffected. Water inflow into the unsaturated zone during Q_{in} creates strong horizontal as well as vertical water flow component in the near stream riparian zone. This results in complete flushing of the solute source layer from the near stream zone where the unsaturated zone is filled with recently entered stream water. Solutes from the near stream area are mobilized and transported away from the bank both vertically upward by a capillary rise effect as well as horizontally away from the stream. The highest solute mass is observable directly in areas where saturation is high (dark red area around the 100% saturation line), while there is also visible increase in solute mass in areas between 5 (blue dashed line in Figure 3) and 100% saturation.

To illustrate the effect of Q_{in} on riparian solute mobilization, we observe the water and solute mass changes in a near stream cell located within the unsaturated zone at $x = 5$ m and $y = 0.9$ m (indicated by the blue dot in Figure 3). The change in saturation (S_w), solute concentration (C), solute mass (M), and vertical velocity (V_z) within the cell are shown in Figure 4. Clearly at the time, when the S_w within the cell starts increasing (Figure 4a) by vertical water flow (indicated by V_z in Figure 4d), concentration C (Figure 4b) decreases but solute mass M (Figure 4c) increases within the cell at the same time, indicating that additional solute mass is received from the cell below by upward movement of water (positive V_z in Figure 4d). The solute mass keeps increasing in the cell until the cell reaches nearly full saturation. At this stage water flow starts transporting mass to neighboring cell which is evident from declining mass in Figure 4c until water within the cell is completely replaced by river water of zero solute concentration. The observed vertical water flow can be explained by capillary rise effect on commencement of Q_{in}. Similar behavior of flow and solute movement in variably saturated zone was observed by Silliman et al. (2002) in a laboratory study.

The mobilization of solute within the domain shown in Figure 3 is largely driven by the above mentioned effect of saturation. After the peak of the event, during the falling limb (Figure 3; $T = 1030$ to 1050 h), the curved shape of the groundwater level indicates the movement of water into both directions (into the stream and towards the distant riparian zone), that is, the groundwater level (saturation) in the distant domain is still rising (around $x = 20$ m) leading to an additional mobilization of solutes in the distant domain. At the same time, the groundwater level is declining in the near-stream zone due to the increasing Q_{out} towards the stream. During the falling limb, the decrease in groundwater level in the entire domain, results in a vertical downward movement of the solute mass. The higher solute mass (dark red area at T = 1012 to T = 1100 h) is moving downwards with the lowering of the 100% saturation line indicating solute movement from the unsaturated zone to the saturated zone. At the same time solute is also moving horizontally in the unsaturated zone towards the stream with Q_{out}. The near stream area of the domain ($x < 3$ m) is free of solutes at ($T = 1030$, 1050 h), therefore, no solute export occurs in the beginning of Q_{out}. The solute carrying water reaches the stream ~15 h later (Figure 3; $T = 1080$ h) indicated by increased C_{str}. This explains the lag between starting time of Q_{out} and C_{str}.

At the end of the event ($T = 1100$ h), groundwater levels adjacent to the stream have returned to the pre-event level while in the distant riparian zone ($x > 10$) heads are still high indicating that a part of Q_{in} still remains in the domain. At this stage, a large portion of Q_{out} is already discharged to the stream and solute concentration C_{str} is at the maximum value (Figure 2f) meanwhile lowering of water table resulted in the movement of solute mass from unsaturated part to the groundwater, from where it is transported to the stream. This is visible at time 1200 h, when the groundwater level is almost back to the pre-event conditions, an increased solute mass is observed in groundwater. This increase in solute mass in

