Process and influencing factors of N removal in grassed paving system by $^{15}$N tracing analysis
Tao Chen, Ben Zhang, Jianfeng Li and Mengzi Han

ABSTRACT
The effects of nitrogen (N) transformation and transportation processes under different soil pH, plant species and rainfall intervals were studied by using a $^{15}$N isotope tracing technique in a simulated grassed paving system. The results showed that the grassed paving systems with three plants including Zoysia matrella (Z), Eleusine indica (E) and Liriope graminifolia (L), were effective at removing NH$_4^+$-N, NO$_3^-$-N, total nitrogen (TN), and chemical oxygen demand (COD) from rainfall runoff. However, there was no significant difference of TN removal among these three-plant species and a certain soil pH. The experiment showed that when the rainfall interval was 5 days, the grassed paving system could remove 65.8–76.8% of runoff TN in 17 detention days. The N conversion was dominated by soil adsorption, plant uptake, microbial assimilation, and nitrification during 0–5 d. While the main N reactions were through denitrification and dissimilatory nitrate reduction to ammonium during 5–14 d.

Key words | $^{15}$N isotope tracing, denitrification, DNRA, grassed paving system, nitrification

INTRODUCTION
In recent years, a large area of hardened pavement in the city has changed the natural circulation properties of the soil, vegetation and infiltration layer, and reduced the system integrity of the urban watershed (Hou et al. 2014). Previous pavement was a typical measure to reduce rainwater runoff and pollutant load by reducing the urban impervious area to alleviate the problem of urban rainwater runoff (Crookes et al. 2017). As one of the common pervious pavements, the grassed paving system was composed of a permeable base layer filled with gravel, a permeable sub-base layer filled with graded aggregate, a leveling layer filled with sand and a surface layer of concrete or plastic grids with vegetation (Starke et al. 2011). Due to the functions of protecting the surface ecology and enhancing the ground strength, grassed paving was increasingly used in parks and residential areas, parking and a variety of leisure venues.

Grassed paving systems have shown many beneficial features such as removal of rainwater pollutants, recharge of groundwater and the reduction of runoff volumes and peak flows (Mohammadinia et al. 2018). The plastic pavers filled with grass could reduce runoff volumes by 95% compared with a conventional asphalt surface (Dreelin et al. 2006). The peak discharge was reduced by 40–55% for the ecotrihex paver and 45–60% for the Turf cell. Meanwhile, the removal rates of total nitrogen (TN) loads were 64–74% for the ecotrihex paver and 78–81% for the Turf cell (Jayasuriya & Kadurupokune 2013).

The removal of N pollutants in grassed paving system mainly relies on soil adsorption, absorption by plants, microbial assimilation, dissimilatory nitrate reduction to ammonium (DNRA), nitrification and denitrification (Maltaiolandry-Landry et al. 2009), thus it may be affected by different environmental conditions. Soil pH was one of the major factors affecting soil chemical, physical and biological properties. As microbially mediated processes, soil N transformations are expected to be strongly influenced by soil pH (Cheng et al. 2015). Moreover, it has been shown that the choice of plant species may be important for N removal, particularly where the biofilter media contain significant amounts of in situ N (Payne et al. 2014). Also, rainfall intervals (RI) affect the system’s pollutant removal capacity by affecting the degree of contaminant accumulation in the system.

The purpose of this laboratory study was to explore the contributions of soil adsorption, plant uptake, microbial assimilation, DNRA, nitrification and denitrification in a...
grassed paving system under the above-mentioned conditions by isotope tracking analysis, and to quantify the performance as well as N transformation and transportation processes in it.

**METHODS**

**Experiment design**

**Column design**

The experiment column unit was a square box structure made of plexiglass and PVC drains, as in Figure 1. The 400 mm filter layer consisted of sandy loam layer (consists of 40% loam, 40% coarse sand and 20% fine sand), a 180 mm sand transition layer (30 mm medium sand, diameter 0.25–0.50 mm; 150 mm graded broken stone, diameter 0.075–26.5 mm), and a 150 mm gravel layer (diameter 20–30 mm) for drainage with an embedded drain pipe which was connected to the sampling outlet.

