Environmental Science
Processes & Impacts

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

rsc.li/process-impacts

Effects of atmospheric deposition nitrogen flux and its composition on soil solution chemistry from a red soil farmland, southeast China

Jian Cui,[*ab] Jing Zhou, [*a] Ying Peng,[c] Andrew Chan,[d] and Jingdong Mao[e]

Abstract

A detailed study on the solution chemistry of red soil in South China is presented. Data are collected from two simulated column-leaching experiments with an improved setup to evaluate the effects of atmospheric N deposition (ADN) composition and ADN flux on agricultural soil acidification using a ^{15}N tracer technique and an *in-situ* soil solution sampler. Results show that solution pH values decline regardless of the increase of NH_4^+/NO_3^- ratio in ADN composition or ADN flux, while exchangeable Al^{3+}, Ca^{2+}, Mg^{2+}, and K^+ concentrations increase at different soil depths (20, 40, and 60 cm). Compared with the control, ADN (60 kg ha^{-1} yr^{-1} N, NH_4^+/NO_3^- ratio of 2:1) decreases solution pH values, increases solution concentrations of NO_3^--N, Al^{3+}, Ca^{2+} and Mg^{2+} at the middle and lower soil depths, and promotes their removal. NH_4^+-N was not detected in red soil solutions of all the three soil layers, which might be attribute to effects of nitrification, absorption and fixation in farmland red soil. Some of the NO_3^--N concentrations at 40-60 cm soil depth exceed the safe drinking level of 10 mg L^{-1}, especially when ADN flux is beyond 60 kg ha^{-1} N. These features are critical for understanding the ADN agro-ecological effects, and for future assessment of ecological critical loads of ADN in red soil farmlands.

Keywords: atmospheric nitrogen deposition, flux/composition, soil solution chemistry, agricultural

[a] *Institute of Soil Science, Chinese Academy of Sciences, Nanjing, 210008, China. Email: zhoujing@issas.ac.cn; cuijian@cigit.ac.cn*

[b] *Chongqing Institute of Green and Intelligent Technology, Chinese Academy of Sciences, Chongqing, 400714, China*

[c] *Nanjing Institute of Geography and Limnology, Chinese Academy of Sciences, Nanjing, 210008, China*

[d] *Division of Environment, Faculty of Engineering, University of Nottingham Malaysia Campus, Semenyih, 43500, Malaysia*

[e] Department of Chemistry and Biochemistry, Old Dominion University, Norfolk, VA 23529-0126, USA

red soil, column-leaching experiment

1 Introduction

Human activity has significantly altered the global nitrogen (N) cycling in the last several decades, resulting in increased atmospheric N deposition (ADN) worldwide.[1-3] China is the third highest ADN flux region in the world.[4] However, related ADN research concerning the substantial use of fertilizer N in farmlands, especially in agricultural ecosystems, is still in its infancy.[5, 6]

Existing research mainly focuses on the quantification of ADN flux in agroecosystems, and the negative effects of ADN on soil acidification and ecological degeneration, especially in forest ecosystems.[7-9] In fact, due to several control programs including the adjustment of energy structure and current agricultural fertilizer N,[8-11] ADN composition has changed, for example the NH_4^+/NO_3^- ratio in wet ADN has declined since 1980.[12,13] As there is a lack of continuity in previous research on ADN, with study periods limited to one to two years, the ecological effects of ADN composition changes have not been comprehensively investigated.[6,7,13]

Soil acidification (decrease in soil pH) is one of the most important consequences of dramatic increases in anthropogenic acid deposition, including ADN.[2,14] When acid deposition was a major concern, ADN was often ignored as a contributing factor.[15,16] In fact, the effects of ADN in Chinese agro-ecosystems are quite significant,[6,12] and preliminary studies report that more ADN is associated with higher acidification of farmland soils.[17,18]

Usually, researchers equate the effect of ADN with that of fertilizer N on agricultural soil acidifications. It was deduced that the overuse of fertilizer N contributed substantially to regional soil acidification, but ADN made a small contribution to the acidification of agricultural soils across China, based on nationwide survey data and related theories and processes of N cycling.[19] Although the different sources concern the same element, there are significant differences between fertilizer N and ADN.

Firstly, the different applications mean that fertilizer N is usually applied at seeding times or is added at critical moments for crops, while ADN affects field soils at all times. Secondly, the different N components mean that usually one type of N fertilizer is applied and its N component is

fixed, while the composition of ADN is unfixed and its NH_4^+/NO_3^- ratio exceeds unity. Hence, it is interesting to investigate whether ADN and fertilizer N produce the same effect on farmland acidification. However, it is difficult to evaluate the contribution of different N sources from soil, fertilizer and atmospheric deposition using traditional methods, such as the control experiment of no N addition.[16,20]

In China, soil acidification is a major problem in agricultural soils, especially in (sub-) tropical regions.[19] Red soils are widely distributed, accounting for over 20% of the country's total land area.[21] The red soils of China are highly weathered, inherently infertile, generally acidic, and deficient in most essential nutrients.[22] Large amounts of organic matter and nutrients are lost from the cultivated land,[23] making the agro-ecosystems fragile. It has also been observed that ADN is higher and ADN composition also changing in the red soil regions,[6,24] indicating the necessity to evaluate the effects of ADN on soil acidification in red soil fields.

A dynamic content of soil solution chemistry could typify the key progress of soil chemical changes. Usually, a soil column leaching stimulation is used to discuss progresses of soil acidification, nitrification and so on.[25-28] The key factors are the method of adding the solution, and the operability of the leaching setup. Most researchers add their solutions with the same quantity and the same speed during the whole experimental process,[26,28] meaning that real environmental information, such as precipitation, cannot be simulated. As for the leaching setup, soil chemistry is often studied in different soil depths while soil solution chemistry focuses on the leachate.[25,26,28] However, a multistage soil solution and its chemistry are rare for the limit of the leaching setup. An *in-situ* soil solution sampler is feasible in field,[29,30] which helps to overcome the limit.

^{15}N isotope-labeling is the best way to explore N source and distribution.[12,31] This technique can be applied to soil columns and plots for a short-time scale for research into ADN on the soil acidification of farmland.[16] The advantage of ^{15}N isotope-labeling is that it can be used to calculate the amounts of acid produced by marked N to work out the proportion of the acidification attributed to ADN. In order to identify the major processes driving the solution chemical responses of a red soil field in under pressure from ADN and its composition, a soil column leaching experiment has been done with an improved leaching setup and the application of the ^{15}N isotope-labeling

technology in this study. This information is important for future modelling and assessment of ecological critical loads of ADN and its effects in red soil farmlands.

2 Materials and methods

2.1 Materials

2.1.1 Experimental soil

Representative soil samples from the Yingtan station, developed from the quaternary red earth, were collected sequentially from the upper 0-20 cm, middle 20-40 cm and lower 40-60 cm soil layers in farmland for the experiments. The soils were collected using a plat shovel by a cross-section method in three fields. The samples were air dried under shade, ground, mixed thoroughly, and sieved through a 2-mm mesh. The soil samples were analyzed for basic soil properties including soil pH value, soil bulk density (SBD), water holding capacity (SWC), organic matter (SOM), available nutrients including N, phosphorous (P) and potassium (K), base cations (BCs) including K, sodium (Na), calcium (Ca) and magnesium (Mg), total exchangeable bases (TEB, sum of BCs), cation exchange capacity (CEC) and base saturation (BS).[32] The details are shown in Table 1.

