


Quantification of the contribution of nitrogen fertilization and crop harvesting to soil acidification in a wheat-maize double cropping system

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Abstract

Background Over fertilization with nitrogen (N) is considered the main driver of agricultural soil acidification in China. However, the contribution of this driver compared to other causes of soil acidification on intensive croplands has seldom been quantified under field conditions.

Methods We measured the fate of major nutrients, and calculated the related H^+ production, based on the difference between inputs and leaching losses of those nutrients for a wheat-maize rotation system on a moderate acid silty clay loam soil in a two-year field experiment.

Results Topsoil pH decreased 0.3 units in the plots with conventional (current farmer practice) high N fertilization after two years, with a proton production of $13.1 \text{ keq } H^+ \text{ ha}^{-1} \text{ yr}^{-1}$. No apparent changes

in topsoil pH were observed in the plots without N application, in spite of a proton production of $4.7 \text{ keq } H^+ \text{ ha}^{-1} \text{ yr}^{-1}$. Crop uptake was the primary driver of H^+ production, followed by N transformation processes and HCO_3^- leaching in both plots.

Conclusions Nitrogen fertilization had a relative small direct impact on soil acidification due to a very limited nitrate leaching, induced by large N losses to air by denitrification in this specific moderately acid soil, whereas elevated base cation uptake by crops induced by N fertilization indirectly had a relative large impact.

Keywords Soil acidification · Agriculture · N fertilization · Wheat maize · Soil pH · Acid neutralizing capacity

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Introduction

Soil acidification can threaten terrestrial ecosystem functioning and services through altering biogeochemical cycles (Delhaize and Ryan 1995; Hoegh-Guldberg et al. 2007). Species, mobility and availability of elements in soil are significantly affected by soil pH (Brümmer 1986). Under low pH, there is generally a limited availability of nutrients, such as calcium, magnesium, potassium and phosphate, and elevated concentrations of toxic elements, such as aluminium, manganese and heavy metals, which can restrict plant and soil biota growth due to nutrient deficiency and metal toxicity (Kochian et al. 2004; Rengel 1992; Wang et al. 2007).

Soil acidification in response to acid atmospheric deposition, especially due to sulphur dioxide (SO₂) and to a lesser extent nitrogen oxides (NO_x) was first noticed in the 1970s in Europe, originally being held responsible for large-scale forest dieback in view of aluminium toxicity (e.g. Ulrich et al. 1979). Since the middle of the 1980s, deposition of nitrogen (N) compounds, including both NO_x and ammonia/ammonium (NH_x), dominated forest soil acidification as SO₂ deposition declined since the 1980s (de Vries et al. 2015; Van Breemen et al. 1982). Since that time, NO_x deposition also declined and soil acidification slowed down in response to reduced acid deposition in European forest (Kirk et al. 2010). However, the reverse is true for China. This is because air pollution legislation has been implemented in Europe, since the 1980s, causing declining SO₂, NO_x and NH₃ emissions but this has not been the case in China. This country is experiencing an intense atmospheric N pollution with bulk N deposition increasing on average from 13.2 kg N ha⁻¹ yr⁻¹ in 1980s to 21.1 kg N ha⁻¹ yr⁻¹ in 2010s, caused by the increased NH₃ and NO_x emissions in response to elevated N fertilizer use, livestock breeding, transport and coal consumption (Liu et al. 2013). The increased N deposition is accused to cause a widespread and significant soil acidification on natural grasslands (Yang et al. 2012) and forests (Zhu et al. 2016) during 1980s–2000s.

Soil acidification due to (N) compounds does occasionally also happen naturally, due to highly elevated natural N fixation in specific trees followed by nitrification and nitrate leaching (e.g. Van Miegroet and Cole 1984). In Australia and New Zealand extensive soil acidification with aluminium toxicity was also experienced on grassland via biologically fixed N, followed by

leaching of nitrate accompanied with cations from soils and continuous uptake of more cations than anions (Bolan et al. 1991; Edmeades et al. 1983). Subsequently, many management measures were practiced to relieve soil acidification, such as planting deep-rooted perennial species to reduce nitrate loss and the use of lime or other alkaline material to neutralize soil acidification (Ridley et al. 1990).

Identical but more serious acidification has occurred in agriculture ecosystems where abundant N fertilizers are applied and large amount of base cations (BCs) are removed by harvest (Guo et al. 2010). Rates and types of N fertilizer, and cation and anion uptake by plant greatly influence soil acidification on cropland (Bouman et al. 1995; Pierre et al. 1971). Nutrient management measures that have been suggested to relieve soil acidification, apart from application of alkaline material (lime, dolomite, plant ash etc.), includes the application of an appropriate N fertilizer form (nitrate-based and organic fertilizer) at an appropriate application rate, effectively reducing nitrification and N leaching (Goulding 2016; Whalen et al. 2000).

From 1980s to 2000s, the topsoil pH of major Chinese croplands decreased significantly, with the average pH declining between 0.13 and 0.80 units, depending on crops and soil types, which is attributed to excess N fertilizer application (Guo et al. 2010). At current farmers' fertilization practice (209–220 kg N ha⁻¹ per crop season) in Chinese main cereal production areas, the average N surplus (N fertilizer applied in excess of uptake by crops) was 72–82 kg N ha⁻¹ during 2007 and 2009, due to relatively low crop yields (5.7 ton ha⁻¹ for wheat, 7.0 ton ha⁻¹ for rice and 7.6 ton ha⁻¹ for maize) and related low N uptake, indicating poor nutrient management practices (Chen et al. 2014). Many long-term experiments have indeed shown that soil pH has significantly decreased due to long-term application of ammonium- or urea-based N fertilizers in croplands, especially in soils with a low H⁺-buffer capacity in the southern and eastern parts of China (Miao et al. 2010; Zhang et al. 2009).

In view of the potential impacts of soil acidification on crop yields, thus affecting food security, more insight in the quantification of soil acidification rates and the contribution of main drivers of acidification is urgently needed. This allows to understand and quantify the impacts of nutrient management on soil acidification, defined as a change in soil acid neutralizing capacity (ANC) (De Vries and

Breeuwsma 1986; Van Breemen et al. 1984). Input-output budgets of major elements have been used to assess soil acidification in non-agricultural land, but this type of research has until now hardly been carried out in agricultural lands. Here, we describe a field experiment that was conducted to evaluate the impacts of conventional N fertilizer application (current farmer practice) in China on soil acidification by quantifying the acid (H^+) production and consumption, as well as the contributions of N inputs by fertilizer and deposition and the role of vegetation uptake and natural bicarbonate leaching on soil acidification.

Materials and methods

A field experiment was set up with winter wheat and summer maize rotation on a moderately acid soil (pH 5.1 in topsoil of 0–20 cm) to evaluate the impacts of conventional N fertilizer application on soil acidification. This was done by measuring and quantifying the inputs (deposition and fertilizer) and outputs (losses to air and water, harvest removal and accumulation in soil) of N and other major elements, being a prerequisite to calculate H^+ production (H_{pro}). We quantified the contribution of N input via deposition/fertilizer and base cation removal by crop harvesting to acidification, in terms of soil ANC decrease. In addition, we assessed the change in soil exchangeable base cation pool, being a measure for the sensitivity to acidification (ANC decrease).

Location

The field experiment was located at Huangzhuang village (29°03.85'N, 106°11.37'E, 285 m above sea level) with a hilly landscape and humid subtropical climate in Chongqing City, China. During the 2-year experiment (2014–2016), average annual temperature was 18.3 °C, average annual precipitation was 1089 mm and annual relative humidity averaged 89.9%. Soil texture was classified as silty loam, based on a mechanical composition of 20.3% sand, 58.0% silt and 21.7% clay in the topsoil (0–20 cm) using the USDA soil texture classification. According to the FAO soil classification system, the soil was classified as a Cambisol (IUSS Working Group WRB 2014). The physical and chemical properties of the soil at three layers (0–20, 20–40 and 40–

60 cm) are shown in Table 1. The methods that were used to assess those soil properties are given in the Measurements section. The soil is poor in organic carbon (below 1%) and thus also in organic N. The C/N ratio is low (from 6 to 9, indicating a relative strong N enrichment). The results for available P (Bray-P) indicated that P concentrations in the topsoil (0–20 cm, near 75 mg kg⁻¹) are strongly enhanced compared to the subsoil, while a similar but weaker pattern was found for available K (NH₄OAc extractable K, near 200 mg kg⁻¹ in topsoil). The soil has a high P and K supplying capacity, most likely due to P and K that has been accumulated in the last decade in response to over fertilization in the previous rape and sorghum planting.