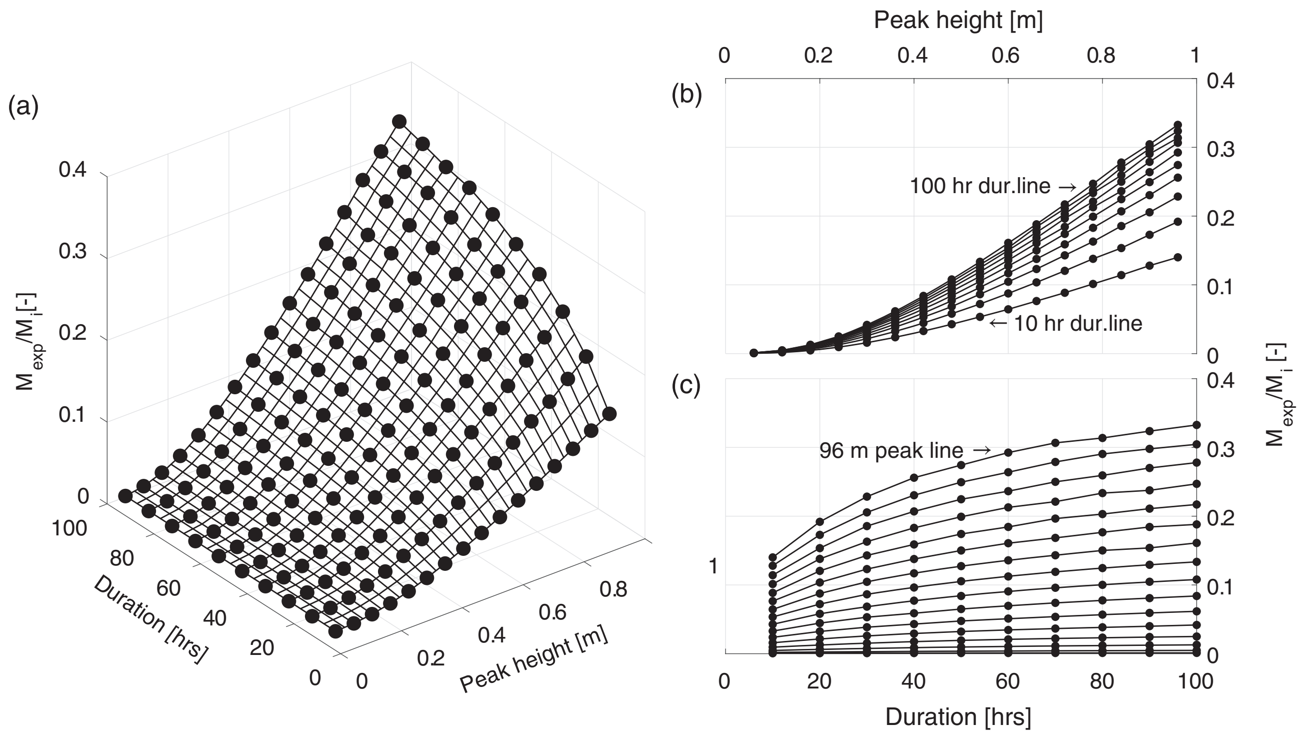

Figure 5. Total solute mass exported into stream in 4000 h (166 days) as a fraction of total solute mass in the domain at pre-event conditions, (a) combined effect of event peak height and duration, (b) effect of event peak height, and (c) effect of event duration.

the groundwater is the result of the gravity driven vertical drainage from the unsaturated zone.

At time 3000 h, we would expect the groundwater to be free from solute; however solute mass is visible even after 9000 h indicating that vertical solute movement from the unsaturated to the saturated parts of the domain continues very long after the end of the flow event. This is due to the slow drainage of Q_{out} from the unsaturated zone as explained in the previous section (see "water exchange time scales") and is consistent with previous studies, for example, McCallum and Shanafield (2016). This explains the long tailing of stream concentration C_{str} in Figure 2f.

The general trends explained above, hold for all simulated scenarios. Flushing of solute mass from near stream riparian zone, longer time periods of Q_{out} and C_{str} were observed in all cases.

Influence of Peak Height and Event Duration on Solute Mass Export towards the Stream

In the following sections, we evaluate the effects of changes in peak height and event duration on cumulative solute export from riparian zone.

Since the cumulative mass export keeps increasing over time long after the flow event, we chose to constrain the output time to 4000 h (166 days) after the beginning of the flow event, the time when water outflow rate falls back to the pre-event flow rate for all of the simulated scenarios.

The solute export to the stream is a function of both event peak height and event duration (Figure 5a). The lines in Figure 5b represent the solute export for varying peaks but equal duration, for example, a 10 h duration line means the solute export for varying peak discharge scenario for equal 10 h duration. Similarly in Figure 5c each peak line represents the export for varying duration with equal peak heights.

For events with peak heights of less than 0.3 m where the infiltrated water does not reach the solute layer, the exported mass remains low and is independent of the actual event peak height (Figure 5b). An increase in the event peak height causes a groundwater level rise into the solute source layer, which results in an increased solute mass mobilization and consequent export. Therefore variations in event peak height have a pronounced effect on solute export. For instance, the solute export on the 100 h duration line (Figure 5b), is increased from 6% for the minimum peak reaching the solute layer (0.36 m) to 33% for the highest peak (0.96 m) Hence for an increment of 0.6 m in peak height, solute export is increased by 5.5 times.