2.1.2 Simulated ADN solution

Based on regional long-term monitored data by our group,[10,24] the average values of annual rainfall, pH in precipitation, ADN and its NH_4^+/NO_3^- ratio were 1785 mm, 4.5, 31 kg ha^{-1} yr^{-1} N and 2.5, respectively for the 2004–2012 period. Considering atmospheric dry inorganic nitrogen deposition, the bulk inorganic deposition flux reached 92 kg ha^{-1} yr^{-1} N.[33] Thus, two group experiments were conducted: 1) simulated ADN composition change with a stable flux (90 kg ha^{-1} yr^{-1} N): with NH_4^+/NO_3^- ratio 1:2, 1:1, 2:1 and 4:1 (four treatments in total); and 2) simulated ADN flux increase with stable composition (NH_4^+/NO_3^- ratio 2:1): 30, 60, 90 and 120 kg ha^{-1} yr^{-1} N (four treatments in total). Every treatment above was carried out in triplicate. All simulated ADN solutions were set at pH 4.5 and made from $^{15}NH_4Cl$, $^{15}NH_4{}^{15}NO_3$, $Na^{15}NO_3$, NaCl, HCl and deionized water. The ^{15}N enrichment is 10% in all three of the ^{15}N-labelled chemicals. In addition, a control treatment (0 kg ha^{-1} yr^{-1} N) was also set at pH 4.5 and made from NaCl, HCl and deionized

water.

2.1.3 Soil column setup

The improved column setup is shown in Fig.1. The detailed setup was as follow: a total of 27 PVC pipes (15 cm inner diameter, 65 cm length) were used to contain three-layer prepared agricultural red soil samples. A porous plate was fixed at the bottom end of each pipe. Five layers of filtering materials (silica sand in the middle and two pieces of paper filters both on top and bottom) were placed on a porous plate to filter the effluents and to prevent soil leakage. The prepared three-layer soil samples were poured into the pipe in the order of the same layer in the farmland. At the same time, two *in-situ* soil solution samplers were placed between two soil layers (between 0-20 cm and 20-40 cm, and between 20-40 cm and 40-60 cm).

2.2Methods

2.2.1 Simulated ADN Progress

Before the ADN progress, the prepared soil columns were placed into a pool with deionized water for ten days to ensure adequate soil condensation. The total ADN solution of 29.14 L in a year, converted into 1665 mm annual rainfall, was added with a sprayer at the end of each month for each soil column. The detailed simulated ADN contents are shown in Table 2. The monthly simulated ADN solution lasted 24 h each time. A protective film with small punctures was applied to the top of the PVC pipes to prevent the rapid evaporation of water from the soil columns. Both sets of experiments began on January 30th 2013 and lasted for 12 months.

2.2.2 Sampling and analysis

Soil solutions at depths of 20 and 40 cm in the soil columns were collected using the *in-situ* soil solution samplers, and soil solutions at depths of 60 cm were collected by Erlenmeyer flasks once the simulated N deposition solution was finished every month. The soil solution pH value was measured using an IQ 150 pH meter (Spectrum Technologies, INC., USA) immediately. Exchangeable aluminum (Al) and BCs were analyzed using an inductively-coupled plasma spectrometer (Optima 8000, PerkinElmer Inc., USA). NH_4^+-N and NO_3^--N were determined using a continuous flow analyzer, AutoAnalyzer 3 (Bran-Luebbe Inc., Germany). The samples with ^{15}N isotopic were from these soil solutions in the depth of 60cm. The ^{15}N atom enrichments (%) of soil

solutions were detected using a stable isotope mass spectrometer (Elementar Isoprime 100, Isoprime Ltd., UK) at the State Key Laboratory of Soil and Sustainable Agriculture, Institute of Soil Science, Chinese Academy of Sciences. Before that, solution NO_3^--N was converted into gaseous N_2O by Cadmium particles which were coated with copper under the condition of solution pH=4.7.[34]

2.2.3 Calculation

The values of main irons in the depth of 60cm were defined as their removals, which were calculated by the formula (1):

$$R_i = C_{it}V_{it} - C_{i0}V_{i0} \quad (1)$$

Where R_i is the removal of the i iron of the t treatment (mg column^{-1} N), C_{it} and C_{i0} were the i concentrations of the t and the control treatments (mg L^{-1} N), V_{it} and V_{i0} was the solution volumes of the t and the control treatments (L column^{-1}), respectively.

The loss of $^{15}NO_3^-$-N ($^{15}R_j$) was calculated by the formula (2):

$$^{15}R_j = E_j C_j V_j \quad (2)$$

where $^{15}R_j$ was the $^{15}NO_3^-$-N loss (mg column^{-1} N), E_j ,C_j and V_j were the ^{15}N atom enrichments (%), NO_3^--N concentrations (mg L^{-1} N) and the solution volumes (L column^{-1}) of the j treatments, respectively.

2.2.4 Statistical analysis

The statistical program SAS 9.0 was performed for all data analyses. A one-way analysis of variance (ANOVA) was used to test for differences ($p<0.05$) in soil solution pH, NO_3^--N, Al^{3+}, BCs, TEB and molar ratios of Al^{3+}/TEB across different ADN fluxes and compositions.

3 Results

3.1 pH value

With the increase of ADN flux (0-120 kg ha^{-1} yr^{-1} N) when the NH_4^+/NO_3^- ratio was kept stable (2:1) and NH_4^+/NO_3^- ratio when its flux was 90 kg ha^{-1} yr^{-1} N, solution pH values declined at every soil depth (Figs.2a, 2c). Fig.2a also shows that in all three soil depths, pH values declined significantly ($p<0.05$) when ADN flux was beyond 60 kg ha^{-1} yr^{-1} N. When NH_4^+/NO_3^- ratio ranged

from 1:2 to 4:1, pH values also declined significantly ($p<0.05$) at the upper soil depths (20 and 40cm) while the same variation was found at the 60cm depth when NH_4^+/NO_3^- ratio ranged from 2:1 to 4:1 (Fig.2c). As for different soil depths of the two experiments, there were no differences for solution pH values between the two shallower depths (20 and 40 cm), which were obviously lower than those at the 60 cm depth.

3.2 Inorganic N

NH_4^+-N was not detected in all of soil solution samples throughout the whole experiment. With the increase of ADN flux (0-120 kg ha^{-1} yr^{-1} N) when the NH_4^+/NO_3^- ratio was kept stable (2:1), solution NO_3^--N values increased in all soil depths (Figs.2b). Moreover, when ADN fluxes were beyond 60 kg ha^{-1} yr^{-1} N, there had significant differences ($p<0.05$) between the ADN flux treatment and the control. Though the similar difference was found between the NH_4^+/NO_3^- ratio treatment and the control, there had no significant differences among the four treatments of NH_4^+/NO_3^- ratio (Fig. 2d). Additionally, NO_3^--N concentration at the 60 cm depth ranged from 2.14–14.47 mg L^{-1} N (Figs. 2b and 2d), so some of the samples exceed the drinking level of 10 mg L^{-1} N, especially when ADN flux is beyond 60 kg ha^{-1} yr^{-1} N. This indicates that ADN might create a risk to human health.

As for NO_3^--N removals and $^{15}NO_3^-$-N loss, they increased linearly ($p<0.05$) with the increase of ADN flux (Figs. 3a and 3b; Table 3) while the increase of NH_4^+/NO_3^- ratio increased them a little (Figs. 3c and 3d; Table 3). During the whole ADN flux experiment, NO_3^--N removals were in the range of 33.54-157.27 mg $column^{-1}$ N, accounting for 63.28%-74.85% of total N additions from the simulated ADN solution (53.01-157.27 mg $column^{-1}$ N). $^{15}NO_3^-$-N loss ranged from 3.25-14.92 mg $column^{-1}$ N, accounting for 9.48%-10.40% of total ^{15}N addition from the simulated ADN solution. During the whole experiment of NH_4^+/NO_3^- ratio, NO_3^--N removals and $^{15}NO_3^-$-N loss were in ranges of 116.28-125.76 and 11.35-12.27 mg $column^{-1}$ N, accounting for 73.11%-79.09% and 9.71%-10.31% of total N and ^{15}N addition from the simulated ADN solution, respectively.

