Nitrogen transport and transformation in artificial groundwater recharge with treated reclaimed municipal wastewater through river utilization

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ABSTRACT

Nitrogen pollution in river-based artificial groundwater recharge using reclaimed municipal wastewater poses a major threat to groundwater drinking water supplies in Beijing, China. Laboratory leaching column experiments simulating recharge were conducted to study nitrogen transformation, transport and leaching. Representative soil vadose zone media from three parts of the Chaobai River were used as filler for the three columns. The media consisted mainly of water-permeable gravel sand, fine sand and less-permeable silty clay, which are the typical streambed in the Huabei plain. The results showed that the attenuation of total nitrogen (TN) was in the order of silty clay column > fine sand column > gravel sand column, which followed the first-order kinetics. The TN attenuation mass was 6.36, 2.05 and 1.33 mg 100 g⁻¹, respectively. The TN decay rate constants were 2.1, 1.7 and 1.6 m⁻¹, respectively. The NO₃⁻-N attenuation mass was 7.68, 1.76 and 1.17 mg 100 g⁻¹, respectively. The denitrification rate constants were 6.5, 3.5 and 2.6 m⁻¹, respectively. The inflection points of TN concentration at different depths were 0.4, 0.5 and 0.8 m, respectively. The same trend was observed in NO₃⁻. The content of NH₄⁺-N was in the range of 0-4 mg L⁻¹ in the early experimental period, while NH₄⁺ was not detected after 15 d. Nitrogen transformation was affected by water temperature; when the temperature was below 5 °C, the conversion of nitrogen did not change significantly with depth and time. Groundwater nitrogen pollution was related to the adsorption and degradation capacity of the soil vadose zone media. To avoid or minimize possible nitrogen contamination of groundwater in artificial groundwater recharge areas, the amount of TN in treated reclaimed municipal wastewater has to be determined and minimized by optimizing reclaimed water treatments and enhancing the ecological purification function of rivers.

INTRODUCTION

China is severely suffering from water shortages, especially in northern arid areas. Artificial groundwater recharge with reclaimed water provides many advantages, such as groundwater supplementation, mitigation of declining groundwater levels, and storage of reclaimed water for later usage [1]. The artificial recharge of several aquifers was successfully accomplished at many locations around the world [2-5]. In most of the arid regions in northern China, river surface runoff comes from secondary wastewater treatment plant effluents, which can impact groundwater quality [6]. The concentration of total nitrogen (TN) in the secondary wastewater treatment plant effluent was between 15 and 20 mg L⁻¹ [7], and even tertiary-treated reclaimed municipal wastewater contains an appreciable concentration of nitrogen, approximately 5-15 mg L⁻¹, which might cause nitrogen pollution in artificially river-recharged aquifers in this area. High nitrogen
accumulation and the free flow of water in the soil profile are pre-conditions for nitrogen leaching into groundwater [8]. Nitrogen can move downward with the percolation of water and might lead to nitrogen pollution in groundwater. Excessive nitrate in groundwater is a significant public health problem in northern China because drinking water in these areas comes from groundwater. The US drinking water standard for nitrate-nitrogen is 10 mg L\(^{-1}\) (EPA, 1980), the same as standards for drinking water quality in China (GB 18918-2002). Excess nitrate can contribute to eutrophication and can also be toxic to some aquatic organisms [9].

In the vadose zone, nitrogen species consist of ammonium, nitrite, nitrate, and organic nitrogen. The predominant form is determined by factors such as pH, DO (dissolved oxygen), temperature, and microbial activity. Therefore, nitrogen transformation and transport during artificial groundwater recharge is a complicated process. Calculation of the N balance is a potentially useful method for predicting the risk of nitrate leaching into groundwater [10]. In this study, a lab-scale leaching column was designed to simulate aquifer recharge to further investigate the fate and transformation of nitrogen. The purpose of the present study was to simulate nitrogen transformation and transport, thus supporting the development of nitrogen pollution prevention and control measures during river-based artificial groundwater recharge using reclaimed municipal wastewater in China.

