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RESEARCH ARTICLE

Soil pH Dynamics and Nitrogen Transformations Under Long-Term Chemical Fertilization in Four Typical Chinese Croplands

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Abstract

Long-term fertilization experiment provides the platform for understanding the proton budgets in nitrogen transformations of agricultural ecosystems. We analyzed the historical (1990-2005) observations on four agricultural long-term experiments in China (Changping, Chongqing, Gongzhuling and Qiyang) under four different fertilizations, i.e., no-fertilizer (Control), sole chemical nitrogen fertilizer (F_N), sole chemical phosphorous and potassium fertilizers (F_{PK}) and chemical nitrogen, phosphorous and potassium fertilizers (F_{NPK}). The significant decline in topsoil pH was caused not only by chemical N fertilization (0.29 and 0.89 ΔpH at Gongzhuling and Qiyang, respectively) but also by chemical PK fertilization (0.59 ΔpH at Gongzhuling). The enhancement of available nutrients in the topsoil due to long-term direct nutrients supply with chemical fertilizers was in the descending order of available P (168-599%)>available K (16-189%)>available N (9-33%). The relative rate of soil pH decline was lower under long-term judicious chemical fertilization (-0.036-0.034 ΔpH yr^{-1}) than that under long-term sole N or PK fertilization (0.016-0.086 ΔpH yr^{-1}). Long-term judicious chemical fertilization with N, P and K elements decreases the nutritional limitation to normal crop growth, under which more N output was distributed in biomass removal rather than the loss *via* nitrate leaching. We concluded that the N distribution percentage of nitrate leaching to biomass removal might be a suitable indicator to the sensitivity of agricultural ecosystems to acid inputs.

Key words: available nutrients, ecosystem, long-term fertilization, N distribution, soil pH

INTRODUCTION

The continuous decline of soil pH generally describes the ecosystem sensitivity to acid inputs. From the perspective of proton budgets, soil pH reflects the dynamic balance between proton production and consumption in a soil-plant system. Proton production processes are categorized as the net addition of

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hydrogen ion (H^+), net nitrification, the dissociation of carbonate and organic acids and the oxidation of sulfur, whereas proton consumption processes are derived from the weathering of soil minerals and the mineralization of soil organic matter (SOM) (van Breemen *et al*. 1983, 1984; de Vries and Breeuwsma 1987; Fujii *et al*. 2008, 2009;). In the well-drained croplands, the direct addition of H^+ *via* deposition and fertilization and the oxidation of sulfur contribute little to proton production (Paces 1985; Barak *et al*. 1997; Goulding and Blake 1998; Guo *et al*. 2010). The main external proton is derived from net nitrification which performs the net ammonium (NH_4^+) input into and the net nitrate (NO_3^-) output from soil layers of main rooting zone, whereas the main internal proton is derived from the dissociation of carbonate and organic acids which performs the excess removal of soil base cations (BCs^+) via biomass harvest and the leaching of bicarbonate (HCO_3^-) and organic acid anions ($RCOO^-$) (van Breemen *et al*. 1984; Fujii *et al*. 2008). Meanwhile, the enhancement of root activity under fertilization also increases the rates of mineral weathering and SOM mineralization (Lesturgez *et al*. 2006; Fujii *et al*. 2009), which consumes almost all internal proton rather than external proton in most steady-state ecosystems (Verstraten *et al*. 1990; Asano *et al*. 2000; Shibata *et al*. 2001). Therefore, the external-internal proton ratio (EIPR) was used to assess the ecosystem sensitivity to acid inputs (van Breemen *et al*. 1984).

Modern agricultural ecosystem is generally characterized as N saturation, i.e., N input greater than the sequestration of N in both plant and SOM, which may cause soil acidification (Stein and van Breemen 1993; Barak *et al*. 1997). Poss *et al*. (1995) defined the neutral N (N_2, NO_X, NH_3, R-NH_2) as the reference state in N transformations to assess proton production and consumption in ecosystems, respectively, compared with the oxidized NO_3^- and the reduced NH_4^+. Nitrogen transformations among the reference states with equal mole equivalents should have no contribution to proton budgets in a closed soil-plant system (Fig. 1; de Vries and Breeuwsma 1987). However, the NO_3^- leaching due to N saturation implies that the proton budgets with equal mole equivalents occurred in the topsoil under neutral N fertilization (Poss *et al*. 1995).

Available nutrients in the topsoil are significantly affected by long-term fertilization with chemical N, P and K elements (Vieira *et al*. 2008; Covaleda *et al*. 2009; Darilek *et al*. 2009). Under high level of available nutrients in the topsoil, the more biomass production implied the larger amount of internal proton (van Breemen *et al*. 1984; Guo *et al*. 2010). However, the response of soil N pool to long-term chemical fertilization was uncertainty (Raun *et al*. 1998; Belay *et al*. 2002; Zanatta *et al*. 2007; Zhang *et al*. 2009a). N volatilization, i.e., the losses of gaseous N (NH_3, N_2, N_2O and so on) from croplands, was associated with the application rate of N fertilizer under fixed soil property and cropping system (Robertson and Vitousek 2009; Guo *et al*. 2010). As a result, based on the N balance in ecosystems, we hypothesized that the rate of NO_3^- leaching and the EIPR would decrease significantly under high level of available nutrients in the topsoil due to long-term judicious chemical fertilization.