Field experiment

Set up of the experiment

Winter wheat and summer maize as an annual rotation were planted during 2014–2016. Wheat was sown after tillage around 7th November in rows with a spacing of 20 cm between the seeds and a row spacing of 27 cm (~100 kg seeds ha⁻¹, ~10 seeds per hole, Field seedling emergence >90%, Varieties: Chuanmai 15 for 2014 and Chuanmai 104 for 2015). Wheat was harvested around 5th May in the following year. Maize was immediately transplanted after the harvest of winter wheat, following a tillage with a hole spacing of 40 cm and a row spacing of 100 cm (about 50,000 plants ha⁻¹, 2 plants per hole, Varieties: Yunuo 8 (waxy corn) for 2015 and Hemuyu 918 (yellow corn) for 2016). Maize was harvested at the end of August and in November, the next round started with wheat sowing, following the same patterns as in the first year. In total, there were four harvests in 2 years (2 for winter wheat and 2 for summer maize). No irrigation was applied during the whole cropping season.

A randomized complete block design was employed with a control (non-N fertilized) plot and an N treatment plot, each including three replicates. The N treatment was set at 240 kg Urea-N ha⁻¹ for wheat (120 kg N ha⁻¹ applied before sowing and 120 kg N ha⁻¹ applied at the tillering stage) and 320 kg Urea-N ha⁻¹ for maize (160 kg N ha⁻¹ applied before transplanting and 160 kg N ha⁻¹ applied at the 12th leaf stage (V12). These are conventional N application rates (farmers' practice in Sichuan during 2005–2010, including chemical and organic fertilizers) (Zhang 2013; Zhu et al. 2018), which are clearly far above regional

Table 1 Characteristics of the soil at three depths (0–20, 20–40 and 40–60 cm)

Depth cm	pH	BD ^a g cm ⁻³	TN ^a %	OC ^a %	CEC meq kg ⁻¹	BS ^a %	Bray-P mg kg ⁻¹	NH ₄ OAc-K mg kg ⁻¹
0–20	5.1	1.37	0.143	0.93	277	75	75.6	219
20–40	5.0	1.44	0.109	0.89	273	71	33.0	167
40–60	5.0	1.45	0.106	0.88	268	85	26.5	181

The soils were sampled before the experiment at nine sampling points across the field and the results represent the average values

^aBD: Bulk Density; TN: Total Nitrogen; OC: Organic Carbon; BS: Base Saturation

recommended N fertilization rates (Wu 2014). Sufficient phosphorus and potassium fertilizers (60 kg P ha⁻¹ and 70 kg K ha⁻¹), being twice as high as the recommended fertilization (Wu 2014), were applied at all plots before sowing/transplanting in the forms of calcium superphosphate and potassium chloride, respectively. All chemical fertilizers were broadcasted on the soil surface, N fertilizer was broadcasted in bands for the second split application and no manure was applied. Plots of 30 m² (5 m wide × 6 m long) were separated by a 20-cm-wide and 10-cm-high dam to minimize the effects of the two adjacent plots and avoid losses of nutrients and water by runoff.

Measurement devices and sampling methods

Bulk deposition (precipitation) samples were collected on a daily basis (8:00 a.m.–8:00 a.m. next day) using a precipitation gauge (SDM6, Tianjin Weather Equipment Inc., China) located 450 m away from the experimental field. The precipitation (rainwater, snow if any) collector was made of a stainless steel funnel connected to a glass bottle (vol. 2000–2500 mL). Precipitation amounts were measured using a measuring cylinder (scale range: 0–10 mm; division: 0.1 mm) coupled with the gauge. The collected samples were thoroughly stirred and then immediately stored in clean polyethylene bottles (60 mL). All daily collected samples were frozen at -18 °C until delivery to the laboratory at China Agricultural University (CAU) for chemical composition analysis, including H⁺ (shown as pH), NH₄⁺, Ca²⁺, Mg²⁺, K⁺, Na⁺, Al³⁺, Fe³⁺, Mn²⁺, H₂PO₄⁻, Cl⁻ and SO₄²⁻. The gauges were cleaned with high-purity water after each collection and once every week in order to avoid cross contamination.

To assess the dry deposition of nitrogen compounds, monthly concentrations of gaseous NH₃, NO₂ and HNO₃, and particulate NH₄⁺ (pNH₄⁺) and NO₃⁻

(pNO₃⁻) were measured using continuous active and passive samplers. DELTA active sampling systems (Denuder for Long-Term Atmospheric sampling), described in detail in Flechard et al. (2011); Sutton et al. (2001), were used to collect NH₃, HNO₃, pNH₄⁺ and pNO₃⁻; while NO₂ samples were collected using Gradko diffusion tubes (Gradko International Limited, UK). The air intakes of the DELTA system and the NO₂ tubes were set at a height of 2 m above the ground.

Ammonia emission was measured by a closed sponge adsorption method (Qianqian Li, unpublished) with approximately 90% nitrogen recovery, developed on the basis of a half open sponge method (Nõmmik 1973; Cantarella et al. 2003). The device consisted of a PVC cylinder (Diameter 20 cm, Height 75 cm) fixed in soil and a PVC cover (Diameter 20 cm, Thickness 5 cm) in which a sponge of 2 cm thickness was fixed. The sponge was saturated with 35 mL PG-mix solution (preparation: mix 200 mL deionized water with 400 mL 85% phosphoric acid and add 60 mL glycerine, then dilute with deionized water to 1000 mL), which is an ammonia adsorbent. The above ground part of the cylinder and the cover were sealed with tape.

Weekly samples were taken in the first month after fertilization and monthly samples in the remaining period until harvest. The sampled sponge was immediately pressed and extracted four times with 50 mL deionized water in a PVC vessel. All extractions were collected together, diluted with deionized water to 1000 mL and immediately injected into a 10 mL centrifuge tube with PES membrane filter caps (0.45 µm Pore, 13 mm Diameter, Tengda Inc., Tianjin, China). All samples were frozen at -18 °C until delivery to the laboratory at China Agricultural University (CAU) for mineral nitrogen analysis.

Leaching was measured by one lysimeter and three suction cups per plot (Fig. S1). In both cases, continuous sampling for one week was carried out after fertilization and weekly sampling for the rest of the period until

harvest. In the time between harvest of maize and planting of wheat (nearly two months), sampling took place at monthly intervals.

The lysimeter (see also Fig. S2) was made up of: 1) a stainless steel square collection box (length: 50 cm) buried at 60 cm soil depth and filled with 2 mm diameter quartz particles to ensure water conductivity; 2) a grass leachate-store bottle (vol. 10000 mL, protected by an PVC cylinder), with its top 20 cm away from the collection box, with two Teflon pipes connected to the air and a sampling device, respectively; and 3) a sampling device consisting of a collection bottle (vol. 10000 mL), a buffer bottle (vol. 500 mL) and a vacuum pump. The suction cups consisted of 2 cm diameter clay pipes, air switches, sampling bottles and air pumps (see also Fig. S3). Suction cups were fixed in the soil at 60 cm deep and no disturbance was allowed within 50 cm of the suction cup.

Samples of the three suction cups per plot were equally mixed into one sample. The two samples (lysimeter and mixed suction cups) per sampling event were immediately stored in clean polyethylene bottles (60 mL). All collected samples were frozen at -18°C until delivery to the laboratory at China Agricultural University (CAU) for chemical composition analysis.

Measurements

Fertilizer composition We used pure urea (no contamination with other elements). The total nutrient composition of P (calcium superphosphate) and K (KCl) fertilizers was based on acid-digestion according to the method by Nziguheba and Smolders (2008). Three concentrated nitric acid (Guaranteed Reagent) samples as reference materials were analysed simultaneously to ensure the accuracy of sample analysis. Anions were analysed by ICS-2100, which consists of a separation column (Dionex Ionpac AS11) and a guard column (Dionex Ionpac AG11). Cations were analysed by DX-600, which consists of a separation column (Dionex CS12A), a guard column (Dionex AG12A), a self-regenerating suppressed conductivity detector (Dionex Ionpac ED50), gradient pump (Dionex Ionpac GP50), and chromatographic box (LC20). The concentrations in the fertilizer are given in (Table 2).

