

Article

Reactive Transport of NH_4^+ in the Hyporheic Zone from the Ground Water to the Surface Water

Ailan Yan ^{1,2,*}, Xianyan Guo ³, Donghui Hu ⁴ and Xiaoyang Chen ^{1,2}

¹ Key Laboratory for Technology in Rural Water Management of Zhejiang Province, Zhejiang University of Water Resources and Electric Power, Hangzhou 310018, China; chengxy@zjweu.edu.cn

² College of Water Conservancy and Environmental Engineering, Zhejiang University of Water Resources and Electric Power, Hangzhou 310018, China

³ Production & Technology Department, Reconnaissance and Design Institute, Qiantang River Administration of Zhejiang Province, Hangzhou 310018, China; guoxianyan2001@163.com

⁴ Hydraulic and Agriculture Engineering Department, Yuyao Water Conservancy Bureau, Yuyao 315402, China; yyhdh@126.com

* Correspondence: yanal@zjweu.edu.cn; Tel.: +86-0571-86929060

Abstract: Nowadays, ammonia nitrogen (NH_4^+) pollution gets more and more attention in drinking water sources. This study investigated the main behavior of biogeochemical NH_4^+ from groundwater to surface water in a hyporheic zone (HZ) sediment from a reservoir. The experiments were conducted using synthetic groundwater to investigate ammonium transformation. The results indicated that ammonium concentration decreased, apparently resulting from the influence of microbial oxidation and ion exchange with Ca^{2+} , Mg^{2+} , K^+ , and Na^+ . However, all the ammonium in the sediment was oxidized, then the adsorbed NH_4^+ became bioavailable by being released back when NH_4^+ concentration decreased in the aqueous phase. The results showed NH_4^+ behavior in a HZ where the aerobic and anaerobic environments frequently exchange, with different hydrological conditions controlled by a strong coupling between microbial activities, geochemistry, hydrology, and ion exchange.

Keywords: hyporheic zone; ammonium (NH_4^+) pollution; biological oxidation; ion exchange



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1. Introduction

Anthropogenic ammonium (NH_4^+) contamination has become a worldwide environmental problem [1,2]. From protecting and managing water resources, it is particularly important to understand the anthropogenic nutrient transformation between the groundwater and surface waters [3,4]. NH_4^+ is a common groundwater contaminant [5,6], primarily originating from septic systems and agricultural nitrogenous fertilizer practices [7], landfill leachate [8], and wastewater disposal practices [9]. As the seasons change and the dry season comes, the surface water level would be lower than the groundwater level, resulting in groundwater discharge to the surface water. At the same time, a lot of the different chemical compositions, including NH_4^+ , will ultimately be delivered to the surface water, which can affect aquatic ecosystem health and drinking water supplies [10].

Lots of studies have extensively focused on NH_4^+ transport processes in surface water, such as streams, rivers, and wetlands [11,12]. The hyporheic zone (HZ) is a biogeochemically active zone [13,14] because it contains strong hydrologic and biogeochemical gradients, and these gradients lead to different redox conditions, which influence the ammonium–nitrogen behavior of biological, chemical, and physical processes [15]. Nitrification, denitrification, and anammox are microbially mediated ammonium reduction pathways [16,17]. Nitrification represents the chemoautotrophic oxidation of NH_4 to NO_3^- [18,19]. Denitrification, on the other hand, is the reduction of dissolved NO_3^- to dinitrogen gas (N_2), which can subsequently return to the atmosphere [20]. Anammox is another way to oxidize NH_4^+ into N_2 through the key intermediates N_2H_4 from NH_4^+

to N₂ in anaerobic conditions, which is generally considered to be less important than denitrification, but in some benthic sediments, anammox can also be up to 60–80% of N loss [21,22].

Lots of studies have shown that the main reaction of ammonium is biogeochemical processes rather than ion-exchange processes [23,24], while some studies showed ion exchange processes were an important control in the dissolved cation transport in the HZ [25–27]. Gooseff and Mcknight's [28] research also showed that cation exchange was an important control in streams, and we believe that this may be important in ammonium biogeochemical processes in HZ too.

The objective of this paper is to explore ammonium transport processes in HZ sediments collected from the Shuangxikou reservoir under different conditions. The microbial community function and structure may be influenced by numerous processes acting over a wide range of spatial and temporal scales in the HZ. We propose that the chemical composition of water flowing through the HZ sediments, and the hydrologic gradient across the HZ, are important controls on the NH₄⁺ transport processes. Besides primary hydrological reactions, ion exchange processes also influence NH₄⁺ transport and inorganic chemistry loads in the HZ sediment. Thus, the results provide important evidence of systematically understanding NH₄⁺ biogeochemical transport and consumption in HZ sediments.