The solute mass export is also positively related to the event duration. However, each line of equal peak height tends to converge to an upper value of mass export with increasing event duration (Figure 5c). This is due to the reason that longer durations push the mobilized solutes away from stream (along *x* dir.), decreasing the availability of solutes to be exported with initial high Q_{out} flow rates. It means, although solute mass export increases with increasing event duration, it has lower impact on solute export compared to the peak height. For instance, the minimum peak height touching the solute layer (0.36 m), solute mass export is 0.14% of the initial

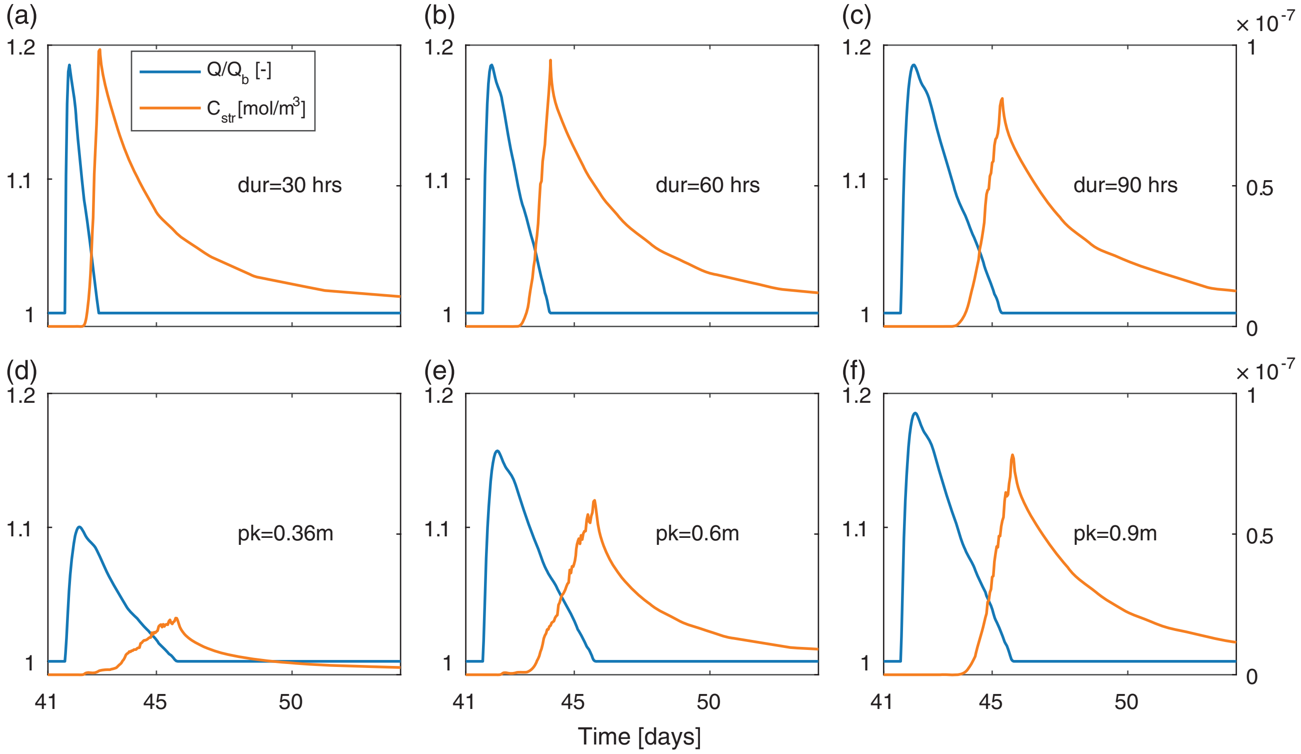

Figure 6. Stream discharge Q/Q_b [−] vs. solute concentration in stream C_{str} [mol/m^3] for (a–c) increasing discharge event duration (30, 60, and 90 h, respectively) for a fixed maximum peak height (0.96 m) (d–f) increasing maximum peak height (0.18, 0.54, 0.96 m) above base flow level, respectively) for a fixed event duration (100 h).

solute mass in the riparian zone for the shortest duration (10 h.) while for the longest duration (100 h) of the same peak height, 0.33% mass is exported. Hence, by an increase of 90 h event duration for the same peak height, mass export is increased by 2.35 times.

The mass export analysis suggests that events with higher peak height result in an increased mobilization and therefore increased solute export while longer durations tend to delay the timing of bank outflow causing retardation in solute export. Therefore, frequent, short-term stream fluctuations will be more efficient than flow event of longer duration with lower peaks in mobilization and consequent export of solutes into the stream. Boutt and Fleming (2009) also demonstrated that frequent stream fluctuations transport solute mass from the stream to the aquifer under zero net water flux by enhancing mixing process inside the aquifer. Gu et al. (2012) found that strong stream events significantly influence the chemistry of both surface water and groundwater by enhancing mixing and reaction efficiency in the near stream zone. They also observed that time frames of chemical activity within riparian zone are much longer than the hydraulic exchange time scales, which is in line with our observations.