3.3 Al^{3+} and BCs

3.3.1 Concentrations

With the increase of simulated ADN flux when the NH_4^+/NO_3^- ratio was kept stable (2:1), there were increased trends for solution Al^{3+}, BCs and TEB concentrations at the three soil depths (20, 40 and 60 cm, Table 4). Al^{3+} concentrations under the ADN flux treatment (60 kg ha^{-1} yr^{-1} N) averaged 18.58 and 29.67 mg L^{-1} at the two depths of 20cm and 40cm, respectively, which significantly higher ($p<0.05$) than those under the control. Similarly, at both 20cm and 40cm depths, Ca^{2+}, Mg^{2+}, K^+ and TEB concentrations under the ADN flux treatment (60 kg ha^{-1} yr^{-1} N) were significantly higher ($p<0.05$) than those under the control. At the 60cm depth, there had significant differences for Al^{3+}, Mg^{2+} and K^+ concentrations between treatments of the ADN flux (90 kg ha^{-1} yr^{-1} N) and the control and those for Ca^{2+} and TEB concentrations between treatments of the ADN flux (60 kg ha^{-1} yr^{-1} N). At all three depths, Na^+ concentrations under the ADN flux (120 kg ha^{-1} yr^{-1} N) were significantly larger ($p<0.05$) than other four treatments and there had no difference among the four treatments.

In the experiment of ADN composition (NH_4^+/NO_3^- ratio ranged from 1:2 to 4:1, ADN kept 90 kg ha^{-1} yr^{-1} N), the increase of NH_4^+/NO_3^- ratio raised solution concentrations of Al^{3+}, BCs and TEB at all the three soil depths (Table 5). Al^{3+} concentrations under the NH_4^+/NO_3^- ratio (2:1) averaged 23.95, 34.33 and 19.09 mg L^{-1} at the 20cm, 40cm and 60cm depths, respectively, which significantly higher ($p<0.05$) than those under the NH_4^+/NO_3^- ratio (1:2). At the 20cm and 60cm depths, Ca^{2+}, Mg^{2+}, K^+ and TEB concentrations under the NH_4^+/NO_3^- ratio (2:1) were significantly larger ($p<0.05$) than those under the NH_4^+/NO_3^- ratio (1:2) while significantly lower ($p<0.05$) than those under the NH_4^+/NO_3^- ratio (4:1), which was similar to concentrations of K^+ and TEB at the 40cm depth.

Al^{3+}/TEB ratio was a comprehensive and important index for red soil solution chemistry. In the control, the ratios were 2.3%, 4.3% and 1.8% at the 20cm, 40cm and 60cm depths, respectively. Whatever the increase of ADN flux and NH_4^+/NO_3^- ratio, the Al^{3+}/TEB ratios increased (Tables 4 and 5). Moreover, Al^{3+}/TEB ratios were higher significantly ($p<0.05$) than that under the control at the three depths when ADN flux was beyond 60 kg ha^{-1} yr^{-1} N. When NH_4^+/NO_3^- ratio ranged from 2:1 and 4:1, Al^{3+}/TEB ratios were larger significantly ($p<0.05$) than that under the control at the

three depths.

3.3.2 Removals

Al^{3+} removal was significant (Fig. 4 and Table 3). When ADN flux ranged from 30 to120 kg ha^{-1} yr^{-1} with the stable NH_4^+/NO_3^- ratio (2:1), Al^{3+} removals were in the range of 0.9-11.0 mg/column. There had significant differences ($p<0.05$) among the three treatments (30, 60 and 120 kg ha^{-1} yr^{-1} N) while the treatment (90 kg ha^{-1} yr^{-1} N) had no differences with the two treatments (60 and 120 kg ha^{-1} yr^{-1} N), respectively (Fig.4a and Table 3). When ADN kept 90 kg ha^{-1} yr^{-1} N, high NH_4^+/NO_3^- ratio treatments (2:1 and 4:1) significantly ($p<0.05$) mobilized Al^{3+} in the soil, but Al^{3+} removal was similar between the two treatments (Fig.4b and Table 3). In the whole process, their Al^{3+} removals are 8.9 and 9.6 mg $column^{-1}$, respectively, higher than ($p<0.05$) those under the other two NH_4^+/NO_3^- ratio treatments.

Extractable BCs removal was dominated by Ca^{2+} (Figs. 5 and Table 3). In the ADN flux experiment, Ca^{2+} removals were in the range of 27.5–146.8 mg $column^{-1}$, accounting for 68.9%–75.6% of the corresponding TEB, while K^+ removal is the lowest (from 1.0 to 9.0 mg $column^{-1}$, only accounting for 2.6%-5.6% of the corresponding TEB). Compared with the control, Ca^{2+} removals increased by 17.11%, 38.51%, 52.96% and 91.17% in the 30, 60, 90 and 120 kg ha^{-1} yr^{-1} N treatments, respectively. When the flux was beyond 60 kg ha^{-1} yr^{-1} N, both Mg^{2+} and K^+ removals increased significantly, and showed obvious differences ($p<0.05$) to the other two treatments (30 and 60 kg ha^{-1} yr^{-1} N, Table 3). Na^+ removal in the 120 kg ha^{-1} yr^{-1} N treatment was higher ($p<0.05$) than those in the other three treatments, which showed little variation amongst themselves (Figs. 5a-5d; Table 3).

Similar to the ADN flux experiment, extractable BCs removal was dominated by Ca^{2+} in the ADN composition experiment (Figs. 5e-5h; Table 3). Over the whole process, Ca^{2+} removals were in range of 49.6–124.3 mg, accounting for 68.9%-80.8% of the corresponding TEB, while K^+ removals were the lowest (1.3-10.8 mg, accounting for 2.1%-6.2% of the corresponding TEB). Difference analysis showed that all the Mg^{2+}, Na^+ and TEB removals in the treatment (NH_4^+/NO_3^-

ratio 1:2) were significantly lower ($p<0.05$) than those in the other three treatments, while both Ca^{2+} and K^+ removals in the treatment (NH_4^+/NO_3^- ratio 1:2) were also significantly lower ($p<0.05$) than those in the 2:1 and 4:1 NH_4^+/NO_3^- ratio treatments.

4 Discussion

The ^{15}N isotope-labeling technique was used to distinguish the N elements from the ADN and soil N. From the ^{15}N abundances, NO_3^--N concentrations, and solution volumes at the 60 cm soil depth, $^{15}NO_3^-$-N loss account 9.76%-10.31% for the corresponding NO_3^--N removals. In the simulated ADN composition experiment it accounts for 9.49%-10.40% of the corresponding NO_3^--N leaching (Figs. 3b and 3d), which is similar to the ^{15}N abundance (10%) of the ADN solutions. This result indicates that ^{15}N isotope-labeling is a feasible tool in the column-leaching experiments. However, the ^{15}N price, including the sampling and analysis fee, is ~20-30 times than that of unlabeled N, which may be the main reason that ^{15}N isotope-labeling is not widely used. Another important reason for underuse of the technique is that most researches focus on forest and grass soils.[25-28] For these soils, ADN is the exogenous N, so it is easy to distinguish the two N sources from ADN and soil N using a conventional experiment. However, in farmland soils, exogenous N includes ADN, fertilizer N and irrigation N, so is difficult to identify the exogenous N using a conventional experiment. Thus, it is necessary to apply the ^{15}N isotope-labeling technology into studies of agricultural soils.