2. Materials and Methods

2.1. Synthetic Water and Sediments

The sediments were collected from the Shuangxikou reservoir, where NH₄⁺ is a contaminant in the benthic sediments. The sediment core was sieved at 2 mm in order to remove plant shatters and stones and then stored at 4 °C before use for the experiments. The sediment was added to the column in a 9.67% moist condition.

In this study, synthetic groundwater (SGW) mimicked the composition of natural waters in this sediment (Table 1). Based on the literature [25] and the determination of the experiment site's groundwater composition, the synthetic GW was made using deionized water (made by Millipore super-Q plus), and its pH was adjusted to 8.2 with CO₂. The SGW was continuously bubbled with nitrogen to squeeze out oxygen till there was no oxygen in the solution before using it for the experiment.

Table 1. Synthetic groundwater.

Chemical	M	mg/L	Ions	mM
NaHCO ₃	1.44×10^{-3}	121.0	Ca ²⁺	1
KHCO ₃	1.60×10^{-4}	16.0	K ⁺	0.16
MgSO ₄ (7H ₂ O)	5.10×10^{-4}	125.7	Mg ²⁺	0.51
CaSO ₄ (2H ₂ O)	3.50×10^{-4}	60.4	Na ⁺	1.44
CaCl ₂ (2H ₂ O)	6.50×10^{-4}	95.6	NO ₃ ⁻	0
KBr		37.2	pH	8.103

2.2. Column Experiment

The fine-grained sediment was packed in a small polymethyl methacrylate column under aerobic (column A) and anaerobic (column B) conditions (Table 2). The moist sediment condition in the column was 9.57%. Column packing was performed in small increments, with 1–1.5 cm thick layers, and a plastic hammer was used to tap the sediment to compact them, as in the natural condition. The top and bottom of the column were covered with porous plates (12 μm pore diameter and 0.30 cm thick) for passing influent and effluent solutions. After the experiment, the moisture content of the sediment was measured after drying (105 °C).

Table 2. Parameters used in the columns.

Column	A (Aerobic)	B (Anaerobic)
Length (cm)	10.5	10.7
A (cm ²)	5.31	5.31
V (mL)	55.74	56.81
Porosity	0.385	0.425
Pore Water (mL)	21.9	24.2
Flow Rate (mL/h)	12.13	11.21
Residence Time (h)	1.803	2.15
Darcy Velocity (cm/h)	2.28	2.11
Sample time (min)	25	25
Cation Exchange Capacity (CEC) (cmol/kg)	4.423	4.423

The SGW solution was injected from the bottom of the column at a constant flow rate of 0.02 mL/min to saturate the column slowly. The saturation process of the two columns took approximately 50 h. After the saturation, the SGW solution containing 2 mM NH₄⁺ was leached into the sediment in column A and column B at a constant flow rate of 0.2 mL/min. When the NH₄⁺ concentration reached 2 mM in the effluent, it is provided with SGW without NH₄⁺ in the influent solution. A high-performance liquid chromatography (HPLC) pump was used to control the flow rate. An automatic fraction collector was used to collect effluent samples. Every sample was collected during the first 2 days and every two samples were collected per pore volume at other times of the experiment. The samples were collected using 3 mL syringes and filtered by a 0.22 µm polytetrafluoroethylene (PTFE) syringe filter. Among the filtrate, 1 mL was used for the measurement of ammonium, 1 mL for anion, and 1 mL for cation.

Br⁻ (KBr 37.2 mg/L) was used in the column as a tracer to determine the dispersion coefficient and other mass transfer properties. It offset the concentration of K within the synthetic groundwater.

2.3. Sample Analysis

The cation exchange capacity (CEC) of the clay fraction and the sediment was measured using sodium acetate and NH₄OAc.

Ammonium chloride stock solution (1000 mg N/L) was prepared by dissolving 0.3819 g NH₄Cl powders (analytical reagent grade) in 100 mL deionized water. The standard samples were prepared to give NH₄⁺ concentrations of 0, 1, 5, 10, 20, and 40 mg/L by adding appropriate amounts of the NH₄Cl stock solution. The ammonium concentration of the samples was determined by HACH Ammonia Salicylate Reagent (high range) using a UV-2501 spectrophotometer (SHIMADZU, Kyoto, Japan) at 655 nm.

