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Abstract

Significant soil pH decrease has been reported in Chinese croplands in response to enhanced chemical fertilizer application and crop yields. However, the temporal and spatial variation of soil acidification rates across Chinese croplands is still unclear. We therefore assessed trends in soil acidification rates across provincial China for the period 1980-2010 by calculating inputs-outputs of major cations and anions in cropland systems. Nitrogen (N) induced proton production increased from 4.7 keq H^+/ha/yr in 1980 to a peak of 11.0 keq H^+/ha/yr in 1996 and remained nearly constant after 2000 at a rate of approximately 8.6 keq H^+/ha/yr. The proton production induced by crop removal increased from 1.2 to 2.3 keq H^+/ha/yr. The total proton production thus increased from 5.9 to 10.9 keq H^+/ha/yr in the 30 years. As a result, the actual acidification rate, reflected by (base) cation losses, accelerated from 2.3 to 6.2 keq H^+/ha/yr and the potential acidification rate, reflected by phosphorus accumulation, accelerated from 0.2 to 1.3 keq H^+/ha/yr. The national averaged total acidification rates were thus estimated to increase from 2.6 to 7.6 keq H^+/ha/yr in the past 30 years.The highest soil acidification rate occurred in the Jiangsu Province with a rate of 17.9keq H^+/ha/yr, which was due to both high N application rates and high base cation removals by crops and crop residues. The combination of elevated N inputs and decreased N use efficiency (NUE) in response to those N inputs, thus enhancing the nitrate discharge, were the main reasons for the accelerated acidification in Chinese croplands. Considering the expected growth of food demand in the future, and the linkage between grain production and fertilizer N consumption, a further acceleration of soil acidification can thus be expected, unless the N inputs is reduced and/or the NUE is increased substantially.

Keywords: Soil acidification; Cropland; Historic change; Element budgets; Regional scale

1. Introduction

To feed the expanding population of China from 0.99 billion in 1980 up to 1.34 billion in 2010, cereal crop production was raised from 321 to 546 Tg/yr. Meanwhile, the nitrogen (N) chemical fertilizer (further denoted as fertilizer) consumption increased by a factor of 3.1 while phosphorus (P) fertilizer application increased by a factor of 5.0 from 1980 to 2010 (National Bureau of Statistics of China, NBSC, http://data.stats.gov.cn/). Inputs of N and P are essential to attain high crop yields, but excessive inputs lead to a waste of fertilizer, which is reflected by a decline in nutrient use efficiency. For example, the partial nitrogen fertilizer productivity (PNFP, being the ratio of crop yield per unit of applied N fertilizer) has decreased from 34 kg/kg N in 1980 to 16 kg/kg N in 2008 in China (Zhang *et al.*, 2011). Increased N and P surpluses (total input minus crop removal (harvest removal and crop residue removal) lead to potential risks of losses of those nutrients to air and water, and subsequent degrading air and water quality (Chen *et al.*, 2014). Environmental impacts of enhanced N deposition on biodiversity in terrestrial ecosystems have increased due to increased ammonia (NH_3) emissions from agricultural activities and N oxides (NO_x) from fossil fuel combustion (Basto *et al.*, 2015, De Vries *et al.*, 2015). Due to an overload of N and P in the last 30 years, widespread eutrophication and pollution of surface and ground water, negatively affecting both biodiversity of aquatic ecosystems and drinking water quality, are now serious challenges for China (Zhang *et al.*, 2011).

In addition, there is also a problem of N induced soil acidification in major Chinese croplands (Guo *et al.*, 2010). Accompanying the discharge of nitrate (NO_3^-), an equivalent amount of cations also leaches from soil, causing a decrease of the acid neutralization capacity (ANC, defined as the sum of (base) cations minus (acid) anions), which is defined as soil acidification (De Vries & Breeuwsma, 1986, Van Breemen *et al.*, 1984). Complete budgets of major elements (cations and anions) in agricultural system should thus be assessed to calculate the acid (proton) production rates by fertilization and the related buffering by (base) cation release and possible anion adsorption. This ANC decrease is in turn the driver for changes in soil pH, which is determined by the sensitivity of a soil to acidification, i.e. the unit change in pH per unit change in ANC.

Until now, soil N, P and K budgets and their historic changes have been evaluated in Chinese cropland at regional scale. This includes soil annual N budgets for the period 1980-2004 by Sun *et al.* (2008) and for 1985 and 2007 by Ti *et al.* (2012) for all provinces in China. In addition, N, P and K budgets for 2009 for six sub-regions in China were given by Li and Jin (2011). However, apart from Ti *et al.* (2012), those studies were only limited to input, crop removal and surplus, with no information on the fate of the surplus in terms of losses to air, water and soil accumulation or release. Furthermore, a full assessment of the budgets of all major cations,i.e. ammonium and base cations (calcium, magnesium, potassium and sodium) and anions (nitrate, sulphate, phosphate, chloride and bicarbonates) are essentially required to assess the acidification rate in Chinese croplands, which is lacking for China.

The objective of this study was therefore to assess the major element inputs and outputs in croplands and the related acid load at provincial and national level in China over the period 1980-2010. This period was chosen since large historical changes in agricultural management in China took place in that period, especially in terms of fertilizer input (Liu *et al.*, 2016). In this study, both inputs by field management (fertilization, manure application, irrigation and seeding) and by other sources (deposition and biological N fixation) were considered. Apart from the output by crop harvest, the fate of surpluses in terms of losses to air and water were also assessed to gain insight in the acidification potential of agricultural management. Budgets of each element were involved to evaluate their relative contribution to the total acidification of arable soils in China.

