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The contribution of natural and anthropogenic causes to soil acidification rates under different fertilization practices and site conditions in southern China

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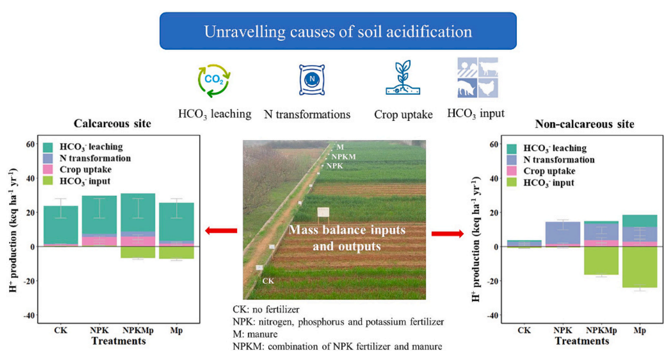
HIGHLIGHTS

- Soil acidification rates were derived for 13 long-term experimental sites.
- The rates varied depending on fertilizer management, land use, soil type and climate.
- Natural bicarbonate leaching dominated soil acidification in calcareous soils and paddy soils.
- Nitrogen fertilizer application dominated soil acidification in non-calcareous upland soils.
- Manure application reduced soil acidification due to enhanced base cation addition.

GRAPHICAL ABSTRACT



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ABSTRACT

Excessive application of mineral fertilizers has accelerated soil acidification in China, affecting crop production when the pH drops below a critical value. However, the contributions of natural soil acidification, induced by leaching of bicarbonate, and anthropogenic causes of soil acidification, induced by nitrogen (N) transformations and removal of base cations over acid anions, are not well quantified. In this study, we quantified soil acidification rates, in equivalents (eq) of acidity, by assessing the inputs and outputs of all major cations and anions, including calcium, magnesium, potassium, sodium, ammonium, nitrate, bicarbonate, sulphate, phosphate and chloride, for 13 long-term experimental sites in southern China. The acidification rates strongly varied among fertilizer treatments and with the addition of animal manure. Bicarbonate leaching was the dominant acid production process in calcareous soils (23 keq ha^{-1} yr^{-1}) and in non-calcareous paddy soils (9.6 keq ha^{-1} yr^{-1}), accounting for 80 % and 68 % of the total acid production rate, respectively. The calcareous soils were strongly buffered, and acidification led no or a limited decline in pH. In contrast, N transformations were the most important driver for soil acidification at one site with upland crops on a non-calcareous soil, accounting for 72 %

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of total acid production rate of 8.4 keq ha^{-1} yr^{-1}. In this soil, the soil pH considerably decreased being accompanied by a substantial decline in exchangeable base cation. Reducing the N surplus decreased the acidification rate with 10 to 54 eq per kg N surplus with the lowest value occurring in paddy soils and the highest in the upland soil. The use of manure, containing base cations, partly mitigated the acidifying impact of N fertilizer inputs and crop removal, but enhanced phosphorus (P) accumulation. Combining mineral fertilizer, manure and lime in integrative management strategies can mitigate soil acidification and minimize N and P losses.

1. Introduction

Soil acidification, usually defined as a decrease in the acid-neutralizing capacity (ANC), is a biogeochemical process leading to soil degradation (De Vries and Breeuwsma, 1987; Guo et al., 2010; Van Breemen et al., 1984). It restricts crop production by decreasing the availability of soil nutrients, such as phosphorus (P) and base cations (BC, including exchangeable potassium (K^+), calcium (Ca^{2+}), magnesium (Mg^{2+}), and sodium (Na^+)). At low pH (<4.5) the release of toxic elements is higher as shown for aluminium (Al), manganese (Mn) and heavy metals, inhibiting crop and root growth (Fenn et al., 2006; Kochian et al., 2015; Yan et al., 1992; Zhang et al., 2020; Zhang et al., 2016). Cereal production losses due to acidification are expected to increase from 4 % to 24 % during 2010–2050 due to a strong pH decline unless mitigation measures are applied (Zhu et al., 2020). In China, around 47 % of total croplands has soil pH levels lower than 6.5, being defined as non-calcareous (unpublished data from China's Ministry of Agricultural and Rural Affairs). From these croplands 15 % has a pH lower than 5.5, which may affect food production.

Soil acidification is a naturally occurring process, driven by the leaching of bicarbonate (HCO_3^-) and organic anions ($RCOO^-$), being the leakages in the natural CO_2 cycle (De Vries and Breeuwsma, 1987; Sparks, 2003). In addition, acidification can naturally occur in soils with trees or crops with a high biological nitrogen (N) fixation rate, causing enhanced NO_3^- leaching, but in nearly all cases the natural N cycle is almost closed and the same holds for the sulphur (S) cycle. However, soil acidification has been greatly accelerated by human activities in recent decades, especially by the increasing use of nitrogen (N) fertilizers, in large parts of the world and especially in China and also by enhanced emissions of SO_2, thus causing losses in the N and S cycle (De Vries and Breeuwsma, 1987; De Vries et al., 2021; Tian and Niu, 2015). Extensive use of N fertilizers causes the production of protons (H^+) by nitrification of ammonium (NH_4^+) and subsequent nitrate (NO_3^-) leaching whereas the nitrate is associated with BC to counteract the H^+ production (Bouman et al., 1995; Hao et al., 2020; Wang et al., 2018; Zhang et al., 2016). In addition, the continuous removal of edible crops leads to excess removal of base cations over anions, i.e. phosphate ($H_2PO_4^-$), sulphate (SO_4^{2-}) and chloride (Cl^-), with subsequent H^+ release from roots (Duan et al., 2004). In soils, the produced H^+ is buffered either by calcium carbonate ($CaCO_3$) in calcareous soils or the release of exchangeable BC in non-calcareous soils, reflected by soil $CaCO_3$ or BC pool changes (De Vries et al., 1994; De Vries et al., 1989; Ulrich, 1983). Furthermore, adsorption of acid anions such as $H_2PO_4^-$ and SO_4^{2-} also neutralize the H^+ production and causes a decrease in acid-neutralizing capacity. In China, over half of the soils is calcareous with carbonate dissolution strongly buffering the pH. Leaching of HCO_3^-, combined with enhanced NO_3^- leaching, can be an important cause for high decalcification rates, thus threatening the buffering capacity on the longer term (Raza et al., 2020).