**MATERIALS AND METHODS**

1. **Vadose Zone Soil Samples**

The Chaobai River vadose zone aquifer media were mainly composed of water-permeable gravel sand in the northern section, fine sand in the middle section and less-permeable silty clay in the southern section, in Beijing of Huabei plain. Simulation columns numbered 1, 2, and 3 were filled with representative soil vadose zone media from the three parts of the ChaoBai River, which is a typical streambed in northern China (Table 1).

<table>
<thead>
<tr>
<th>Medium category</th>
<th>CEC (cmol kg(^{-1}))</th>
<th>TOC (%)</th>
<th>Clay mineral composition (%)</th>
<th>Clay content (%)</th>
<th>Bulk density (g cm(^{-3}))</th>
<th>Effective porosity</th>
<th>Permeability coefficient (m d(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>gravel sand</td>
<td>0.03</td>
<td>0.18</td>
<td>10.4</td>
<td>10.9</td>
<td>2.02</td>
<td>0.12</td>
<td>1.13</td>
</tr>
<tr>
<td>fine sand</td>
<td>0.03</td>
<td>0.18</td>
<td>14.4</td>
<td>8.2</td>
<td>1.67</td>
<td>0.14</td>
<td>1.42</td>
</tr>
<tr>
<td>Silty clay</td>
<td>0.10</td>
<td>0.63</td>
<td>33.7</td>
<td>32.5</td>
<td>2.13</td>
<td>0.12</td>
<td>1.05</td>
</tr>
</tbody>
</table>

The hydrogeological cross-sectional north-to-south view (Fig. 1) shows that the shallow aquifers stratigraphic number of 80 m increased from north to south as the lithology of the aquifer changed from gradient gravel to fine sand. The overall lithologies of the river were mainly water-permeable gravel sand in the northern section, fine sand in the middle section, and less-permeable silty clay in the southern section.

2. **Raw Water**

Raw water used for lab-scale experiments was tertiary effluent from the YinWenJiChao Reclaimed Water Treatment Plant in Beijing (Table 2). The process stages are ozone oxidation, a membrane bioreactor, chemical phosphorus removal and disinfection. The water samples for this study were collected and stored in the dark for a maximum of 3 d.

2.1. **Lab-scale column recharge system**

The lab-scale installations are shown schematically in Fig. 2. From the feed tank, the raw water was pumped into three aquifer treatment columns with the same flow rate. The three aquifer treatment columns were the same size, 0.20 m in diameter and 1.55 m in height, with a packed-bed height of 1.2 m and a supporting layer height of 0.15 m. They were operated under saturated conditions to simulate aquifer behavior during river-based groundwater recharge with reclaimed municipal wastewater. The flow rate was approximately 1 m d\(^{-1}\). The background leaching system was the same size as the lab-scale columns. Samples from the background leaching system were taken every 7 d, while for lab-scale column recharge system every 3 d. The two systems operated for 3 to 7 months. The room temperature was 20 ± 5 °C.

2.2. **Analytical methods**

The concentration of NH\(_4\)^+ was determined via a colorimetric method, NO\(_3^-\) and NO\(_2^-\) concentrations were determined with an ion analyzer chromatographic system (ICS-2000 Dionex, USA). The concentration of TN was determined by the alkaline potassium

<table>
<thead>
<tr>
<th>Material</th>
<th>NH(_4)^+</th>
<th>TN</th>
<th>NO(_3^-)-N</th>
<th>NO(_2^-)-N</th>
<th>Na(^+)</th>
<th>K(^+)</th>
<th>Ca(^{2+})</th>
<th>Mg(^{2+})</th>
<th>Cl</th>
<th>SO(_4^{2-})</th>
<th>HCO(_3^-)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.0 ± 2.2</td>
<td>6.7 ± 8.5</td>
<td>4.9 ± 9.5</td>
<td>0.2 ± 1.5</td>
<td>99</td>
<td>18</td>
<td>63</td>
<td>24</td>
<td>93</td>
<td>69</td>
<td>317</td>
</tr>
</tbody>
</table>
persulfate method using ultraviolet spectrophotometry (GB11894-89).