The effluent pH was determined immediately after sampling. The influent pH was 8.2. The cations (including K⁺, Mg²⁺, Ca²⁺, Na⁺) in the aqueous samples were measured using inductively coupled plasma-Mass Spectrometry (ICP-MS, Perkin-Elmer, Nexion350). The NO₃⁻, NO₂⁻, SO₄²⁻, Br⁻, and Cl⁻ concentrations in aqueous samples were determined with an ion chromatograph (ICS-1500).

3. Results

3.1. Characteristics of the Sediment and Column Samples

The sediment from the Shuangxikou reservoir consists of 45% >2 mm size materials and 55% of small particles (<2 mm), which were used in the experiments. After wet-sieving, 10.7% of silt/clay materials is responsible for the <2-mm size fraction. The silt/clay size materials contained both expansible (smectite, vermiculite) and nonexpansible (muscovite, biotite) clay minerals. The organic content of the sediment was 15.6 g/kg.

The CEC value of the studied sediment was 4.423 cmol/kg, and the concentrations of NH₄⁺-N, NO₃-N, and NO₂-N in the sediment, were 14.7, 59, and 4 µM, respectively. The

pH value of the influent SGW was 7.8–8.2, indicating that the solution was slightly alkaline. The parameters used in the columns are in Table 2. The porosity, pore water, flow rate, residence time and Darcy velocity (flow rate (mL/h) dividing by A (cm²)) were measured values. The Br (Kbr) breaking curve in columns A and B were symmetric (Figure 1). PV is the period of the experiment.

$$PV = \frac{\text{Samplpe time(d)} \times 24}{\text{Resident(h)}} = \frac{\text{Samplpe time(d)} \times 24 \times \text{flow rate(mL/h)}}{\text{pore water(mL)}}$$

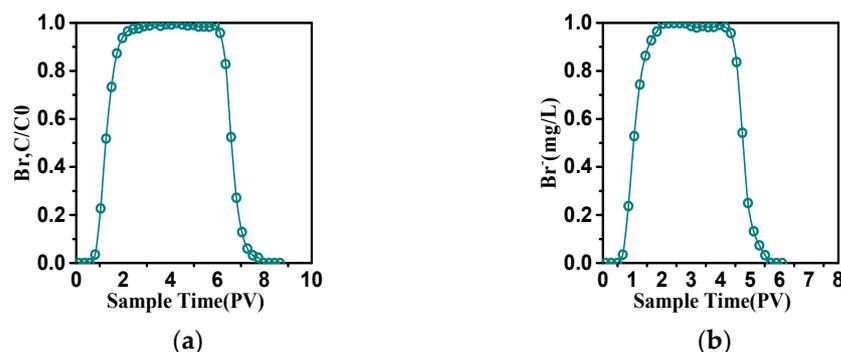


Figure 1. Br breakthrough curve. (a) Column A. (b) Column B.

3.2. NH₄⁺ Concentration Changes in SGW under Aerobic/Anaerobic Condition

The NH₄⁺ concentration was determined in the ground-water effluent to investigate the transfer behavior of NH₄⁺ in the sediment. The results showed that, in the beginning, no NH₄⁺ was detected in the effluent, indicating that the input NH₄⁺ was absorbed by the sediment (Figure 2). When the sediment adsorption was saturated, the NH₄⁺ concentration was in a rising state to the maximum value; then it decreased from its peak after the influent solution without NH₄⁺ was provided. It can be seen that the peak value of NH₄⁺ was 1.81 mM under the aerobic condition (Figure 2a), suggesting part of the ammonium was likely involved in the reaction, and the concentration was supposed to be 0.19 mm at least, while it can reach 2.0 mM under anaerobic conditions (Figure 2b). In other words, the behavior of NH₄⁺ passing through the column was different under different conditions, and it is more reactive by matching the maximum of NH₄⁺ under aerobic conditions (Figure 2a).