The contribution of natural and anthropogenic sources to soil acidification can be quantified by a mass balance approach where all inputs and outputs of major cations (especially NH_4^+, Ca^{2+}, Mg^{2+}, K^+, Na^+) and major anions (especially NO_3^-, SO_4^{2-}, $H_2PO_4^-$ and Cl^-) are quantified (De Vries and Breeuwsma, 1987; Van Breemen et al., 1984). Such assessments have often done for forest ecosystems (De Vries et al., 2003) but much less in agricultural soils. An exception Hao and co-workers, who assessed soil acidification rates in various cropping systems in China using measured inputs and outputs of the above mentioned elements, showing that soil acidification rates vary across crop rotation systems and fertilization strategies (Hao et al., 2022; Hao et al., 2018; Hao et al., 2020; Meng et al., 2013). For example, NH_4^+ fertilizers induced higher acidification rates than urea fertilizers, and soil acidification rates were substantially higher in wheat-maize rotations than in rice-fallow and rice-wheat rotations (Hao et al., 2022). However, their experiments were done on loamy clay soils with limited NO_3^- leaching rates, thereby reducing the impacts of N transformations on soil acidification. A more comprehensive quantification of the impacts of fertilizer and manure management on soil acidification as a function of land use, soil properties and climate are essential to identify the main contributors of soil acidification under different site conditions and to identify appropriate management strategies.

The southern China region is the main crop producing area in China, where soil acidification has been identified as a main threat (Hao et al., 2020; Zhang et al., 2022). Optimizing N fertilizer type and reducing excess application of N seem appropriate measures to mitigate acidification but given the climatic conditions the N losses will likely continue even at low N input levels (Wang et al., 2023). Replacing N fertilizers with manure can partly counteract acidification given its BC content, counteracting the acidifying impact of N (Cai et al., 2015; Cai et al., 2021). This shift in fertilization strategy should be combined with innovations in stable management and application technologies (Hao et al., 2020; Zeng et al., 2017) to reduce NH_3 emissions from manure to minimize N deposition and associated soil acidification of non-agricultural soils (indirect effect). In addition, intermittent liming remains required to avoid too low pH values, thereby avoiding HCO_3^- leaching of the added lime. Because the impact of fertilizer and manure management on the acidification rate is affected by soil properties and crop management (Fageria and Baligar, 2008), insight in those factors is needed to select appropriate fertilizer management on regional scale. This dependency on local and regional site conditions is confirmed by strong differences in acidification rates among long-term experimental sites across southern China. For example, long-term addition of mineral N fertilizers leads to a strong decline in soil pH where the addition of manure increased the soil pH in Qiyang site (Cai et al., 2015) but the same treatments showed minor differences in soil pH in the Minhou site (Fang et al., 2015). Understanding the contribution of natural and anthropogenic sources of acidification is key to mitigate the adverse impacts of soil acidification.

In this research, we used data from 13 long-term experimental sites in southern China with variable land use types, fertilizer application (type and dose), manure application, climate, and soil properties to unravel the contribution of natural and anthropogenic sources of acidification. The experiments were mainly set up to study the fate of N and P and not so much for soil acidification. Consequently the experiments only included data on the inputs and crop removal of N, P and K. However, by extending the datasets with information on the inputs and crop removal of the base cation Ca^{2+}, Mg^{2+} and Na^+, combined with the anions SO_4^{2-}, Cl^- and HCO_3^- information on soil acidification rates can be derived. We did so by quantifying the all relevant input and output fluxes for the above mentioned major cations and anions and assessed the impacts of management strategies on these fluxes and related acidification rates. The experiments included 6 calcareous and 7 non-calcareous soils. The impacts of fertilization management (the rate and type of mineral fertilizer and organic manure) and land use types, soil type (calcareous and non-calcareous soils) and climate (precipitation surplus) on soil acidification rates were evaluated for the main driving processes (i) N transformations (ii) crop uptake of cations over anions and (iii) HCO_3^- leaching. Estimated changes in carbonate contents and exchangeable BC contents were used to validate the estimated soil acidification rates. We hypothesized that (i) main drivers for soil acidification are HCO_3^- leaching in calcareous soils and N fertilizer induced NO_3^- leaching in non-calcareous soils and (ii) pH changes in calcareous soil are very limited, while the pH decline in non-calcareous soils will depend on the soil acidification rates and the acid buffer capacity, being strongly related to the soil cation exchange capacity.

2. Methods and materials

2.1. Study sites

The 13 long-term experimental sites in southern China, which were established by the institutes of Chinese Academy of Agricultural Sciences and Chinese Academy of Sciences and started between 1981 and 1993, were designed to investigate the effects of mineral fertilizer and manure on soil fertility and crop yield. The experimental sites were in the provinces Anhui, Jiangxi, Hunan, Guizhou, Chongqing and Fujian. Experimental details for each site are given in Table 1. The sites cover the main cropping systems of southern China, including paddy soil (Rice-Rice and Rice), upland-paddy soil (Rice-Wheat and Wheat-Rice), and upland soil (Wheat-Soybean, Wheat-Maize, and Maize). The fertilizer treatments include: no fertilization as control (CK), combinations of mineral N, P and K fertilizers (NPK), combinations of mineral fertilizers and manure (NPKM), and manure only (M). The main mineral fertilizers used were urea (N, 46 %), calcium phosphate and potassium chloride. Manure types include pig, cattle, and chicken manure. The annual N, P, K fertilizer input rates under different fertilizer and manure treatments of each site are given in Tables S1, S2 and S3.

