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Nitrogen cycles within the stream-to-riparian continuum under flood waves

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By using a 2D-coupled flow and solute transport and reaction model across the stream-to-riparian continuum, this paper systematically studied the nitrogen-cycling processes driven by a flood wave and their spatial-temporal distributions. The influences on hyporheic nitrogen removal of different waves that vary by amplitude (A), duration (T), wave-type parameter (r) and rising duration (t_p) were investigated. During the surface-water-infiltration period, the aerobic respiration, nitrification and denitrification in the hyporheic zone were gradually enhanced, and aerobic respiration was dominant. During the groundwater-backflow period, the reactions gradually weakened, and the role of denitrification was improved. The consumption of each solute continuously increased in the whole process, and the groundwater-backflow period corresponded to a larger consumption but at a smaller consumption rate. The reaction rates in space from high to low were as follows: riparian phreatic zone > variable saturated zone > stream bed. Hyporheic nitrogen removal increased with increasing A , T and t_p and with decreasing r , which was contrary to the change rule of nitrogen removal efficiency. The hyporheic nitrogen removal exhibited a good linear relationship with the polynomial ' $A \cdot T \cdot t_p / r$ ', which had great predictive significance.

Introduction

The rapid fluctuations and lateral spreads of flood events greatly change the hydrological regime within the stream-floodplain system (Sawyer et al., 2009; Gerecht et al., 2011; Liu et al., 2018) and affect the hydrochemical indexes in the hyporheic zone (HZ) (Curry et al., 1994; Arntzen et al., 2006; Hanrahan, 2008; Jeon and Lee, 2015). The effect of a flood event on hydrochemical indexes is through the following two ways. (1) The solutes are carried into the HZ during the surface water infiltration, or the HZ behaves as a source of solutes during the groundwater discharging. (2) The solutes in the HZ undergo

a series of chemical reactions that change the corresponding hydrochemical indexes.

Current studies on the hydrochemical reactions in the HZ under flood events focus on the nitrogen cycles. In the processes of hyporheic exchange and nitrogen cycles, surface water is usually rich in dissolved oxygen (i.e., O_2), dissolved organic carbon (DOC) and nutrients, whereas these contents in groundwater are generally lower (Dahm et al., 1998). Therefore, when surface water level rises and recharges groundwater, it carries much of O_2 into the HZ. In aerobic environment, NH_4^+ is converted into NO_3^- by the action of nitrobacteria (i.e., nitrification), which contributes to the NO_3^- source of the aquifer. Simultaneously, O_2 and DOC also undergo aerobic respiration, thereby promoting the degradation of organic matter. When surface water level falls, heterotrophic microorganisms in the HZ preferentially use NO_3^- as an electron acceptor in the absence of oxygen to promote their metabolism and convert NO_3^- to N_2 and N_2O (i.e., denitrification). According to Böhlke and Denver (1995) and Marzadri et al. (2011), the threshold concentration of O_2 for denitrification in stream sediment is 3 mg/l, assuming NO_3^- is completely reduced to N_2 .

Scholars have conducted a lot of researches on the hyporheic nitrogen cycles under flood events through field tracer tests. For example, Stanley and Boulton (1995) studied the nitrogen cycles in stream-floodplain system under alternating wet and dry processes, indicating that the concentrations of nitrates and dissolved oxygen drop sharply during flood attenuation. Moreover, with weakening hyporheic exchange, the HZ reaches an extremely hypoxic state (O_2 concentration <0.5 mg/L), and the nitrate nitrogen concentration is also at a lower level (<0.02 mg/L), after which denitrification dominates. Roley et al. (2012) conducted an in situ measurement and analysis of the nitrate concentration and nitrification rate in the HZ under flood events in Shatto Creek, USA. The authors' results showed that nitrification rate in the floodplain area gradually increases with the expansion of flood-submerged area and has different performances in the process of flood rise-peak-fall. Harvey et al. (2013) investigated denitrification in the HZ by injecting $^{15}NO_3^-$ in the upstream of Sugar Creek, USA, and the HZ plays a dominant role in the denitrification process of the river system. Moreover, the denitrification rate is proportional to the magnitude of hyporheic exchange.