RESULTS AND DISCUSSION

1. Nitrogen Contamination in Leachate in Background Leaching Experiment

The concentrations of TN, NO$_3^-$ and NH$_4^+$ over time in background leaching tests are shown in Fig. 3. Different concentrations of TN were detected in the leachate of the three background leaching columns. The concentration of TN followed the same trend in all three leaches. The TN concentration decreased quickly over the first 10 d. Subsequently, the change in TN concentration was more gradual from 10 to 60 d. The TN concentrations were all less than 0.1 mg L$^{-1}$ from 60 to 80 d. The TN concentrations of columns # 1 and 3 were from 0-0.8 mg L$^{-1}$ after 12 d, while the TN concentration of column # 2 was between 0-0.7 mg L$^{-1}$ after 21 d, a slight lag. This was probably due to the different characteristics of the media packed in the columns. In the leachate, the TN concentration of column # 1 is the highest in the three columns. During leaching of the blank sample, the highest TN concentration was detected in the leachate of column # 1. The TN includes inorganic nitrogen species such as NO$_3^-$, NO$_2^-$, and NH$_4^+$ and organic nitrogen found in proteins, amino acids, organic amines, etc. [11], while the TN was mainly composed of NH$_4^+$ at the beginning of the experiment.

After 80 d, TN concentrations increased, especially for column # 3. However, the concentrations were all less than 0.8 mg L$^{-1}$. Due to the concentration of NO$_3^-$-N, NO$_2^-$-N and NH$_4^+$-N were less than 0.05 mg L$^{-1}$; the TN mainly included organic nitrogen, which came from biofilm shedding from the soil filler media. Because microbial adhesion was poor in column # 3, which had a large porosity, the biofilms easily fell off.

In column # 3 and 2, NO$_3^-$-N and NH$_4^+$-N were occasionally detected below 0.04 mg L$^{-1}$. However, the result was different in column # 1. For the first 11 d, the concentration of NH$_4^+$-N was relatively high, nearly equal to TN, while the concentration of NO$_3^-$-N was below 0.09 mg L$^{-1}$. NO$_3^-$-N was detected between 45 and 60 d, and the highest concentration reached was 0.09 mg L$^{-1}$. The experiments were carried out in the pH range of 7 to 8.5, which was conducive to nitrification and converted NH$_4^+$ into NO$_3^-$ by nitrifying bacteria; furthermore, NO$_3^-$ would then enter the groundwater more easily during artificial recharge.

2. TN Contamination in Groundwater

TN accumulation in the leachate from different soil profiles showed high variance among different depths in each recharging system using treated reclaimed municipal wastewater. TN concentrations ranged from 0.1 to 8.3 mg L$^{-1}$ after the second day in the three leaches and varied greatly at different depths. On the first day, there was no effluent because the solution did not fully penetrate the columns. On the second day, the TN concentration was high in the effluent at different depths, which was different from other days. The TN concentrations in the leaching of the upper layer were higher than in the raw water, which was due to the dissolution of soil nitrogen in the three columns. The TN concentrations gradually decreased with increasing depth, but the degradation
rates were different in the three columns. The results showed that the attenuation effect of TN was in the order of silty clay column > fine sand column > gravel sand column (Fig. 4). The inflection points of TN concentration at different depths were 0.4, 0.5 and 0.8 m. In column # 3, the migration depth of TN was the maximum. This was closely related to the soil texture of the filler media and its physicochemical properties. TN concentration decreased mainly due to the physical adsorption of NH$_4^+$ by the medium, nitrification of NH$_4^+$, and the denitrification of nitrate and nitrite. In column # 3, the coarse gravel sand filler contained less organic carbon and clay content, which resulted in a smaller CEC (cation exchange capacity) value and consequently poorer adsorption and biodegradation of TN. Denitrification is mainly controlled by microbial activities, which requires available organic carbon and an absence of oxygen [12]. However, in column # 1, the silty clay filler contained a higher organic carbon and clay content, which resulted in a higher CEC value and improved removal of TN.