2.2. Basic soil properties and climate data

Soil samples (0–20 cm depth) were collected each year using a soil auger. To obtain a representative sample from the plot, ten cores of soils were collected at random from each treatment plot using a 5 cm inner diameter auger and thoroughly mixed to one composite sample. The soil samples were air dried, ground, sieved to pass through a 1.0 mm sieve, and stored in sealed glass jars for analysis. Soil samples were analysed for soil basic soil properties, including soil mineralogy (clay, sand, and silt), soil bulk density, soil organic carbon (SOC) content and soil pH (Bao, 2000). Soil texture was classified according to the United Nations Food and Agriculture Organization (FAO) soil classification system. The cutting ring method was used to measure soil bulk density. The dichromate oxidation method was used to measure SOC. Soil pH was determined with a pH electrode in a 1:2.5 soil/distilled water suspension (Cai et al., 2015). CEC was calculated with the equation of soil pH, clay and SOC (Helling et al., 1964).

The SOC content and soil pH were measured yearly. Soil base cations (BC) in non-calcareous soils and calcium carbonate (CaCO3) in calcareous soils were measured for selected long-term sites and years in 2021 (Table S4). BC was determined by displacement with 1 M ammonium acetate (pH 7) and measured by ICP-Optical Emission Spectrometer (Varian 715-ES) (Hao et al., 2022). The $CaCO_3$ content was measured by measuring gas volume method (Bao, 2000).

Daily climate data for precipitation, temperature and sunshine hours were derived from the nearest meteorological station per site (http://data.cma.cn/). An overview of site properties is given in Table 2.

2.3. Calculation of acid production and acid consumption rates

Soil acidification is an acid production-consumption process where both the production and consumption of H^+ can be quantified via a mass balance approach where inputs and outputs are quantified for all relevant cations and anions, including ammonium (NH_4^+), nitrate (NO_3^-), BC (Ca^{2+}, Mg^{2+}, Na^+, K^+), bicarbonate (HCO_3^-), sulphate (SO_4^{2-}), phosphate ($H_2PO_4^-$) and chloride (Cl^-).

2.3.1. Calculation of net acid production rate

The annual net acid (proton) production in soils was calculated by the total H^+ production, due to both natural and anthropogenic processes, minus the HCO_3^- input. The total H^+ production (keq ha^{-1}) originates from HCO_3^- leaching, N transformation processes, crop uptake, and net H^+ input, as the leaching of $RCOO^-$ hardly occurs on croplands (Xu et al., 2022):

Table 1
Location, crop rotations, and fertilizer and manure treatments used for different crop rotations in 13 long-term experimental sites of southern China.

Province	Site	Location	Crop type	Start Year	Manure type	Treatments
Sichuan	Suining	30°10′N 105°03′E	Rice-Wheat	1982	Pig manure	CK, NPK, M, NPKM
Chongqing	Beibei	30°26′N 106°26′E	Rice-Wheat	1991	Chicken manure	CK, NPK, NPKM
Anhui	Mengcheng	33°13′N 116°37′E	Wheat-Soybean	1982	Pig manure Cattle manure	CK, NPK, NPKM
Guizhou	Guiyang	26°11′N 106°07′E	Maize	1993	Cattle manure	CK, NPK, NPKM, M
Guizhou	Guiyang	26°11′N 106°07′E	Rice	1994	Cattle manure	CK, NPK, NPKM, M
Hubei	Wuchang	30°28′N 114°25′E	Wheat-Rice	1981	Pig manure	CK, NPK, NPKM
Jiangxi	Jinxian	28°35′N 116°17′E	Rice-Rice	1981	Pig manure	CK, NPK, M
Jiangxi	Jinxian	28°35′N 116°17′E	Rice-Rice	1981	Pig manure	CK, NPK, 2NPK, NPKM
Hunan	Wangcheng	28°37′N 112°80′E	Rice-Rice	1981	Pig manure	CK, NPK
Jiangxi	Nanchang	28°57′N 115°94′E	Rice-Rice	1984	Pig manure	CK, NPK, NPKM
Hunan	Qiyang	26°45′N 111°52′E	Rice-Rice	1982	Cattle manure	CK, NPK, NPKM, M
Hunan	Qiyang	26°45′N 111°52′E	Wheat-Maize	1990	Pig manure	CK, NPK, NPKM, M
Fujian	Minhou	26°13′N 119°04′E	Rice-Rice	1983	Cattle manure	CK, NPK, NPKM

Table 2
Initial soil conditions and climate of 13 long-term experimental sites in southern China. The distinction between calcareous and non-calcareous soils was based on the mean pH during the whole experiment. CaCO3 values below 0.3 % were set as a limit for a calcareous soil unless pH stayed high during the experiment.

Site	Soil type	Initial pH	Mean pH[a]	SOC[b] ($g\ kg^{-1}$)	Clay (%)	$CaCO_3$ (%)[c]	CEC $_{pH=7}$ [d] ($mmol\ kg^{-1}$)	Bulk density ($g\ cm^{-3}$)	PRE[e] (mm)	TEM[e] (°C)	SSH [e] (h)
Suining	Calcareous	8.6	8.3	9.2	47	Not measured	317	1.30	927	19	1227
Beibei		7.7	8.0	14	31	0.42 (1990)	236	1.38	1105	18	1294
Mengcheng		7.4	6.9	6.0	19	1.12 (2012)	136	1.40	872	15	2352
Guiyang		7.0	6.9	26	65	0.15 (2012)	484	1.17	1071	15	1354
Guiyang		6.6	7.0	18	64	Not measured	450	1.17	1150	15	1354
Wuchang		6.3	7.0	16	55	0.12 (2012)	389	1.19	1300	17	2080
Jinxian	Non-Calcareous	6.9	5.6	16	41	0.16 (2010)	304	1.17	1537	18	1950
Jinxian		6.9	5.5	16	41	0.16 (2010)	304	1.19	1537	18	1950
Wangcheng		6.6	5.9	20	39	0.15 (2007)	305	1.18	1370	17	1610
Nanchang		6.5	6.2	15	23	–	191	1.19	1600	18	1610
Qiyang		6.0	6.1	12	44	–	308	1.19	1255	18	1610
Qiyang		5.7	5.7	6.7	44	0.03 (2000)	290	1.19	1255	18	1610
Minhou		5.0	5.0	13	28	–	214	1.25	1351	20	1813