2. Materials and methods

2.1 Acidification assessment

Acidification is primarily manifested by leaching of cations from the soil, which is driven by anion leaching, either by bicarbonate or organic anions due to a leaking natural carbon (C)cycle or by nitrate or sulphate due to a disturbed N or sulphur (S) cycle, mostly caused by human interference (De Vries & Breeuwsma, 1986, De Vries *et al.*, 2015).The quantification of input-output budgets of major element (cations and anions) has widely been used to assess the acidification of forest ecosystem since 1980s (e.g. Van Breemen *et al*. (1984) and De Vries and Breeuwsma (1987)). Based on the same fundamental principles of mass balance and charge balance, we applied this method to agricultural ecosystems. The annual total acidification (H_{tot}) in cropland was quantified by the sum of (base) cation losses and acidic anion accumulation in the soil (De Vries & Breeuwsma, 1987), which was derived by assessing the inputs and outputs of all major cations and anions (NH_4^+, K^+, Ca^{2+}, Mg^{2+}, Na^+, H^+, NO_3^-, SO_4^{2-}, $H_2PO_4^-$, Cl^-, HCO_3^-) in the system.

The H^+ production rate due to N was calculated on the basis of the NH_4^+ input plus net NO_3^- output (acidification induced by a disturbed N cycle), according to (Van Breemen *et al*. (1984); De Vries and Breeuwsma (1987)):

H^+ production by N transformation: $H_N = NH_{4,in}^+ - NO_{3,in}^- + NO_{3,dis}^- - NH_{4,dis}^+$ (1)

Where $_{in}$ and $_{dis}$ denote the total input and discharge losses from the root zone.

In this study, we assumed that nitrification is complete in all agricultural soils. This implies that all N leaches as NO_3^-, implying the production of two protons when N enters the soil as NH_4^+ (see also Eq. 1). Note that this coincides with the production of two protons during nitrification of $NH_4^+$to NO_3^-. When N enters as organic N, only one proton is produced, in line with the occurrence of mineralization, consuming one proton, followed by nitrification, producing two protons. Finally, when N enters as NO_3^-there is no proton production since nitrification did not occur (see further De Vries and Breeuwsma(1987), for the relation between N cycling and acid production).

The H^+ production due to the elements removal by harvesting crops and crop residue was calculated as:

H^+ production by vegetation: $H_{rem} = BC_{rem} - An_{rem}$ (2)

Where $_{rem}$ denotes the net removal by crop harvest and crop residue, *BC* stands for the base cations (Ca^{2+}, Mg^{2+}, K^+, Na^+) and *An* for Anions (SO_4^{2-}, $H_2PO_4^-$). Note that cations can potentially also include aluminum, but this hardly occurs above pH 4.5, and crop lands hardly ever have pH values below 4.5 and the cations are denoted as base cations (BC).

According to De Vries and Breeuwsma (1987), one of the most important processes of H^+ consumption is release of BC in exchange to H^+ in solution followed by discharge, which calculated as the net losses of base cations from the soil, HBC_{loss}, called actual acidification (H_{act}). Inversely, the accumulation of the anions in the soil, HAn_{acc}, called potential acidification (H_{pot}), as the accumulated anions can release and leaching in the future causes an acidification risk. The sum of the two process was defined as the total acidification (H_{tot}) in the assessment:

$$H_{tot} = HBC_{loss} + HAn_{acc} \qquad (3)$$

With

H^+ consumption by soil base cation release: $HBC_{loss} = BC_{dis} - BC_{in} + BC_{rem}$ (4)

H^+ consumption by soil anion accumulation: $HAn_{acc} = An_{in} - An_{dis} - An_{rem}$ (5)

. Note that anions were limited to elements available in soil, i.e. P and S, whose accumulation leads to ANC decline (see e.g. Van Breemen *et al.* (1984) and De Vries and Breeuwsma (1987)).

Apart from soil processes, neutralizing the acid input, some fertilizers also contain bicarbonate, which may buffer the incoming acidity unless the bicarbonate is leached out at the same rate as the input. Finally, there is a net OH^- input associated with all element inputs, which can be calculated by a charge balance, and this also buffers the incoming acidity unless the OH^- output equals the input. These H^+ consumption processes were calculated as:

H^+ consumption by net HCO_3^- inputs: $H_C = HCO^-_{3,in} - HCO^-_{3,dis}$ (6)

H^+ consumption by net OH^- input: $H_H = OH^-_{in} - OH^-_{dis}$ (7)

Note that the H^+ consumption processes calculated by adding Eq. (4) – (7) equal the sum of proton production processes by N transformations and vegetation uptake (Eq.(1) and (2)).

The unit used in all the above-mentioned equations was keq/ha/yr. The calculations that were used to transfer kg/ha/yr to keq/ha/yr are given in Table A.1 of the Supplementary material.

2.2 Input-output budget calculations

Annual inputs of each element over the period 1980-2010 in cropland were assessed according to:

$$X_{in} = X_{fert} + X_{manu} + X_{fix} + X_{seeds} + X_{irri} + X_{dep} \quad (8)$$

Where *X* denotes the anions and cations, e.g. NH_4^+, NO_3^-, $H_2PO_4^-$, K^+, Ca^{2+}, Mg^{2+}, Na^+, SO_4^{2-}, Cl^-, H^+ and HCO_3^- and the subscripts denote the element inputs (X_{in}) by chemical fertilizer (X_{fert}), manure (X_{manu}), biological fixation (X_{fix}), irrigation (X_{irri}), seed (X_{seeds}) and atmospheric deposition (X_{dep}). Note that biological N fixation (X_{fix}) is only relevant for nitrogen. H^+ was calculated as the difference between anion and cations.

Annual outputs of each element over the period 1980-2010 in cropland were assessed according to:

$$X_{out} = X_{rem} + X_{air} + X_{dis} + X_{acc} \quad (9)$$

Where X_{rem} is the output of elements by removal of harvested parts, which include the grains, fruits, tubers, etc. and crop residues, X_{air} are emissions of ammonia and nitric oxide

(NO), nitrous oxide (N_2O) and dinitrogen (N_2) due to denitrification, X_{dis} are discharge losses including runoff and leaching losses and X_{acc} is the accumulation in soil. Note that gaseous emissions are only relevant for nitrogen. Also note that the sum of the element losses to air and water and the accumulation in soil is equal to the element surplus, X_{sur}, being the difference between total element inputs and removal by harvest and crop residues.