3. TN Attenuation

Figure 5a shows the fitting curve of TN attenuation rate constants in the three columns. The average TN concentration at different depths is represented by $C_i$ and the influent concentration is $C_i$. The TN decay rate constants were 2.1, 1.7 and 1.6 m$^{-1}$ for column 1, 2 and 3, respectively, which were calculated by fitting curves to the concentration with relation to the depth. The results showed that the attenuation of TN was in the order of silty clay column (# 1) > fine sand column (# 2) > gravel sand column (# 3).

It can be seen from Fig. 5a that the curves were better fitted to columns 2 and 3 than to column 1. Because the concentration fell too fast in column 1, in which silty clay had a strong adsorption capacity, it was not consistent with ideal first order fitting curve dynamics. In column 3, the gravel sand had a weak adsorption capacity and fewer biofilm, in which TN attenuation rate did not change significantly with the increasing depth.

Figure 6a shows the TN attenuation mass (Eq. 1) in the three columns; the outflow was approximately 2.48 L d$^{-1}$ in each column. This rate best simulated the
actual water infiltration in the Chaobai River, where the infiltration rate was approximately 1 m d⁻¹. The TN attenuation mass was 6.36, 2.05 and 1.33 mg 100 g⁻¹, for column 1, 2 and 3, respectively.

TN attenuation of unit mass = \( \frac{(C_{in1} - C_{out1})Q_1 + (C_{in2} - C_{out2})Q_2 + \cdots + (C_{inN} - C_{outN})Q_N}{\text{Total weight of soil}} \)  

\( C_{inN} \): influent TN concentration on day N  
\( C_{outN} \): effluent TN concentration on day N

4. Nitrate Contamination in Groundwater

The NO₃⁻ accumulation in the leachate from different soil profiles showed high variance among different depths in each recharging system. The results showed that the attenuation effect of NO₃⁻ was in the order of silty clay column > fine sand column > gravel sand column (Fig. 7). The variation of the NO₃⁻ concentration with depth was different than that of TN. On the first day, there was no effluent because the solution did not penetrate the columns. On the second day, the NO₃⁻ concentration was high in the influent and effluent of different depths, which was different from other days. From day 8 to 72, an obvious attenuation of NO₃⁻ was observed at various soil depths. The inflection points of the nitrate-N concentration at different depths were 0.4, 0.4 and 0.8 m, for column 1, 2 and 3, respectively. The trend was similar to that of TN, although the concentrations were much lower. The NO₃⁻-N concentration was below 0.5 mg L⁻¹ at depths greater than 0.6 m in column # 1 after the second day. The concentration of NO₃⁻ was much lower than that of the influent at depths greater than 0.4 m in all three columns after the second day because DO concentration decreased with increasing depth, which resulted in denitrification. The attenuation rate of NO₃⁻ was positively correlated with organic matter content and soil CEC.

5. Nitrate Attenuation

Figure 5b shows the fitting curve of NO₃⁻ attenuation rate constants in the three columns. The average NO₃⁻-N concentration at different depths is represented by \( C_o \), and the influent concentration is \( C_i \). The NO₃⁻-N decay rate constants were 6.5, 3.5 and 2.6 m⁻¹, for column 1, 2 and 3, respectively, which were calculated by fitting curves to the concentration with relation to the depth. The attenuation effect of NO₃⁻ was the same as that of TN, in the order of silty clay column (# 1) > fine sand column (# 2) > gravel sand column (# 3).