[a] The mean soil pH under CK treatment during the experiment period of each sites.
[b] SOC, soil organic carbon.
[c] Numbers in parentheses are the years in which the sample was measured.
[d] CEC $_{pH=7}$, The CEC at pH 7 ($mmol\ kg^{-1}$) was calculated based on the measured data of soil pH, soil clay and SOC with the equation (Helling et al., 1964): $CEC = (0.44*pH + 3)*Clay + (5.7*pH - 5.9)*SOC$

which pH value in this equation is 7, clay is soil clay content (%), and SOC is soil organic carbon (%).
[e] PRE, TEM and SSH is annually mean of precipitation, temperature, and sunshine hours, respectively.

$$H_{pro,total}{}^{+} = H_{pro,HCO_3{}^{-}}{}^{+} + H_{pro,N}{}^{+} + H_{pro,uptake}{}^{+} + H_{pro,H}{}^{+} \quad (1)$$

The H^+ production of these four processes was calculated by input-output budget for all related cations and anions (De Vries and Breeuwsma, 1987; Hao et al., 2022; Zhu et al., 2018).

First, the H^+ production by natural soil acidification due to HCO_3^- leaching ($H_{pro,HCO_3{}^{-}}{}^{+}$, keq ha^{-1}) was calculated as:

$$H_{pro,HCO_3{}^{-}}{}^{+} = HCO_{3le}{}^{-} \quad (2)$$

where HCO_{3le}^- represent the leaching of HCO_3^-. We ignored the leaching of organic anions ($RCOO^-$) as this is negligible compared to bicarbonate in agricultural soils (Xu et al., 2023).

Second, the H^+ production from N transformations ($H_{pro,N}{}^{+}$, keq ha^{-1}) was calculated by:

$$H_{pro,N}{}^{+} = (NH_{4in}{}^{+} - NH_{4le}{}^{+}) + (NO_{3le}{}^{-} - NO_{3in}{}^{-}) \quad (3)$$

where NH_{4in}^+ and NO_{3in}^- represent the input of ammonium and nitrate from mineral fertilizer and manure, atmospheric deposition and biological fixation, and NH_{4le}^+ and NO_{3le}^- represents the leaching flux outside the rooting zone.

Third, the H^+ production due to element removal by harvested crops ($H_{pro,uptake}{}^{+}$, including grain and straw, keq ha^{-1}) was calculated by net removal of cations minus net removal of anions:

$$H_{pro,uptake}{}^{+} = BC_{uptake} - An_{uptake} \quad (4)$$

where BC_{uptake} represents the uptake of Ca^{2+}, Mg^{2+}, K^+ and Na^+ and An_{uptake} represents the removal of major anions include SO_4^{2+}, $H_2PO_4^-$ and Cl^-. Note that the uptake of nitrogen (NH_4^+ and NO_3^-) has been included in Eq. (1), and the uptake of Al^{3+}, Fe^{2+} and HCO_3^- by crops was assumed to be negligible.

Lastly, the H^+ production ($H_{pro,H}{}^{+}$, keq ha^{-1}) was calculated as:

$$H_{pro,H}{}^{+} = H_{in}{}^{+} - H_{le}{}^{+} \quad (5)$$

where H_{in}^+ and H_{le}^+ represent the input and leaching of H^+, respectively. The input of H^+ was neglected and set to zero. The total leaching of H^+ was estimated based on soil pH (see details in 2.4).

The total proton production by natural and anthropogenic causes can, however, be counteracted due to HCO_3^- input (HCO_{3in}^-), mainly due to by input of manure. The total HCO_{3in}^- (keq ha^{-1}) is calculated as the difference in cations and anions inputs (following charge balance principles) as follows:

$$H_{con,HCO_3{}^{-}}{}^{+} = HCO_{3in}^{-} = H_{in}^{+} + NH_{4in}^{+} + BC_{in} - SO_{4in}^{2-} - H_2PO_{4in}^{-} - Cl_{in}^{-} - NO_{3in}^{-} \quad (6)$$

In all experiments in which manure was included, the input of NH_4^+ and NO_3^- does not need to be accounted for since N enters the soil as organic N and the H^+ input by manure is negligible due to the high pH.

Thus, the net H^+ production ($H^+_{pro,\ net}$) was calculated as:

$$H_{pro,net}{}^{+} = H_{pro,total}{}^{+} - H_{con,HCO_3{}^{-}}{}^{+} \quad (7)$$

2.3.2. Calculation of soil acid consumption rate

Soil acidification is buffered by changes in soil $CaCO_3$ levels for calcareous soils and the release of BC in non-calcareous soils on the one hand and anion adsorption on the other (De Vries and Breeuwsma, 1987). The total BC release (keq ha^{-1}) can be estimated as the change between total BC inputs and losses:

$$BC_{release} = BC_{uptake} + BC_{le} - BC_{in} - BC_{we} \quad (8)$$

where BC_{uptake}, BC_{le}, BC_{in} and BC_{we} represent the BC removed by crop harvests, lost by leaching, BC input by deposition, mineral fertilizer and manure application, and BC input by soil weathering, respectively. Note that the leaching of aluminium was neglected due to lack of experimental data and the fact that Al^{3+} leaching starts to occur below pH 4.5, which hardly occurs at the experimental sites.