Effects of Event Hydrograph Shape on Stream Water Solute Concentration

Since solute export starts with the onset of $Q_{out,}$ (bank outflow) a time delay between the peak in stream discharge and peak concentration of stream water was expected. Figure 6 depicts the stream discharge and concentration change during the stream flow event. Generally, stream concentrations start increasing during the falling limb of the flow event, reaching a maximum value near the end of the flow event. The fixed time of peak concentration at the end of discharge event for all of the simulated scenario is due to the decline in Q_{out} as shown in Figure 6e, which is caused by the turning point in the positive hydraulic gradient i_5 in the near stream zone (Figure 6d). An increase in the duration of the flow causes a damping effect on the concentration peak in the stream water (Figure 6a to 6c). However, tail concentrations are elevated with increasing duration indicating a retardation effect of the event duration on stream concentration as explained in the previous sections. The time difference between the peak discharge (Q_{max}) and peak concentration (C_{str_max}) is increasing with increasing event duration. The increasing time lag and damping of concentration peak is related to the longer Q_{in} duration which initially pushes the mobilized solute mass horizontally away from the stream as well as delays the starting time of Q_{out} and corresponding J.

In contrast, an increase in the event peak height results in a significant increase in the peak stream concentration (Figure 6d to 6f). Higher concentration peaks for higher inflow are due to the water saturation of an increasing portion of the solute source and thus a more efficient mobilization. Therefore, higher peaks release more solute without delaying the solute release from the riparian zone. However, this does not hold for event peaks where the solute source layer is not tapped into by the rising groundwater levels. In such cases no direct solute mobilization is possible and the solute export is mainly caused by diffusion and gravitational solute movement through the unsaturated zone resulting in delayed concentration peaks.

The time lag between Q_{max} and C_{str_max} is constant for scenarios of varying peaks and fixed duration, provided the peak height is high enough to reach the solute layer (Figure S3c), while it is linearly increasing with event duration for scenarios of constant peak height (Figure S3d). This is due to two reasons: a) longer durations induce longer Q_{in} resulting in later starting times for Q_{out} and b) longer Q_{in} pushes the solute mass further away from the near stream zone. As a result, the part of Q_{in} which entered the riparian zone after the solute has been pushed away from the near stream zone may drain back to the stream without having been in significant contact with the solute, causing a significant time lag between the starting times of Q_{out} and J.

Overall, higher and shorter events result in higher and earlier release of solutes and increased total solute mass export resulting in higher and earlier peak C_{str_max} whereas increase in duration results in retardation in release of solute mass resulting in delayed and damped peak C_{str}.

Our results are mainly in line with the concentration-discharge relations found in field studies. Especially, the significant lag between peak discharge and solute peak in stream water has been also observed by many field studies (e.g., Hangen et al. 2001; Inamdar et al. 2004; Pellerin et al. 2012; Welch et al. 2015). In line with our modeling results, they concluded that the rise in groundwater table mobilizes DOC but with a delayed maximum groundwater level compared to the maximum stream stage, leading to delayed solute concentration peak in stream water. Mei et al. (2014) concluded that the time lag is mainly controlled by event duration and hydraulic connectivity between groundwater and stream. Xie et al. (2016) also observed time lag increase with increasing event duration. These studies have suggested that bank inflows have significant effects on the chemical conditions of both stream water and groundwater. In this context, our results give detailed insights into the process of the solute mobilization and export to the stream.

Model Limitations and Future Studies

Our modeling setup represents a simplified riparian zone with reduced process complexity as we exclusively study the effect of stream discharge scenarios on solute mobilization and transport processes. For example, in our model the riparian aquifer is homogeneous and isotropic in both effective porosity and hydraulic conductivity, similar to the study of McCallum et al. (2010). Therefore, we did not account for any highly conductive zones although they may facilitate fast preferential flow and transport that potentially exists in riparian aquifers (Beven and Germann 1982). In turn, layers of lower permeability may reduce the zone of water exchange and solute removal (Chen and Chen 2003). However, since sediment properties will hardly change during short-term stream discharge events the comparative metrics derived in our study are likely the same as for the heterogeneous case.

In this study, recharge by precipitation was not simulated, although it is potentially an important process for water and solute mobilization (Nielsen et al. 1986; Xie et al. 2016). Recharge can mobilize solutes during infiltration and also contributes to the rise of the water table. However to test the additional effect of recharge, we simulated a scenario with a constant recharge of 2 mm at the top surface during the entire period of the flow event and compared the total solute export with the scenario without additional recharge. We found that the overall solute export is enhanced by factor 5.6 after 300 h when a major portion of Q_{out} has been released to the stream and by factor 5.9 after 5000 h when Q_{out} reaches the pre-event level. This clearly indicates that the addition of vertical recharge will significantly increase the overall amount of solute export. However, for a thorough analysis of the effect of groundwater recharge future modeling scenarios should consider rain events with realistic timing and amount of water per time.