All fluxes of inputs and outputs were derived from total flows at provincial level and divided by the arable land area in each province (Taiwan, Hong Kong and Macao are not included due to the data limitation). An overview of the data sources that were used to assess the budgets at province level are given in Table A.2 .The details with respect to the assessment of inputs and outputs are given in the supplementary material.

3. Results

3.1 National average element budgets in the period 1980-2010 in Chinese croplands

Calculated average inputs and outputs of all major elements in Chinese croplands for the years 1980 and 2010 are shown in Table A.4 and annual changes during the period 1980-2010 are shown in Fig. 1 and Fig. A.4. The nitrogen (N) and phosphorus (P) inputs increased from 120 kg N/ha/yr and 14.4 kg P/ha/yr in 1980 to 311 kg N/ha/yr and 57.5 kg P/ha/yr in 2010, respectively (Fig. 1a, b). These enormous changes were mainly caused by the rapid increase of N and P chemical fertilizer application, whose percentage of total input increased from 60.3% and 65.9% in 1980 to 73.1% and 82.0% in 2010, respectively. Similarly, inputs of base cations (BC) increased from 113 kg/ha/yr in 1980 to 295 kg/ha/yr in 2010, mainly by elevated fertilizer (39.9%) and manure application (48.5%). Chloride

(Cl) inputs showed also a sharp rise from 19.3 to 120 kg Cl/ha/yr in the period 1980-2010 (Fig. A.4). However, the other accompanying anions with N and P fertilizer, sulphate (SO_4^{2-}) and bicarbonate (HCO_3^-), decreased from 1.2 to 0 kg S/ha/yr and from 32.0 to 21.7 kg HCO_3-C/ha/yr during the period 1980-2010, respectively (Fig. 1d and Fig. A.4). These significant declines were mainly due to the transformation of N fertilizer types from ammonium bicarbonate and ammonium sulphate to urea (Fig. A.1). Nevertheless, total S inputs in 2010 (27.9 kg S/ha/yr) almost doubled compared with those in 1980 (15.1 kg S/ha/yr) due to elevated atmospheric S deposition.

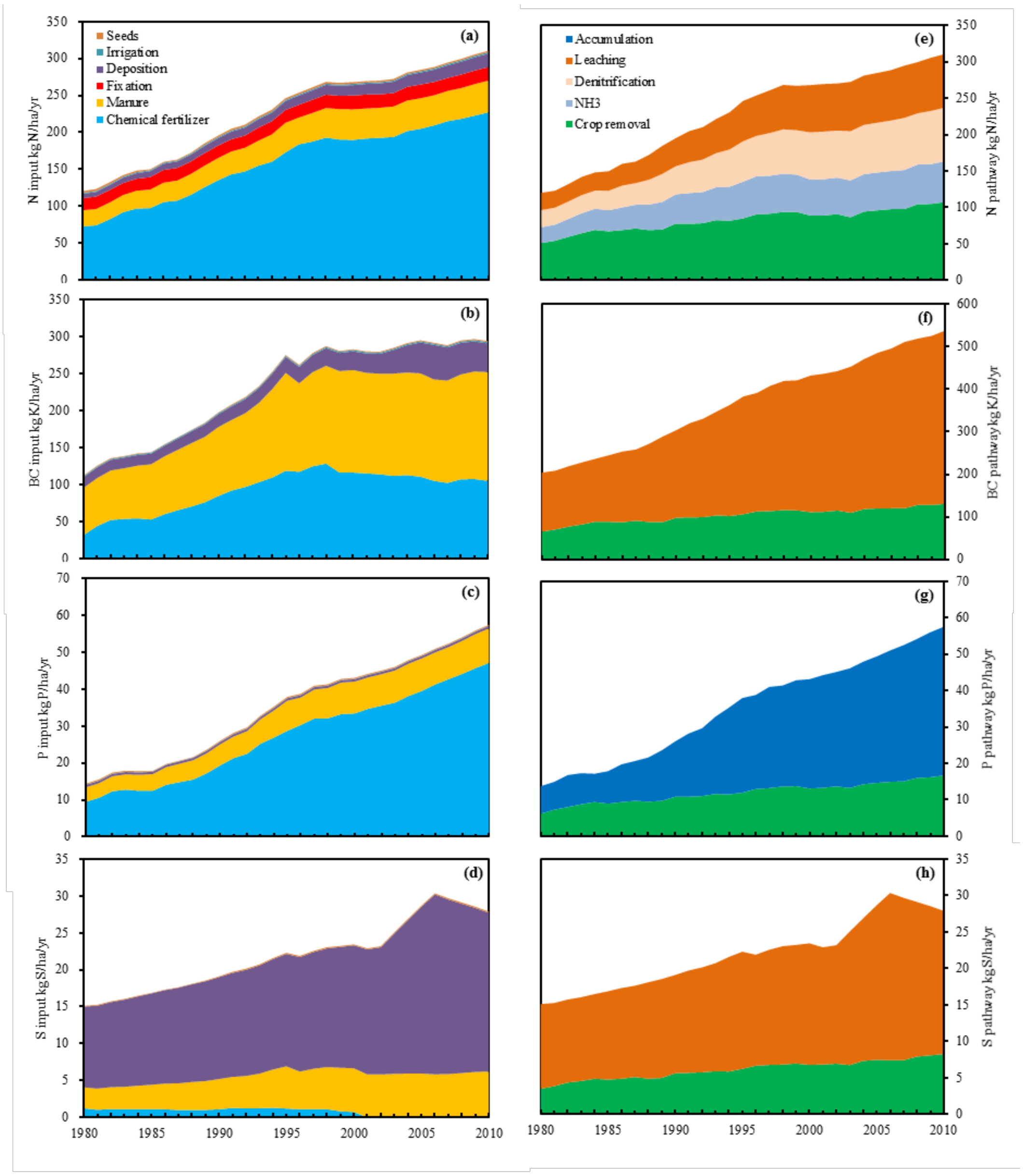

Fig. 1 Annual input-output budgets for N, P, BC and S in China during 1980-2010. The inputs of N, P, BC and S are given in the graphs (a), (b), (c) and (d) on the left and the output of N, P, BC and S in the graphs (e), (f), (g) and (h) on the right.