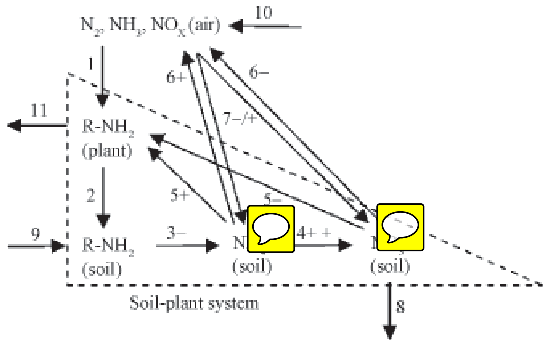

Fig. 1 Proton budgets in nitrogen transformations of agricultural ecosystem. 1, biological N_2 fixation; 2, N returning (straw, stubble and litter); 3, ammonification; 4, nitrification; 5, N uptake; 6, N volatilization; 7, N deposition; 8, nitrate leaching; 9, N fertilization (R-NH_2, NH_4^+ or NO_3^-); 10, N emission from livestock, industry and traffic; 11, N output from biomass removal. The symbols "+" and "–" indicate proton production and consumption with equal mole equivalents in the soil-plant system, respectively.

In major Chinese croplands, from the red soil to black soil in humid regions or even the fluvo-aquic soil in semi-arid regions, topsoil pH has significantly decreased since the 1980s (Darilek *et al*. 2009; Guo *et al*. 2010; Zhang *et al*. 2012). The proton budgets from N cycling and biomass removal were calculated in four main cropping systems, respectively (Guo *et al*. 2010). However, the theoretical association between proton budgets and soil pH dynamics is still unknown particularly under long-term fertilization in croplands. The objectives of this study were 1) to understand soil pH dynamics and soil acidification rate under long-term different chemical fertilizations in four typical soils of China and 2) to assess the ecosystem sensitivity to acid inputs based on the proton budgets in N transformations of agricultural ecosystem.

RESULTS

Soil pH dynamics during 1990-2005

Long-term chemical fertilization had significant impacts on topsoil pH although it varied among sites and treatments (Table 1; Fig. 2). Topsoil pH under the control treatment at each site remained stable and had no significant differences compared with the initial pH value despite some fluctuations over the study period. The significant decline in topsoil pH was shown under chemical N fertilization at Gongzhuling (0.29 ΔpH) and Qiyang (0.89 ΔpH) and under chemical PK fertilization at Gongzhuling (0.59 ΔpH). The interactive effects of chemical N and PK fertilization (N×PK) on topsoil pH only appeared at Chongqing.

Table 1 Means soil pH (±SD) in the topsoil (0-20 cm) during 1991-2005 at the four study sites

Items\Site	Changping	Chongqing	Gongzhuling	Qiyang
Treatments				
Control	8.19±0.17 a	7.77±0.16 b	7.61±0.18 c	5.72±0.35 b
F_N	8.11±0.18 a	7.32±0.44 a	7.21±0.34 b	4.65±0.74 a
F_{PK}	8.13±0.10 a	7.21±0.56 a	6.91±0.47 ab	5.46±0.38 b
F_{NPK}	8.13±0.14 a	7.41±0.29 ab	6.72±0.60 a	4.76±0.48 a
ANOVA	0.496	0.030	<0.001	<0.001
Chemical N fertilization				
Control, F_{PK}	8.16±0.14	7.49±0.49	7.26±0.50	5.59±0.38
F_N, F_{NPK}	8.12±0.16	7.36±0.37	6.97±0.54	4.70±0.62
ANOVA	0.304	0.335	0.012	<0.001
Chemical PK fertilization				
Control, F_N	8.15±0.18	7.55±0.40	7.41±0.34	5.18±0.79
F_{PK}, F_{NPK}	8.13±0.12	7.31±0.44	6.82±0.54	5.11±0.56
ANOVA	0.690	0.082	<0.001	0.525
Chemical N×PK fertilization				
ANOVA	0.282	0.021	0.370	0.132

Control, no-fertilizer; F_N, sole chemical nitrogen fertilizer; F_{PK}, sole chemical phosphorous and potassium fertilizers; F_{NPK}, chemical nitrogen, phosphorous and potassium fertilizers. The same letter in the same column indicates no significant difference (Duncan, P<0.05) among treatments.