Furthermore, in our study solute transport is purely conservative, although in natural aquifers, sorption and reaction may alter solute export to the stream. Incorporating reactions into future modeling scenarios would highlight the effect of solute mobilization on spatial extent and efficiency of solute turn-over.

Summary and Conclusions

Infiltration and exfiltration of water into and out of riparian soils during stream flow events may lead to solute exchange between streams and their connected riparian zones. In this study, we have investigated the effect of stream discharge events on solute mobilization in riparian zones and the subsequent export of solutes to the stream. The dynamics of riparian solute mobilization and transport were simulated for stream discharge scenarios of varying peak height and durations.

Our results show that the magnitude and timing of bank inflows, outflow and therefore solute mass outflux from the riparian zone into the stream is controlled by the shape of the discharge event (i.e., event peak height and duration). The initially unsaturated conditions in parts of the riparian soils allow higher inflow rates in significantly shorter times than the subsequent bank outflows. The bank outflows typically start during the falling limb of the stream flow event, when the local hydraulic gradient reverses back to gaining conditions. A significant fraction of the infiltrated water was discharged back to the stream until the end of the flow event. However, a small fraction of outflow remained in the bank, and was discharged back to the stream over a longer period of time after the flow event. Upon infiltration of stream water, the water level in the riparian zone rises resulting in the mobilization of solutes residing in the previously unsaturated zone. The export of mobilized solutes into the stream occurs in two stages. In the first stage, the bulk of the mobilized solute is transported by the direct bank outflow from the riparian zone resulting in peak concentration at the end of flow event. Bank outflow driven export lasts for a relatively short period of up to 12 days, while during the second stage solute mass from zones of increased saturation moves vertically downward to the saturated zone under the influence of gravity. This drainage process from the unsaturated zone is very slow and is responsible for the long tailing of stream concentration (>400 days) after the event.

Both event peak height and event duration enhance solute mass export. However, in comparison to the event duration, peak height plays a dominant role for the total solute mass exported. The timing of change in stream concentration is directly linked to the timing of the bank outflows which in turn depends on the hydraulic gradient near the stream. The time lag between peak discharge and peak concentration increases with event duration as longer durations delay the reversal of the local hydraulic gradient from negative (losing) to positive (gaining).

Our findings are consistent with previous studies (e.g., Boutt and Fleming 2009; Gu et al. 2012; Mei et al. 2014; Sawyer et al. 2014). It also supports the idea that the export of the riparian solutes during bank outflows is dominantly controlled by the fluctuations in near stream hydraulic gradients (Welch et al. 2015). Another important finding is that presence of an unsaturated zone can lead to long-term solute export into the stream after the flow event. For a field based evaluation of the effects of stream flow events on river solute loads, measurement windows have to be long enough to capture the delayed response caused be solute mobilization from the unsaturated soil zone. The prolonged stays of stream water in the riparian zone provide opportunity for long-term reactions and therefore have important implications for both stream and groundwater quality.

Acknowledgments

This study was funded by Higher Education Commission Pakistan and German Academic Exchange Service (Project ID: 57076459). We are thankful to the editors, Steffen Birk, Olivier Bour, and one anonymous reviewer for their reviews and feedback on the manuscript.

Authors' Note

The authors do not have any conflicts of interest or financial disclosures to report.

Supporting Information

Additional Supporting Information may be found in the online version of this article. Supporting Information is generally *not* peer reviewed.

Figure S1. Selected discharge scenarios of varied peak height and duration used in simulations (shortened list). Tick marks on x and y axes indicate duration of events (h) and peak height (m), respectively.

Figure S2. Fraction of bank inflow water remaining in the riparian zone (green line), corresponding solute export (orange line) out of the riparian zone (top) and change in saturation within the riparian zone during and after the flow event (bottom). The vertical line indicate starting time of bank outflow, end time of flow event and time when major part of the outflow has discharged back to the stream, respectively.

Figure S3. Effects of event hydrograph shape on stream water solute concentration. (a, b) Peak concentration in stream (C_{str}) with increasing peak discharge and duration. (c, d) Time lag in starting time of bank outflow (Q_{out}) and stream concentration (C_{str}).

References

Bartsch, S., S. Frei, M. Ruidisch, C.L. Shope, S. Peiffer, B. Kim, and J.H. Fleckenstein. 2014. River-aquifer exchange fluxes under monsoonal climate conditions. *Journal of Hydrology* 509: 601–614. https://doi.org/10.1016/j.jhydrol.2013.12.005.

Beven, K., and P. Germann. 1982. Macropores and water flow in soils. *Water Resources Research* 18, no. 5: 1311–1325. https://doi.org/10.1029/WR018i005p01311

Biron, P.M., A.G. Roy, F. Courschesne, W.H. Hendershot, B. Côté, and J. Fyles. 1999. The effects of antecedent moisture conditions on the relationship of hydrology to hydrochemistry in a small forested watershed. *Hydrological Processes* 13, no. 11: 1541–1555.