Element outputs from land occurred by crop removal, discharge to ground and surface water and (or) gaseous emissions, with the remained part accumulating in the soil. With increased crop yields, net element removal by harvest increased continuously during the period 1980-2010. This increase was mainly due to increased removal of harvested parts, while the crop residue removal stayed relatively constant due to an increasing fraction of crop residue return to the soil (Fig. A.3). The N net removal increased from 51.2 kg N/ha/yr in 1980 to 108 kg N/ha/yr in 2010, while the ratio of N removal to total N input decreased from 42.6% to 34.6%. This decrease is associated with an increased N surplus (Table A.3). As with N surplus, NH_3 emission increased from 21.7 to 55.8 kg N/ha/yr, while N_2O and NO emission increased from 1.9 and 0.9 kg N/ha/yr to 4.0 and 2.0 kg N/ha/yr, respectively. Eventually, the strongly increased N fertilizer application elevated the N discharge losses from 23.7 to 73.7 kg N/ha/yr in the period 1980-2010. Similar to N, increased surpluses also occurred for S and Cl, lead to increasing discharge losses from the soil (Table A. 6). Accompanying with these anions, discharge losses of BC increased from 117 to 387 kg/ha/yr during the period 1980-2010, even though the BC surplus increased from 47.8 to 164 kg/ha/yr (Table A.4). The difference between BC outputs (Fig. 1g) and BC inputs (Fig. 1c) denotes the BC loss from the soil, being the actual soil acidification.

3.2 National average acidification rates between 1980 and 2010 in Chinese croplands

Fig. 2a shows the proton production in Chinese croplands by N transformations and and crop removal between 1980 and 2010. With a continuously increasing N input, proton production increased from 4.7 keq H^+/ha/yr in 1980 to a peak of 11.0 keq H^+/ha/yr in 1996(Fig. 2a). Thereafter, a slight decline occurred due to a decrease of ammonium based N fertilizer use and an increase in urea input (Fig. A.1 and Fig. 1a). Proton production was nearly constant since 2000, at an acidification rate of approximately 8.6 keq H^+/ha/yr (Fig. 2a). In combination with the proton release induced by crop removal, that increased from 1.2 to 2.3 keq H^+/ha/yr, the total proton production thus increased from 5.9 to 10.9 keq H^+/ha/yr in 30 years, being an increase by a factor 1.8.

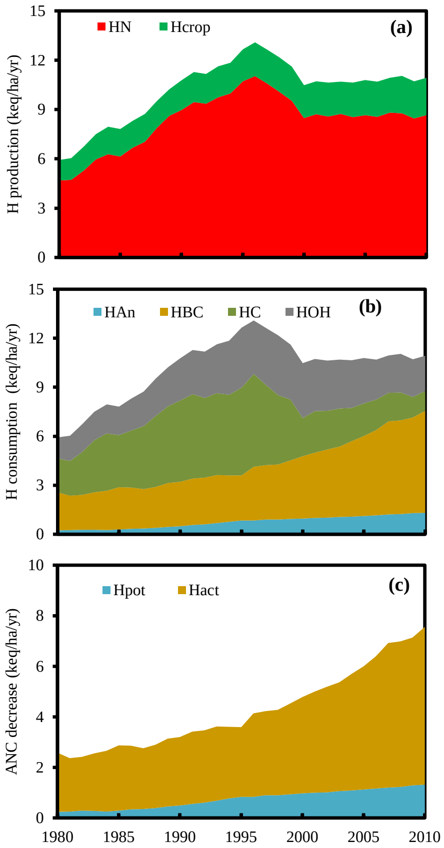

Fig. 2 The proton production by N transformations (HN) and crop removal (Hcrop) (a) and the proton consumption by base cation loss (HBC), anion accumulation (HAn), HCO_3^-(HC) and OH^- input (HOH) (b) and the related soil acidification (c), being the sum of base cation loss (actual acidification, H_{act}) and anion retention (potential acidification, H_{pot}).

Besides the protons neutralized by net OH^- and HCO_3^- inputs, the rest was neutralized by loss of base cations and accumulation of anions (Fig. 2b). The neutralization by BC losses increased from 2.3 to 6.2 keq H^+/ha/yr during the period 1980-2010, which reflected the enhanced actual acidification rate (H_{act}). The neutralization by P accumulation increased from 0.2 to 1.3 keq H^+/ha/yr during the period, implying an elevated risk of potential acidification (H_{pot}) when released again. The total acidification (H_{tot}) thus accelerated from 2.6 keq H^+/ha/yr in 1980 to 7.6 keq H^+/ha/yr in 2010, as shown in Fig. 2b.

3.3 Spatial variation in elements and acidification budgets

The element application at provincial level showed big variations across China, with relative differences between provinces staying rather constant during the period 1980-2010 (Fig. A.5-A.8). N, BC and P inputs in the northeast and northwest of China were generally lower than the inputs in the central and south of China. These enhanced inputs have improved the crop yield and element removal by harvest, simultaneously, even under an increasing crop residues return fraction (Fig. A.3). However, the surpluses in 2010 were much higher compared to 1980 (Fig.A.5-A.8), being either emitted to water and air or accumulated in soil (especially P).

The largest potential acidification by P accumulation occurred in the Fujian, Henan and Hubei Provinces, with rates greater than 2.4 keq H^+/ha/yr (Fig. 3). The most severe actual acidification by base cation loss occurred in the central and southern part of China, where actual acidification rates were greater than 12 keq H^+/ha/yr in 2010 in the Jiangsu, Henan and Hubei Provinces.