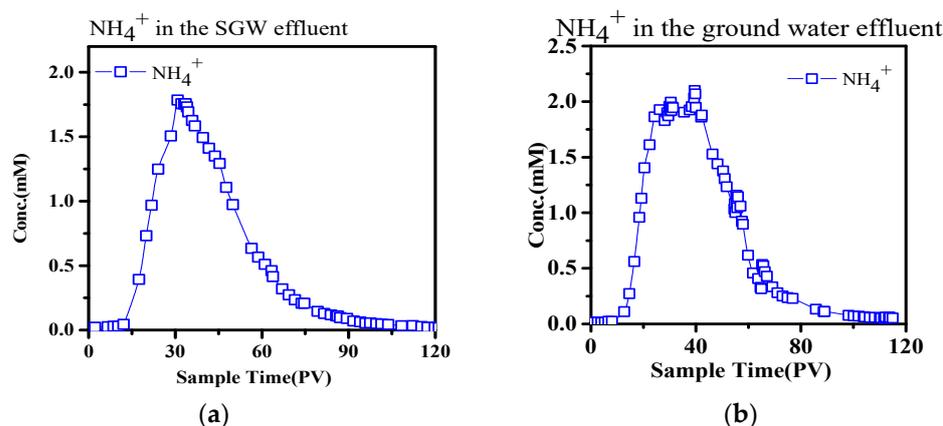


Figure 2. The kinetic curves of NH₄⁺ in the ground-water effluent under aerobic conditions (a) and anaerobic conditions (b).

3.3. NH₄⁺ Microbial Oxidation in SGW under Aerobic/Anaerobic Condition

NO₃⁻, NO₂⁻, and N₂H₄ concentrations were measured in the ground-water effluent to investigate the transfer behavior of NH₄⁺ in the sediment. The results showed oxidation-reduction reactions, such as nitrification and other biological processes, are important in

the migration and transformation process of NH_4^+ from the ground-water to the surface water. Under aerobic conditions, the NH_4^+ concentration decreased continuously. NO_2^- was an intermediate product during the NH_4^+ oxidation as its concentration first increased and then decreased with time, and NO_3^- was the final product. Namely, in the presence of oxygen, it occurred to nitrification, but the biological reaction did not happen immediately, or the degree of biological reaction was mild; for the reaction products NO_3^- were not detected immediately (Figure 3a). NH_4^+ was oxidized to NO_2^- , and there was no NO_3^- (Figure 3b); obviously, it showed the denitrification process had existed in the absence of oxygen. In addition, N_2H_4 was detected in the experiment (Figure 3c), even though the N_2H_4 concentration was very low, as we know it is the key intermediate from NH_4^+ to N_2 in the anaerobic ammonium oxidation (anammox) process. It can be hypothesized that the anammox reactions took place, except denitrification, under anaerobic conditions.