Element concentrations in deposition, emission and leachate The measurements of N compounds in monthly dry deposition are given in Xu et al. (2015). The bulk deposition and leaching samples were filtered through a

PES membrane filter (0.45 μm , Tengda Inc., Tianjin, China). Ammonium (NH_4^+) and nitrate (NO_3^-) in filtered solutions, including NH_4^+ in extracted emission samples, were measured with an AA3 continuous-flow analyser (Bran + Luebbe GmbH, Norderstedt, Germany). Major cations (Ca^{2+} , Mg^{2+} , K^+ , Na^+ , Al^{3+} , Fe^{3+} and Mn^{2+}) and phosphate (H_2PO_4^-) were measured with inductively coupled plasma-atomic emission spectrometry (ICP-AES, OPTIMA 3300 DV, Perkin-Elmer, USA). Water-soluble anions (Cl^- , SO_4^{2-}) were analysed by Dionex ICS-2100. HCO_3^- was measured by acid titration (standard acid corrected by Na_2CO_3 : 0.5xxx M $1/2\text{H}_2\text{SO}_4$, indicator: methyl orange). High-purity water samples were used as reference materials.

Crop yields and nutrient concentrations in grain and straw All plants in 3 yield-test zones (zones of $100\text{ cm} \times 108\text{ cm}$ for wheat, implying 20 (60) plant holes in each zone (total zones) and of $100\text{ cm} \times 440\text{ cm}$ for maize, implying 11(33) plant holes in each zone (total zones)) were harvested to estimate yields at maturity. At harvest, plants were divided into grain and straw to determine the above-ground biomass and nutrient removal in both the edible parts and the crop residues. The samples were immediately sent to a local laboratory, where they were washed with deionized water, oven-dried at 70°C to constant weight and then weighed. Grain and straw yields (kg ha^{-1}) were calculated using the weights divided by the area.

Plant samples were grinded with a stainless steel grinder (JSP-1500A, Jinsui, Zhejiang, China) and digested with $\text{HNO}_3\text{-H}_2\text{O}_2$ in a microwave accelerated reaction system (CEM, Matthews, NC, USA). The concentrations of P, Ca, Mg, K, Na, Al, Fe and Mn in the digested solutions were determined by ICP-AES (OPTIMA 3300 DV, Perkin-Elmer, USA). IPE126 maize plant and IPE200 maize shoots (Wageningen University, The Netherlands) were used as reference materials. Subsamples were mineralized using $\text{H}_2\text{SO}_4\text{-H}_2\text{O}_2$, after which the N concentration was determined using the Kjeldahl method (Horowitz 1970). Nutrient removals (kg ha^{-1}) by grain and straw (crop residues) were calculated by multiplying the crop yield (grain biomass) and crop residues (straw biomass) with nutrient concentrations in grain and straw, respectively.

Soil properties Soil properties of the three soil layers (0–20, 20–40 and 40–60 cm) were measured at the beginning and after every crop season (half year) as follows:

Table 2 Chemical compositions of the applied N, P and K fertilizers (unit: g kg⁻¹)

Fertilizers types	N	Al ³⁺	Ca ²⁺	Fe ³⁺	K ⁺	Mg ²⁺	Mn ²⁺	Na ⁺	H ₂ PO ₄ ⁻	Zn ²⁺	Cl ⁻	SO ₄ ²⁻
Urea*	464	–	–	–	–	–	–	–	–	–	–	–
NH ₄ Cl	254.0	0.0	0.0	0.0	0.0	0.0	0.0	7.1	0.0	0.0	655.0	5.7
Calcium superphosphate	–	2.6	247.4	2.3	0.9	6.9	0.1	0.2	171.1	0.0	4.9	548.5
KCl	–	0.1	0.5	0.5	506.3	0.4	0.0	8.9	0.0	0.0	468.1	12.3

* Urea data is from the product (pure urea) table with N content (46.4%)

Soil pH (H₂O) was determined using a 1:2.5 soil water ratio with a pH meter (S220 Seven Compact pH/ion, Mettler Toledo, Switzerland). Soil cation exchange capacity (CEC) was determined using the buffered ammonium acetate method at pH 7 and the contents of exchangeable base cations (BCs: Ca²⁺, Mg²⁺, K⁺, Na⁺) were determined by ICP-AES (OPTIMA 3300 DV, Perkin-Elmer, USA). Nitrate and ammonium in soils was extracted with 0.01 M CaCl₂ solution. The concentrations of NH₄⁺-N and NO₃⁻-N were measured with AA3 continuous-flow analyser (Bran + Luebbe GmbH, Norderstedt, Germany). The soil organic carbon content (OC) was determined using the Schollenberger procedure (1945). The total nitrogen content (TN) was measured by the Kjeldahl method (Bremner 1965) and the clay content was determined using the standard pipet method (Gee and Bauder 1986). Bray-P was measured by an extraction method with 0.025 M HCl and 0.03 M NH₄F (Bray and Kurtz 1945).

Data evaluation

Assessment of deposition and leaching

Total deposition of N compounds was assessed by adding the measured daily bulk deposition and the calculated dry deposition of those compounds. Bulk deposition was calculated by multiplication of measured daily rainwater fluxes with measured daily concentrations in rainwater. The dry deposition flux of Nr species was calculated by multiplying monthly measured concentrations of gaseous NH₃, NO₂ and HNO₃, and particulate NH₄⁺ (pNH₄⁺) and NO₃⁻ (pNO₃⁻) and a modeled dry deposition velocity (Vd) (Pan et al. 2012; Schwede et al. 2011). The value used for Vd was a monthly average local value calculated by the GEOS-Chem chemical transport model (CTM) (Bey et al. 2001). Detailed information about the calculation can be found in Xu et al. (2015).

Total deposition of all other elements was assessed by multiplying the measured daily bulk deposition with the ratio of total deposition to bulk deposition using literature information on the ratio of elements in throughfall and bulk precipitation. For P the ratio was set at 2.2, based on China averaged data published by Du et al. (2016). For SO₄²⁻ and BCs, we used values of 1.4 and 1.1 based on Zhu et al. (2016).

Total element loss by leaching was calculated by multiplication of weekly water fluxes with weekly concentrations in leachates. Water fluxes (Litre m⁻² per week) were calculated by division of the measured weekly water/leachate volume (L) from the lysimeter with the area of the lysimeter (0.5 m × 0.5 m) (see also Fig. S2).

Assessment of N mineralization

Soil N mineralization for all plots was assumed to be equal to the no N fertilized (control) plots (Cui et al. 2008). Based on previous calculation methods (Cabrera and Kissel 1988; Olf et al. 2005), N mineralization in the control plot was calculated as plant N uptake, corrected for natural input, accumulation and loss fluxes, according to:

$$N_{\text{MIN}} = N_{\text{upt}} + \text{NH}_{3,\text{em}} + N_{\text{le}} + N_{\text{min,end}} - N_{\text{min,start}} - N_{\text{dep}} \quad (1)$$

where MIN represents soil mineralization; upt represents plant uptake by aboveground biomass (straw and grain); em represents emission loss; le represents leaching loss; N_{min,start} and N_{min,end} represents the amount of mineral N in a soil layer of 0–60 cm before planting and after harvest and dep represents input via dry and wet deposition, respectively. Both N fixation and denitrification were assumed to be negligible in this approach. N fixation is very low in cereals i.e. approximately 5 kg N ha⁻¹ yr⁻¹ (Herridge et al. 2008; Smil 1999), accounting for 1% of the N fertilization in this study.

Denitrification is also likely to be negligible for the control plot, because the sum of soil mineral N retention and N outputs (N uptake, NH₃ emission and N leaching) exceeded N external input (N deposition) (Table 3) and there was hardly N surplus to be denitrified. This could be balanced by soil mineralization.

Assessment of element and acidity budgets

The acidity budget, which is the key budget to identify soil acidification, was calculated by aggregating the various H⁺ production and consumption processes, (all in keq ha⁻¹ yr.⁻¹) (De Vries and Breeuwsma 1987).