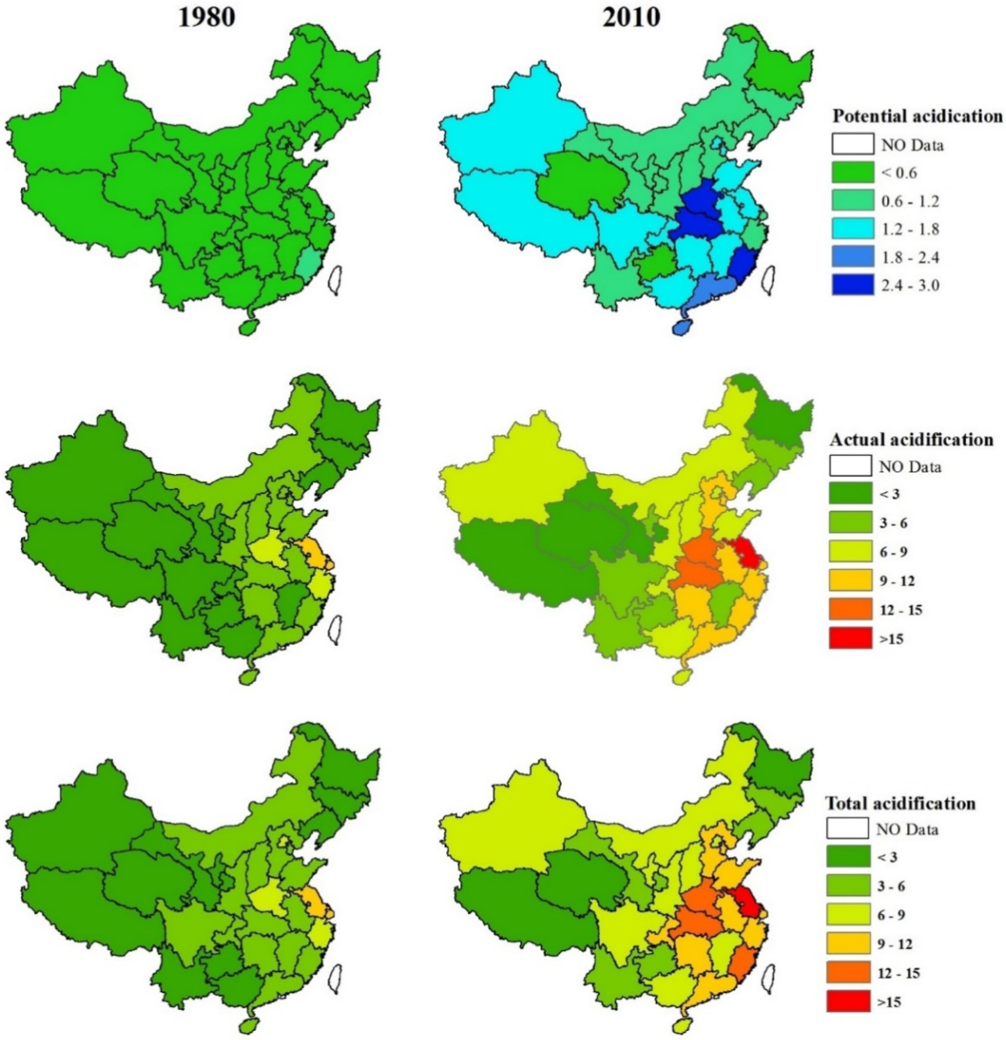

Fig. 3 Provincial potential acidification by anion accumulation (top), actual acidification by base cation loss (middle) and total acidification (bottom) in 1980 (left) and 2010 (right). Unit is keq H^+/ha/yr.

In 1980, there were only two provinces whose total acidification rates were greater than 9 keq H^+/ha/yr (Shanghai and Jiangsu), while this increased to 13 provinces in 2010 (Fig. 3). Among the 13 provinces, there were four provinces (Fujian, Henan, Hubei and Jiangsu) with total acidification rates greater than 12 keq H^+/ha/yr, with one province (Jiangsu) being even higher than 15 keq H^+/ha/yr. In short, soil acidification in Chinese croplands has increased significantly over the last 30 year at both national and provincial levels.

4. Discussion

4.1 Uncertainties in the element budgets and acidification assessment

Due to the variability in the various sources of inputs and outputs, there are also uncertainties in the calculated element budgets and acidification. Regarding the inputs, the main driver for acidification is the N input for which reasonable estimates are available at least at national and also at provincial level. Considering a total cropland area of 130 million hectare, we estimated an N input by fertilizer and manure of 29.5 TgN/yr and 5.6 TgN/yr in 2010, which is quite comparable to estimates of 28.9 TgN/yr and 5.9 TgN/yr, respectively by Gu *et al.* (2015). Crop removal estimates are quite certain at national scale considering the national statistics on crop yields. However, the largest uncertainties are in the assessed denitrification and discharge losses of nitrate, as the latter drives the N induced acidification rate.

In our study,we assumed that half of the N_{rest} (which is the N surplus corrected for NH_3 emission as: N_{rest}=N_{sur}- NH_3) discharged from the root zone, and that the remainder was denitrified. As a result, the contributions of N output fluxes to the total N output were 37.7% for crop removal, 19.1% for NH_3 emission, 21.6% for denitrification, and 21.6% for discharge from the root zone. The assumption was made on the basis of previous research by Ma *et al.* (2010) and Liu (unpublished), who estimated that on average about 25% and 17% of N_{rest} was leached at 100 cm soil depth, respectively. This result was combined with information on the changes in N leaching fraction with soil depth (Li & Li, 2000), since we focused our study on the root zone, being the top 30 cm of the soil. By using those data, we assumed that half of the N surplus leached from the root zone, and that the remainder was denitrified and subsequently emitted to the air. The actual acidification rates thus increased from 2.3 to 6.2 keqH^+/ha/yr during the period 1980-2010. The discharge fraction has, however, quite a large uncertainty and this mainly affects the calculated acidification rates. We thus evaluated the uncertainties in the acidification rates by assuming a range in the N discharge fraction of 35-65% of the N_{rest}. Results showed that the actual acidification shows always an increasing trend but the increase was from 1.8 to 4.7keqH^+/ha/yr assuming that 35% of N_{rest} is leached and from 2.8 to 7.8keqH^+/ha/yr when 65% of N_{rest} is leached, respectively (Fig. 4).