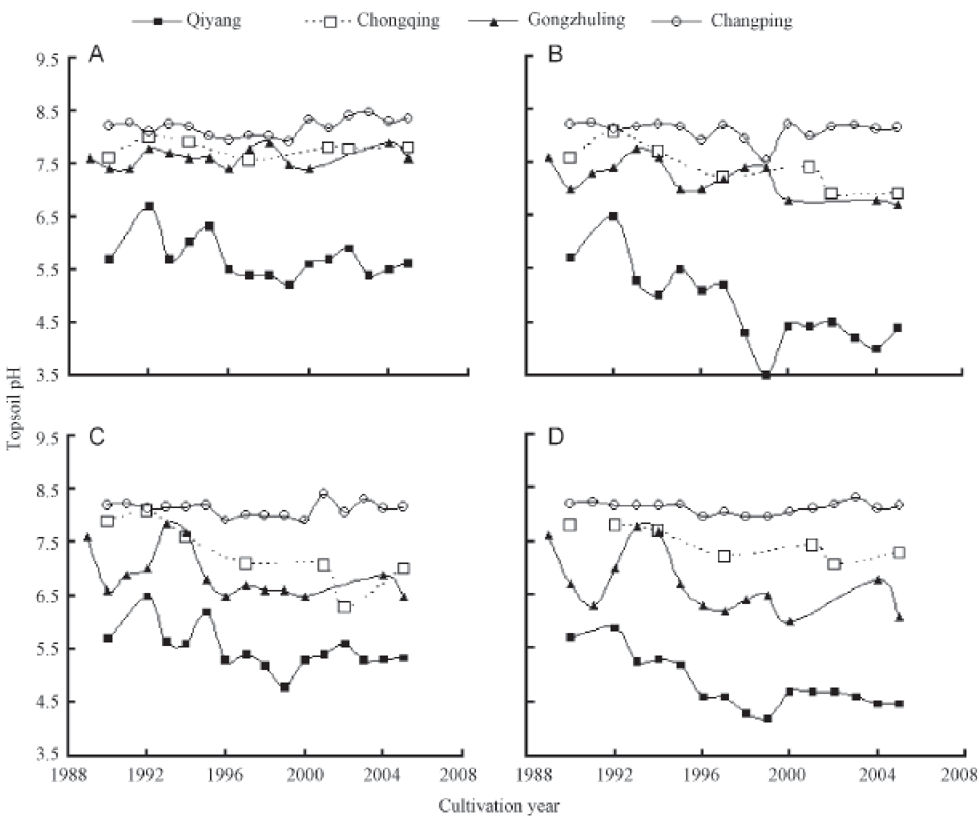

Fig. 2 Dynamics of topsoil pH during 1990-2005 under the Control (A), F_N (B), F_{PK} (C) and F_{NPK} (D) treatments at the four study sites.

Available nutrients in the topsoil during 1990-2005

Available N, P and K contents in the topsoil reflected the level of available nutrients in the topsoil under different amendments with chemical N, P and K fertilizers (Table 2). Chemical N fertilization significantly increased available N content by 7.2 and 22.1 mg kg^{-1} at Chongqing and Qiyang, respectively. Chemical PK fertilization significantly increased available P content by 13.15-23.89 mg kg^{-1} at all study sites and available K content by 11-120 mg kg^{-1} at all sites except for Gongzhuling. Therefore, the direct nutrients supply with chemical fertilizers significantly increased available P content by 168-599%, followed by available K content by 16-189% and available N content by 9-33% in the topsoil. However, long-term chemical N fertilization also indirectly decreased available P content at Changping (3.94 mg kg^{-1}) and available K content at Chongqing (13.5 mg kg^{-1}) and Qiyang (59.1 mg kg^{-1}). And long-term chemical PK fertilization indirectly increased available N content at Chongqing (6.8 mg kg^{-1}) and Gongzhuling (22.1 mg kg^{-1}). The interactive effects of chemical N and PK fertilization (N×PK) only appeared on available P content at Changping and on available K content at Chongqing and Qiyang, respectively.

Rates of soil pH decline under long-term different fertilizations

The relative rate of soil pH decline was higher under long-term sole PK (0.016-0.068 ΔpH yr^{-1}) or N (0.020-0.086 ΔpH yr^{-1}) fertilization than that under long-term judicious PK (-0.036-0.019 ΔpH yr^{-1}) or N (-0.025-0.034 ΔpH yr^{-1}) fertilization (Fig. 3). Therefore, it was crucial to maintain high level of available nutrients in the topsoil under long-term judicious chemical fertilization for alleviating soil acidification in croplands.

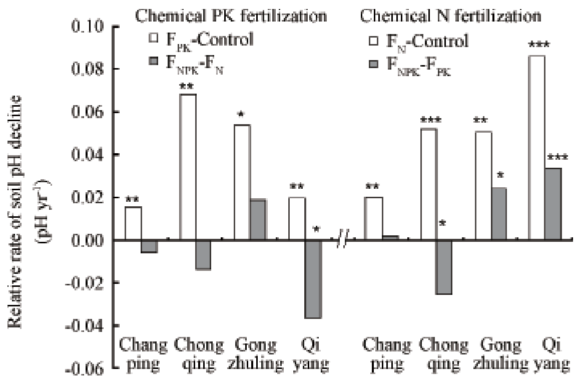

Fig. 3 Rates of soil pH decline under sole PK (F_{PK}-Control) or N (F_N-Control) fertilizations and judicious PK (F_{NPK}-F_N) or N (F_{NPK}-F_{PK}) fertilizations, respectively. *, ** and *** indicate significant linear correlation in the relative rate of soil pH decline at *P*<0.05, *P*<0.01 and *P*<0.001, respectively.