Table 3 The average major element budgets (keq ha⁻¹) for the control plot (a) and the N treated plot (b) during the complete observation period (Nov. 2014 – Aug. 2016)

Sources	Average element budgets in soil of 0–60 cm					
	NH ₄ ⁺ -N	NO ₃ ⁻ -N	BCs ^a	ACs ^a	AAs ^a	HCO ₃ ⁻ -C
a: Control plot						
Input to land						
Atmospheric deposition	3.49	1.83	5.35	0.07	4.53	0.00
Mineral fertilizer	0.00	0.00	67.13	1.93	68.75	0.00
N mineralization	7.39					
Total input	10.88	1.83	72.48	2.00	73.28	0.00
Output from land						
Crop removal	11.40		7.10	0.94	2.21	0.00
NH ₃ emission	0.60					
Denitrification		0.00				
Leaching	0.17	0.18	35.67	0.41	34.07	0.67
Actual soil accumulation ^b	-0.15	0.51	13.77	-2.31	-	0.00
Total output	12.71		56.54	-0.96	-	0.67
Balance ^c	0.00		15.94	2.96	-	-0.67
b: Urea treatment						
Input to land						
Atmospheric deposition	3.49	1.83	5.35	0.07	4.53	0.00
Mineral fertilizer	40.00	40.00	67.13	1.93	68.75	0.00
N mineralization	7.39					
Total input	50.88	41.83	72.48	2.00	73.28	0.00
Output from land						
Crop removal	40.60		20.36	1.27	3.88	0.00
NH ₃ emission	2.70					
Denitrification		40.64				
Leaching	0.40	4.55	55.91	0.53	51.14	0.48
Actual soil accumulation ^b	-0.24	4.06	-19.24	1.89	-	0.00
Total output	92.71		57.03	3.69	-	0.48
Balance ^c	0.00		15.45	-1.69	-	-0.48

^a BCs indicates base cations (Ca²⁺, Mg²⁺, K⁺, and Na⁺), ACs indicates acid cations (Al³⁺, Fe³⁺, and Mn²⁺), AAs indicates acid anions (Cl⁻, H₂PO₄⁻, and SO₄²⁻, but only latter two for crop removal)

^b Actual soil accumulations were the measured soil available nutrients (end value minus start value), including soil mineral N and exchangeable base and acid cations

^c Balance equals all inputs minus all outputs, also considered as the difference between the calculated surplus and actual soil accumulation

*Nitrification was not showed here for the unknown nitrogen uptake forms by plants, and did not affect the calculation of N cycle as an intermediate process in N transformation

The H^+ production by N transformations ($H_{\text{pro,N}}$) was calculated as:

$$H_{\text{pro,N}} = \text{NH}_4^+_{\text{in}} - \text{NH}_4^+_{\text{le}} + \text{NO}_3^-_{\text{le}} - \text{NO}_3^-_{\text{in}} \quad (2)$$

where 'in' represents input via fertilizer and deposition and 'le' present leaching losses from the root zone. Here, we treated the Urea-N input as if it was NH_4NO_3 , since NH_4NO_3 has an equal acidification potential as urea after urea hydrolysis is completed.

The H^+ production by net HCO_3^- leaching ($H_{\text{pro,HCO}_3}$) was calculated as

$$H_{\text{pro,HCO}_3} = \text{HCO}_3^-_{\text{le}} - \text{HCO}_3^-_{\text{in}} \quad (3)$$

where inputs via fertilizer and deposition were almost negligible in this study.

The H^+ production by plant uptake of cations and acid anions ($H_{\text{pro,upt}}$) was calculated as:

$$H_{\text{pro,upt}} = \text{Cat}_{\text{upt}} - \text{An}_{\text{upt}} \quad (4)$$

where cations (Cat) includes both base cations (Ca^{2+} , Mg^{2+} , K^+ , and Na^+) and acid cations (Al^{3+} , Fe^{3+} , and Mn^{2+}) and Anions (An) are limited to SO_4^{2-} and H_2PO_4^- .

The total H^+ production ($H_{\text{pro,total}}$) was calculated as:

$$H_{\text{pro,total}} = H_{\text{pro,N}} + H_{\text{pro,HCO}_3} + H_{\text{pro,upt}} \quad (5)$$

Soil acidification includes actual acidification and potential acidification. In line with De Vries and Breeuwsma (1987), we defined actual acidification as net cation loss, and potential acidification as net anion accumulation. The soil ANC change (ΔANC) by cations (Cat)/ acid anions (An) and the total soil ANC change were calculated as:

$$\begin{aligned} \text{Actual soil acidification } (\Delta\text{ANC}_{\text{Cat}}) \\ = \text{Cat}_{\text{out}} - \text{Cat}_{\text{in}} = \text{Cat}_{\text{upt}} + \text{Cat}_{\text{le}} - \text{Cat}_{\text{in}} \end{aligned} \quad (6)$$

$$\begin{aligned} \text{Potential soil acidification } (\Delta\text{ANC}_{\text{An}}) \\ = \text{An}_{\text{in}} - \text{An}_{\text{out}} = \text{An}_{\text{in}} - \text{An}_{\text{upt}} - \text{An}_{\text{le}} \end{aligned} \quad (7)$$

$$\Delta\text{ANC} = \Delta\text{ANC}_{\text{Cat}} + \Delta\text{ANC}_{\text{An}} \quad (8)$$

Two calculation approaches were used to define nutrient use efficiency. The agronomic one, also called recovery efficiency (Cassman et al. 2002), was used to assess fertilizer efficiency by comparing N treated plots with control plots. Note however that P and K fertilizers were applied at the same rates in both control and N treated plots. Therefore, the P and K use efficiencies calculated by

the approach above only indicate the effect of N addition on the P and K fertilizer use efficiencies, rather than the real P and K fertilizer efficiency by comparing P or K fertilization and no fertilization. The agronomic nutrient use efficiency ($\text{NUE}_{\text{agronomic}}$) was calculated as:

$$\begin{aligned} \text{NUE}_{\text{agronomic}}(\%) \\ = (\text{Nutrient}_{\text{upt,t}} - \text{Nutrient}_{\text{upt,c}}) / \text{Nutrient}_{\text{fer}} \times 100 \end{aligned} \quad (9)$$

where Nutrient represents Nitrogen (N), Phosphorus (P) or Potassium (K); t and c represent N treated and control plots, respectively; fer represents fertilizer rate (all in $\text{kg ha}^{-1} \text{ yr}^{-1}$).

Another calculation method is the environmental nutrient use efficiency, which gives an indication of the surplus and the related accumulation in soil and losses to air and water, using the uptake divided by input without considering control plots. The environmental nutrient use efficiency ($\text{NUE}_{\text{environ}}$), was calculated as:

$$\text{NUE}_{\text{environ}}(\%) = \text{Nutrient}_{\text{upt}} / \text{Nutrient}_{\text{input}} \times 100 \quad (10)$$

where input represents all the nutrient input via atmospheric deposition, fertilization (All in $\text{kg ha}^{-1} \text{ yr}^{-1}$). Note that no manure and organic residue were added in the study and biological N fixation was considered negligible.

The NH_3 emission fraction (fr_{NH_3} , %) was calculated as:

$$\text{fr}_{\text{NH}_3} = (\text{NH}_{3,\text{em,t}} - \text{NH}_{3,\text{em,c}}) / \text{N}_{\text{fer}} \times 100 \quad (11)$$

In calculating denitrification, nitrification had no effect on the calculation of denitrification (see also Table S1, where we assumed three optional patterns of nitrogen uptake to calculate nitrification). Based on the input – output mass balance, denitrification and the denitrification fraction (fr_{de} , %) in N treated plot were calculated as:

$$\text{Denitrification} = \text{N}_{\text{in}} + \text{N}_{\text{MIN}} - \text{N}_{\text{upt}} - \text{NH}_{3,\text{em}} - \text{N}_{\text{le}} - \text{N}_{\text{acc}} \quad (12)$$

$$\text{fr}_{\text{de}} = \text{Denitrification} / (\text{N}_{\text{in}} + \text{N}_{\text{MIN}} - \text{N}_{\text{upt}} - \text{NH}_{3,\text{em}} - \text{N}_{\text{acc}}) \times 100 \quad (13)$$

where acc represents soil net accumulation ($\text{N}_{\text{min,end}}$ minus $\text{N}_{\text{min,start}}$). In the calculation, N runoff is not included, since runoff was avoided by building dams (10 cm height) between plots in this study.

Actual changes in soil exchangeable BCs pool (keq ha^{-1}) were directly measured before planting and after harvest. The soil BCs pool of 0–60 cm depth is too large

to find significant changes within such a short period. So exchangeable soil BCs pools of 0–20 cm, 20–40 cm and 40–60 cm were measured, respectively. The changes were compared with the soil residual BCs calculated by a mass as $\Delta\text{Exchangeable BC pool} = \text{BC}_{\text{in}} - \text{BC}_{\text{upt}} - \text{BC}_{\text{le}} - \text{BC}_{\text{weathering}}$.