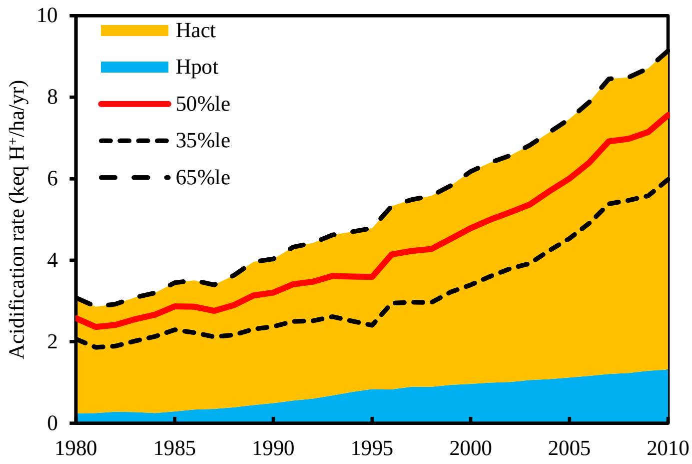

Fig. 4 Sensitive analysis of total acidification assuming that 35% (35%le), 50% (50%le, reference run) and 65% (65%le) of the N_{rest}(total N input minus NH_3-N emission minus and crop N removal) being leached. H_{act} and H_{pot} denote the actual acidification rate and potential acidification rate, respectively.

There are also uncertainties in the assumptions with respect to the behaviour of the various other ions, especially that of the anions Cl^-, SO_4^{2-}, $H_2PO_4^-$, HCO_3^- and $RCOO^-$. We assumed that both Cl^-, SO_4^{2-} behave like a tracer, with no adsorption taking place in soil. Unlike Cl^-, SO_4^{2-} can be adsorbed to the soil, but in most ecosystems SO_4^{2-} adsorption is very limited. For example, De Vries *et al* (2007) found that on average SO_4^{2-} output was nearly equal to SO_4^{2-} input at 121 intensively monitored forest plots, implying that SO_4^{2-} was hardly adsorbed. Kopáček*et al*., (2014) even reported that agricultural land was a small net source of sulphate and forest soils changed from a sink to a source of sulphate in the late 1980s during the period 1960-2010 in a large central European catchment (Upper Vltava river, Czech Republic). Therefore, we made the assumption that SO_4^{2-} adsorption was negligible. Most likely, the uncertainty in soil acidification related to this assumption is negligible compared to the uncertainty induced by the fate of N behaviour and the related nitrate loss. This also holds for the leaching of $RCOO^-$. We made an estimate of this term by multiplying water fluxes, ranging from 100 to 400mm/yr, with estimated concentrations of $RCOO^-$ using the method of Oliver *et al*. (1983). Calculations were made for a DOC concentration of 5 mg C/L, being representative for the root zone (Walmsley *et al*., 2011) and a pH ranging from 4.5-7.0. The $RCOO^-$ fluxes thus calculated varied between 0.033 to 0.20 keq/ha, being very small compared to leaching of NO_3^-.

4.2 Spatial variation of element budgets and acidification rates across China

More than 70% of the arable land is distributed in the eastern part of China, where about 80% of China's cereal production takes place (National Bureau of Statistics of China, NBSC). Acidification rates in the eastern part were greater than in the western part of China in both of 1980 and 2010 (Fig. 3). The averaged total acidification rates in the east (5.1 keq H^+/ha/yr in 1980 and 9.8 keq H^+/ha/yr in 2010) were about 2.7 times to that in the west (1.5 keq H^+/ha/yr in 1980 and 5.3 keq H^+/ha/yr in 2010). The disparate acidification rates in the two regions can be ascribed to inconsonant elements input-output budgets. For example, in 2010, the average N inputs were 369 and 232 kg N/ha/yr and the average N removals by harvest were 114 and 64 kg N/ha/yr in the east and in the west, respectively (Fig. A.5). As a consequence, greater N surpluses were estimated for the east (255 kg N/ha/yr) than for the west (169 kg N/ha/yr), which can lead to more BC losses to ground and surface water, accompanied by nitrate losses (De Vries and Breeuwsma, 1987).

Moreover, higher yield levels in the east than in the west lead caused more BC losses by harvest removal. For example, in 2010, the cereal yields in the east and west were 4450 and 2836 kg/ha (NBSC), and BC removal in the east was thus 1.5 times higher than in the west (Fig. A.6). As a consequence, actual acidification rates, reflected by net soil BC losses (the difference between inputs and outputs by harvest removal and discharge) in the east (8.34 keq H^+/ha/yr) were 1.9 times higher than in the west (4.34 keq H^+/ha/yr) in 2010 (Fig. 3).

Similarly, variations in potential acidification (Fig. 3), reflected by anion accumulation in soil, can be explained by the variations in the P budget (Fig. A.7). Higher P surpluses imply a potential risk of P discharge and related BC loss. For example, in 2010, P inputs were 65.1 and 40.7 kg P/ha/yr, and P removals were 18.4 and 11.1 kg P/ha/yr in the eastern and western part of China, respectively (Fig. A.7). As a result, P surpluses of 46.8 and 29.6 kg P/ha/yr in the east and west led to a potential acidification of 1.51 and 0.95 keq H^+/ha/yr in 2010, respectively.

The largest acidification in China was found in the Jiangsu Province with a total average rate of 17.9 keq H^+/ha/yr in 2010, followed by the Henan (14.8 keq H^+/ha/yr), Hubei (14.7 keq H^+/ha/yr) and Fujian (14.1 keq H^+/ha/yr) Provinces (Fig. 3). In Jiangsu, proton production by N inputs (515 kg N/ha/yr) was up to 16.2 keq H^+/ha/yr, which was 1.9 times higher than the national average (8.6keqH^+/ha/yr) in 2010. Moreover, the BC losses by crop removal (4.2 keq H^+/ha/yr) were also slightly higher than the national average (3.3 keq H^+/ha/yr). However, the BC inputs in Jiangsu (7.5 keq H^+/ha/yr) were comparable to the national average (7.6 keq H^+/ha/yr). As a consequence, the estimated actual acidification rate in the Jiangsu Province in 2010 was 2.6 higher than the national average. In conclusion, unbalanced inputs, i.e. enormous N but few BC, led to the high acidification rates in the Jiangsu Province, as well as the eastern part of China.