At present, researches on the mechanism of hyporheic nitrogen cycles focus on topographic factors and rely on numerical simulation. For example, Bardini et al. (2012) simulated the nitrogen cycles in the HZ driven by streambed dunes under steady flow conditions. The authors found that the availability of DOC determines whether the stream bed is the source or sink of nitrate. Bardini et al. (2013) further clarified that sediment heterogeneity has minimal effect on stream bed nutrient dynamics compared with stream bed morphology. Hu et al. (2014) emphasized that ignoring the micro-morphology in the large stream bed structure will underestimate the discharge of nitrate nitrogen from the HZ to the stream. Gu et al. (2007) studied the effects of flow and biogeochemical conditions on nitrate reduction in stream bed through indoor flume test and numerical simulation. They found that nitrate concentration of groundwater drainage is controlled by groundwater discharge rate and by the rates of aerobic respiration and denitrification.

However, studies on the mechanism of hyporheic nitrogen cycles driven by flood events are lacking. Gu et al. (2012) was the first to simulate the effects of flood waves on hyporheic exchange and nitrogen cycles. The lateral exchange in the riparian zone greatly improves the efficiency of hyporheic nitrogen removal. Furthermore, they revealed positive correlations between nitrogen removal and wave amplitude, duration, bank storage and maximum solute storage. However, their model did not consider nitrification, which might play a lead role in short hyporheic exchange paths and hydrological retention time (Zarnetske et al., 2011). Shuai et al. (2017) built an improved flow-solute transport model and explored the effects of surface-groundwater hydraulic gradient, aquifer hydraulic conductivity and dispersivity on hyporheic nitrogen removal under flood waves. The study's results indicated that when surface water is in gaining condition, large aquifer hydraulic conductivity and dispersivity lead to great hyporheic nitrogen removal and efficiency. Similarly, Trauth et al. (2018) revealed that aerobic respiration and denitrification efficiency in the HZ increase correspondingly with the increase of amplitude and duration of flood wave through numerical simulations.

In summary, the understanding of mechanism of hyporheic nitrogen cycles driven by flood waves is unclear. Understanding of spatial-temporal distribution of hydrochemical characteristic quantities in a stream bed, riparian phreatic zone and variable saturated zone is lacking. Moreover, although previous studies fully discussed the influence of wave amplitude and duration on nitrogen cycles, the parameters characterizing the roundness and skewness of a wave remain unexamined. Hence, this study aims to solve the following three problems: (1) revealing the dynamics of reaction rates, solute consumption and consumption rates of hyporheic nitrogen cycles in response to a flood wave; (2) illustrating the variations of solute concentrations, solute plumes and reaction rates in stream-to-riparian continuum; and (3) systematically exploring the influence of four typical wave parameters on hyporheic nitrogen removal.

Methods

Site and Model Descriptions

This study adopted the field test and flow model from Liu et al. (2019), based on which the solute transport and reaction model were

coupled. The field site (128°12'18"E, 38°13'15"N) is located in the upstream of the Inbuk stream, Korea, where the stream stage amplitude and duration are able to reach 1 m and 5 days respectively due to seasonal flooding. Several piezometers were installed across the stream-to-riparian continuum at intervals of 10m for evaluating the hyporheic exchange between surface water and groundwater. And some chemical indexes in the surface water and groundwater were also measured.

Governing Equations

The model coupled Richard's Equation (Voss, 1984) and convection-dispersion-reaction Equation (1), as follows:

$$\frac{\partial}{\partial t}(\theta C_j) - \nabla \cdot (\theta \mathbf{D} \nabla C_j) + \nabla \cdot (\mathbf{q} C_j) = R_j \quad (1)$$

where θ is the water content, C_j is the concentration of solute j , $\mathbf{D}$ is the hydrodynamic dispersivity tensor, $\mathbf{q}$ is the Darcy velocity vector, R_j is the reaction rate of solute j and t is the time.

The nitrogen-cycling processes involved in this model included aerobic respiration, nitrification and denitrification. DOC was represented by the chemical formula 'CH₂O', and all the reaction equations were as follows:

The Multiple-Monod kinetics model was used to characterize the aforementioned nitrogen-cycling processes (Molz et al., 1986). R_j in Equation (1) was expressed by the following formula:

$$R_{\text{O}_2} = -\theta V_{\text{AR}} X_{\text{AR}} y_{\text{O}_2} \left(\frac{C_{\text{DOC}}}{K_{\text{DOC}} + C_{\text{DOC}}} \right) \left(\frac{C_{\text{O}_2}}{K_{\text{O}_2} + C_{\text{O}_2}} \right) - \theta V_{\text{NT}} X_{\text{NT}} (1 - y_{\text{O}_2}) \left(\frac{C_{\text{NH}_4}}{K_{\text{NH}_4} + C_{\text{NH}_4}} \right) \left(\frac{C_{\text{O}_2}}{K_{\text{O}_2} + C_{\text{O}_2}} \right) \quad (5)$$

$$R_{\text{NH}_4} = -\theta V_{\text{NT}} X_{\text{NT}} \left(\frac{C_{\text{NH}_4}}{K_{\text{NH}_4} + C_{\text{NH}_4}} \right) \left(\frac{C_{\text{O}_2}}{K_{\text{O}_2} + C_{\text{O}_2}} \right) \quad (6)$$

$$R_{\text{NO}_3} = \theta V_{\text{NT}} X_{\text{NT}} \left(\frac{C_{\text{NH}_4}}{K_{\text{NH}_4} + C_{\text{NH}_4}} \right) \left(\frac{C_{\text{O}_2}}{K_{\text{O}_2} + C_{\text{O}_2}} \right) - \theta V_{\text{DN}} X_{\text{DN}} \left(\frac{K_I}{K_I + C_{\text{O}_2}} \right) \left(\frac{C_{\text{DOC}}}{K_{\text{DOC}} + C_{\text{DOC}}} \right) \left(\frac{C_{\text{NO}_3}}{K_{\text{NO}_3} + C_{\text{NO}_3}} \right) \quad (7)$$

$$R_{\text{DOC}} = -\theta V_{\text{AR}} X_{\text{AR}} y_{\text{O}_2} \left(\frac{C_{\text{DOC}}}{K_{\text{DOC}} + C_{\text{DOC}}} \right) \left(\frac{C_{\text{O}_2}}{K_{\text{O}_2} + C_{\text{O}_2}} \right) - \theta V_{\text{DN}} X_{\text{DN}} \left(\frac{K_I}{K_I + C_{\text{O}_2}} \right) \left(\frac{C_{\text{DOC}}}{K_{\text{DOC}} + C_{\text{DOC}}} \right) \left(\frac{C_{\text{NO}_3}}{K_{\text{NO}_3} + C_{\text{NO}_3}} \right) \quad (8)$$

where C_{O_2} , C_{NH_4} , C_{NO_3} and C_{DOC} are the concentrations of O₂, NH₄⁺, NO₃⁻ and DOC, respectively; R_{O_2} , R_{NH_4} , R_{NO_3} and R_{DOC} are the reaction rates for O₂, NH₄⁺, NO₃⁻ and DOC, respectively; V_{AR} , V_{NT} and V_{DN} are the maximum specific uptake rates of the substrate for aerobic respiration (AR), nitrification (NT) and denitrification (DN), respectively; X_{AR} , X_{NT} and X_{DN} are the biomass of the functional microbial group facilitating the different reaction components for AR, NT and DN, respectively; K_{O_2} , K_{NH_4} , K_{NO_3} and K_{DOC} are the half-saturation con-

stands for O_2 , NH_4^+ , NO_3^- and DOC, respectively; K_i is an inhibition constant; y_{O_2} is the O_2 partition coefficient; and U_{AR} , U_{NT} and U_{DN} ($U = VX$) are the lumped specific maximum microbial reaction rates for AR, NT and DN, respectively.

Boundary Conditions and Input Parameters

The concentrations for O_2 , NO_3^- and NH_4^+ on the stream-aquifer boundary were set based on measured values of 5, 5 and 0.05 mg/L, respectively (Fig. 1). It was also set to 5 mg/L for DOC to compare better the degree of reaction of each solute owing to the lack of DOC concentration in surface water. Moreover, a conservative solute boundary condition (Na^+) was also set, which was completely consistent with that of NO_3^- . The initial values of all solutes in the model were set to zero and were uniformly distributed. The longitudinal and transverse dispersivity of the model were set to 0.1 and 0.01 m, respectively, according to the model scale and the empirical values. Other biochemical parameters were also determined by basing on the empirical values of previous similar studies (Table 1).

Quantifications of Nitrogen Cycles

For multi-component reactive solutes (O_2 , NH_4^+ , NO_3^- and DOC), the consumption of solute j (M_{rem-j}) at any time during water-level fluctuation was obtained by the following:

$$M_{rem-j} = \int_0^T \int_{\Omega} \theta R_j d\Omega dt \quad (9)$$

where T is the total simulation time and Ω is the study area.