Table 2 Means available N, P and K content (mg kg^{-1}) in the topsoil (0-20 cm) during 1991-2005 at the four study sites

Items\Site	Available N content				Available P content				Available K content			
	Changping	Chongqing	Gongzhuling	Qiyang	Changping	Chongqing	Gongzhuling	Qiyang	Changping	Chongqing	Gongzhuling	Qiyang
Treatments												
Control	58.0 a	78.8 a	112.3 a	67.8 a	3.38 a	3.26 a	7.77 a	5.77 a	71.8 a	77.0 a	114.2 a	71.0 a
F_N	60.8 a	89.6 b	116.8 ab	93.4 b	3.20 a	2.75 a	7.84 a	4.77 a	70.5 a	74.1 a	110.9 a	55.6 a
F_{PK}	58.3 a	89.0 b	123.5 ab	67.2 a	20.57 c	24.19 c	19.63 b	27.64 b	87.2 b	106.7 b	121.7 a	234.7 c
F_{NPK}	64.3 a	91.8 b	126.1 b	85.8 b	12.88 b	17.88 b	22.29 b	30.68 b	77.2 a	82.7 a	113.4 a	131.9 b
ANOVA	0.613	0.005	0.064	<0.001	<0.001	<0.001	<0.001	<0.001	0.001	<0.001	0.872	<0.001
Chemical N fertilization												
Control, F_{PK}	58.1	83.9	117.9	67.5	11.98	13.73	13.70	16.70	79.5	91.9	118.0	152.9
F_N, F_{NPK}	62.6	90.7	121.4	89.6	8.04	10.31	15.06	17.73	73.8	78.4	112.2	93.8
ANOVA	0.244	0.014	0.367	<0.001	0.021	0.078	0.511	0.735	0.077	<0.001	0.549	<0.001
Chemical PK fertilization												
Control, F_N	59.4	84.2	114.5	80.6	3.29	3.01	7.81	5.27	71.1	75.6	112.6	63.3
F_{PK}, F_{NPK}	61.3	90.4	124.8	76.5	16.72	21.04	20.96	29.16	82.2	94.7	117.6	183.3
ANOVA	0.618	0.024	0.012	0.348	<0.001	<0.001	<0.001	<0.001	0.001	<0.001	0.604	<0.001
Chemical N×PK fertilization												
ANOVA	0.666	0.143	0.804	0.423	0.028	0.134	0.531	0.505	0.168	0.004	0.799	0.001

The same letter in the same column indicates no significant difference (Duncan, *P*<0.05) among treatments.

N transformations under the F_N and F_{NPK} treatments

During total study period (1991-2005), N transformations of agricultural ecosystems were different among treatments and sites (Table 3; Fig. 4). Under the control treatment, the rate of soil N change was significantly positive at Chongqing (2.18 kmol N ha^{-1} yr^{-1}), but slightly negative at Changping, Gongzhuling and Qiyang (-1.97- -0.66 kmol N ha^{-1} yr^{-1}). Based on the N balance of ecosystem under the control treatment, the calculated values of N deposition were 2.98, 9.64, 2.38 and 0.77 kmol N ha^{-1} yr^{-1} at Changping, Chongqing (including the N input from irrigation and autotrophic N_2-fixed by algae during the rice season), Gongzhuling and Qiyang, respectively. Nitrogen volatilization that was associated with the application rate of N fertilizer (11.79-21.43 kmol N ha^{-1} yr^{-1}) ranged from 2.36 to 8.57 kmol N ha^{-1} yr^{-1} at the four study site. The N in biomass removal increased by 4.1-8.8 kmol N ha^{-1} yr^{-1} under chemical N fertilization and by 0.9-4.0 kmol N ha^{-1} yr^{-1} under chemical PK fertilization. Compared with the value under the F_N treatment, the rate of NO_3^- leaching under the F_{NPK} treatment decreased by 7.58, 8.67, -1.09 and 0.70 kmol N ha^{-1} yr^{-1} at Changping, Chongqing, Gongzhuling and Qiyang, respectively. Meanwhile, the amendment of chemical PK with N fertilizers increased the N in biomass removal (from 41±25% to 55±15%) but decreased the N loss *via* NO_3^- leaching (from 37±21% to 22±20%) in the distribution percentage of N output fluxes (Fig. 4). As a result, the calculated values of EIPR were distinctly lower under treatment F_{NPK} than F_N at all sites except for Gongzhuling. There was significant and positive correlation (r=0.99, n=6) between EIPR and the rate of soil pH decline under the F_{NPK} and F_N treatments at all sites except for Changping (Fig. 5).