4. 3 Decreased nutrients use efficiency and its impacts on environment

Even though increased fertilizer application improved crop yields significantly, there was still a decreased nutrient use efficiency and enhanced nutrient waste (Fig.5), associated with an N surplus and P surplus that increased on average from 69 to 203 kg N/ha/yr and 8.2 to 41 kg P/ha/yr, respectively in the period 1980-2010. The surplus N is either emitted to air as NH_3 or NO and N_2O after (de)nitrification, or discharged by leaching to groundwater and runoff to surface water (Galloway *et al.*, 2008), while the P surplus accumulates in soil, increasing soil fertility, but ultimately leaches to ground and surface water (Li *et al.*, 2015). In our assessment, nationwide N_2O emissions from agroecosystems more than doubled from 249 to 522 Gg N/yr and NO emissions increased from 122 to 264 Gg N/yr, from 1980 to 2010. What's even worse, besides the greenhouse gas (GHG) emission, the discharge losses increased from 3.1 to 9.6 Tg N /yr during the period. Increased eutrophication occurrences were reported in this period (Wang *et al.*, 2016), attributed to the fertilizer and manure use in agroecosystems (Strokal *et al.*, 2014). On the other hand, N surpluses can also leach to groundwater which supplies 20% of the drinking water in China and this causes enlarged risks of gastric and oesophageal cancers(Gao *et al.*, 2016). A recent research showed that the nitrate concentration in more than 25% of samples of groundwater taken under croplands during 2000-2009 exceeded the World

Health Organization (WHO) recommended maximum value of 11.3 mg NO_3-N/L(Gu *et al.*, 2013).

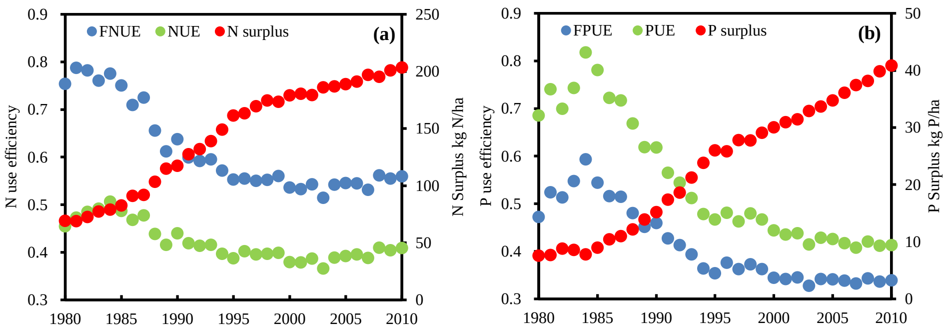

Fig. 5 Decreased nutrient use efficiencies and increased nutrients surplus ofN (a) and P (b). Where, NUE and PUE denote the element N, P use efficiency, which calculated as sum crop uptake divided to total input; Similar for FNUE and FPUEdenote fertilizer N and P use efficiency respectively, calculated as sum crop uptake divided to chemical fertilizer N and P input, respectively.

Similarly, P surpluses increased from 8.2 to 40.8 kg P/ha/yr during the period, which result in an increased soil P content, in line with a reported increase in national averaged soil Olsen P contents from 7.4 mg/kg in 1980 to 20.7 mg/kg in 2006(Li *et al.*, 2011). In summary, excessive nutrients application in agricultural system led to increased waste of nutrients and decreased nutrients use efficiency, and enlarged threats to air quality and water security.

4. 4 Future acidification risks in China's croplands

To feed the increased Chinese population from 0.99 billion in 1980 to 1.34 billion in 2010, cereal production increased from 321 to 546 Tg, and N fertilizer consumption increased from 9.4 to 29.5 Tg N/yr during that period (NBSC). Our data shown a significant positive relationship between acidification rates and the increase in both grain production and N fertilizer consumption (Fig. 6a). This result is driven by the fact that such a raised N application improves crop yield, but also causes elevated nitrate discharge losses, accompanied by accelerated base cation losses from the soil (De Vries *et al.*, 2015). Thus, the acidification rate showed a negative relationship with the FNUE fertilizer N use efficiency) and PNFP (partial nitrogen fertilizer productivity), as shown in Fig.6b.

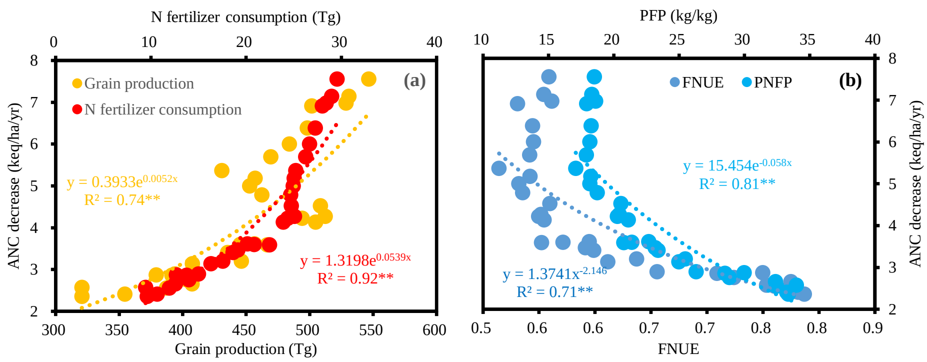

Fig. 6 Regression analysis between the soil acidification rate and (a) the N fertilizer consumption and grain production and (b) the PNFP and fertilizer N use efficiency (FNUE). Where, gain production includes cereal, tuber and legumes; PNFP, (Partial N fertilizer productivity, calculated as grain production divided to N consumption); and T denotes 10^{12}.