The consumption rate (R_{rem-j}) of solute j was obtained by deriving M_{rem-j} with respect to t :

$$R_{rem-j} = \frac{dM_{rem-j}}{dt} \quad (10)$$

The consumption efficiency (N_{rem-j}) of solute j was further determined by the following:

$$N_{rem-j} = \frac{M_{rem-j}}{M_{in-j}} \quad (11)$$

where M_{in-j} is the maximum storage of solute j in the aquifer:

$$M_{in-j} = \int_0^{t_F} C_0 q(t) dt \quad (12)$$

where C_0 is the initial concentration of surface water, t_F is the surface water infiltration time and q denotes the exchange flux between the surface water and groundwater, which is obtained by integrating the normal velocity (v_n) along the stream-aquifer interface:

$$q = \int_0^l v_n dl \quad (13)$$

where l is the length of the stream-aquifer interface.

In addition, the average reaction rate ($\bar{R}_j$) of solute j within the study domain was further determined by the following:

$$\bar{R}_j = \frac{d[M_{rem-j}/Q(t)]}{dt} \quad (14)$$

where $Q(t)$ is the aquifer storage, which is obtained by integrating the q mentioned above over time.

$$Q(t) = \int_0^t q dt \quad (15)$$

Model Scenarios

As Inbuk Stream is subjected to seasonal flooding and reservoir drainage throughout the year, the surface water level exhibits approximately sinusoidal fluctuation (Liu et al., 2019), as follows:

$$h(t) = h_0 + A \sin \left[\left(\frac{t}{R} \right)^{-\ln 2 / \ln (\frac{t}{T})} \pi \right] \quad (16)$$

where h_0 is the elevation of stream bottom, A is the amplitude characterizing the height of a flood wave, T is the duration characterizing the width of a flood wave, r is the wave type parameter characterizing the roundness of a flood wave, and t_p is the rising duration characterizing the skewness of a flood wave.

The range of each parameter was roughly determined based on the measured stream water level data from 2014 to 2016, and a variety of waveforms of different A , T , r and t_p were generalized (Fig. 2).

Figure 1. Conceptual flow-transport-reaction coupling model across the stream-to-riparian continuum. The dotted boundary denotes the submerged area. The blue points denote the observation points in stream bed, riparian phreatic zone and riparian variable saturated zone with the same distance from the stream-aquifer interface.

Table 1. Input parameters of flow-transport-reaction coupling model

Parameters	Values	Units
Hydrodynamic Model Parameters		
Saturated hydraulic conductivity (K) ^(a)	3.47E-5	[m/s]
Effective porosity (n_e) ^(a)	0.41	[-]
Specific storage (S_0) ^(a)	0.0001	[1/m]
Residual saturation (s_r) ^(a)	0.146	[-]
Maximum saturation (s_s) ^(a)	0.96	[-]
van Genuchten parameter (ξ) ^(a)	7.5	[1/m]
van Genuchten parameter (n) ^(a)	1.95	[-]
Longitudinal dispersivity (D_L) ^(b)	0.1	[m]
Longitudinal/Transverse dispersivity ratio (D_L/D_T) ^(b)	0.01	[-]
Water Quality Model Parameters		
O ₂ concentration in surface water ^(c)	5	[mg/L]
NH ₄ ⁺ concentration in surface water ^(c)	0.05	[mg/L]
NO ₃ ⁻ concentration in surface water ^(c)	5	[mg/L]
DOC concentration in surface water ^(c)	5	[mg/L]
Na ⁺ concentration in surface water ^(c)	5	[mg/L]
O ₂ , NH ₄ ⁺ , NO ₃ ⁻ , DOC, Na ⁺ concentration in the aquifer and recharge water ^(c)	0	[mg/L]
Maximum specific uptake rate for AR (U_{AR}) ^(d,e,f)	2	[mg/L/d]
Maximum specific uptake rate for NI (U_{NI}) ^(d)	1.05	[mg/L/d]
Maximum specific uptake rate for DN (U_{DN}) ^(d,e,f)	2	[mg/L/d]
Half saturation constant for O ₂ (K_{O_2}) ^(d,e,f)	1	[mg/L]
Half saturation constant for NH ₄ ⁺ (K_{NH_4}) ^(d,e)	0.5	[mg/L]
Half saturation constant for NO ₃ ⁻ (K_{NO_3}) ^(d,e,f)	1	[mg/L]
Half saturation constant for DOC (K_{DOC}) ^(d,e,f)	5	[mg/L]
O ₂ inhibition constant (K_I) ^(d,e)	1	[mg/L]
O ₂ partition coefficient (γ_{O_2}) ^(d)	0.64	[-]

^(a)Identified parameters of flow model (Liu et al., 2019).