DISCUSSION

Under long-term application of chemical N fertilizers, an overall decreasing trend of topsoil pH was reported in various agricultural ecosystems (Vieira *et al*. 2008; Covaleda *et al*. 2009; Zhang *et al*. 2009b; Huang *et al*. 2010; Malhi *et al*. 2011; Schroder *et al*. 2011). While the large temporal variations of soil pH, i.e., soil pH dynamics in the long-term scales were less reported. Lal (1997) reported that topsoil pH rapidly decreased by 0.6-1.2 ΔpH in the first three years and then remained stable in the next five years under intensive monocropping of maize in West Africa, and a similar phenomenon was reported under a 27-yr rotation of maize-soybean-wheat in Northeast China

Table 3 Nitrogen transformations in agricultural ecosystem (kmol N ha^{-1} yr^{-1}) during 1991-2005 at the four study sites

Site	Treatment	Deposition	Fertilization	Change in soil[1)]	Biomass removal[2)]	Volatilization[3)]	Leaching[4)]	EIPR[5)]
Changping	Control	2.98	0.00	-1.97^{ns}	4.95 a	0.00	--	--
	F_N	2.98	21.43	-1.30^{ns}	7.10 b	8.57	10.04	1.41
	F_{PK}	2.98	0.00	-1.18^{ns}	5.62 ab	0.00	--	--
	F_{NPK}	2.98	21.43	-1.04^{ns}	14.42 c	8.57	2.46	0.17
Chongqing	Control	9.64	0.00	2.18^{*}	7.27 a	0.00	--	--
	F_N	9.64	20.75	-0.45^{ns}	13.27 b	5.19	11.97	0.90
	F_{PK}	9.64	0.00	0.98^{ns}	9.08 a	0.00	--	--
	F_{NPK}	9.64	20.75	5.15^{**}	16.23 c	5.19	3.30	0.20
Gongzhuling	Control	2.38	0.00	-0.76^{ns}	3.14 a	0.00	--	--
	F_N	2.38	11.79	-1.12^{ns}	11.32 b	2.36	1.61	0.14
	F_{PK}	2.38	0.00	-3.11^{**}	3.36 a	0.00	--	--
	F_{NPK}	2.38	11.79	-3.71^{**}	12.83 c	2.36	2.69	0.21
Qiyang	Control	0.77	0.00	-0.66^{ns}	1.42 a	0.00	--	--
	F_N	0.77	21.43	1.83^{ns}	3.66 b	3.21	13.50	3.69
	F_{PK}	0.77	0.00	-3.70^{**}	2.65 ab	0.00	--	--
	F_{NPK}	0.77	21.43	-2.48^{*}	8.67 c	3.21	12.80	1.48

[1)] *, ** and "ns" indicate significant linear correlation in the rate of soil N change at P<0.05, P<0.01 and no significant, respectively.

[2)] The same letter indicates no significant differences (Duncan, P<0.05) among treatments at each site.

[3)] Nitrogen volatilization was 40, 25, 20 and 15% of N fertilization rate according to initial soil pH and cropping system at Changping, Chongqing, Gongzhuling and Qiyang, respectively (Robertson and Vitousek 2009; Guo *et al*. 2010).

[4)] Leaching=Deposition+Fertilization-Change in soil-Biomass removal-Volatilization.

[5)] EIPR (external-internal proton ratio)=Leaching/Biomass removal.

(Zhang *et al*. 2008). However, topsoil pH was not significantly changed in the initial short-term scales (2002-2005) but did significantly decrease by more than 1.0 ΔpH in the medium-term scales (1986-2005) under an oat/maize/beans/wheat random rotation in the infertile volcanic soil in Mexican (Covaleda *et al*. 2009). In this study, topsoil pH rapidly decreased at Gongzhuling but increased at Chongqing and Qiyang in the initial 3-5 yr (Fig. 2).

According to the theory of proton budgets, the biogeochemical processes of soil acidification were quantified (van Breemen *et al*. 1983, 1984; Fujii *et al*. 2008). In the semiarid Great Plains of United States, the leaching of NO_3^- contributed 59-66% of proton budgets, which may result to the decline of 0.30-0.33 ΔpH in the topsoil during 1989-2003 (Tarkalson *et al*. 2006). The acidity of topsoil (0-25 cm) increased in autumn due to the excess soil nitrification over the NO_3^- uptake, and then 2.4 kmol ha^{-1} yr^{-1} of proton budget *via* the leaching of NO_3^- produced during the humid early winter (Poss *et al*. 1995). Soil pH rapidly decreased by 1.2 units after a dry growth season, which was accompanied by a large amount of NO_3^- accumulation in the topsoil, and soil pH returned to normal level in the next suitable growth season (van Breemen *et al*. 1982). In this study, soil pH under the F_N treatment rapidly decreased at Qiyang (from 4.30 to 3.50) and Changping (from 7.95 to 7.55) during 1998-2000, which might be due to the large decrease of the N in removed biomass (2.2 to 0.7 kmol N ha^{-1} yr^{-1} at Qiyang and 8.3 to 5.4 kmol N ha^{-1} yr^{-1} at Changping, respectively). Correspondingly, a rapid pH increase under the F_{NPK} treatment at Gongzhuling (from 6.30 in 1991 to 7.80 in 1993) might be due to a distinct increase of the N in removed biomass (9.66, 12.02 and 16.28 kmol N ha^{-1} yr^{-1} in 1991, 1992 and 1993, respectively). Therefore, the phytoavailability of N in ecosystems may be closely responsible for soil pH dynamics in the short-term scales.