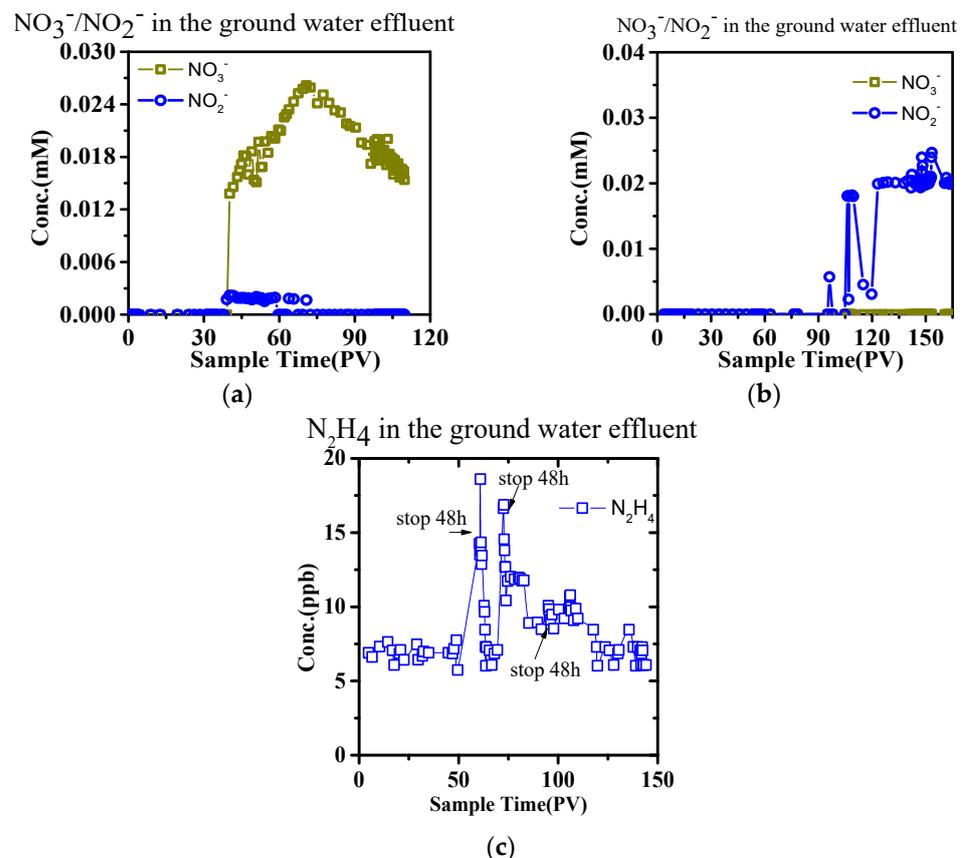


Figure 3. The kinetic curves of NO_3^- and NO_2^- in the ground-water effluent under aerobic conditions (a), anaerobic conditions (b), and N_2H_4 in the effluent under anaerobic conditions (c).

3.4. Ion Exchange for NH_4^+ in SGW under Aerobic Condition

The Ca^{2+} , Mg^{2+} , K^+ , and Na^+ concentrations were analyzed to investigate the effect of ion exchange on the transformation of NH_4^+ . The results indicated that the Ca^{2+} , Mg^{2+} , K^+ , and Na^+ ion exchange process with each other was evident, and they could affect NH_4^+ behavior (Figures 4 and 5). The dynamic trend of ion exchange with Ca^{2+} and Mg^{2+} was similar, which was opposite to the NH_4^+ concentration trend in the ground effluent. However, the trend of K^+ concentration was different from Ca^{2+} and Mg^{2+} . From the results, it provided important insights into NH_4^+ behavior in HZ; namely, ammonium ion exchange and the rate of oxidation were affected by the groundwater with chemical condition exchange.

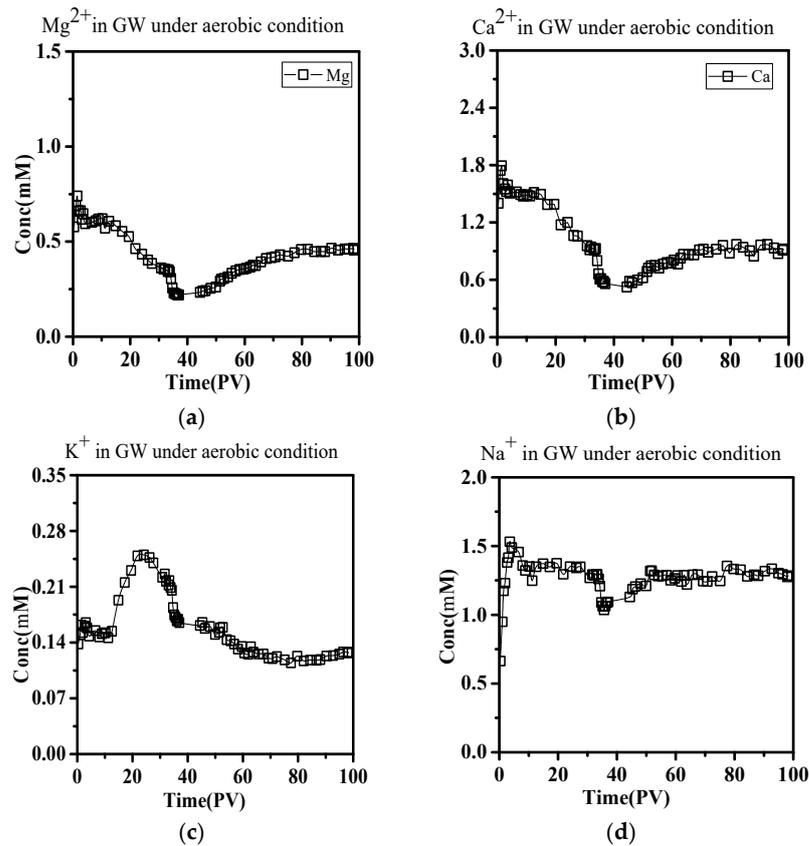


Figure 4. The ion exchange kinetic curves of Mg^{2+} (a), Ca^{2+} (b), K^+ (c) and Na^+ (d) with NH_4^+ in SGW under aerobic conditions.