Bishop, K., H. Grip, and A. O'Neill. 1990. The origins of acid runoff in a hillslope during storm events. *Journal of Hydrology* 116, no. 1: 35–61. https://doi.org/10.1016/0022-1694(90)90114-D

Bishop, K., C. Pettersson, B. Allard, and Y.-H. Lee. 1994. Identification of the riparian sources of aquatic dissolved organic carbon. *Environment International* 20, no. 1: 11–19. https://doi.org/10.1016/0160-4120(94)90062-0

Boano, F., C. Camporeale, R. Revelli, and L. Ridolfi. 2006. Sinuosity-driven hyporheic exchange in meandering rivers. *Geophysical Research Letters* 33, no. 18. https://doi.org/10.1029/2006GL027630

Boutt, D.F., and B.J. Fleming. 2009. Implications of anthropogenic river stage fluctuations on mass transport in a valley fill aquifer. *Water Resources Research* 45, no. 4. https://doi.org/10.1029/2007WR006526

Burt, T.P., G. Pinay, F.E. Matheson, N.E. Haycock, A. Butturini, J.C. Clement, S. Danielescu, D.J. Dowrick, M.M. Hefting, A. Hillbricht-Ilkowska, and V. Maitre. 2002. Water table fluctuations in the riparian zone: comparative results from a pan-European experiment. *Journal of Hydrology* 265, no. 1: 129–148.

Cardenas, M.B., and J.L. Wilson. 2007. Hydrodynamics of coupled flow above and below a sediment–water interface with triangular bedforms. *Advances in Water Resources* 30, no. 3: 301–313. https://doi.org/10.1016/j.advwatres.2006.06.009

Castelle, A.J., A.W. Johnson, and C. Conolly. 1994. Wetland and stream buffer size requirements—A review. *Journal of Environmental Quality* 23, no. 5: 878–882. https://doi.org/10.2134/jeq1994.00472425002300050004x

Chen, X., and X. Chen. 2003. Stream water infiltration, bank storage, and storage zone changes due to stream-stage fluctuations. *Journal of Hydrology* 280, no. 1–4: 246–264. https://doi.org/10.1016/S0022-1694(03)00232-4

Cooper, H.H., and M.I. Rorabaugh. 1963. Ground-water movements and bank storage due to flood stages in surface streams. 1536–J. Geological Survey Water Supply Paper. Washington: USGS.

Creed, I.F., and L.E. Band. 1998. Export of nitrogen from catchments within a temperate forest: Evidence for a unifying mechanism regulated by variable source area dynamics. *Water Resources Research* 34, no. 11: 3105–3120.

Creed, I.F., L.E. Band, N.W. Foster, I.K. Morrison, J.A. Nicolson, R.S. Semkin, and D.S. Jeffries. 1996. Regulation of nitrate-n release from temperate forests: A test of the n flushing hypothesis. *Water Resources Research* 32, no. 11: 3337–3354.

Diem, S., M. Rudolf von Rohr, J.G. Hering, H.-P.E. Kohler, M. Schirmer, and U. von Gunten. 2013. Nom degradation during river infiltration: Effects of the climate variables temperature and discharge. *Water Research* 47, no. 17: 6585–6595. https://doi.org/10.1016/j.watres.2013.08.028

Doble, R., P. Brunner, J. McCallum, and P.G. Cook. 2012. An analysis of river bank slope and unsaturated flow effects on bank storage. *Ground Water* 50, no. 1: 77–86. https://doi.org/10.1111/j.1745-6584.2011.00821.x

Duval, T.P., and A.R. Hill. 2006. Influence of stream bank seepage during low-flow conditions on riparian zone hydrology: Influence of bank seepage. *Water Resources Research* 42, no. 10. https://doi.org/10.1029/2006WR004861

Frei, S., K.H. Knorr, S. Peiffer, and J.H. Fleckenstein. 2012. Surface micro-topography causes hot spots of biogeochemical activity in wetland systems: A virtual modeling experiment. *Journal of Geophysical Research – Biogeosciences* 117, no. G4: G00N12. https://doi.org/10.1029/2012JG002012

Gassen, N., C. Griebler, U. Werban, N. Trauth, and C. Stumpp. 2017. High resolution monitoring above and below the groundwater table uncovers small-scale hydrochemical gradients. *Environmental Science & Technology* 51, no. 23: 13806–13815. https://doi.org/10.1021/acs.est.7b03087

van Genuchten, M.T. 1980. A closed-form equation for predicting the hydraulic conductivity of unsaturated soils1. *Soil Science Society of America Journal* 44, no. 5: 892–898. https://doi.org/10.2136/sssaj1980.03615995004400050002x