Long-term application of chemical fertilizers significantly affected the level of available nutrients in the topsoil and crop production (Tables 2 and 3). In a N-limited ecosystem, long-term supply of chemical PK fertilizers caused the excessive accumulation of free phosphate and potassium ions ($H_2PO_4^-$, K^+) in the topsoil, which could generate strong acid and affect soil exchangeable Ca^{2+} and Mg^{2+} (McAndrew and Malhi 1992; Chen *et al*. 2011), leading to the decline in soil acid buffering capacity and soil acidification. In a PK-limited ecosystem, accordingly, long-term supply of chemical N fertilizer could not increase the sequestration of N in both plant and SOM but the excessive accumulation of NO_3^- in the topsoil, leading to the leaching of NO_3^- and soil acidification (Fig. 3, Table 2). As a result, the judicious chemical fertilization with suitable N, P and K nutrients not only increased the phytoavailability of NO_3^-, Ca^{2+}, Mg^{2+} and so on, but also decreased the leaching loss of these nutrients, soil acidification was thus alleviated in croplands (Belay *et al*. 2002).

In modern agricultural ecosystems, N fertilization is a necessary practice to avoid excessive consumption of soil N pool (Robertson and Vitousek 2009). However, the responses of chemical fertilization on

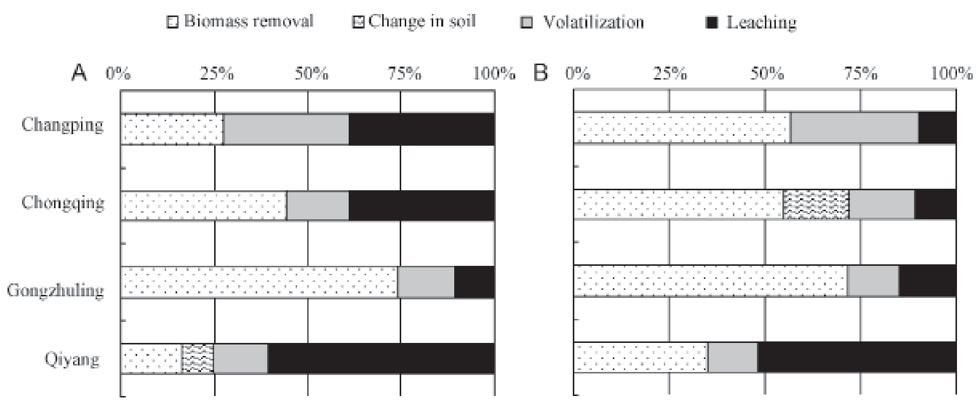

Fig. 4 Distribution percentage of N output fluxes under the F_N (A) and F_{NPK} (B) treatments during 1990-2005.

soil N change varied at the four study sites (Zhang *et al*. 2009a). At the same time, other N input fluxes such as atmospheric deposition, irrigation, biological N_2 fixation and SOM mineralization should not be neglected in some an agricultural ecosystem either. The calculated values of N deposition at the four study sites were proved to be credible according to the observations on N deposition over the same periods in China (Nakagawa *et al*. 2001; Hu *et al*. 2007; Hou *et al*. 2012). N deposition was high at Changping, Chongqing and Gongzhuling, which are close to big cities of Beijing, Chongqing and Changchun, respectively, whereas N deposition was low at Qiyang which locates in a remote countryside area. However, N deposition might be underestimated if the N in biomass removal was limited by soil basic fertility and then the N loss *via* the leaching of NO_3^- occurred in the topsoil, just as the red soil with humid climate at Qiyang. Although the percentage of N volatilization in N fertilization at the four sites may be controversy, the comparison on EIPR between the F_{NPK} and F_N treatments at each site still was feasible (Table 3). When the EIPR was more than 0.30, a forest ecosystem became more sensitive to acid inputs, which would cause the rapid decline in soil pH, the biological effects of aluminum toxicity and the degradation of productivity (van Breemen *et al*. 1984). Assuming that the threshold value (EIPR=0.30) was also suitable to an agricultural ecosystem, the ecosystem sensitivity to acid inputs in this study were high under the F_N treatment at Changping, Chongqing and Qiyang and under the F_{NPK} treatment at Qiyang (Fig. 5).

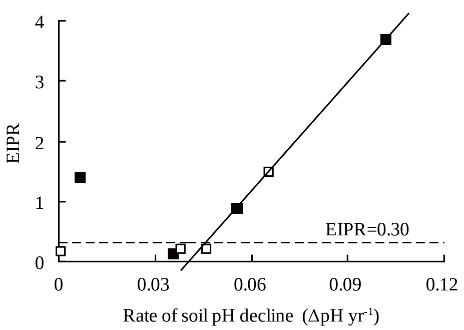

Fig. 5 Relationships between EIPR and the rate of soil pH decline under the F_N (■) and F_{NPK} (□) treatments.

Soil pH was also affected by soil acid buffering capacity and texture in the long-term scales (Vieira *et al*. 2008; Covaleda *et al*. 2009; Zhang *et al*. 2010). In the four study sites, the highest value of acid buffering capacity in the fluvo-aquic soil may lead to the minimum variation and decline of soil pH at Changping, and the lowest value of acid buffering capacity in the red soil may lead to the maximum variation and decline of soil pH at Qiyang (Table 4). In a light textured soil, the proton produced in the topsoil is prone to leak, consequently pH remains stable in the topsoil and a rapid acidification appears in the deep soil layers (Lesturgez *et al*. 2006; Noble *et al*. 2008). In this study, the decline of 0.20 ΔpH in the deep soil layer (80-100 cm) compared with the topsoil (0-20 cm) was occurred under F_{NPK} treatment at Changping in 2001 (data not shown), which probably attribute to the low clay content (10%) and soil parent material with coarse river sediments at this site.