Soil NH_4^+-N absorption and leaching depend on cation exchange, the fixing capacity of soil, the concentration of other cations in solution and so on.[27,35,36] In our study, solution NH_4^+-N concentrations were not detected in the two experiments, which was in agreement with other findings in red soil, China.[26,35] The possible reasons were as follows:

1) Soil adsorption. Generally, red soil is clay and a variable charge soil. The surface of the clay minerals is negatively charged, which absorbs NH_4^+-N to the surface and further to make it immobilized from soil solution. Chang et al.[37] found it was remarkable that red soil absorbed NH_4^+-N and the rate of absorption was quick (only 30min).

2) Other cations. BCs especially for Na^+ and Ca^{2+} leaching benefited to NH_4^+-N fixation in

soil.[36,38] In the study, Na^+ was one of balance cations in simulated ADN solution. Moreover, Ca^{2+} concentrations under treatments of ADN flux and its NH_4^+/NO_3^- ratio were higher than those under the control (Tables 4 and 5). Both Na^+ and Ca^{2+} trended to increase distances of crystal layers, [36,38] which benefited to NH_4^+-N fixation and reduce concentrations of red soil solution NH_4^+-N.

3) Nitrification. Ammonium and soil pH are the most important environmental factors that influence soil nitrification.[39,40] Some studies showed that nitrification was rather weak in acidic soil with lower pH.[40,41] However, recent studies found that nitrification still affected in acidic farmlands with pH values of 4.4-4.9.[38,42] It indicated that there were still ammonia-oxidizing archaea communities or higher pH values in parts of soils though the averaged pH values (the measured values) were low in the soils.[38] In the present study, NO_3^--N removal under the conditions of ADN flux (90 kg ha^{-1} yr^{-1} N) and the NH_4^+/NO_3^- ratio (1:1) was 118.6 mg $column^{-1}$ N (Table 3), accounting for 74.57% of total N addition (NH_4NO_3, 159.04 mg $column^{-1}$ N) . In theory, NO_3^--N removal was 79.52 mg $column^{-1}$ N, which was lower than the measured value (118.6 mg $column^{-1}$ N). This indicates that the nitrification might affect ~ 29.52 mg $column^{-1}$ N, accounting for 18.56% of total N addition (NH_4NO_3, 159.04 mg $column^{-1}$ N) in the progress. The detailed and real mechanism still need to discuss for the red soil nitrification in the further.

At present, related ADN critical load has mostly focused on ADN flux[43-46] while effects of ADN composition have been ignored. It was evaluated that the ADN critical load was 40 kg ha^{-1} yr^{-1} N for soil acidification in south China.[45,47] In this paper, the key NH_4^+/NO_3^- ratio was found to be 2:1 and the key ADN flux was 60 kg ha^{-1} yr^{-1} N for the red soil solution chemistry. This suggests that these two key indices could be the ADN thresholds for farmland acidification. The NH_4^+/NO_3^- ratio also declined in China,[12] hence ADN composition should be an important index for ecological critical load models in future research.

Though soil solution chemistry is a significant index for evaluating soil acidification, there is still a need for more information from soil chemistry including pH value, Al^{3+}, BCs, CEC, soil buffering capacity, N status and plant growth. Some research in forest and grass soils has shown that ADN, especially for NH_4^+-N addition, appears to promote the speed of nitrification, increase

soil net N mineralization, and consequently decrease soil pH value, and increase BCs removal and Al^{3+} concentration to further accelerate the process of soil acidification.[16, 48,49] Related research in farmland red soil will be published in due course.

5 Conclusion

Leaching experiments with an improved setup were done for discussing effects of ADN on agricultural red soil solution chemistry. In the experiment, different precipitation intensities were simulated, which is more representative of the real situation. Moreover, the ^{15}N isotope-labeling technique was used to distinguish the N elements from the ADN and soil N. The results showed that there are decreased trends for solution pH values, and increased trends for solution NO_3^--N, Al^{3+}, BCs and TEB concentrations at the three soil depths (20, 40 and 60 cm) when ADN fluxes or NH_4^+/NO_3^- ratios in ADN composition increased. $^{15}NO_3^-$-N loss account 9.76%-10.31% for the corresponding NO_3^--N removals, which is similar to the ^{15}N abundance (10%) of the ADN solutions. As for iron removals, Al^{3+} removal was significant. Extractable BCs removal was dominated by Ca^{2+}, which accounting for 68.9%–80.8% of the corresponding TEB. In general, the key points were 60 kg ha^{-1} yr^{-1} N for ADN flux with the stable NH_4^+/NO_3^- ratio (2:1) and 2:1 for NH_4^+/NO_3^- ratio in ADN composition with the kept flux (90 kg ha^{-1} yr^{-1} N), respectively. That's to say, the possible ADN critical load for red soil acidification were 60 kg ha^{-1} yr^{-1} N for ADN flux and 2:1 for NH_4^+/NO_3^- ratio in ADN composition in the farmland, separately.

Acknowledgments

This work is supported by the National Natural Science Foundation of China (41201206, 41173094). Especial thanks are given to the anonymous reviewers for their constructive comments, which have greatly improved the manuscript.

References

1 S. C. Doney, N. Mahowald, I. Lima, R. A. Feely, F. T. Mackenzie, J. Lamarque and P. J. Rasch, *PNAS*, 2007, **104**(37): 14580-14585.

2 N. Gruber and J. N. Galloway, *Nature*, 2008, **451**:293-296.

3 D. S. Reay, F. Dentener, P. Smith, J. Grace and R. A. Feely, *Nature Geoscience*, 2008, **1**: 430-437.

4 A. Richter, J. P. Burrows, H. Nub, C. Granier and U. Niemeier, *Nature*, 2005, **437**: 129-132.

5 X. Y. Liu, K. Koba, C. Q. Liu, X. D. Li and M. Yoh, *Environ. Sci. Technol.*, 2012, **46**(22): 12557–12566.

6 J. Cui, J. Zhou, H. Yang and Y. Q. He, *Soils*, 2015, **47**(2): 245-251 (in Chinese).

7 C. M. Clark and D.Tilman, *Nature*, 2008, **451**: 712-715.

8 T. Larssen, L. Duan and J. Mulder, *Environ. Sci. Technol.*, 2011, **45**: 1192-1198.

9 B. Zhao, S. X. Wang, J. D. Wang, J. S. Fu, T. H. Liu, J. Y. Xu, X. Fu and J. M. Hao, *Atmos. Environ.*, 2013, **77**: 453-463.

10 J. Cui, J. Zhou, Y. Peng, Y. Q. He, H. Yang, J. D. Mao, M. L. Zhang, Y. H. Wang and S. W. Wang, *Atmos. Environ.*, 2014, **89**:102-108.

11 H. Kros, M. M. Bakker, P. Reidsma, A. Kanellopoulos, S. J. Alam and W. Vries, *Landscape Ecol.*, 2014, **30**(5): 1-15.

12 X. J. Liu, Y. Zhang, W. X. Han, A. H. Tang, J. L. Shen, Z. L. Cui, P. Vitousek, J. W. Erisman, K. Goulding, P. Christrie, A. Fangmeier and F. S. Zhang, *Nature*,2013, **494**: 459-463.

13 Y. L. Jia, G. R. Yu, N. P. He, X. Y. Zhan, H. J. Fang and W. P. Sheng, *Sci. Rep.*, 2014, **4**: 3763.

14 T. L. Greaver, T. J. Sullivan, J. D. Herrick, M. C. Barber, J. S. Baron, B. Cosby, M. E. Deerhake, R. L. Dennis, J. B. Dubois, C. L. Goodale, A. T. Herlihy, G. B. Lawrence, L. L. Liu, J. A. Lynch and K. J. Novak, *Front. Ecol. Environ.*, 2012, **10**(7):365-372.