The 54 biofilter columns were divided into three groups based on their vegetation type. The filters were planted with either Zoysia matrella, Eleusine indica, or Liriope graminifolia, labelled as Z, E and L, because they are commonly used in grassed paving systems. Then each group was divided into three groups of six replicates based on their soil pH (6.40, 7.17 and 8.24), numbered as Z₆.₄₀, Z₇.₁₇, and Z₈.₂₄, etc.

These six replicates were destroyed for sampling on the 2nd, 5th, 7th, 10th, 13th and 17th days. The columns were placed in a greenhouse located in Beijing (China).

**Stormwater dosing**

With reference to the measured road rainfall runoff pollutant data in Beijing, synthetic stormwater of typical concentrations for the target pollutants was used by mixing $^{15}$N isotope-labeled K$_{15}$NO$_3$, NH$_4$Cl, glucose reagent with deionized water to consistently match the target pollutant concentrations (Table 1). Each column was filled with water on the 1st and 5th day to simulate a rainfall interval of 5 days.

**Parameters measured**

The original soil was neutral (pH = 7.17) and then divided into three groups, one was adjusted to acid soil (pH = 6.40) with plaster (CaSO$_4$), one was adjusted to alkaline soil (pH = 8.24) with plant ash (K$_2$CO$_3$), and the other was kept neutral. The test of soil pH was performed according to Figure 2(a). After construction and planting, the biofilter columns were leached to simulate the saturation process in the structural layers and to remove the original salts and unstable organic matter in the soil and fillers. Therefore, the response of the systems to stormwater during the dosing and sampling period could be measured.

![Figure 1](https://iwaponline.com/wst/article-pdf/78/3/611/482228/wst078030611.pdf) | Design of laboratory-scale biofilter columns of (a) the grassed paving system in the greenhouse, (b) standard column design with outflow at the bottom.
After the pretreatment, the filters were run for 17 days. Samples from biofilter columns for analyzing were performed according to Figure 2(b).

The concentrations of NO$_2$-N, NO$_3$-N, NH$_4$+ -N, TN and chemical oxygen demand (COD) in the leachate and soil extracts were determined by HACH DR6000 UV spectrophotometer. The isotopic abundance of 14N-NO$_3$, 14N-NH$_4$+, 15N-TN, 15N-NO$_3$, 15N-NH$_4$, 15N-TN in the leachate and soil extracts was evaluated by isotope mass spectrometer. Soil oxidation-reduction potential (ORP) was measured by STEH-100 soil oxidation-reduction potentiometer. Soil moisture content (MC) and temperature were determined by Decagon EM50. And soil pH was determined by soil ZD-06 pH.

### Data calculation and analysis

All isotope test results use Equations (1) and (2) to convert isotope abundances of 15N to atomic percentages.

The results of the mass spectrometer are expressed in $\delta^{15}$N(‰) and calculated as follows:

$$\delta^{15}N(‰) = \left( \frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) \times 1000 \quad (1)$$

The 15N isotope accounts for the percentage of N atoms in the sample (atom%), which is derived from the following formula:

$$\text{atom}\% = 100 \times \frac{R_{\text{sample}}}{R_{\text{sample}} + 1} \quad (2)$$

where $R_{\text{sample}}$ is 15N/14N of the sample; $R_{\text{standard}}$ is standard 15N/14N;

The calculation of the 15N content in a solid sample, such as plants and soils, is calculated as follows:

$$15N_{s} = m_{s} \times (\text{atom}\%_{s} - \text{atom}\%_{b}) \times TN_{s} \quad (3)$$

where $m_{s}$ is solid sample dry weight (mg); atom$%_{s}$ is mass percentage of 15N atoms in solid sample; atom$%_{b}$ is the background mass percentage of 15N atoms in solid sample; TN$%_{s}$ is mass percentage of TN in solid sample;

The 15N content of 15N-NH$_4$ and 15N-NO$_3$ in leachate, is calculated as follows:

$$15N_{l} = V_{l} \times (\text{atom}\%_{l} - \text{atom}\%_{b}) \times C_{l} \quad (4)$$

where $V_{l}$ is the total volume of leachate (L); atom$%_{l}$ is percentage of 15N atoms in leachate samples; atom$%_{b}$ is N natural abundance of 0.365%; $C_{l}$ is N concentration in leachate (mg/L).