CONCLUSION

In four typical soils of Chinese croplands, long-term (1990-2005) application of chemical fertilizers significantly affected the pH value and the level of available nutrients in the topsoil and N transformations in ecosystems. The significant decline in soil pH with variations at each site not only occurred under chemical N fertilization but also under chemical PK fertilization. The enhancement of available nutrients in the topsoil due to long-term direct nutrients supply with chemical fertilizers was in the descending order of available P>available K>available N. The relative rate of soil acidification was lower under long-term judicious chemical fertilization than that under long-term sole N or PK fertilization. Compared with the sole N or PK fertilization, judicious chemical fertilization with N, P and K firstly increased the level of available nutrients in the topsoil for better crop growth, whilst the N output was distributed more in biomass removal than nitrate leaching. The N distribution percentage of nitrate leaching to biomass removal might be a suitable indicator to the sensitivity to acid inputs in agricultural ecosystems.

MATERIALS AND METHODS

Site descriptions and cropping systems

A series of long-term experiments have been conducted to monitor soil fertility and fertilizer efficiency in major cropping systems throughout China since 1990 (Xu *et al*. 2006). The four study sites (Changping, Chongqing, Gongzhuling and Qiyang) have distinct climatic conditions and topsoil properties (Table 4). Changping and Gongzhuling are located in the north China with temperate semi-humid climate, whereas Chongqing and Qiyang in the south China with subtropical humid climate. Three cropping systems (wheat-maize, wheat-rice and single maize) were included. The wheat (*Triticum aestivum*) cultivars Nong 8693 (from November to June), Xinongmai 1 (from November to May) and Xiangmai 11 or 12 (from November to May) were grown at Changping, Chongqing and Qiyang, respectively. The maize (*Zea mays*) cultivars Tangkang 5 (from July to November), Daiyu 13 or Zhengdai 958, etc. (from April to September) and Yedai 4 or 13 (from April to July) were grown at Changping, Gongzhuling and Qiyang, respectively. The rice (*Oryza sativa*) cultivars Shanyou 63, Eryou 868, etc. were grown from May to August at Chongqing.

Fertilization and management

A total of 12 treatments with different amendments of chemical N, P and K fertilizers, organic manure and straw were consistently designed at all the study sites (Xu *et al*. 2006; Duan *et al*. 2011). The plot size for each treatment was 200, 120, 400 and 196 m^2 at Changping, Chongqing, Gongzhuling and Qiyang, respectively. Four treatments, i.e., control, F_N, F_{PK} and F_{NPK} were chosen to compare the effects of chemical N, PK and N×PK fertilizations. Fertilizer application rates for the treatments were presented in Table 5. At Changping, Chongqing and Gongzhuling, all P and K and 60% of N were as base fertilizer and 40% of N was as top application at the jointing stage, whereas all N, P and K were as base fertilizer at Qiyang. Annual deep plowing with cattle or machinery was conducted at all study sites. No irrigation was conducted during the growing seasons except for the rice season at Chongqing. Grains and aboveground straw were harvested completely from each plot, respectively. Other field managements were the same as the local practices.

Soil sampling and chemical analysis

Topsoil samples (0-20 cm) were collected in October or November once per year. Air-dried soils were sieved

Table 4 Locations, climatic conditions and topsoil properties at the four study sites

Site characteristics	Changping	Chongqing	Gongzhuling	Qiyang
Locations				
Latitude (°N)	40.22	30.43	43.50	26.75
Longitude (°E)	116.23	106.43	124.80	111.87
Altitude (m, a.s.l.)	70	266	220	120
Climatic types	Warm temperate semi-humid	Subtropical humid	Mild temperate semi-humid	Subtropical humid
Annual air temperature (°C)	13.0	18.3	7.3	18.1
Effective cumulative temperature (°C)	4500	5190	2800	5600
Frost-free days	210	330	144	300
Annual sunshine hours	2561	938	2624	1406
Precipitation (mm yr^{-1})	568	1136	607	1417
Water surface evaporation (mm yr^{-1})	2301	900	1400	1374
Properties of topsoil (0-20 cm) in 1990				
Parent material	Coarse river sediments	Weathered neutral purple mudstone	Alluvial loess-like clay	Quaternary red earth
China classification	Brown fluvo-aquic soils	Purple soils	Black soils	Red soils
FAO classification	Haplic Luvisols	Eutric Regosols	Luvic Phaeozems	Ferralic Cambisols
Clay content (< 2 μm, %)	10.2	26.8	31.1	41.0
Acid buffering capacity (mmol H^+ pH^{-1} kg^{-1}) [1)]	158.71	32.79	68.84	24.48
Bulk density (g cm^{-3})	1.42	1.38	1.19	1.19
pH	8.22	7.60	7.60	5.70
Organic matter (g kg^{-1})	12.2	24.0	22.4	13.6
Total N (g kg^{-1})	0.80	1.25	1.42	1.07
Total P (g kg^{-1})	1.60	0.67	1.53	0.45
Total K (g kg^{-1})	17.3	21.1	24.6	13.7
Available N (mg kg^{-1})	36.0	93.0	114.0	79.0
Available P (mg kg^{-1})	4.6	4.3	11.8	13.9
Available K (mg kg^{-1})	78	88	158	104

[1)] Acid buffering capacity was determined by curves of pH after the addition of sodium hydroxide or sulfuric acid solutions at known concentrations (0.004-0.08 mol L^{-1}) (Vieira *et al*. 2008).