15 X. Chen, J. Mulder, Y. Wang, D. Zhao and R. Xiang, Environ. *Geochem. Health*, 2004 **26**: 179-186.

16 J. Huang, J. M. Mo, W. Zhang and X. K. Lu, *Acta Ecologica Sinica*, 2014, **34**:302-310.

17 J. D. Wang, X. M. Gao, D. Y. Chen, Y. C. Zhang, X. J. Xu, Y. W. Ning and Y. H. Hu, *J. Soil Water Conserv.,* 2009, **23**(4):118-122 (in Chinese).

18 J. Cui, J. Zhou, Y. Peng, Y. Q. He, H. Yang and J. D. Mao, *Atmos. Environ.*, 2014, **82**: 121-129.

19 J. H. Guo, X. J. Liu, Y. Zhang, J. L. Shen, W. X. Han, W. F. Zhang, P. Christie, K. W. T. Goulding, P. M. Vitousek and F. S. Zhang, *Science*, 2010, **327**: 1008-1010.

20 X. K. Xu, L. Han and X. B. Luo, *Climatic Environ. Res.*, 2012, **17**(5): 628-638 (in Chinese).

21 Y. Q. He, Sci. Press, Beijing, 2008 (in Chinese).

22 G. Q. Chen, W. L. Fu, Y. C. Luo, W. L. Gao, S. G. Li and H. Yang, *Environ. Sci.*, 2014, **35**(12), 4686-4694 (in Chinese).

23 Z. L. He, X. E. Yang and V. C. Baligar, *Commun. Soil Sci. Plan.,* 2001, **32**(7-8): 1251-1263.

24 J. Cui, J. Zhou, Y. Peng, Y. Q. He and A. Chan, *Plant Soil*, 2012, **359**: 387-395.

25 M. E. Hodson and S. J. Langan, *Environ. Pollut.*, 1999, **104**: 11-19.

26 B. H. Sun, Z. Y. Hu, J. L. Lv, L. N. Zhou and C. K. Xu, *Acta Ecologica Sinica*,2006, **26**(6): 1872-1881 (in Chinese).

27 M. Zarabi and M. Jalali, *Environ. Monit. Assess.,* 2012, **184**: 7607-7622.

28 X. J. Wen, X. Q. Duan and D. C. Zhang, *Environ. Earth Sci.*, 2013, **69**: 843-853

29 X.S. Luo, L. Cang, X.Z. Hao, L.Z. Li and D.M. Zhou, *Soils*, 2007, **39**(6):943-947 (In Chinese).

30 X. Wang, J. Cui and J. Zhou, *Soils*, 2011, **43**(3):382-387 (in Chinese).

31 H. G. Zechmeister, A. Richter, S. Smidt, D. Hohenwallner, I. Roder, S. Maringer and W. Wanek, *Environ. Sci. Technol.*, 2008, **42**: 8661-8667.

32 R. K. Lu, Chinese Agricultural Scientech Press: Beijing, 2000 (In Chinese).
33 J. Cui, J. Zhou, H. Yang, J. N. Liang and X. L. Liu, *Environ. Sci.*, 2009, **30**(8): 2221-2226 (in Chinese).
34 Y. C. Cao, Y. Han, H. Y. Tao, X. Wang, D. L. Sun, Y. F. Sun and X. L. Sun, *Acta Pedologica Sinica*, 2015, **52**(1): 212-219 (in Chinese).
35 R. K. Lu, Z. Y. Shi and Q. W. Lai, *Chinese J. Soil Sci.*, 2000,**31**(4): 156-158(in Chinese)
36 Y. H. Sun and Y. Z. Zhang, *J. Hunan Agri. Univ. (Nat. Sci.)*, 2002, **28**(2):171-176 (in Chinese).
37 K. Chang, S. Q. Sun and F. C. Yin, *J. Anhui Agri. Sci.*, 2014, **42**(3):728,745 (in Chinese).
38 D. L. Tong and R. K. Xu, *Plant Nutrit. Fertil. Sci.*, 2012, **18**(4):853-859 (in Chinese)
39 J. P. Shen, L. M. Zhang and J. Z. He, *J. Soils Sediment.*, 2014, **14**:1861-1868.
40 K. L. Sahrawat, *Plant Soil*, 1982, **65**(2):281-286.
41 H. X. Li, F. Hu, M. Q. Liu, G. X. Cai and X. H. Fan, *Soils*, 2000, **32**(4):194-197, 214 (in Chinese)
42 B. Z. Wang, Y. Zheng, R. Huang, X. Zhou, D. M. Wang, Y. Q. He and Z. J. Jia, *Appl. Environ. Microb.*, 2014, **80**(5):1684-1691.
43 L. Duan, J. M. Hao, S. D. Xie and Z. P. Zhou, *Environ. Sci.*, 2002, **23**(2): 7-12 (in Chinese)
44 A. Nordin, J. Strengbom, J. Witzell, T. Nasholm and L. Ericson, *Ambio*, 2005, **34**(1): 20-24.
45 H. B. Fan and Y. Z. Huang, *J. Plant Physiol. Mol. Biol.*, 2006, **32**(4):395-402 (in Chinese).
46 G. Linder, W. Brumbaugh, P. Neitlich and E. Little, *Open J. Air Pollut.*, 2013, **2**:76-99.
47 J. Y. Kim, Y. S. Ghim, S. B. Lee, K. C. Moon, S. G. Shim, G. N. Bae and S. C. Yoon, *Water Air Soil Poll.*, 2009, **205**(1-4):259-272.
48 B. Hu, Y. Q. Wang, Y. J. Wang, B. Wang, H. L. Zhang, P. Guo and C. X. Liu, *Res. Environ. Sci.*, 2015, **8**(3): 418-424 (in Chinese).
49 B. Z. Houlton and S. L. Morford, *Soil,* 2015, **1**: 381-397.

TABLES

Table 1 Red soil chemical properties

Soil layer (cm)	pH	SBD (g cm^{-1})	SWC (%)	SOM (g kg^{-1})	AN (mg kg^{-1})			BCs (cmol (+) kg^{-1})				CEC (cmol kg^{-1})	TEB	BS (%)
					N	P	K	K^+	Na^+	Mg^{2+}	Ca^{2+}			
0-20	4.56	1.34	23.05	9.32	46.87	14.27	195.0	0.35	0.16	2.21	0.52	18.82	3.24	17.2
20-40	4.67	1.41	26.28	3.76	18.03	0.80	82.5	0.22	0.16	2.14	0.36	18.41	2.88	15.6
40-60	4.75	1.45	31.30	3.66	21.63	1.32	57.5	0.18	0.13	2.17	0.35	19.69	2.83	14.4

Table 2 Addition of ADN every month in 2013 (unit: kg ha^{-1} month^{-1} N)

Treatment [a)]	Jan [b)]	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
0	0	0	0	0	0	0	0	0	0	0	0	0
30	1.45	2.36	3.36	4.27	5.09	5.09	1.64	2.18	1.09	0.82	1.45	1.18
60	2.91	4.73	6.73	8.55	10.18	10.18	3.27	4.36	2.18	1.64	2.91	2.36
90 [c)]	4.36	7.09	10.09	12.82	15.27	15.27	4.91	6.55	3.27	2.45	4.36	3.55
120	5.82	9.45	13.45	17.09	20.36	20.36	6.55	8.73	4.36	3.27	5.82	4.73

Note: a) The unit of every treatment was kg ha^{-1} yr^{-1} N. The N rates of these five treatments were converted into 53.01, 106.03, 159.04, 212.05 mg/column, respectively.

b) Jan–Dec were the abbreviations for 12 months in one year. The corresponding volumes of the monthly solutions were 1.4, 2.3, 3.3, 4.2, 5.0, 5.0, 1.6, 2.1, 1.1, 0.8, 1.4 and 1.2 L, respectively, converted into 79, 130, 187, 238, 283, 283, 91, 119, 62, 45, 79 and 68 mm rainfall every month.

c) The monthly ADN additions were performed for the group experiment of simulated ADN composition change with NH_4^+/NO_3^- ratios of 1:2, 1:1, 2:1 and 4:1.