### Table 1

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Inflow concentration</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>7.4</td>
<td>Sulphuric acid (H$_2$SO$_4$)</td>
</tr>
<tr>
<td>NO$_3$-15N</td>
<td>5.0 mg/L</td>
<td>Potassium nitrate (K$^{15}$NO$_3$)</td>
</tr>
<tr>
<td>NH$_4$+ -N</td>
<td>5.0 mg/L</td>
<td>Ammonium chloride (NH$_4$CL)</td>
</tr>
<tr>
<td>TN</td>
<td>10.0 mg/L</td>
<td>N addition</td>
</tr>
<tr>
<td>COD$_{ex}$</td>
<td>150.0 mg/L</td>
<td>Glucose (C$<em>6$H$</em>{12}$O$_6$)</td>
</tr>
<tr>
<td>C/N</td>
<td>15</td>
<td>–</td>
</tr>
</tbody>
</table>

Figure 2 | Pretreatment for analysis of (a) planting soil pH, (b) biofilter columns.
The $^{15}$N content of soluble organic nitrogen is $^{15}$N-TN minus $^{15}$N-TIN ($^{15}$N-NH$_4^+$ + $^{15}$N-NO$_3^-$) in leachate. Similar for $^{14}$N content of soluble organic nitrogen.

The N material balance in this experiment includes the following:

1. N-NO$_3^-$ and N-NH$_4^+$ in leachate indicate the amount of non-participating parts of N.
2. Soil adsorption. The contents of $^{15}$N-NO$_3^-$ and $^{14}$N-NH$_4^+$ in the soil were measured to indicate the amount of $^{15}$N-NO$_3^-$ and $^{14}$N-NH$_4^+$ adsorbed to the soil.
3. Soil microbial assimilation. The sum of $^{15}$N-organic in soil and effluent was calculated as microbial assimilation of $^{15}$N-NO$_3^-$ and $^{14}$N-NH$_4^+$.
4. Plant uptake. $^{15}$N in each plant indicates the amount of $^{15}$N-NO$_3^-$ absorbed by plant, and the difference of $^{14}$N content in each plant before and after the test indicates $^{14}$N-NH$_4^+$ absorbed by plant.
5. DNRA. The sum of $^{15}$N-NH$_4^+$ in soil and effluent indicates DNRA effect.
6. Nitrification and denitrification. Since the influx in this experiment contains only $^{15}$N-NO$_3^-$ and $^{14}$N-NH$_4^+$, the $^{14}$N-NO$_3^-$ detected from the soil and leachate in the system were used to determine nitrification of $^{14}$N-NH$_4^+$. Denitrification of $^{15}$N-NO$_3^-$ was deduced from the material balance of $^{15}$N (Harrison et al. 2012). The amount of $^{15}$N added to the experiment minus the amount absorbed by the plant, remaining in the leachate, assimilated by microorganisms, and depleted in DNRA was $^{15}$N consumed by denitrification. The volatile $^{14}$N-NH$_4^+$ was calculated using material balance.

RESULTS AND DISCUSSION

Changes of soil ORP and MC during experiment

Since most denitrification-related enzymes can be induced to synthesize under hypoxic conditions, moisture and O$_2$ content are important factors that affect denitrification. Both of them affect soil denitrification indirectly by affecting soil redox potential (Korol et al. 2016).

As shown in Figure 3(a), the changes of soil ORP under different plant species and soil pH were similar in grassed paving systems. Soil ORP was 650–655 mV for each system at the beginning of the experiment. During 0–5 d, DO was consumed in the system, soil ORP decreased gradually and dropped to 122–324 mV on day 5. When the second influx was filled into the system, soil ORP increased to over 600 mV. During 5–17 d, soil ORP decreased until reached the lowest level of −100 mV to 24 mV on day 13, then gradually increased to 88–132 mV on day 17. As shown in Figure 3(b), soil MC of the whole experiment showed a gradual downward trend from 0.370 m$^3$/m$^3$ on the first day until 0.170 m$^3$/m$^3$ on day 17 due to significant evapotranspiration, only increased on day 5 due to influx.