Table 5 Fertilizer application rates (N-P-K, kg ha^{-1} yr^{-1}) at the four study sites

Treatment	Changping		Chongqing		Gongzhuling	Qiyang	
	Wheat	Maize	Wheat	Rice	Maize	Wheat	Maize
Control	0-0-0	0-0-0	0-0-0	0-0-0	0-0-0	0-0-0	0-0-0
F_N	150-0-0	150-0-0	135-0-0 (150-0-0)	150-0-0	165-0-0	90-0-0	210-0-0
F_{PK}	0-33-37	0-33-37	0-26-50 (0-33-62)	0-26-50 (0-33-62)	0-36-68	0-16-30	0-37-70
F_{NPK}	150-33-37	150-33-37	135-26-50 (150-33-62)	150-26-50 (150-33-62)	165-36-68	90-16-30	210-37-70

Data in brackets are the fertilizer application rates during 1991-1996. Chemical fertilizers were applied as urea (N), calcium superphosphate (P) and potassium chloride or potassium sulfate (K), respectively.

through 2.0 mm mesh to determine pH by the electrode mothod (1:1 w/v soil/water), and were ground to 0.25 mm to determine organic matter by the wet combustion method, total N by the semi-micro-Kjeldahl method, total P by the $HClO_4$ and H_2SO_4 digestion plus colorimetric method, total K by the HF and $HClO_4$ digestion plus flame emission photometry, and available N by the alkaline-diffusion method, available P by the $NaHCO_3$-extraction method and available K by the NH_4OAc-extraction method. Grains and aboveground straw were collected after crop maturity and were ground to 1.0 mm to determine total N, P and K concentrations by the H_2SO_4-H_2O_2 digestion method. All determination methods see details in Bao (2000).

Calculation of N transformations in agricultural ecosystem

In an open agricultural ecosystem without leguminous crops, six fluxes of N input-output, i.e., deposition, fertilization, biomass removal, change in soil, volatilization and NO_3^- leaching, were involved in the calculation of N transformations (Fig. 1; Avila-Segura 2004; Guo *et al*. 2010). N deposition averaged in the study period (1991-2005) at each site was approximately calculated by the N in biomass removal minus the N change in soil under the control treatment. The N in biomass removal was the amount of harvested biomass by the N concentrations in grains and aboveground straw, respectively. Nitrogen volatilization was assumed to be 15-40% of N fertilizer (urea) according to the initial topsoil pH and cropping system at each site (Robertson and Vitousek 2009; Guo *et al*. 2010). The rate of soil N change (N_{soil}, kmol N ha^{-1} yr^{-1}) was considered to be a linear change of total N (b, g kg^{-1} yr^{-1}) by the bulk density (D, g cm^{-3}) in the topsoil (0-20 cm).

$$N_{soil}=b\times D\times 0.2\times 10000\div 14 \quad (1)$$

Therefore, the rate of NO_3^- leaching under N fertilization was the subtraction of N outputs (biomass removal, volatilization and change in soil) from N inputs (deposition and fertilization) based on the N balance in an ecosystem.

$$N_{leaching}=N_{deposition}+N_{fertilzation}-N_{soil}-N_{biomass}-N_{volatilization} \quad (2)$$

In agricultural ecosystem, the fluxes of N and BCs^+ in biomass removal were approximately equal in mole equivalents (Duan *et al*. 2004). Moreover, the leaching of HCO_3^- and $RCOO^-$ was trivial and can be neglected compared with the leaching of NO_3^- in croplands with chemical N fertilizer (de Vries and Breeuwsma 1987; Tarkalson *et al*. 2006; Vieira *et al*. 2008; Fujii *et al*. 2009). Therefore, we simplified the calculation of EIPR as shown bellow to assess the ecosystem sensitivity to acid inputs in agricultural ecosystem.

$$EIPR=N_{leaching}/N_{biomass} \quad (3)$$

Statistical analysis

Considering each year during 1991-2005 as the random effect (Duan *et al*. 2011), we tested the significant differences among the four treatments in soil pH, available N, P and K content and the N in biomass removal by one-way ANOVA at the probability level of less than 0.05. The orthogonal effects of chemical N and PK fertilizations on soil pH, available N, P and K content were tested by two-way ANOVA at the probability level of less than 0.05. Linear regression analysis was used to determine the rates of soil pH decline and soil N change during 1991-2005. Data processing and analysis were performed using SPSS 17 (IBM SPSS Statistics, Belgium).

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