It can be seen from Fig. 5b that the values of \( R^2 \) for NO₃⁻ were higher than for TN in all three columns. The NO₃⁻ decay rates were higher than those of TN,
and the concentration of NO$_3^-$-N was below 6.3 mg L$^{-1}$ except for in the influent on the first day. The DO concentration decreased with the increasing soil depth, which resulted in weakened nitrification and enhanced denitrification.

Figure 6b shows the NO$_3^-$ attenuation mass in the three columns. The NO$_3^-$-N attenuation mass was 7.7, 1.8 and 1.2 mg 100 g$^{-1}$, for column 1, 2 and 3, respectively. The attenuation effect of NO$_3^-$ had the same trend as TN. It can be seen that the attenuation mass of nitrate was slightly less than that of TN in columns 1 and 2 because there was a substantial amount of organic nitrogen. The organic nitrogen present in the water was previously confirmed by filtration through 0.45-μm membranes. TN reduction was mainly due to denitrification. However, the amount of NO$_3^-$ attenuation mass was higher than that of TN in column 1 because of TN leaching from the soil. In the blank soil leaching experiments, the concentration of TN in column # 1 was approximately two times that of columns # 2 and 3. NO$_3^-$ can be attenuated by adsorption or biodegradation, while organic nitrogen might be converted to inorganic nitrogen. The conversion of organic nitrogen did not reduce TN, which resulted in the lower attenuation rate.

6. Influence of Temperature on Nitrogen Transformation and Transport

The concentrations of TN and NO$_3^-$ at different depths of the vertical infiltration recharge columns were greatly affected by temperature as shown in Fig. 8. When the temperature was below 15 °C, the change in the TN and NO$_3^-$ concentrations was insignificant. The concentrations at different depths were almost equal to the influent concentration. With increasing temperature, the concentration of nitrate and TN significantly decreased with increasing depth. Denitrification was more obviously affected by temperature. A suitable temperature for nitrification is 16-35 °C; when the temperature is too high or too low, nitrification is weakened. When the temperature was less than 0 °C or more than 40 °C, nitrification almost stopped [13]. The highest denitrification rate was reached when the water temperature was 35 °C. Little change was observed in the denitrification rate from 35-60 °C. Because nitrification and denitrification are affected by temper-
ature, nitrogen transformation did not significantly change with depth at low temperatures [14].

Because nitrification and denitrification rate in reclaimed municipal wastewater treatment plant is also affected by water temperature, the effluent concentrations of TN and NO₃⁻ were higher in winter than in summer [15]. Thus, the TN and NO₃⁻ contents in recharge water were higher in winter than in summer.

CONCLUSIONS

The pollutant removal efficiency of nitrogen was significantly higher for silty clay than for gravel sand and fine sand. The TN decay rate constants for the silty clay column, fine sand column and gravel sand column were 2.1, 1.7 and 1.6 m⁻¹, respectively. The NO₃⁻ decay rate constants were 6.5, 3.5 and 2.6 m⁻¹, respectively. Therefore, reclaimed wastewater recharge groundwater should be applied to an aquifer with a high silty clay content. Moreover, nitrification and denitrification are greatly affected by temperature, which resulted in a very poor nitrogen removal capability in underground soil aquifers at low temperatures. For this reason, artificial groundwater recharge using reclaimed municipal wastewater should be supervised during the winter to avoid nitrogen accumulation in the groundwater. Although using rivers to artificially recharge an aquifer with tertiary-treated wastewater is an effective method, to avoid or minimize possible nitrogen contamination of groundwater in artificial groundwater recharge areas, the amount of TN in treated reclaimed municipal wastewater must be determined and minimized by optimizing reclaimed water treatments and enhancing the ecological purification function of rivers.

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REFERENCES

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