The future food demand is expected to increase in China, promoted by diet shifts to more meat consumption by an increasingly rich urban population and a continuous increase of the total population(Bai *et al.*, 2016, Ma *et al.*, 2013). At the current N fertilizer use efficiency (FNUE), applying more N to gain high yields would further aggravate the nitrate discharge losses and acidification rates of croplands. Considering the potential effects on crop yield below a threshold soil pH (Baquy *et al.*, 2017), this may even lead to a crop yield decline with a further decrease in NUE and thus a declining trend in food production in the future. In other words, crop yield improvement should not come at the expense of more N application but by increasing the FNUE to reduce the N application and mitigate the nitrate discharge losses and acidification of cropland. This is crucial to achieving food security and mitigate soil acidification rates in Chinese croplands.

A comprehensive assessment on N management practices to increase the FNUE was carried out by Xia *et al.*,(2017). Measures that were evaluated were all related to the so-called 4 R strategy, i.e. adding the right fertilizer type (nitrification inhibitor, urease inhibitor), at the right place (deep placement), the right time (higher splitting frequency) and the right amount (lower basal N fertilizer and optimal N rate based on soil N test). Results showed that these measures can improve yields by 1.3-10.0%, increase the FNUE by 8.0-48.2% and reduce the N leaching by 13.6-37.3%. The application of integrated soil-crop system management (ISSM, which designs the system on the basis of local environment, crop varieties selection, sowing dates, densities and advanced nutrient management) can even reduce the N surplus around zero (varying from -9 to 16 kg N/ha) in China's cereal cultivation (Chen *et al*., 2014). Recent meta-analysis of results in China also showed that the PNFP (Partial nitrogen fertilizer productivity) in the highest yield group was almost twice as high as the all farmers averaged group, which implies that a reduction of about 40% in N application and an increase of approximately 30% in grain production are possible (Cui *et al*., 2014).

Another way to reduce the soil acidification is a change from NH_4^+ to NO_3^- based fertilizers. This change in N fertilizer types (Fig. A.1) was the reason for the relative constant acidification rate that was found after 2000 (Fig. 2b), as it counteracted the effect of an increased N fertilizer rate (Fig. 1a) during the period 2000-2010.The proportion of ammonia nitrogen and urea in Chemical N fertilizer was 46% and 53% in 1997, respectively, while it changed to 19% and 79%in 2010. This reduced the acidification potential of the added fertilizers since transformation of one mole ammonia to nitrate, that is subsequently leached from the soil, produces two equivalent H^+, whereas this is only one equivalent H^+ when urea-nitrogen is transformed to nitrate (De Vries and Breeuwsma, 1987; Zeng *et al.*, 2017).

Besides measures to reduce N application and enhance NUE, another option to decrease cropland soil acidification is an increase in the application of alkaline materials, such as manure and limestone, to neutralize the produced protons. Liming has been widely recommended to manage soil acidification (Goulding, 2016; Zhu *et al*., 2016). However, this management approach is impractical in some areas due to supply shortages and high costs (Shi *et al*., 2017; Xu and Coventry, 2003).However, replacing part of the chemical N fertilizer by manure can significantly alleviate soil acidification as shown in both modelling research (Zhu *et al*., accepted) and long-term observations (Cai *et al*., 2015). Straw return, which is expected to increase on the future, also reduces soil acidification by returning BC to the soil (Zeng *et al*., 2017), but the effect is weaker than manure application (Sun *et al*., 2015). In general, the fundamental approach to alleviate soil acidification in cropland is to reduce the N inputs and/or increase the net BC inputs to the soil.

5. Conclusions

This paper provides a comprehensive assessment and evaluation of soil acidification rates n Chinese croplands at provincial and national levels by an assessment of all major element budgets. Significant yield production was driven by elevated element inputs from chemical fertilizer, manure and deposition, especially of N, P and K. However, negative effects induced by a decreasing fertilizer use efficiency and increasing soil acidification occurring simultaneously. We estimated a China averaged total acidification rate that increased from 2.6 to 7.6keq H^+/ha/yr in the period 1980-2010, with rates higher than 9 keq H^+/ha/yr in thirteen provinces in 2010, while such rates only occurred in two provinces in 1980. The combination of elevated N inputs and decreased N use efficiency was the main reason for the accelerated acidification in Chinese croplands. Considering the expected growth of food demand in the future, and the linkage between grain production and fertilizer N consumption, a further acceleration of soil acidification can thus be expected, unless the N fertilizer application is reduced and/or the N use efficiency is increased.

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Abbreviations:

An: Anions (NO_3^-, SO_4^{2-}, $H_2PO_4^-$, Cl^- and HCO_3^-)

BC: base cations, i.e. K^+, Ca^{2+}, $Mg^{2+}$and Na^+

H_{act}: actual acidification rates, being the net base cations losses from soil

H_{pot}: potential acidification rates, being the anions accumulate in the soil

H_{tot}: total acidification rates, being the sum of actual acidification and potential acidification

ISSM: integrated soil-crop system management

NBSC: National Bureau of Statistics of China

N_{rest}: N rest, being the difference between total inputs, crop removal and NH_3 emission

NUE: nitrogen use efficiency

FNUE: nitrogen fertilizer use efficiency

PNFP: partial nitrogen fertilizer productivity

X: element of N, P, K, Na, Ca, Mg, C, S, Cl, H

X_{acc}:element *X*accumulation in soil

X_{air}: gaseous emissions losses from the soil

X_{dep}:element X input to the soil by atmospheric deposition

X_{dis}: element X discharge from the root zone

X_{fert}:element X input to the soil by chemical fertilizer

X_{fix}:element X input to the soil by biological fixation

X_{in}: element X input to the soil

X_{irri}:element X input to the soil by irrigation

X_{seeds}:element X input to the soil by seed

X_{sur}:element X surplus, being the difference between total inputs and crop removal

X_{manu}:element X input to the soilby manure

X_{rem}: element X removal from the soil by crop harvest and crop residue removal

Supplementary material

The supplementary material describes in detail the assessment of element inputs and outputs, including four Tables and eight Figures with data and results.

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