The adsorption of anions ($An_{accumulation}$) was limited to phosphorus adsorption, assuming that sulphate adsorption can be neglected (Details are given in Text S1 and Fig. S1) and this was calculated as:

$$An_{accumulation} = \left(H_2PO_{4_{in}}{}^{-} - H_2PO_{4_{le}}{}^{-} - H_2PO_{4_{uptake}}{}^{-}\right) + \left(SO_{4in}{}^{2-} - SO_{4le}{}^{2-} - SO_{4uptake}{}^{2-}\right) \quad (9)$$

where the subscripts *uptake*, *le* and *in* represent $H_2PO_4^-$ and SO_4^{2-} removed by crop harvests, loss by leaching, and input by deposition, mineral fertilizer, and manure application, respectively. Since sulphur adsorption is neglected, the SO_4^{2-} leaching and crop uptake together equals the SO_4^{2-} input. We assumed that leaching of $H_2PO_4^-$ is negligible, implying that P accumulation equals to the soil P surplus (input minus crop removal). In other words, our study assumed $An_{accumulation}$ being equal to $P_{accumulation}$, which was calculated as:

$$P_{accumulation} = An_{accumulation} = H_2PO_{4_{in}}{}^- - H_2PO_{4_{uptake}}{}^- \tag{10}$$

Thus, total soil H^+ consumption rate was calculated by:

$$H_{con,total} = BC_{release} + P_{accumulation} \tag{11}$$

2.4. Data and calculation for assessing elements input and output

All data sources needed for the calculation of net acid production and soil consumption rate calculation are given in Table S5, including inputs by mineral fertilizer, manure, deposition, fixation (only for N), and output data by crop uptake, and leaching. The annual N, P, K fertilizer input rates under different fertilizer treatments of each site are given on Tables S1, S2 and S3. The fluxes of all related elements were usually in kg ha^{-1} yr^{-1} while the unit used to calculate soil acidification rate was keq ha^{-1} yr^{-1}. The method to transfer kg ha^{-1} yr^{-1} to keq ha^{-1} yr^{-1} is given in Table S6.

2.4.1. Element input via fertilization (mineral fertilizer and manure)

Mineral fertilizer application was recorded annually, including the use of urea (for N), calcium phosphate (P, Ca and S), and potassium chloride (K and Cl). The element input was calculated by multiplying the application rate (kg ha^{-1}) with the element composition (%). The manure application rate was recorded each year, of which the element input of C, N, P, K, Ca, Mg, Na, S and Cl was calculated by multiplying the manure application rate with the element concentration (measured yearly for C, N, P and K). The element content of Ca, Mg, S and Cl were determined in 2021 for pig manure (from Jinxian and Qiyang sites) and cattle manure (from Minhou site) using microwave digestion and inductively coupled ICP-Optical Emission Spectrometer (Varian 715-ES). For those sites where manure was not sampled, we used element concentrations derived from National Agro-tech Extension & Service Centre (NATESC) records for different manure type (Table S7). Note that N inputs as urea and manure were both regarded as 50 % NH_4^+ and 50 % NO_3^- because of their same acidification potential as NH_4NO_3 (Zeng et al., 2017).

2.4.2. Element input via atmospheric deposition and N fixation

The element input from atmospheric deposition was not recorded but were derived from published data at provincial level (Zhu et al., 2018). The N input via fixation was estimated per crop type using data from literature. The N fixation equalled 80 kg ha^{-1} yr^{-1} for soybean (Li and Jin, 2011; Smil, 1999), 25 kg ha^{-1} yr^{-1} for rice (Giller, 2001) and 5 kg ha^{-1} yr^{-1} for maize (Herridge et al., 2008; Smil, 1999), and the N input was also regarded as 50 % NH_4^+ and 50 % NO_3^-.

2.4.3. Element output via crop uptake

The crop element removal of N, P, K, Ca, Mg, Na, Cl and S by harvesting was calculated by multiplying the yield of crop grain and straw (kg dry mass ha^{-1} yr^{-1}) with the element concentrations (g kg^{-1}). The amount of crop grain and straw was collected and weighed annually and a sample was taken of to measure N, P and K concentrations. To gain insight in the crop removal of other relevant cations and anions, the concentrations of Ca, Mg, Na, Cl and S were determined for both grain and straw samples collected from Jinxian, Qiyang, Guiyang, Beibei and Minhou sites during 2010–2020. Element concentrations were determined by microwave digestion and inductively coupled ICP-Optical Emission Spectrometer (Varian 715-ES). When crop element data were missing, default element per crop type was extracted from literature (Zhu et al., 2018) (Table S8).

2.4.4. Element output via losses to air and water

The N losses include emission via volatilization (NH_3), denitrification (N_2O, NO and N_2) and leaching of nitrate (NO_3^-) from the rooting zone to groundwater and surface water. Note that we assumed that ammonium (NH_4^+) is fully nitrified to NO_3^-, and that the change in soil N is negligible on the long term, indicating that all N losses to water are only in form of nitrate. The leaching of nitrate ($NO_{3le}{}^-$) was calculated as:

$$NO_{3le}{}^- = \left(N_{in} - N_{uptake} - N_{\text{amonia emission}}\right) \times fr_{le} \tag{12}$$

where N_{in}, N_{uptake} and $N_{ammonia\ emission}$ refers to the total N input (mineral fertilizer and manure application, deposition and fixation), N removed by crop harvests, and N losses by volatilization, respectively. The fr_{le} refers to the N surplus fraction that is leached, being dependent on soil texture, land use and precipitation surplus. The leaching fraction is adapted from European leaching fractions from Velthof et al. (2009) using soil dependent correction functions of Gao et al. (2016). Details on this derivation are given in the Text S2. These initial estimations of the leaching fraction are subsequently adapted using an optimization procedure to minimize the difference between calculated BC stock change (via the mass balance approach) and the measured BC change from the Hunan-Qiyang (Wheat-Maize) and Fujian-Minhou (Rice-Rice) experimental sites. The ammonia emission was calculated as function of the N rate, fertilizer type, clay content and mean annual temperature following the procedure from Wang et al. (2021). More details are given in Text S3.