All fluxes were measured except the weathering rate, which is negligible small (estimated near $0.6 \text{ keq ha}^{-1} \text{ yr}^{-1}$ for a Purple Soil by Duan et al. (2002), comparing to the BCs input (near $36 \text{ keq ha}^{-1} \text{ yr}^{-1}$) via fertilization and deposition (Table 3).

Statistical analysis

Repeated-measures analysis of variance (ANOVA) was used to test the effects of fertilization on soil pH and soil exchangeable base cations. When the ANOVA results were significant, the Tukey's Honestly Significance Difference (HSD) test was used to determine the significance of the difference between means at $P < 0.05$. All the statistical analyses were conducted using IBM SPSS Version 23.0 (IBM Corp., Armonk, NY, USA). Figures were drawn using OriginPro 2015 (OriginLab Corporation, Northampton, MA, USA).

Results

Input-output budgets of major nutrients, and nutrient use efficiencies

The average input-output budgets of N, base cations (BCs), acid cations (ACs), acid anions (AAs) and bicarbonate ion (HCO_3^-) for control and N treated plots during two years are presented in Table 3.

Nitrogen

Atmospheric deposition and soil mineralization during the two years contributed 5.32 and $7.39 \text{ keq N ha}^{-1}$ (approximately 37.2 and $51.7 \text{ kg N ha}^{-1} \text{ yr}^{-1}$), respectively. N deposition consisted of 66% NH_4^+ -N and 34% NO_3^- -N and contributed 5.7% of the total N input by both N fertilizer and N deposition in the N treated plot. Compared to the control plot, N application significantly enhanced all the N output pathways (Table 3). N removal by crop was the largest or second largest output, respectively in control and N treated plots, accounting for 89.8 and 43.8% of the

total N input, respectively. In the N treated plot, N losses through NH_3 emission, denitrification and leaching equalled 2.9%, 43.9 and 5.3% of the total N input, whereas this was only 4.7%, 0.0 and 2.8% in the control plot. The calculated fractions of N that were emitted to air as NH_3 , fr_{NH_3} , and as N_2 , N_2O or NO_x via denitrification of the N surplus, fr_{de} , averaged 2.6 and 89.9% in the N treated plot during the two years, being similar in the 1st year and 2nd year (Table 4). Denitrification was thus the major N loss pathway in the N treated plot, accounting for 43.8% of the N input and even 89.9% of the N surplus, being comparable to crop N removal. In leaching water, NO_3^- -N was dominant in the N treated plot, being 11 times as high as NH_4^+ -N, while NO_3^- -N and NH_4^+ -N were almost equal in the control plot. Only 2.8 and 4.5% of the total N input was retained in soil for the control and N treated plots, respectively.

In summary, in the control plot, crop removal was the dominant N output, whereas denitrification was negligible and both N leaching and NH_3 emission were very limited (Table 3). In the N treated plot, 44% of the N input was used by crop uptake, but also here both N leaching and NH_3 emission were very limited since the N surplus (N input minus N uptake) was mainly denitrified (nearly 90%) and partly retained in soil.

Table 4 NUE, PUE, KUE, fr_{NH_3} and fr_{de} for 1st year, 2nd year and two years in N treated plots

Index (%)		1st year	2nd year	Two years
$\text{NUE}_{\text{Agron.}}$ *		29.7	43.3	36.5
$\text{PUE}_{\text{Agron.}}$		10.0	18.5	14.3
$\text{KUE}_{\text{Agron.}}$		90.1	141.2	115.6
$\text{NUE}_{\text{Environ.}}$ *	Control	72.8	64.4	69.1
	N treated	37.9	46.5	42.1
$\text{PUE}_{\text{Environ.}}$	Control	16.7	16.2	16.5
	N treated	26.7	34.7	30.7
$\text{KUE}_{\text{Environ.}}$	Control	69.2	42.2	55.7
	N treated	155.8	179.1	167.4
fr_{NH_3}		2.4	2.9	2.6
fr_{de}		90.2	89.6	89.9

Note that NUE, PUE and KUE could also be calculated for the control plots when using the environmental definition

* Agron. represents Agronomic Use Efficiency, only for N treated plot; Environ. represents Environmental Use Efficiency, for control and N treated plots

* fr_{NH_3} and fr_{de} are only for N treated plot

Base cations, acid cations, acid anions and bicarbonate

During the two years, high BCs and AAs inputs in both plots were mainly due to the enormous Ca^{2+} and SO_4^{2-} inputs through P fertilizer (calcium superphosphate containing $\text{Ca}(\text{H}_2\text{PO}_4)_2$ and CaSO_4) with high concentrations of Ca^{2+} and SO_4^{2-} (see also Table 2 and Table S2). Ca^{2+} and SO_4^{2-} were also the dominant ions in deposition input (see also Table S2). The ACs input was relative low and mainly coming from fertilizer. Leaching was the dominant output of BCs and AAs in both plots, occupying 49.2 and 46.5% of the total BCs and AAs input in the control plot, respectively, and 77.1 and 69.8% in the N treated plot. Crop removal was a much less important output of BCs and AAs, being equal to 9.8 and 3.0% of the total input in the control plot, respectively, while being 28.1 and 5.3% in the N treated plot. However, crop removal was the largest ACs output, being 47 and 64% of the total input in the control plot and N treated plot, respectively. The results of calculated nutrient surplus (inputs minus uptake) showed that the surplus of BCs, ACs and AAs in the control plot were 90.2, 53.0 and 97.0% of the total BCs, ACs and AAs input, respectively, higher than those in the N treated plot (72.0 for BCs, 36.5% for ACs and 94.7% for AAs). The difference between inputs and outputs was expressed as a balance in Table 3, showing a similar difference in BCs and varied in ACs. Since the accumulated AAs in soil was not measured, the balance of AAs was not available.

HCO_3^- input was zero both by local acid rain (pH averaged 5.4 ± 0.1) and by fertilizers. HCO_3^- -C leaching was 28% lower in the N treat plot as compared to the control plot, in line with the acidification of the N treated plot.

Nutrient use efficiencies

During the two years, agronomic use efficiencies NUE, PUE and KUE in the N treated plot were 36.5, 14.3 and 115.6%, being lower than the environmental ones of 42.1, 30.7 and 167.4%, respectively (Table 4). The fluctuations of nutrient use efficiencies between the 1st year and 2nd year for both plots were caused by the differences in aboveground biomass and nutrient concentration (Table S3 and Table S4), especially for the N treated plot.

Drivers of soil acidification

An overview of the contribution of the drivers of soil acidification in the control plot and N treated plots during the two years of wheat-maize cropping, i.e. H^+ production by N, HCO_3^- and crop removal are presented in Fig. 1a. The soil ANC changes are shown in Fig. 1b. The total H^+ production in the N treated plot during the 1st, 2nd and two years was significantly higher than in the control plot. However, the patterns of H^+ production were quite similar (Fig. 1a). The uptake_{Cat+An} dominated the H^+ production in both plots, occupying 61(65/55) and 68(66/69)% of the total H^+ production in control and N treated plot during the two years (1st/2nd year), respectively, followed by N transformation which contributed 31(26/37) and 27(29/25)%. HCO_3^- leaching had only a weak effect on H^+ production in both plots, being 8(8/7) and 5(5/5)% of the total H^+ production, respectively. On the other hand, the patterns of soil ANC change between years/plots varied. Generally, both plots had a decrease in soil ANC during all three periods. In the control plot, the decline was due to a larger net accumulation of anions (-14.0 , -23.0 and $-37.0 \text{ keq ha}^{-1}$) as compared to cations (9.8 , 20.4 and 30.3 keq ha^{-1}) during the two years. In the N treated plot, the decrease in soil ANC was completely due to a high loss of cations ($-10.8 \text{ keq ha}^{-1}$, mainly via leaching loss) whereas the accumulation of anions was nearly negligible (0.04 keq ha^{-1}) in the 1st year. In the 2nd year, there was a net accumulation of cations (7.1 keq ha^{-1}), but much lower than the accumulation of anions ($-18.3 \text{ keq ha}^{-1}$) thus causing a decrease in soil ANC, similar to the pattern of the control plot. In the N treated plot, soil ANC decreased greatly during the two years, because of net anion accumulation ($-18.3 \text{ keq ha}^{-1}$) and much less due to net cation loss (-3.7 keq ha^{-1}).