^(b)Literature empirical values (Fetter, 2000; Gelharet et al., 1992; Neuman, 1990; Schulze-Makuch, 2005).

^(c)Measured values.

^(d)Literature empirical values (Zarnetske et al., 2012).

^(e)Literature empirical values (Lee et al., 2006; Shuai et al., 2017; Gu et al., 2012; Hu et al., 2014).

^(f)Literature empirical values (Gu et al., 2007).

Figure 2. Schematic diagram of a flood wave.

Results

Dynamics of Solute Transformations in Response to a Flood Wave

Fig. 3 showed the dynamics of average reaction rates, solute consumption and consumption rates in response to hyporheic exchange flux. The processes were roughly divided into three periods. (1) Surface-water-infiltration period ($0.5 < t < 2.35d$). The average reaction rate of each solute gradually increased (Fig. 3b), and the consumption and consumption rate increased accordingly (Fig. 3c, d), but their trends gradually slowed down in the latter half. (2) Groundwater-backflow period with the intensity gradually approaching the maximum value ($2.35 < t < 3.1d$). As the solute concentrations decreased, the average reaction rate and consumption rate dropped sharply (especially of DOC and O₂), and the increasing trend of solute consumption slowed down. (3) Groundwater-backflow period with the intensity gradually approaching zero ($t > 3.1d$). Solute concentration in the HZ gradually

Figure 3. Change processes of surface water-groundwater exchange flux (a), average solute reaction rates (b), consumption rates (c) and consumption (d) within the study domain.

approached the initial value, and the average reaction rate and consumption rate decreased with slow trends. By contrast, the solute consumption continued to increase in a very gradual trend.

Spatial-temporal Features of Nitrogen Cycles Driven by a Flood Wave

Fig. 4 showed the distributions of hydraulic head and solute concentrations (O_2 , NH_4^+ , NO_3^- , DOC and Na^+) across the stream-to-riparian continuum at typical moments of a flood wave (base case). During the rising limb ($0.5 < t < 1.25d$), O_2 , NO_3^- , DOC and Na^+ solute plumes were constantly expanding, whereas the range of NH_4^+ plume changed slightly due to the lower actual concentration. During the falling limb before $t = 2d$, O_2 , NO_3^- , DOC and Na^+ plumes were still expanding, but the NH_4^+ plume shrank considerably. As the surface water level continued to fall (e.g., $t = 2.5d$), groundwater switched to recharge surface water. Hence, O_2 , NO_3^- , DOC and Na^+ plumes no longer expanded, and NH_4^+ was almost completely oxidized by O_2 . At the end of the

flood (i.e., $t = 3.5d$), the plumes of O_2 and DOC begin to be markedly smaller than that of NO_3^- , while the NO_3^- plume is slightly smaller than that of Na^+ . In the next long flood recession period ($3.5 < t < 20d$), all the solute plumes were constantly shrinking at different speeds: $DOC > O_2 > NO_3^- > Na^+$. Although NO_3^- consumed slowly in the whole process, it consumed relatively fast in the recession period.

The shape of the solute plume in the stream-to-riparian continuum was similar to the envelope surface of tracer particles (Chen et al., 2003), which meant that in the vertical direction, the closer to the stream centre, the more shallowly the solute was transported. By comparison, in the lateral direction, the closer to the initial groundwater level, the more widely the solute was transported. To compare the nitrogen-cycling processes for different areas (stream bed, riparian phreatic zone and riparian variable saturated zone), observation points were set in each area. Fig. 5a-d showed that during the surface-water-infiltration period, the concentration for each solute in the riparian phreatic and riparian variable saturated zones almost increased in the same way. The increase in magnitude and speed were larger than that in the streambed. Similar variation trends were found for reaction rate of each chemical process (Fig. 5e-g). During the groundwater-backflow period, the decline rate of concentration in space from high to low was as follows: riparian phreatic zone > variable saturated zone > stream bed. However, the decline of reaction rate in space from high to low was as follows: variable saturated zone > riparian phreatic zone > stream bed.