Denitrification may occur when the ORP was below 200 mV (Kralova et al. 1992). It can be seen from Figure 3(a) that denitrification can occur in 9–17 d. Soil MC indirectly affects denitrification rate by affecting the partial pressure of oxygen. It showed that denitrification rate was lower when soil moisture was less than 20%, and the highest rate when the content was more than 30% (Ryden et al. 1987). As shown in Figure 3(b), that denitrification may occur in 0–14 d. To sum up, denitrification may occur

![Figure 3 | Changes of soil ORP and MC in grassed paving system.](https://iwaponline.com/wst/article-pdf/78/3/611/482228/wst078030611.pdf)
in 9–14 d according to integrated ORP and soil moisture changes.

The contents of ammonia, nitrate, nitrite, TN and COD in leachate

As shown in Figure 4(a), the concentration of NH$_4^+$-N in leachate dropped rapidly from 5.00 mg/L to 1.24–1.74 mg/L during 0–5 d. It abruptly reached 6.24–6.74 mg/L when the second influx was filled, and then declined rapidly during 5–7 d, slightly increased on day 10, and finally decreased to 1.56–1.69 mg/L on day 17. The system can reach 83.1–84.4% ammonia removal rate at 5 d rainfall interval. At the end of the experiment, planting grass L was more effective at removing NH$_4^+$-N than other plants.

As shown in Figure 4(b), the concentration of NO$_3^-$-N in leachate increased at first and then decreased during 0–5 d, until it dropped to 3.03–3.99 mg/L on day 5. It abruptly reached 8.03–9.01 mg/L when the second influx was filled, then decreased gradually to 2.00–4.10 mg/L during 5–17 d, which indicated that the system could reach 59–80% nitrate removal rate at 5 d rainfall interval. At the end of the experiment, planting grass L was more effective in removing nitrate than other plants.

As shown in Figure 4(c), the concentration of NO$_2^-$-N in leachate showed an increasing trend during 0–10 d and increased to 0.19–0.21 mg/L on day 10, then gradually decreased to 0.08–0.11 mg/L during 10–17 d.

As shown in Figure 4(d), the concentration of TN in leachate gradually decreased from 10.00 mg/L to 5.02–6.20 mg/L during 0–5 d. It increased abruptly to 15.0–16.2 mg/L when the second influx was filled, then gradually decreased to 4.63–6.83 mg/L during 5–17 d, which indicated that the removal efficiency of TN could reach 65.8–76.8% at 5 d rainfall interval. The three plants had no significant difference in TN removal.

As shown in Figure 4(e), the concentration of COD in the leachate decreased gradually during 0–5 d, and dropped to 9–25 mg/L on day 5. The concentration of COD was changed to 165–175 mg/L when the second influx was filled, then decreased to 9–19 mg/L gradually during 5–17 d, which indicated that the COD removal efficiency of grassed paving system can reach 93.6–97.0% at 5 d rainfall interval. At the end of the experiment, the COD removal efficiency of planting Z was lower than that of other plants.

Soil pH had no significant effect on the removal of ammonia and nitrate in each system. When soil pH was 6.4–8.24, the effect of removing TN was slightly weakened with the increase of soil pH, while the COD removal efficiency of each system increased with the increase of soil pH.

In sum, the adsorption of NH$_4^+$-N and NO$_3^-$-N by soil inorganic particles, the uptake of NH$_4^+$-N and NO$_3^-$-N by plants and nitrification may exist in the system during 0–9 d. During 9–17 d, denitrification rate was fast and may be accompanied by the occurrence of DNRA.