Table 3 NO_3^--N, $^{15}NO_3^-$-N, Al^{3+}, and BCs removals under different atmospheric deposition N fluxes and its NH_4^+/NO_3^- ratios (Units: mg column^{-1})

Treatments		NO_3^--N	$^{15}NO_3^-$-N	Al^{3+}	Ca^{2+}	Mg^{2+}	K^+	Na^+	TEB
ADN flux (kg ha^{-1} yr^{-1} N)	30	33.54c	3.25c	0.93 c	27.54 c	5.03 b	0.98 c	4.72 c	38.26 c
	60	73.86 b	7.43b	2.35 b	61.99 b	7.92 b	2.93 bc	11.75 b	84.59 b
	90	119.05ab	12.38a	8.95 ab	85.25 b	21.14 a	6.94 b	10.27 b	123.60 ab
	120	157.27 a	14.92a	11.00 a	146.76 a	23.37 a	9.05 a	43.18 a	222.35 a
NH_4^+/NO_3^- ratio	1:2	116.27 a	11.35a	-0.73 c	49.58 c	5.50 c	1.27 c	5.04 c	61.39 c
	1:1	118.64 a	12.16 a	4.81 b	65.28 bc	11.87 b	3.67 bc	9.18 b	90.01 b
	2:1	119.05 a	12.27 a	8.95 a	85.52 b	21.14 a	6.94 b	10.34 b	123.94 ab
	4:1	125.76 a	12.21 a	9.56 a	124.34 a	26.00 a	10.84 a	11.97 a	173.16 a

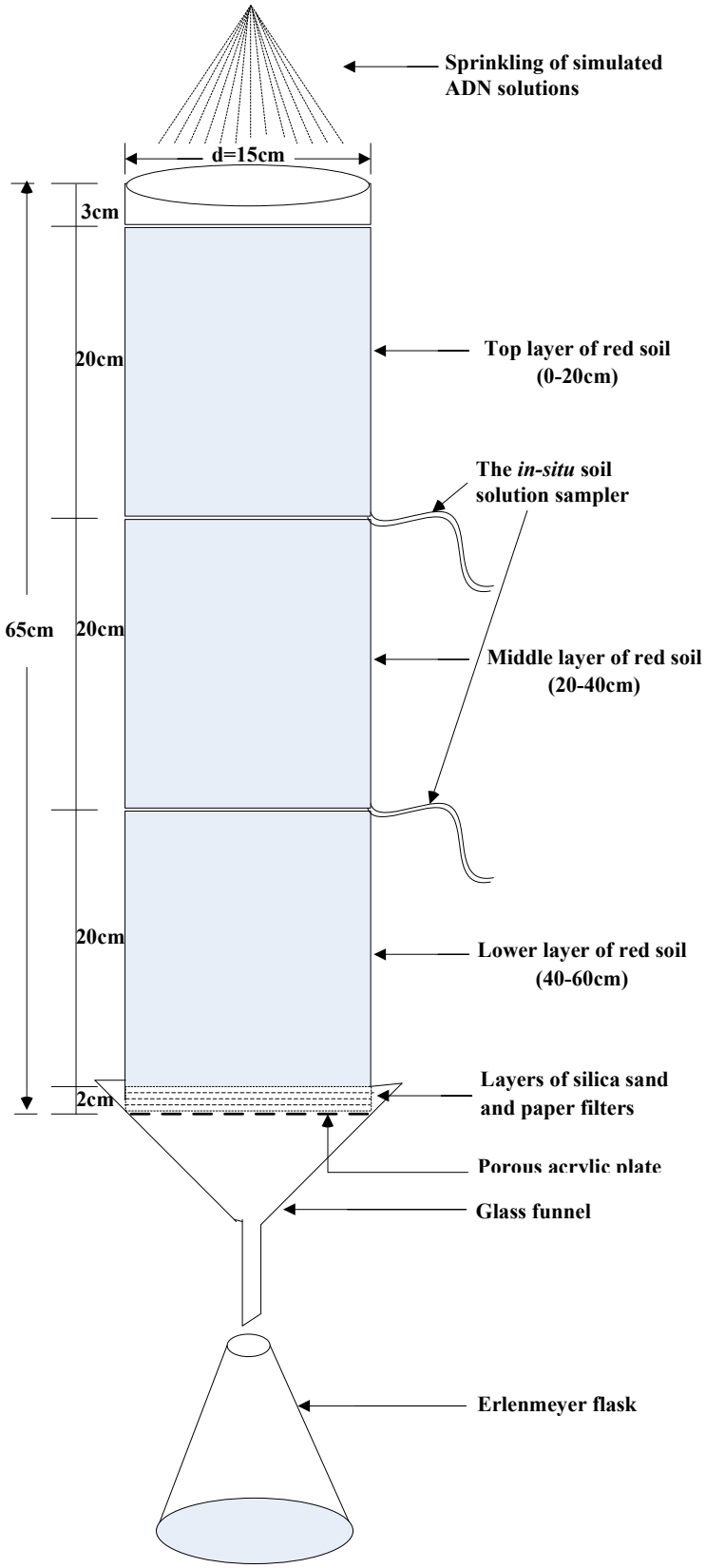
Note: CK indicates the control. Data followed by the same letter(s) in the same columns are not significantly different at $p<0.05$. This also applies to Tables 4 and 5. The leachate amounts were 1.4, 2.3, 3.3, 4.2, 5.0, 5.0, 1.6, 2.1, 1.1, 0.8, 1.4 and 1.2 L columns^{-1} during Jan–Dec, respectively.

Table 4 Effects of ADN flux on Al^{3+}, BCs and Al^{3+}/TEB of red soil solutions at different depths

Soil layer (cm)	ADN flux (kg ha^{-1} yr^{-1} N)	Al^{3+} (μmol L^{-1})	BCs (μmol L^{-1})				TEB (μmol L^{-1})	Al^{3+}/TEB (%)
			Ca^{2+}	Mg^{2+}	K^{+}	Na^{+}		
20	0	5.69 c	79.72 d	20.98 d	48.67 c	95.66 b	245.04 d	2.3 c
	30	11.17 c	122.30 c	35.68 c	69.04 b	99.74 b	326.75 c	3.4 b
	60	18.58 b	149.52 bc	50.93 b	92.08 a	108.53 b	401.06 b	4.6 a
	90	23.95 ab	176.48 ab	59.99 ab	96.85 a	110.93 b	444.25 b	5.4 a
	120	28.14 a	197.90 a	68.67 a	101.73 a	159.13 a	527.43 a	5.3 a
40	0	15.04 c	151.02 c	46.69 c	32.81 d	118.32 b	348.84 c	4.3 b
	30	20.43 bc	200.38 bc	63.93bc	42.27 cd	129.55 b	436.13 bc	4.7 b
	60	29.67 b	247.62 b	75.14 b	46.62 bc	131.96 b	501.33 b	5.9 a
	90	35.15 ab	257.45 b	83.32 ab	57.05 b	125.63 b	523.46 b	6.7 a
	120	45.00 a	338.83 a	104.43 a	74.12 a	191.08 a	708.47 a	6.4 a
60	0	7.20 b	202.10 d	52.14 b	21.73 b	119.57 b	395.55 d	1.8 b
	30	9.05 b	244.04 cd	61.94 b	23.24 b	125.04 b	454.27 cd	2.0 b
	60	10.19 b	275.48 bc	65.51 b	24.53 b	128.33 b	493.85 bc	2.1 b
	90	19.09 a	306.80 b	87.14 a	28.49 a	124.09 b	546.52 b	3.5 a
	120	20.32 a	371.62 a	97.01 a	30.16 a	173.58 a	672.37 a	3.0 a