Gerecht, K.E., M.B. Cardenas, A.J. Guswa, A.H. Sawyer, J.D. Nowinski, and T.E. Swanson. 2011. Dynamics of hyporheic flow and heat transport across a bed-to-bank continuum in a large regulated river. *Water Resources Research* 47, no. 3. https://doi.org/10.1029/2010WR009794

Gift, D.M., P.M. Groffman, S.S. Kaushal, and P.M. Mayer. 2010. Denitrification potential, root biomass, and organic matter in degraded and restored urban riparian zones. *Restoration Ecology* 18, no. 1: 113–120. https://doi.org/10.1111/j.1526-100X.2008.00438.x

Grabs, T., K. Bishop, H. Laudon, S.W. Lyon, and J. Seibert. 2012. Riparian zone hydrology and soil water total organic carbon (toc): Implications for spatial variability and upscaling of lateral riparian toc exports. *Biogeosciences* 9, no. 10: 3901–3916. https://doi.org/10.5194/bg-9-3901-2012

Gu, C., W. Anderson, and F. Maggi. 2012. Riparian biogeochemical hot moments induced by stream fluctuations. *Water Resources Research* 48, no. 9. https://doi.org/10.1029/2011WR011720

Hangen, E., M. Lindenlaub, C. Leibundgut, and K. Von Wilpert. 2001. Investigating mechanisms of stormflow generation by natural tracers and hydrometric data: A small catchment study in the black forest, Germany. *Hydrological Processes* 15, no. 2: 183–199.

Hefting, M., J.C. Clement, D. Dowrick, A.C. Cosandey, S. Bernal, C. Cimpian, A. Tatur, T.P. Burt, and G. Pinay. 2004. Water table elevation controls on soil nitrogen cycling in riparian wetlands along a european climatic gradient. *Biogeochemistry* 67, no. 1: 113–134.

Hill, A.R. 1996. Nitrate removal in stream riparian zones. *Journal of Environmental Quality* 25, no. 4: 743–755. https://doi.org/10.2134/jeq1996.00472425002500040014x

Hill, A.R., K.J. Devito, S. Campagnolo, and K. Sanmugadas. 2000. Subsurface denitrification in a forest riparianzone: Interactions between hydrology and supplies ofnitrate and organic carbon. *Biogeochemistry* 51, no. 2: 193–223. https://doi.org/10.1023/A:1006476514038

Hornberger, G.M., K.E. Bencala, and D.M. McKnight. 1994. Hydrological controls on dissolved organic carbon during snowmelt in the snake river near Montezuma, Colorado. *Biogeochemistry* 25, no. 3: 147–165.

Inamdar, S.P., S.F. Christopher, and M.J. Mitchell. 2004. Export mechanisms for dissolved organic carbon and nitrate during summer storm events in a glaciated forested catchment in New York, USA. *Hydrological Processes* 18, no. 14: 2651–2661. https://doi.org/10.1002/hyp.5572

Mayer, K.U., E.O. Frind, and D.W. Blowes. 2002. Multicomponent reactive transport modeling in variably saturated porous media using a generalized formulation for kinetically controlled reactions. *Water Resources Research* 38, no. 9: 13–1–13–21. https://doi.org/10.1029/2001WR000862

Mayer, P.M., S. Reynolds, T. Canfield, and M. Mccutchen. 2005. *Riparian Buffer Width, Vegetable Cover, and Nitrogen Removal Effectiveness: A Review of Current Science and Regulations. EPA/600/R-05/118*. Washington, DC: U.S. Environmental Protection Agency.

McCallum, J.L., and M. Shanafield. 2016. Residence times of stream-groundwater exchanges due to transient stream stage fluctuations. *Water Resources Research* 52, no. 3: 2059–2073. https://doi.org/10.1002/2015WR017441

McCallum, J.L., P.G. Cook, P. Brunner, and D. Berhane. 2010. Solute dynamics during bank storage flows and implications for chemical base flow separation. *Water Resources Research* 46, no. 7. https://doi.org/10.1029/2009WR008539

Mei, Y., G.M. Hornberger, L.A. Kaplan, J.D. Newbold, and A.K. Aufdenkampe. 2014. The delivery of dissolved organic carbon from a forested hillslope to a headwater stream in southeastern Pennsylvania, USA. *Water Resources Research* 50, no. 7: 5774–5796. https://doi.org/10.1002/2014WR015635

Millington, R.J. 1959. Gas diffusion in porous media. *Science* 130, no. 3367: 100–102. https://doi.org/10.1126/science.130.3367.100-a

Mualem, Y. 1976. A new model for predicting the hydraulic conductivity of unsaturated porous media. *Water Resources Research* 12, no. 3: 513–522. https://doi.org/10.1029/WR012i003p00513