The leaching of H^+ and HCO_3^- to groundwater and surface water was calculated by multiplying the precipitation surplus (mm) with H^+ and the HCO_3^- concentration (mmol L^{-1}) in soil solution via

$$H_{le}{}^+ = [H^+] \times PS \times 10 \tag{13}$$

$$HCO_{3le}{}^- = \left[HCO_3^-\right] \times PS \times 10 \tag{14}$$

where PS is the precipitation surplus (mm) leaving the root zone and discharging to the groundwater, being calculated with the MetHyd water balance model (Bonten et al., 2016), $[H^+]$ is the H^+ concentration and $[HCO_3^-]$ is the bicarbonate concentration. Inputs for MetHyd includes daily meteorological data (average temperature, precipitation, sunshine hours), soil bulk density, soil organic carbon (SOC) content and water-holding capacity derived from clay and sand contents. Daily meteorological data were downloaded from China Meteorological Data Service Centre (AMDSC). In addition, data on irrigation were added in case of paddy rice, assuming an annual input of 736 mm based on He et al. (2020), and half of that amount in case of a combination of paddy rice with an upland crop (wheat or maize) or bare soils. Calculated annual precipitation surpluses per site are given in Table S9, together with the use data for precipitation, irrigation and the calculated evapotranspiration. The range in evapotranspiration was limited, varying from 458 to 698 mm yr^{-1}. The precipitation surplus thus mainly depended on the input by precipitation and irrigation and varied from 414 to 1777 mm per year. The paddy soils, we also includes irrigation using a fixed irrigation values of 736 mm per year (He et al., 2020) in assessing the precipitation surplus. For upland, the irrigation was neglected. The H^+ concentration being calculated from the soil pH and $[HCO_3^-]$ is the bicarbonate concentration. In calcareous soils (soil $CaCO_3$ content higher than 0.3 % and/or mean soil pH under CK treatment is higher than 6.5), bicarbonate originates from the dissociation of CO_2 and dissolution of $CaCO_3$. In these soils, $[HCO_3^-]$ was calculated from the partial pressure of CO_2 (De Vries and Breeuwsma, 1986) following:

$$log\left(\left[HCO_3^-\right]\right) = -1.94 + log(pCO_2)/3 \tag{15}$$

where pCO_2 is the partial pressure of CO_2 in soil solution, which was set at 15 mbar for upland soil and 50 mbar for paddy soil, respectively (De Vries and Breeuwsma, 1986; Greenway et al., 2006), and 25 mbar for upland-paddy soil (Details on this calculation are given in the Text S4).

For non-calcareous soils, linked in this study to sites with a soil

$CaCO_3$ content lower than 0.3 % and/or a mean soil pH lower than 6.5, bicarbonate concentration is formed by the dissolution of CO_2. The bicarbonate concentration in these soils was calculated from the partial pressure of CO_2 and soil pH via:

$$[HCO_3^-] = (KCO_2 * pCO_2)/[H] \tag{16}$$

where KCO_2 is the product of Henry's law constant for the equilibrium between CO_2 in soil water and soil air, being set at $10^{-7.8}$ mol^2 l^{-2} bar^{-1} and pCO_2 is the partial CO_2 pressure in the soil.

Based on the charge balance, the leaching of BC was calculated by the total anions minus proton leaching:

$$BC_{le} = NO_{3le}{}^- + Cl_{le}{}^- + SO_{4le}{}^{2-} + H_2PO_{4_{le}}{}^- + HCO_{3le}{}^- - H_{le}{}^+ \tag{17}$$

where leaching of $H_2PO_4^-$ was neglected due to poor mobility of available P in soils. We assumed that $H_2PO_4^-$ adsorption equals the P surplus (Hao et al., 2022; Hao et al., 2018) and leaching of SO_4^{2-} was calculated by the difference between SO_4^{2-} inputs and SO_4^{2-} uptake, as the adsorption of SO_4^{2-} was considered negligible. Since there is also no Cl^- adsorption in the soil (Hao et al., 2022), the leaching of chloride also equals the soil surplus of chloride, being the difference between Cl^- input and uptake.

2.5. Data analysis

We assessed relationships between the main causes of acid production, including HCO_3^- leaching, N transformations and crop uptake and their main drivers, including soil pH and precipitation surplus for HCO_3^- leaching, N surplus for N transformations and crop yield for crop uptake, while distinguishing between paddy and upland soils and between calcareous and non-calcareous soils. The linear or non-linear relations were derived by regression analysis. Data calculation and statistics were performed with Excel 2013, and SPSS 24.0. Figures were performed with Origin 2016 and R 4.2.0.

3. Results

3.1. Mean acid production and consumption rates and their drivers

3.1.1. Net acid production rates

The contribution of natural and anthropogenic drivers to the net H^+ production rate, originating from HCO_3^- leaching, N transformation processes and crop uptake, minus the HCO_3^- input, varied across the sites due to differences in soil types (calcareous versus non-calcareous soils), land use types (paddy rice versus upland crops) and fertilizer and manure management practices (Fig. 1, Tables S10 and S11). The net acid production rate of calcareous soils was much higher than that of non-calcareous soils, with a mean value of 23 keq ha^{-1} yr^{-1} and 7.5 keq ha^{-1} yr^{-1}, respectively. This was due to the much higher acid production rate by HCO_3^- leaching in calcareous soils. Paddy soils always had higher acid production rates than upland soils, mainly induced by higher HCO_3^- leaching caused by a higher CO_2 pressure, but the acid production rates due to N transformations were lower caused by the dryer circumstances going from paddy soils to upland soils. The mean acid production rates for these two land use types were 8.8 (paddy) and 1.6 (upland) keq ha^{-1} yr^{-1} for non-calcareous soils and 28 (paddy) and 13 (upland) keq ha^{-1} yr^{-1} for calcareous soils.

In calcareous soils, natural acidification by HCO_3^- leaching was the most dominant driver affecting acidification regardless of land use types and fertilizer treatments, accounting on average for 80 % of the total acid production rate, followed by crop uptake (11 %) and N transformations (9.0 %). The net soil acid production rate of the mineral fertilizer treatment (NPK) was higher than in the treatments in which manure was (also) applied (NPKM and M). This is due to the high input of HCO_3^- caused by the application of organic fertilizers. The difference in HCO_3^- input between long-term test sites depends on the amount and type of fertilizer applied.