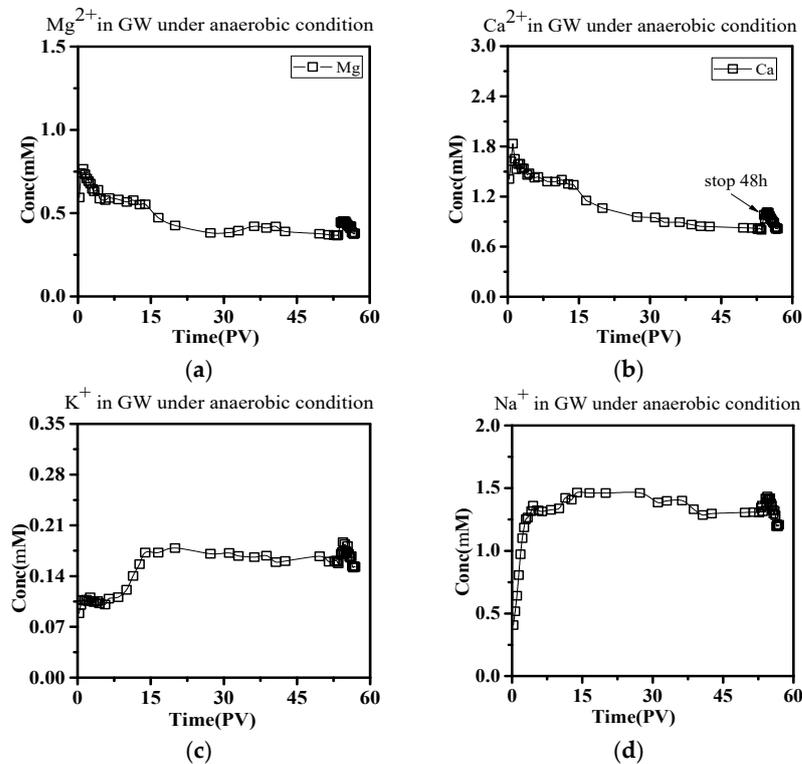


Figure 5. The The ion exchange kinetic curves of Mg^{2+} (a), Ca^{2+} (b), K^+ (c) and Na^+ (d) with NH_4^+ in GW under anaerobic conditions.

4. Discussion

The HZ is a special biological community system, so a series of reactions will occur when various external pollutants enter the HZ. According to the literature [29,30], there exist at least four reactions for ammonia nitrogen in sediment, including ammonification (nitrification and anammox), adsorption (ion exchange), DNRA—dissimilatory nitrate reduction to ammonium, and assimilatory (organic N). Apparently, depending on the geochemical properties of sediments and the properties of the groundwater flow system in the HZ, the migration and transformation process of NH_4^+ in the HZ is affected not only by the microbial-induced phase transition but also by physical and chemical processes, such as adsorption (including cation exchange). Thus, the behavior of NH_4^+ was a dynamic process. The Redox environment (DO concentration), pH value, temperature, electron donor (organic carbon, reducing iron or sulfur), microorganism, salinity, redox potential, substrate concentration, ion exchange, and other factors may affect the activity of microbes and then affect the migration and transformation of ammonia in sediments. However, it was not clear which one is the key factor affecting the behavior of ammonia in the HZ. This study found that once NH_4^+ enters the HZ, the microbial oxidation-reduction reaction and cation exchange would occur. Under different hydrological conditions, NH_4^+ shifted into NO_3^- in the presence of oxygen, and NH_4^+ shifted into NO_2^- , even N_2H_4 , under anaerobic conditions, obviously confirming that the transport and transformation of NH_4^+ were associated with microbial activities. Nevertheless, the effect of nitrification, denitrification, and anammox was proportional to NH_4^+ concentration. Moreover, the ion exchange reactions shifted NH_4^+ to the sorbed phase with Ca^{2+} , Mg^{2+} , K^+ , and Na^+ . As the result of ion exchange adsorption of NH_4^+ , the bioavailability of NH_4^+ was reduced by decreasing the aqueous NH_4^+ concentration. However, the sorbed NH_4^+ desorbed with the oxidation of NH_4^+ , and all NH_4^+ was oxidized in the sediment. The results showed that the adsorption of NH_4^+ and microbial oxidation interacted with each other in the sediment systems. The NH_4^+ temporal changes and its dissolved concentration with time were collectively controlled by the mutual interactions. This will lead to NH_4^+ behavior being collectively controlled by a strong coupling between microbial activities, ion exchange geochemistry, and hydrology. In addition, nitrates can be reduced by microorganisms to produce NH_4^+ that may be carried in groundwater. Therefore, when simulating and understanding NH_4^+ , or more generally, N behavior, the complex coupling requires careful consideration between NH_4^+ oxidation, sorption, and production from microbial reduction and ion exchange sites.

In summary, the HZ is a complex and changeable environmental system, and the migration and transformation of ammonia nitrogen is also a complex biogeochemical coupling process in HZ sediment.

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