Table 5 Effects of ADN composition (NH_4^+/NO_3^- ratio) on Al^{3+}, BCs and Al^{3+}/TEB of red soil solutions at different depths

Soil layer	NH_4^+/NO_3^- ratio	Al^{3+} (μmol L^{-1})	BCs (μmol L^{-1})				TEB (μmol L^{-1})	Al^{3+}/TEB (%)
			Ca^{2+}	Mg^{2+}	K^+	Na^+		
20 cm	CK	5.69 d	79.72 d	20.98 d	48.67 c	95.66 b	245.04 d	2.3 d
	1:2	16.56 c	147.74 c	42.16 c	78.31 c	113.33 a	381.54c	4.3 c
	1:1	16.84 c	146.80 c	50.27 bc	81.22 c	103.75a	382.04c	4.4 c
	2:1	23.95 b	176.48b	59.99 b	96.85b	110.93a	444.25b	5.4 b
	4:1	34.30 a	237.78a	80.22 a	106.78a	114.08a	538.86a	6.4 a
40 cm	CK	15.04 d	151.02 c	46.69 c	32.81 d	118.32 b	348.84 c	4.3 c
	1:2	26.94 c	235.65b	72.78 b	45.39 c	130.71a	484.52b	5.6 b
	1:1	28.70 c	239.55b	77.17 b	49.13 c	122.50a	488.36b	5.9 b
	2:1	34.33 b	259.55b	83.32 b	57.05b	125.11a	525.04b	6.5 a
	4:1	41.46 a	329.79a	99.79 a	63.93 a	125.95a	619.45a	6.7 a
60 cm	CK	7.20 c	202.10 d	52.14 c	21.73 c	119.57 b	395.55 d	1.8 bc
	1:2	6.43 c	265.96 c	62.27 c	23.52 c	117.60b	469.34c	1.4 c
	1:1	11.95 b	288.77bc	72.06 c	25.34 c	121.30ab	507.47bc	2.4 b
	2:1	19.09 a	307.51b	87.14 b	28.49b	124.32ab	547.46b	3.5 a
	4:1	20.29 a	361.74a	96.96 a	32.17 a	127.58a	618.45a	3.3 a



411

412 **Fig. 1** Schematic sketch of the experimental setup.

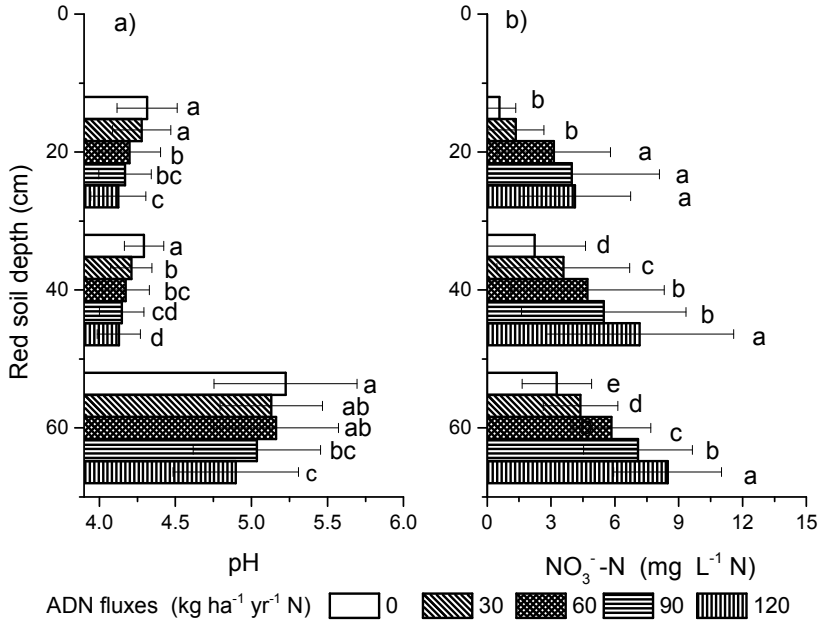
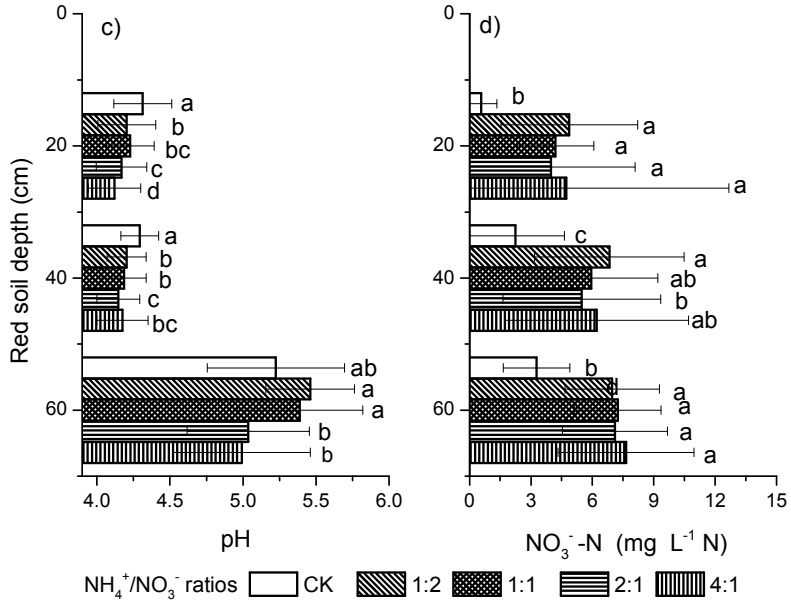
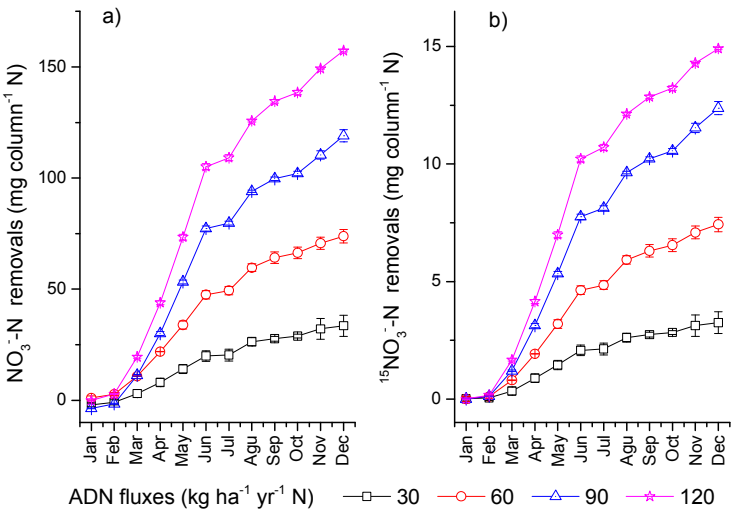


Fig. 2 Atmospheric nitrogen deposition (ADN) on solution pH value and NO_3^- concentration at different red soil depths. a-b in the up-left were effects of ADN flux with a stable composition (NH_4^+/NO_3^- ratio was 2:1) and c-d were effects of ADN composition (NH_4^+/NO_3^- ratio) with a stable ADN flux (90 kg ha^{-1} yr^{-1} N), respectively. The vertical bars denote standard errors. These letters of a, b, c, d and e in the right of the vertical bars indicate the difference with 5% level (n=36).