Analysis of N removal pathways

Adsorption of $^{14}$N-NH$_4$ and $^{15}$N-NO$_3$ by soil inorganic particles

As shown in Figure 5(a), on day 2, the amount of $^{14}$N-NH$_4$ adsorbed by soil with plant L was 0.22–0.24 mg, then declined. On day 7, it reached the maximum of 0.38–0.40 mg after the second influx on day 5, then decreased continuously during 7–17 d. The grassed paving system with plant L had the strongest adsorption capacity of ammonia, followed by Z and E. As shown in Figure 5(b), on day 2, the amount of $^{15}$N-NO$_3$ adsorbed by soil with plant L was 0.10–0.15 mg, then declined. On day 7, it reached the maximum of 0.19–0.23 mg, then decreased continuously during 7–17 d. The grassed paving system with plant L had the strongest adsorption capacity of nitrate, followed by E and the worst of Z.

As can be seen from the comparison of Figure 5(a) and 5(b), at the end of the experiment, the amount of $^{14}$N-NH$_4$ in the soil extract of grassed paving system with plant Z, E and L was 3.17–4.25, 1.82–2.11 and 3.33–4.75 times of that of $^{15}$N-NO$_3$, respectively.

The adsorption capacity of soil inorganic particles to ammonia was significantly higher than that of nitrate because soil particles are usually negatively charged, while the positively charged NH$_4^+$ was more easily adsorbed by the soil. Compared with tillage soils, woodland and grassland soils have a stronger soil adsorption of NH$_4^+$-N due to their abundant organic matter and more 2: 1 clay minerals. NH$_4^+$-N soil adsorption was very rapid, usually within a dozen minutes to complete (Davidson et al. 2010). Corre et al. (2006) using isotope tracing techniques showed that 10% to 30% of the labeled $^{15}$N-NH$_4$ in forest soils could be immobilized by adsorption. In this study, on day 2, the soil adsorption of NH$_4^+$-N in the grassed paving system with plant Z, E and L plants had been completed, reaching 20.0–22.0%, 17.2–18.3% and 22.0–23.5%, respectively.

NO$_3^-$-N reduction requires enzyme as a catalyst. Therefore, the reaction of NO$_3^-$-N and soil organic matter was a biological process, while NO$_2^-$-N can quickly react with
Figure 4 | Changes of NH$_4^+$-N, NO$_3^-$-N, NO$_2^-$-N, TN, and COD concentration in leachate.
soil organic matter non-biologically. Thus, if NO_3^-N was first reduced to NO_2^-N, NO_2^-N will be non-biological binding with the organic matter. During the initial 2 days, the soil adsorption of ^15N-NO_3^-C_0 in the grassed paving system with plant Z, E and L plants has been completed, reaching 10–11.1%, 10.3–11% and 10–13%, respectively.

In this experiment, soil pH had little effect on the biosynthesis of inorganic N, which may be due to the smaller pH range of the selected soil.

**Plant uptake of N**

It was showed that the amount of ^14N-NH_4^+ and ^15N-NO_3^-C_0 absorbed by plants in grassed paving systems kept increasing slowly since the initial experiments and reached the maximum on day 17 (Figure S1, available with the online version of this paper). Plant L had the strongest uptake of NH_4^-N, followed by Z, while E was the worst. There were no significant differences among the three plants and soil pH on the adsorption of nitrate. The amount of ^14N-NH_4^+ absorbed by L at the end of the experiment was about 1.45 to 1.73 times that of ^15N-NO_3^-C_0.

The uptake of ammonia by plant roots was mainly the process of converting ammonia into amino acids under the action of various enzymes such as glutamine synthetase and glutamate synthetase. Ammonia can be directly involved in amino acid synthesis reaction after being absorbed by plants. The plant roots can efficiently absorb nitrate from soil solutions through several low-affinity and high-affinity nitrate-proton anti-transporters on the plasma membrane and, eventually, assimilate most of the absorbed nitrate to organic N compounds (Noguero & Lacombe 2016). The first step was the reduction of nitrate to nitrite under the catalytic conditions of nitrate reductase in the cytoplasm. The second step was that plant cells transfer nitrite produced by nitrate reduction from the cytoplasm into the plastids of chloroplasts or root cells of leaf cells, in which nitrite reductases reduce nitrite to ammonium. Therefore, plants need more energy to absorb nitrate than to absorb ammonia. The experiment showed that inorganic N uptake capacity of three kinds of plants were in the order of L > Z > E. Soil pH had no significant effect on the uptake of inorganic N by the three plants, probably due to the smaller pH interval selected in the experiment.