Hyporheic Nitrogen Removal under Different Flood Waves

Table 2 showed the variations of M_{in-NO_3} , M_{rem-NO_3} and N_{rem-NO_3} under different flood waves. The trends of M_{rem-NO_3} and M_{in-NO_3} were almost the same, which were positively correlated with A , T and t_p , but negatively correlated with r . However, N_{rem-NO_3} showed the opposite trend with M_{rem-NO_3} or M_{in-NO_3} . Fig. 6 showed the fitting relationship between M_{rem-NO_3} and the polynomial ' $A * T * t_p / r$ ' with the correlation coefficient being $R^2 = 0.82$, which suggested a good correlation.

Discussion

Mechanism of Flood-wave-driven Solute Transformations

During the surface-water-infiltration period, the solute consumption and consumption rate increased with increasing solute reaction rate (Fig. 3b-d), but their trends gradually slowed down in the latter half. This trend arose because the intensity of recharge from surface water to aquifer gradually decreased (Fig. 3a), resulting in a slower rise in solute concentration, which was an important indicator affecting chemical reaction. Thus, with increasing concentration of each solute during the surface-water-infiltration period, the corresponding chemical reactions were strengthened, especially aerobic respiration. Although the reaction rate of NO_3^- increased during this period, the magnitude was relatively small due to the inhibition of rich O_2 . During the groundwater-backflow period, the reaction rates for DOC and O_2 decreased significantly, whereas the reaction rate of NO_3^- decreased minimally. These findings indicated that with decreasing O_2 concentration, its inhibition decreased, and the role of denitrification improved. From Fig. 3d, the consumption of each solute was constantly increasing

Figure 4. Distributions of hydraulic head and solute concentrations across the stream-to-riparian continuum at typical moments of a flood wave.

Table 2. NO_3^- maximum storage ($M_{\text{in-NO}_3}$), NO_3^- removal ($M_{\text{rem-NO}_3}$) and NO_3^- removal efficiency ($N_{\text{rem-NO}_3}$) under different water waves

Parameters		Conditions	$M_{\text{in-NO}_3}$	$M_{\text{rem-NO}_3}$	$N_{\text{rem-NO}_3}$
Different flood wave parameters	Amplitude, A ($T = 3$, $r = 2.0$, $t_p = T/4$)	0.2	4.744	1.034	21.80%
		0.4	8.534	1.698	19.90%
		0.6	12.244	2.321	18.96%
		0.8	15.953	2.937	18.41%
		1.0	19.707	3.548	18.00%
	Duration, T ($A = 0.6$, $r = 2.0$, $t_p = T/4$)	1	6.520	1.372	21.04%
		2	9.724	1.886	19.40%
		3	12.244	2.321	18.96%
		4	14.428	2.693	18.67%
		5	16.364	3.058	18.69%
	Wave type parameter, r ($A = 0.6$, $T = 3$, $t_p = T/4$)	1.2	13.801	2.577	18.67%
		1.5	13.114	2.463	18.78%
		2.0	12.244	2.321	18.96%
		2.5	11.495	2.207	19.20%
		3.0	11.082	2.119	19.12%
	Rising duration, t_p ($A = 0.6$, $T = 3$, $r = 2.0$)	$T/6 = 0.5$	11.346	2.172	19.14%
		$T/5 = 0.6$	11.786	2.24	19.01%
		$T/4 = 0.75$	12.244	2.321	18.96%
		$T/3 = 1$	12.729	2.391	18.78%
		$T/2 = 1.5$	13.071	2.445	18.71%

*The shaded area corresponds to the base case (i.e., $A = 0.6$ m, $T = 3$ d, $r = 2.0$ and $t_p = T/4 = 0.75$ d). Different flood wave parameters are generated based on the base case by changing only one parameter at a time and keeping the remaining parameters unchanged.

during the flood event. Each solute consumed faster when surface water infiltrated into the aquifer, while it consumed more slowly when the groundwater flowed back. However, the consumption of each solute during the surface-water-infiltration period was smaller than that during the groundwater-backflow period. This result was due to the fact that the hydrological retention time during the groundwater-backflow period was much longer than that in the surface-water-infiltration period, which provided sufficient reaction time for each chemical process.