Soil pH and exchangeable base cations

Changes in soil pH and exchangeable BCs for the two plots at three soil depths (0–20, 20–40 and 40–60 cm) are presented in Fig. 2, including soil pH of four crop seasons after harvest and the original and final soil exchangeable BCs after the two years. There was no significant difference in soil pH in the control plot at each depth after the four crop seasons as compared to the original value, whereas a significant decline was

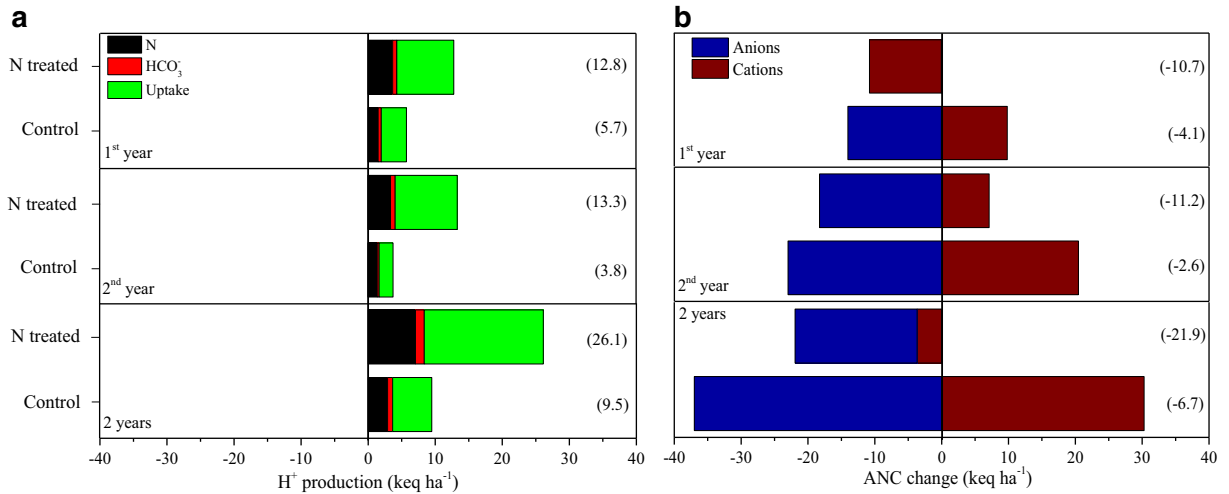


Fig. 1 H⁺ production (a) and acid neutralizing capacity (ANC) change (b) of control and N treated plots in the first year (top), second year (middle) and two years (bottom). *Uptake in Fig. 1a denotes the net effect of cation uptake and anion uptake

observed in the N treated plot at 0–20 cm, 20–40 cm (except 2nd wheat season) and 40–60 cm (except 1st maize and 2nd wheat seasons). Total soil exchangeable BCs pools slightly fluctuated in the control and N treated plots at each depth relative to the original soil. However, various changes were found between different base cations. Compared to the original, soil exchangeable Na⁺ pools of both plots at three depths

significantly decreased, and soil exchangeable K⁺ pools generally stayed stable except for the 0–20 cm in the N treated plot with a significant decline. Similar to K⁺, most soil exchangeable Mg²⁺ pools also were stable except the 40–60 cm in the N treated plot with a significant decline. Large and complex changes appeared in the soil exchangeable Ca²⁺ pool. The Ca²⁺ pool at 0–20 cm showed a significant increase in the

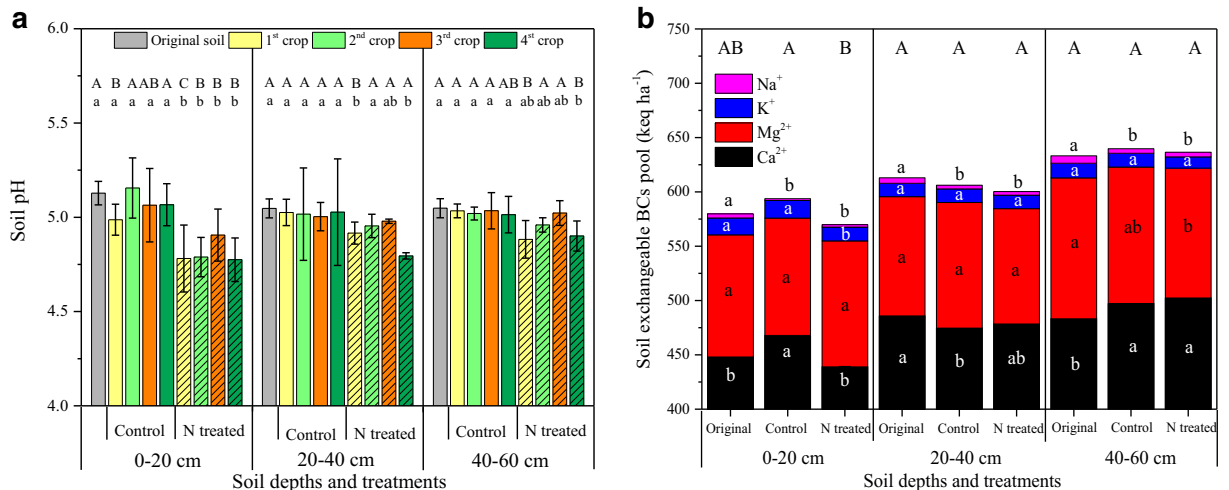


Fig. 2 Changes in soil pH (±S.D.) (Fig. 2a, left) and exchangeable cations (Fig. 2b, right) of control and N treated (Urea) plots at 0–20 cm, 20–40 cm and 40–60 cm depth. *In Fig. 2-a, the uppercase denotes the statistical difference in soil pH between the original soil, control plot and N treated plot in the same crop season at the each soil depth; lowercase above bars denotes the statistical difference in soil pH between original soil and control/N treated plot, respectively, covering all crop seasons at each soil depth. *In Fig.

2-b, the uppercase denotes the statistical difference in soil exchangeable cations pool between the original soil, control plot and N treated plot at each soil depth; the lowercase denotes the statistical difference in each exchangeable cation (Ca²⁺, Mg²⁺, K⁺ and Na⁺) between the original soil, control plot and N treated (Urea) plot at each soil depth. *One-way ANOVA was used, and *P* < 0.05

control plot and no significant change in the N treated plot. At 20–40 cm, there was a significant decrease in the control plot and without any change in the N treated plot. The Ca^{2+} pool significantly increased at 40–60 cm in both plots.

Discussion

Fate of nitrogen and N use efficiency

Ammonia emission

During the two years, the NH_3 emission in the N treated plots was 4.5 times higher than the control plots, caused by increased NH_4^+ in soil as urea application and consequent hydrolysis (Table 3) (Ferguson et al. 1984). The average proportions of NH_3 emission to the total N input in the control plot (4.7%) was higher than the treated plots (3.0%) for the lower N input in the control plots. The NH_3 emission fraction of fertilizer in the N treated plots, fr_{NH_3} , was 2.7%.

Our result is in line with an estimated emission fraction for wheat of 2.1% in the Taihu region (Ju et al. 2009), but it is much lower than results of Yan et al. (2003) who estimated an fr_{NH_3} of 13.7% for uplands in China at a national scale. Most likely, the low NH_3 volatilization rate was due to a low NH_4^+ concentration in the soil and a relative low soil pH, both reducing NH_3 emission. Generally, the transformation rate from NH_4^+ to NH_3 is faster at high pH (Frey et al. 1981). Although urea hydrolysis will cause a temporary increase in soil pH, compared to other regions the soil pH was low (5.1) and there was a very low urease activity ($1.36 \text{ mg N kg}^{-1} \text{ dry soil h}^{-1}$) in this field found by Li (2014). The low urea hydrolysis likely limited NH_4^+ concentrations in soil solution. In addition, the high soil CEC, especially with high exchangeable Ca^{2+} , is beneficial to surface adsorption of NH_4^+ thus inhibiting the transformation of NH_4^+ to NH_3 in soil solution (Anderson 1962; Terman 1980).

The high precipitation rate (above 1000 mm/yr) during the growing season (e.g. the maize seasons, Fig. S5) might also have reduced NH_3 emission through leaching the urea or NH_4^+ into the deeper soil where it was retained (Craig and Wollum 1982; Ernst and Massey 1960). High intensity rainfall (25 mm for one time) effectively inhibits NH_3 emission after urea application (Bouwmeester et al. 1985). In summary, the low

soil pH (5.1) and high soil CEC (277 meq kg^{-1}) (Fig. 2b) in combination with the high rainfall rate are likely the reasons for the low NH_3 emission rate. Besides, the closed method used in this study may have underestimated NH_3 emissions as it reduces the effect of wind, which is conducive to NH_3 diffusion (Bouwmeester and Vlek 1981). In addition, the closed method might also change soil microbial activity via reducing the O_2 concentration, further affecting the NH_3 emission.