In non-calcareous soils, the main acid production process was different among land use types and fertilizer treatments. HCO_3^- leaching was the most dominant driver in paddy soils (accounting for 68 % of total acid production rate) and N transformations was the most important driver in the maize-wheat cropping system at Qiyang (accounting for 72 % of total acid production rate). As with calcareous soils, lower net acid production rates were found under manure application since HCO_3^- input mitigated soil acidification.

3.1.2. Soil acid consumption rates

The total soil H^+ consumption rate differed across the experiments in response to fertilizer and manure management practices, land use and soil types (Fig. 2, Tables S10 and S11). In calcareous soils, the release of BC was by far the most dominant process controlling the H^+ consumption among all treatments, while P accumulation had only a minor contribution (at max 4.8 keq ha^{-1} yr^{-1} as observed in the maize cropping system in Guiyang). Despite an increase of P accumulation in the treatments with manure (NPKM or M), they had the lowest consumption rates since manure decreased the BC release. In for non-calcareous soils, BC release dominated in treatments without organic manure (CK and NPK). In manure-treated plots (NPKM and M in Jinxian, Qiyang and Minhou), there was even base cation accumulation due to high BC inputs and here P accumulation was the most dominant H^+ consumption process.

3.2. Impacts of management and site conditions

3.2.1. Impacts on net acid production rates

To illustrate how natural and anthropogenic sources affected the acid production in the long-term experiments, we assessed the variations in acid production rate of HCO_3^- leaching, nitrogen transformations and crop uptake versus site properties. This included soil pH, and precipitation surplus for HCO_3^- leaching (Fig. 3), the nitrogen surplus for N transformations (Fig. 4) and crop yield for crop uptake (Fig. 5), while distinguishing and use types (paddy, upland and their combination) and soil types (calcareous and non-calcareous soils). As produced H^+ was also consumed by HCO_3^- input from manure application, we also explored the effects of manure dose and types on HCO_3^- input rate (Fig. 6).

3.2.1.1. HCO_3^- leaching. HCO_3^- leaching was calculated as a function of soil pH and precipitation surplus, where the soil pH varied from 4.0 up to 7.5 and the annual precipitation surplus varied from 110 mm to >2000 mm (Fig. 3 and S1). The H^+ produced by HCO_3^- leaching varied from 0.01 to almost 77 keq ha^{-1} yr^{-1}. The HCO_3^- leaching increased linearly with precipitation surplus in calcareous soil at a given CO_2 pressure, with 28 to 34 eq ha^{-1} per mm surplus ($P < 0.001$, Fig. 3 a). The upward trend was greatest in paddy soil due the highest CO_2 pressure (50 mbar). In non-calcareous soils, pH generally affected HCO_3^- leaching in a larger extent than precipitation surplus. When the soil pH varied between 5 and 7, the HCO_3^- leaching was non-linearly related to soil pH ($P < 0.001$, Fig. 3 b).

3.2.1.2. Nitrogen transformations. The nitrogen surplus (total N inputs minus crop N removal and N-NH_3 emission) varied from zero to 298 kg N ha^{-1} yr^{-1}, driving the N leaching and associated H^+ production (Fig. 4). The N surplus varied more in the calcareous compared to the non-calcareous soils, and it was the lowest in paddy soil, followed by upland soils and upland-paddy soils. The acidity production by N transformations linearly increased with the N surplus (Fig. 4) in all soils with the highest increase in the upland soils (54 eq per kg N surplus) and the lowest in the paddy soils (10 eq per kg N surplus).