**Microbial assimilation of N**

As shown in Figure S2 (available online), the amount of ^14N-NH_4^+ and ^15N-NO_3^-C_0 assimilated in the grassed paving systems kept increasing gradually until reaching the maximum on day 17. The microbial assimilation of ^14N-NH_4^+ in grassed paving system with plant L was strongest, Z and E were weaker. The reason may be that the root system of grass L was more developed, providing more suitable micro-environment for microbial growth, thereby enhancing the assimilation of ammonia. The microbial assimilation of ^15N-NO_3^-C_0 in the grassed paving system with these three plants had little difference. When soil pH was 7.17, microbial assimilation of ^14N-NH_4^+ and ^15N-NO_3^-C_0 in the grassed paving systems with three kinds of plants were the strongest, while they were the weakest when soil pH was 8.24, probably because the alkaline conditions inhibited the microbial activity.
At the end of the experiment, the amount of assimilated $^{14}\text{N-NH}_4^+$ was about 2.4 times of $^{15}\text{N-NO}_3^-/C_0$. Microorganisms preferentially utilize ammonia as N source. From the perspective of reductase synthesis, the presence of ammonia either inhibits the synthesis of nitrate reductase, or blocks the entry of nitrate into the cell, or inhibits the activity of the enzyme, or inhibits the activity of the synthesis of nitrate synthase, resulting in microorganisms using less nitrate compared to ammonia. The energy required for assimilation of ammonia by microorganisms is less than that of nitrate.

**Nitrification and denitrification**

As shown in Figure 6(a) and 6(b), during 0–2 d, the amount of $^{14}\text{N-NH}_4^+$ consumed by nitrification was relatively high, and the amount of $^{15}\text{N-NO}_3^-$ consumed by denitrification was quite low, because soil ORP > 200 mV was favorable for nitrification. During 2–5 d, the amount of $^{14}\text{N-NH}_4^+$ consumed by nitrification gradually decreased and the amount of $^{15}\text{N-NO}_3^-$ consumed by denitrification gradually increased. Because dissolved oxygen (DO) in the system was continuously depleted, soil ORP gradually decreased and nitrification was inhibited. During 5–7 d, the amount of $^{14}\text{N-NH}_4^+$ consumed by nitrification abruptly increased and reached the maximum on day 7. The $^{15}\text{N-NO}_3^-$ consumed by denitrification hardly changed. This was mainly due to the second influx on day 5. The concentration of ammonia and nitrate in the system increased and the ORP was increased, which was favorable for nitrification and unfavorable to denitrification. During 7–14 d, the amount of $^{15}\text{N-NO}_3^-$ consumed by denitrification gradually increased. At this point, soil system ORP was less than 200 mV and denitrification was dominant.

As shown in Figure 6(a), $^{14}\text{N-NH}_4^+$ consumed by nitrification increased with increasing soil pH, which affected soil nitrification by influencing the amount, type and activity of nitrobacteria in the soil. As shown in Figure 6(b), soil pH had little effect on the amount of $^{15}\text{N-NO}_3^-$ consumed by denitrification. Under natural conditions, the optimal pH for denitrification was 6–8. Low pH value can significantly reduce denitrification rate. When the pH value was less than 6, nitric oxide reductase and nitrous oxide reductase are inhibited. Denitrification rate decreased with the decrease of pH, while the high pH value enhanced the competition of DNRA with denitrifying substrate nitrate.

**DNRA**

As shown in Figure 7(a), the DNRA effects of the grassed paving system firstly increased and then decreased, due to soil ORP > 200 mV in the initial stage of the experiment. During 2–5 d, the amount of $^{15}\text{N-NO}_3^-$ consumed by DNRA increased significantly, because soil ORP < 200 mV and the system was under anaerobic or hypoxic conditions. During 5–7 d, the amount of $^{15}\text{N-NO}_3^-$ consumed by DNRA increased very slowly because of the secondary influx on day 5 and the soil system was under an aerobic condition with ORP > 200 mV again. During 7–13 d, the amount of $^{15}\text{N-NO}_3^-$ consumed by DNRA increased very slowly because of the secondary influx on day 5 and the soil system was under an aerobic condition with ORP > 200 mV again. During 13–17 d, the amount of $^{15}\text{N-NO}_3^-$ consumed by DNRA gradually increased to 0.23–0.25 mg on day 13. As the experiment progressed, system DO was continuously depleted and it was under anaerobic condition, therefore DNRA was significantly enhanced. During 13–17 d, the amount of $^{15}\text{N-NO}_3^-$ increased.