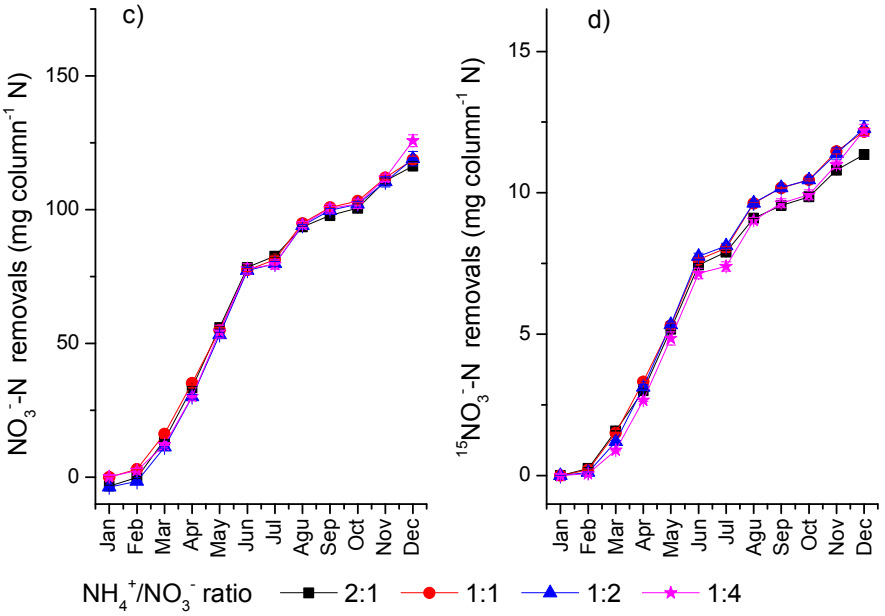
Continued Fig. 2



421

422 Fig.3 Cumulative dynamics of NO_3^--N and $^{15}NO_3^-$-N removals. a and b showed effects of ADN

423 fluxes while c and d showed effects of NH_4^+/NO_3^- ratio, respectively.



424

425 Continuted Fig.3

426

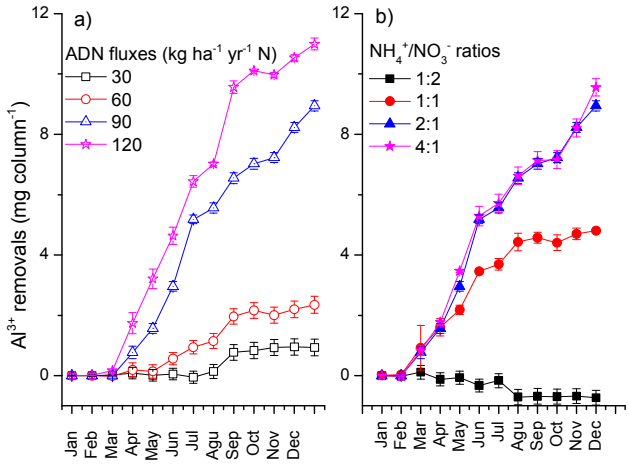


Fig.4 Cumulative dynamics of Al^{3+} removals. a and b showed effects of ADN fluxes and NH_4^+/NO_3^- ratio, respectively.

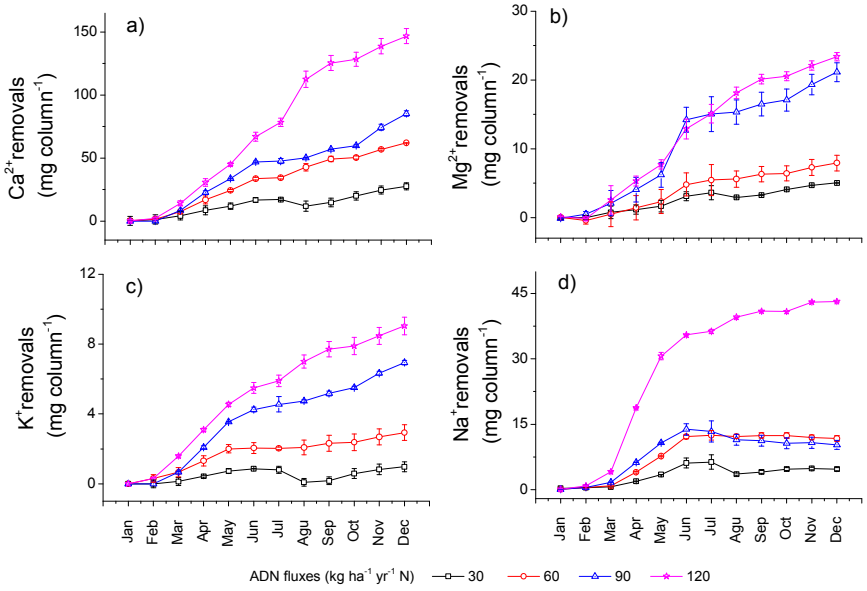
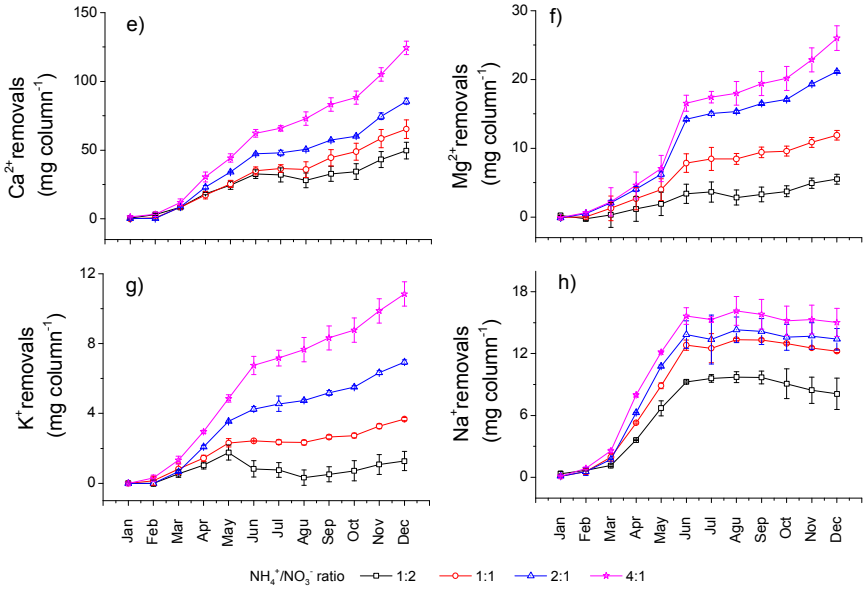


Fig.5 Cumulative dynamics of BCs removals. a-d showed effects of ADN fluxes and e-h showed effects of NH_4^+/NO_3^- ratio, respectively.



Continuted Fig. 5

Human activity has significantly altered the global nitrogen (N) cycling in the last several decades, resulting in increased atmospheric deposition N (ADN) worldwide. Existing research focuses on the quantification of ADN flux in agroecosystems, and the negative effects of ADN on soil acidification and ecological degeneration in forest ecosystems. However, related ADN composition research, especially in agricultural ecosystems, is still in its infancy. This study manages to provide an improved experiment setup to study effects of effects of ADN and its composition on red soil solution chemistry of a farmland, which is useful for future modelling and assessment of ecological critical loads of ADN and its effects in red soil farmlands.