Nitrate leaching and denitrification fractions

NO_3^- leaching, being the N related driver of soil acidification was very low in this study, only accounting for 3.9 and 5.6% to the total N input in control and N treated plots, respectively, due to the high denitrification. Our results were much lower than the estimated 38.9% for typical wheat-maize cropping systems in the North China Plain reported by Guo et al. (2010), but nearly same as Ju et al. (2009) who reported an N leaching fraction of 3.4% for wheat in the Taihu region in southern part of China. Other studies in the Sichuan Basin showed that NO_3^- leaching was 7–20% of the total N input on a loam soil with pH 8.3 (Zhu et al. 2009) and about 6.5% on an acid soil with pH 5.1 (Kuang 2016). The large difference in N leaching fractions was due to the distinct differences in climate and soil properties between regions across China, leading to different mechanisms of N losses. In northern China (e.g. North China Plain), the high N accumulation or N surplus in soil led to a high N leaching risk during the heavy rain due to limited denitrification caused by low available carbon sources and soil moisture (Ju et al. 2004; Liu et al. 2003b; Wan et al. 2009). Conversely, excessive precipitation and high temperature in southern China favour the N loss via denitrification compared to the upland in northern China (Ju et al. 2009). Denitrification is generally low under natural conditions, whereas it is greatly enhanced in response to N addition (Su et al. 2017). The calculated denitrification accounted for 44% of the N input in the N treated plot, and even nearly 90% of the N surplus (the calculated fr_{de} value). However, this value is rather uncertain. We used an N mass balance to calculate the unknown denitrification, implying that the value depends on accurate estimates of crop N uptake, N mineralization, NH_3 emission, N leaching and N accumulation. Although N runoff was supposed to be negligible by building dams (20 cm wide, 10 cm high) between

plots, the dams might have been a little bit narrow to fully avoid runoff to adjacent plots but they were the only choice under local field conditions. The most main uncertain N flux was NH_3 emission, that could have been underestimated by the closed method (see above), implying that denitrification may have been overestimated (Eq. 12). In addition, crop N uptake may have been underestimated since the part that is taken by crop residues, mainly roots, has not been estimated and this may be approximately 12.2 and 3.4% of the aboveground N uptake (shoots and grains) of maize (Rimski-Korsakov et al. 2012) and wheat (Recous et al. 1988), respectively. This may also have caused a limited overestimate in denitrification for the N treated plot. Despite these limitations, the overall N loss to air (NH_3 and denitrification) in the N treated plots, being 54.2% of the applied N fertilizer, close to the 45.6% found in the wheat under high N fertilizer input in Tai regions (Ju et al. 2009). The value would be 38.3% if excluding the effects of N deposition and soil N mineralization. The range of 38–54% indicates the uncertainty in the estimate.

The calculated denitrification fraction is in the upper part of the range of 60–90% that was reported for arable land on with moist clay soils in the Netherlands by De Vries et al. (2003). The high denitrification was likely due to the relatively high clay content (21.7%) in the topsoil and the favourable meteorological conditions (high temperatures and potential wet soil conditions induced by the local high precipitation and high relative humidity (see also Fig. S5). As an H^+ consumption process, high denitrification in the N treated plot reasonably weaken the N-related soil acidification. However, we notice that the low organic carbon (below 1%) (Table 1) may limit the microbial mediated process of denitrification due to less available dissolved organic carbon supply. So, there may have been an overestimation in denitrification caused by the underestimated NH_3 emissions by the close-chamber method.

Soil mineral N accumulation

After two years, soil mineral N accumulation only accounted for 4% of the total N input in N treated plot. Residual N in soil was always stable during every crop season (Table S5), implying a limited N supply from fertilizer being available to the subsequent crop. During the first rotation cycle (1st and 2nd crop seasons), N inputs in both plots tended to accumulate in soil during

the 1st crop season with limited precipitation, becoming available for uptake and denitrification during the subsequent crop, the latter being dominant due to high precipitation and reduced soil condition, similar to findings reported for a wheat-rice system by Fan et al. (2007). In the second rotation cycle (3rd and 4th crop seasons), lower soil accumulation during 3rd crop season was likely due to the increased N leaching caused by several heavy rainfalls (daily precipitation >10 mm, Fig. S5). Compared to the 4th crop season, extreme rainfalls accompanying high denitrification during 2nd crop season likely lowered soil residual N.

Generally, nitrate, rather than ammonium, dominated the soil N_{min} except for the two wheat seasons (1st and 3rd crop seasons) of the control plots, where ratios of $\text{NH}_4^+\text{-N}$ to $\text{NO}_3^-\text{-N}$ in soil mineral N were 2.5:1 and 1.1:1, respectively. The low soil pH (pH_{water} measured in a soil to water ratio of 1:2.5 was 5.1, being most likely lower in the field situation) will have inhibited nitrification (see e.g. Dancer et al. 1973). In addition, the high soil N_{min} in the first crop season in the control and N treated plots (Table S5) was due to the fertilizer residue of the previous crops (rape and sorghum), where slow-release fertilizers were applied. There was also a high proportion of soil $\text{NH}_4^+\text{-N}$ in the 1st crop season for the N treated plots. Apart from fertilizer residue, the low soil pH will also have shifted the equilibrium of urea hydrolysis to more NH_4^+ production via H^+ -induced promoting urea-C forming $\text{H}_2\text{CO}_3/\text{CO}_2$, rather than remaining as HCO_3^- and CO_3^{2-} in the soil solution.

Soil N mineralization

Soil N mineralization in this study was calculated from the non-N fertilized plots and assumed to be the same for the N treated plots. This was done since denitrification can be assumed negligible in the unfertilized plot, while this is not the case for the N fertilized plot. In those plots, the unknown denitrification rate implies that soil N mineralization cannot be derived by an N balance (see Eq. 1) Actually, soil N mineralization is likely affected by N application (Georgel and Gypsi 2007), implying an unknown uncertainty in soil N mineralization rates in the N treated plots, which in turn leads to uncertainties in the calculation of the NUE and denitrification. The usual calculation of N mineralization, without considering the N deposition and N losses to air/water by NH_3 emission and N leaching (Cui et al. 2008) would overestimate N

mineralization in this study, since N deposition exceeded the sum of the latter two losses (Table 3).

Nitrogen use efficiency

During the two years, a low agronomic NUE of 36.5% and environmental NUE of 42.1% was observed in the N treated plot, similar to results of (Yan et al. 2014), who reported an agronomic NUE (or RE_N) near 43% during the period 2005–2010 and an environmental NUE near 40% in 2010 for Chinese croplands. The low NUEs led to the high N losses (low leaching, low NH_3 emission and potential high denitrification).

Fate of cations and anions

Base cations, acid cations and acid anions

The budget of N addition not only enhanced the N cycle, but also altered the fate of other nutrients, in terms of crop removal, leaching and soil accumulation. These processes cause changes in the soil ANC, due to (base) cation loss (actual acidification) and/or anion accumulation (potential acidification). Elevated BCs, ACs and AAs in crop removal were due to the enhanced plant growth due to N addition (Table S2). Compared to the control plot that received the same amount of nutrients except N as the N treated plots, the leaching loss of most cations greatly increased and led to the consequent soil acidification in the N treated plot. Increased H^+ production in response to N addition and crop uptake enhanced cation concentrations in the soil solution by exchanging H^+ against cations absorbed by soil (De Vries and Breeuwsma 1987). The major nutrients in leaching were Ca^{2+} and SO_4^{2-} (Table S2), mainly due to inputs of those elements with P fertilization (Table 2). Further, compared to the control plots, the soil exchangeable base cations decreased with increased leaching losses in the N treated plots. The high balance in BCs (Table 3) is partly due to the uncertainty induced by the spatial variability in sampled soil and the large soil exchangeable BCs pool hardly being changed (about 600 keq ha^{-1} per 20 cm depth) (Fig. 2b), which also applies to AAs and ACs.