Nielsen, D.R., M.T. Van Genuchten, and J.W. Biggar. 1986. Water flow and solute transport processes in the unsaturated zone. *Water Resources Research* 22, no. 9S: 89S–108S. https://doi.org/10.1029/WR022i09Sp0089S

Pellerin, B.A., J.F. Saraceno, J.B. Shanley, S.D. Sebestyen, G.R. Aiken, W.M. Wollheim, and B.A. Bergamaschi. 2012. Taking the pulse of snowmelt: In situ sensors reveal seasonal, event and diurnal patterns of nitrate and dissolved organic matter variability in an upland forest stream. *Biogeochemistry* 108, no. 1–3, 183: 183–198. https://doi.org/10.1007/s10533-011-9589-8

Rassam, W., C.S. Fellows, R.D. Hayr, H. Hunter, and P. Bloesch. 2006. The hydrology of riparian buffer zones; two case studies in an ephemeral and a perennial stream. *Journal of Hydrology* 325, no. 1–4: 308–324. https://doi.org/10.1016/j.jhydrol.2005.10.023

Sandén, P., S. Karlsson, A. Düker, A. Ledin, and L. Lundman. 1997. Variations in hydrochemistry, trace metal concentration and transport during a rain storm event in a small catchment. *Journal of Geochemical Exploration* 58, no. 2: 145–155. https://doi.org/10.1016/S0375-6742(96)00078-7

Sawyer, A.H., L.A. Kaplan, O. Lazareva, and H.A. Michael. 2014. Hydrologic dynamics and geochemical responses within a floodplain aquifer and hyporheic zone during hurricane sandy. *Water Resources Research* 50, no. 6: 4877–4892. https://doi.org/10.1002/2013WR015101

Silliman, S.E., B. Berkowitz, J. Simunek, and M.T. van Genuchten. 2002. Fluid flow and solute migration within the capillary fringe. *Ground Water* 40, no. 1: 76–84. https://doi.org/10.1111/j.1745-6584.2002.tb02493.x

Simmons, R.C., A.J. Gold, and P.M. Groffman. 1992. Nitrate dynamics in riparian forests: Groundwater studies. *Journal of Environmental Quality* 21, no. 4: 659–665. https://doi.org/10.2134/jeq1992.00472425002100040021x

Squillace, P.J., E.M. Thurman, and E.T. Furlong. 1993. Groundwater as a nonpoint source of atrazine and deethylatrazine in a river during base flow conditions. *Water Resources Research* 29, no. 6: 1719–1729.

Trauth, N., and J.H. Fleckenstein. 2017. Single discharge events increase reactive efficiency of the hyporheic zone. *Water Resources Research* 53, no. 1: 779–798. https://doi.org/10.1002/2016WR019488

Trauth, N., C. Schmidt, M. Vieweg, U. Maier, and J.H. Fleckenstein. 2014. Hyporheic transport and biogeochemical reactions in pool-riffle systems under varying ambient groundwater flow conditions. *Journal of Geophysical Research – Biogeosciences* 119, no. 5: 910–928. https://doi.org/10.1002/2013JG002586

Trauth, N., C. Schmidt, M. Vieweg, S.E. Oswald, and J.H. Fleckenstein. 2015. Hydraulic controls of in-stream gravel bar hyporheic exchange and reactions. *Water Resources Research* 51, no. 4: 2243–2263. https://doi.org/10.1002/2014WR015857

Vidon, P.G.F., and A.R. Hill. 2004. Landscape controls on nitrate removal in stream riparian zones. *Water Resources Research* 40, no. 3. https://doi.org/10.1029/2003WR002473

Vidon, P., S. Marchese, and S. Rook. 2017. Impact of hurricane irene and tropical storm lee on riparian zone hydrology and biogeochemistry: Hurricane impacts on riparian zone hydrology and biogeochemistry. *Hydrological Processes* 31, no. 2: 476–488. https://doi.org/10.1002/hyp.11045

Welch, C., G.A. Harrington, and P.G. Cook. 2015. Influence of groundwater hydraulic gradient on bank storage metrics. *Groundwater* 53, no. 5: 782–793. https://doi.org/10.1111/gwat.12283

Wondzell, S.M., and F.J. Swanson. 1996. Seasonal and storm dynamics of the hyporheic zone of a 4th-order mountain stream. Ii: Nitrogen cycling. *Journal of the North American Benthological Society* 15, no. 1: 20–34.

Xie, Y., P.G. Cook, and C.T. Simmons. 2016. Solute transport processes in flow-event-driven stream–aquifer interaction. *Journal of Hydrology* 538, no. July: 363–373. https://doi.org/10.1016/j.jhydrol.2016.04.031