Principle of Spatiotemporal Variations of Flood-wave-driven Nitrogen Cycles

Generally, each solute plume expanded during the rising limb of surface water level and shrank during the falling limb. However, O_2 , NO_3^- and DOC plumes showed expansion trends during a preceding period of the falling limb, because the aquifer was still recharged by the surface water although the surface water level declined, and the solute amount being carried into the HZ was much more than the reaction removal. NO_3^- plume was the largest, because aerobic respiration

and nitrification were strong at this period, whereas denitrification was limited by rich O_2 . Moreover, nitrification produced some extra NO_3^- . Although both O_2 and DOC underwent aerobic respiration, less O_2 participated in nitrification, whereas more DOC participated in denitrification, thereby resulting in the plume of O_2 being slightly larger than that of DOC.

By comparing the variations in the concentration of O_2 , NO_3^- and DOC in three areas, we found that DOC concentration decreased the most, followed by O_2 and then NO_3^- , which indicated that aerobic respiration was dominant in the whole process. This result was supported by comparing Fig. 5(f) and (g). The oxidation rate during a flood wave was about four times than that of denitrification rate. The reason the consumption of DOC was markedly higher than that of O_2 was that the denitrification rate in which DOC was involved was significantly higher than the nitrification rate that O_2 was involved in, which was supported by comparing Fig. 5(e) and (g). The denitrification rate was about thrice that of the nitrification rate. In addition, the overall reaction rate of each process in stream bed was smaller than that in the riparian zone, which was due to the relatively shallow but wide aquifer, resulting in a smaller amount of solute being carried into the vertical

Figure 5. Variations in solute concentration and reaction rate of each solute at different regional observation point units under a flood wave. SB, RPZ and RVSZ denote stream bed, riparian phreatic zone and riparian variable saturated zone, respectively.

Figure 6. Dimensionless relationship between hyporheic nitrogen removal (M_{rem-NO_3}) and ' $A*T*t_p/r$ '.

zone than that being carried into the lateral zone. In the riparian zone, the overall reaction rate of each process in the riparian variable saturated zone was smaller than that in the riparian phreatic zone, because a part of the solute in the variable saturated zone was absorbed by soil particles and remained there, thereby decreasing the overall solute concentrations within the region and reducing the reaction rates.

Implication of a Flood Wave on Hyporheic Nitrogen Removal

During a flood wave condition, nitrogen removal in the HZ (M_{rem-NO_3}) was positively correlated with the polynomial ' $A*T*t_p/r$ ' composed of the wave parameters. However, N_{rem-NO_3} showed the opposite trend with M_{rem-NO_3} . The main reason was that as A , T and t_p increased or as r decreased, the aquifer storage increased accordingly, leading to an increase in M_{in-NO_3} and M_{rem-NO_3} . By comparison, M_{in-NO_3} increased more than M_{rem-NO_3} , which accordingly resulted in the decrease of the ratio of M_{rem-NO_3}/M_{in-NO_3} (i.e., N_{rem-NO_3}). The relationship between M_{rem-NO_3} and ' $A*T*t_p/r$ ' can be used to predict the amount of hyporheic nitrogen removal according to an actual flood wave at the site. The amplitude, duration and rising duration of a flood wave are intuitive and easy to measure. The wave type parameter r can be roughly obtained by an empirical polynomial, which is the fitting relationship between ' $\Delta T/T$ ' and r . ΔT denotes the span of two points at the height of ' $A/2$ ' on the wave graph.

Conclusions

This paper systematically studied the hyporheic nitrogen cycles driven by flood waves using a 2D flow-transport-reaction model. The main findings were as follows:

(1) When surface water infiltrated into the aquifer, the solute concentrations in the HZ increased accordingly, thereby resulting in gradual enhancements of aerobic respiration, nitrification and denitrification, of which aerobic respiration was dominant. When groundwater flowed back, all the chemical reaction processes were gradually weakened, of which the role of denitrification was improved.

(2) In the whole flood duration, solutes in the HZ were continuously consumed, with the consumption in the groundwater-backflow period being greater, although the corresponding reaction rates were

slower. In space, the reaction rate of each chemical process from high to low was: riparian phreatic zone > variable saturated zone > stream bed.

(3) A good linear relation existed between the hyporheic nitrogen removal and the polynomial of each parameter ' $A*T*t_p/r$ ', $R^2=0.82$. As A , T and t_p increased and r decreased, the nitrogen removal in the HZ increased accordingly, whereas the removal efficiency showed the opposite trend.

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