*Figure 6* | $^{14}\text{N-NH}_4^+$ consumed by nitrification, $^{15}\text{N-NO}_3^-$ consumed by denitrification.
consumed by DNRA decreased gradually to 0.16–0.18 mg. This was because the soil MC of the system was greatly reduced after day 13, the oxygen in the air gradually entered the soil system, and the soil ORP gradually increased, which was unfavorable to the reaction of DNRA.

The results showed that DNRA effects of the grassed paving systems increased with increasing soil pH. The neutral and alkaline conditions could enhance the competition of DNRA process for denitrifying substrate (NO$_3^-$). As shown in Figure 7(b), the trend of $^{15}$N-NO$_2^-$/C$_0$ changes of DNRA intermediate was similar to that of $^{15}$N-NO$_3^-$/C$_0$ consumed by DNRA.

**Quantitative analysis of N removal pathways in the grassed paving system**

Figure 8 shows the final N migration and conversion of the grassed paving system with plant L at soil pH of 7.14 as an example. 3.3% of $^{15}$N-NO$_3^-$ and 10.5% of $^{14}$N-NH$_4^+$ were adsorbed by soil inorganic particles. 7.7% of $^{15}$N-NO$_3^-$ and 11.43% of $^{14}$N-NH$_4^+$ were absorbed by plants. 6.6% of $^{15}$N-NO$_3^-$ and 15.24% of $^{14}$N-NH$_4^+$ were degraded by microorganisms, nearly one third of $^{14}$N-NH$_4^+$ were converted to $^{14}$N-NO$_3^-$ through nitrification, and 9.5% of $^{15}$N-NO$_3^-$ were converted to $^{15}$N-NH$_4^+$ through DNRA. Over half of...
\[ ^{15}\text{N}-\text{NO}_3^- \] was removal by denitrification, and 19.2% of \[ ^{14}\text{N}-\text{NH}_4^+ \] was volatilized out of the system. In total, the grassed system could remove 73.8% of TN, 12.8% of \[ ^{14}\text{N}-\text{NO}_3^- \], 8.6% of \[ ^{14}\text{N}-\text{NH}_4^+ \], 22.1% of \[ ^{15}\text{N}-\text{NO}_3^- \], and 9.0% of \[ ^{15}\text{N}-\text{NH}_4^+ \] were found in the leachate.

**CONCLUSIONS**

The results showed that the grassed paving systems with three plants were good for removing NH4+-N, NO3--N, TN, and COD from rainfall runoff. However, there was no significant difference in TN removal among these three-plant species and a certain soil pH. The comparisons of plant types in N removal pathways was in Table S1 (available with the online version of this paper).

The experiment showed that when the rainfall interval was 5 days, the grassed paving system could remove 65.8–76.8% of runoff TN in 17 detention days. The N conversion was dominated by soil adsorption, plant uptake, microbial assimilation, and nitrification during 0–5 d. While the main N reactions were mainly through denitrification and DNRA during 5–14 d. Therefore, for rainy climate with short RI, the removal efficiency of ammonia was better, and that of nitrate removal was worse. Plant selection and soil culture should be strengthened to achieve faster TN removal. For rainy areas with long RI, the design of the grassed paving system structure should be strengthened to enhance its anaerobic environment to achieve better TN removal.

As for typical grassed pavement, runoff volume control is usually put in the first consideration. Therefore, structure bearing load and soil saturated hydraulic conductivity are mainly concerned, and COD and TN load were removed together with volume. While for balancing COD and TN control, it is necessary to increase the soil depth and keep suitable outlet height for adequate detention time and anaerobic environment. Also, appropriate plants with developed root systems are recommended.

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