Large parts of the inputs of both cations and anions were retained in the soil at both plots, except for the N treated plot of the first year when extreme rainfall occurred leading to serious leaching during the 2nd crop season, causing a decrease in soil exchangeable base

cations (Fig. S4). Consequently, after two years, an obvious layered distribution of soil exchangeable BCs was observed at three soil layers of 0–20, 20–40 and 40–60 cm (Fig. 2). In the control plot, residual nutrients (almost Ca^{2+}) concentrated at the layers of 0–20 and 40–60 cm and decreased at 20–40 cm. The phenomenon above was likely due to the high nutrient surplus (Table S2) and the intermittent rain-wash/leaching during the alternation of wet (summer-maize) and dry (winter-wheat) seasons (Fig. S5).

Phosphorous and potassium use efficiencies

The phosphate use efficiency (PUE) and potassium use efficiency (KUE) were calculated to check the occurrence of soil accumulation or soil mining. However, in the control plots there was P and K addition and we could thus not assess the actual agronomic PUE and KUE. Generally, 15–20% of the applied P is taken up by crops during the growing season (Li et al. 2011). The overall environmental PUE of Chinese crop production was estimated at 23% in 2005 (Ma et al. 2012). In this study, environmental PUE (16.5 and 30.7% for the control and N treated plots) and agronomic PUE (14.3% for the N treated plot) were low but comparable.

No P was observed in leachates collected at 60 cm depth. Most P is likely adsorbed in soil or precipitated as a Fe/Al/Ca-P complex (Hilton et al. 2010). Accumulation of P in the soil would further increase the P leaching risk. The soil Bray-P of 0–20 cm in the control plot was already beyond the threshold for P leaching since the second crop season (Table S6), which is 78 mg Olsen-P kg^{-1} for croplands in South China (Li et al. 2015). This result implies that long-term P over application will cause potential environmental P pollution. In addition, non-point sources of P in agricultural runoff play an important role in eutrophication (Carpenter et al. 1998). Building dams used in this study to avoid runoff is not a common practice in conventional agriculture. Therefore, runoff could be a very important potential output pathway of P and other elements in some regions.

On the contrary, K had a very high use efficiency. Both the N induced agronomic KUE and environmental KUE were above 100% in the N treated plot (Table 4), implying mining of the soil K pool (Fig. 2b) thus decreasing the soil ANC. The results suggests a strong need for more K application.

Drivers and impacts of soil acidification

In both control and N treated plots, the contribution of drivers of soil acidification, i.e. crop BC removal, N leaching and HCO_3^- leaching were quite similar in both plots, being near 60%, 30 and 10%, respectively. This implies that plant uptake dominated cropland soil acidification in this soil, followed by N fertilizer-induced acidification while the contribution of natural acidification was very low. Compared to the control plot, N fertilizer application can aggravate soil acidification via a) NH_4^+ -N adsorption or NO_3^- leaching and b) elevating base cation nutrient uptake by the N induced elevated plant growth (Fig. 1a). However, N fertilization did not have such a large effect on soil acidification due to high denitrification accounting, for nearly 90% of the total N loss, thus leading to low NO_3^- leaching (Table 3). Guo et al. (2010) reported that N the cycle rather than BCs uptake was the primary contributor to H^+ production in intensive Chinese croplands, with an estimated value of $33 \text{ keq H}^+ \text{ ha}^{-1} \text{ yr}^{-1}$ produced by N cycle and $19 \text{ keq H}^+ \text{ ha}^{-1} \text{ yr}^{-1}$ BCs uptake in wheat-maize cropping systems, respectively. The much larger impact of the N cycle at a comparable N fertilizer input (about $550 \text{ kg N ha}^{-1} \text{ yr}^{-1}$) in both studies is due to two reasons. First, Guo et al. assumed that 90% of the applied N fertilizer was NH_4^+ and 10% is urea (R-NH_2), while we used urea which has only half of the potential H^+ production under the same N application; Second, Guo et al. (2010) assumed a denitrification rate near 2% of the N surplus (0.9% of the total N input), and a leaching rate of more than 90% of the N surplus, whereas we found the opposite in our experiment. The differences of the fate of N may be due to the regional differences on soil and climate between the northern part (Guo's study) and the southern part (this study) of China. Compared to Guo, the acidification due to BC crop removal was also lower, since the yields of grain and straw in this study (8.08 and 9.52) $\text{ton ha}^{-1} \text{ yr}^{-1}$, respectively) were much lower than that of Guo, where the yields of grain and straw were 11.17 and 13.84 $\text{ton ha}^{-1} \text{ yr}^{-1}$ for the wheat-maize cropping system. The grain yields (3.38 ton ha^{-1} for wheat, 4.69 ton ha^{-1} for maize) in this study (Table S3) were also lower than national average yields of 5.32 and 5.81 ton ha^{-1} for wheat and maize, respectively (China 2016), likely due to N-induced increased aboveground biomass aggravated plant lodging during the heavy rain events (Fig. S5). In contrast, the yields of the control plots increased with increased rainfall (Table S7).

As a result of soil acidification, the soil pH and exchangeable BCs significantly changed comparing to the control plot. Soil pH in 0–20 cm declined about 0.3 unit in the N treated plot after two years of planting. Previous studies also pointed out that soil pH decreases under long-term N fertilization (Guo et al. 2010; Zhang et al. 2009). However, a significant decline in exchangeable BCs ($-16.01 \text{ keq ha}^{-1}$) only occurred at 0–20 cm in the N treated plot for the two years, due to a loss of exchangeable Ca^{2+} , K^+ and Na^+ as a result of high leaching of Ca^{2+} and Na^+ and an excess K^+ uptake. The decline in soil exchangeable BCs reflects that, in non-calcareous soils (soil pH < 6.5), exchangeable BCs are the primary acid buffering system (De Vries et al. 1989; Ulrich 1986; Zhang et al. 2017). In this study, the high CEC and BS lead a large exchangeable BCs pool in the surface soil of 0–20 cm (about 570 keq ha^{-1}), implying that it would take a long time to deplete the exchangeable soil BC pool by decreasing $8 \text{ keq ha}^{-1} \text{ yr}^{-1}$ under an intensive agricultural nutrients management (high application combined NPK fertilizers). However, the exchangeable BC pool is extremely variable across China, so this acidification rate could also be a serious threat in other areas. Furthermore, in the typical and primary production areas of wheat-maize located in northern China, the N loss pathways may be different with higher NO_3^- leaching and lower denitrification.

Anthropogenic soil acidification of croplands is difficult to avoid in periodic cereal crops production with high N fertilizer applications. Liming is a common practice to combat soil acidification (Blake et al. 1999; Goulding 2016), but it is hardly practiced in China as it is a labour intensive practice. Until now, liming has only been practiced in regions with serious negative phenomena caused by soil acidification, such as areas with cadmium-enriched rice (Liu et al. 2003a) and with dramatic yield decreases (Zhao et al. 2010). Theoretically, $650 \text{ kg CaCO}_3 \text{ ha}^{-1} \text{ yr}^{-1}$ should be applied to neutralize soil acidification under the conventional fertilizer management based on the results of this study, which is laborious on cereal croplands with limited mechanization, causing high costs (Shi et al. 2017; Xu and Coventry 2003). In addition, surface-applied lime moves slowly through soil profiles and hence is inefficient in ameliorating subsurface soil acidity (Tang et al. 2013). Anyway, optimized nitrogen management is still the prime way to control H^+ production. However, the impacts of improved nutrient and agricultural management practices (e.g. balanced N application rates,

improved N fertilizer types reducing N losses to air and water, enhanced N manure application, containing base cations that imply alkalinity application etc.) on soil acidification still need to be further investigated.

Conclusions

Over-application of N fertilizers on a wheat-maize double cropping system on a light clay soil in Southern China had a lower impact on soil acidification than expected, due to a large denitrification rate and thus a very limited NO_3^- leaching in this specific soil type. Consequently, crop uptake by wheat and maize was the primary driver of H^+ production, followed by N transformation processes and finally the leaching of HCO_3^- , accounting on average for 61%, 31 and 8% of the total H^+ production in the N application plot.

The conventional high N fertilization with related high inputs of P and K fertilizers at the studied wheat-maize rotation system caused a soil acidification of 13.1 keq H^+ production $\text{ha}^{-1} \text{yr}^{-1}$, associated with a 0.3-unit decline in topsoil pH during the two years. Potential soil acidification (9.1 keq $\text{ha}^{-1} \text{yr}^{-1}$) and actual soil acidification (1.9 keq $\text{ha}^{-1} \text{yr}^{-1}$) jointly contributed the soil ANC decline in the N treated plots. The environmental P use efficiency appeared to be low (near 30%) whereas the environmental K use efficiency was very high (more than 150%), implying mining of the adequate K pool in the soil.

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