3.2.1.3. Crop uptake. The total crop biomass, producing H^+ via excess

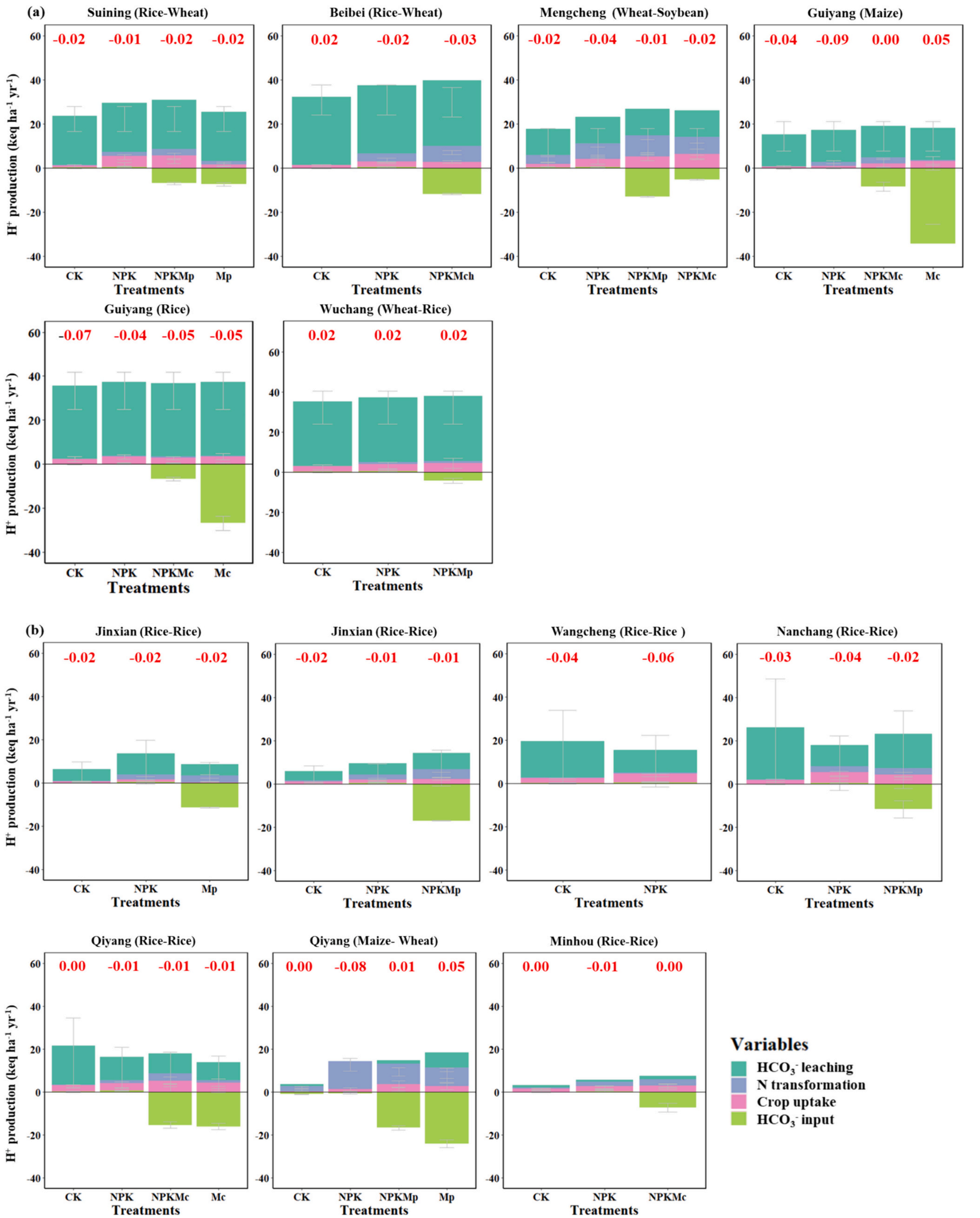

Fig. 1. The net H^{+} production by different source under long-term fertilization for calcareous soils (a) and non-calcareous soils (b). Red numbers represent the mean soil pH change during the experimental trial.

Note: Error bars denote standard deviation. “p” in Mp, NPKMp means the manure type is pig manure, same as “c” and “ch”, it are cattle manure and chicken manure.

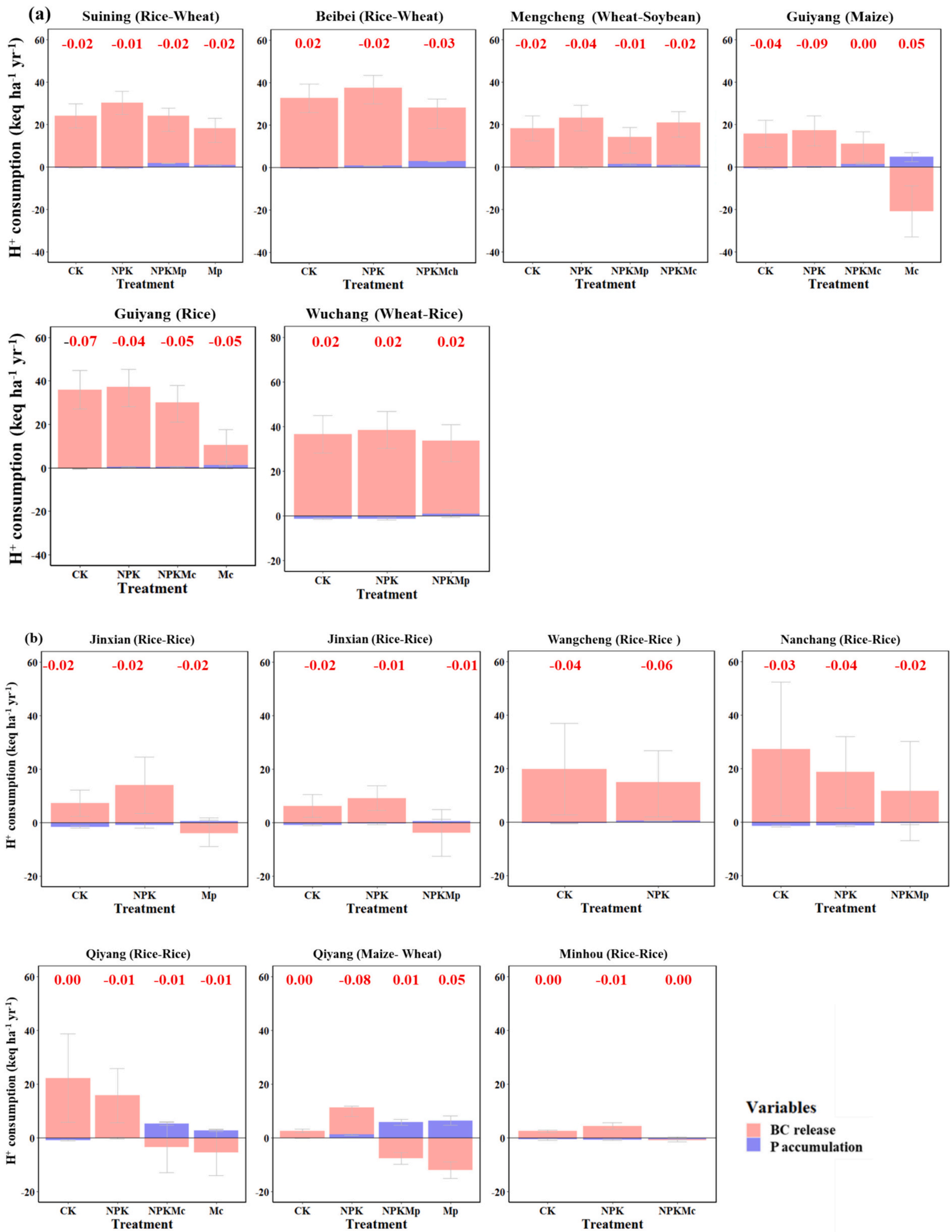

Fig. 2. The soil H^+ consumption by different source under long-term fertilization for calcareous soils (a) and non-calcareous soils (b). Red numbers represent the mean soil pH change during the experimental trial.
Note: Error bars denote standard deviation. "p" in Mp, NPKMp means the manure type is pig manure, same as "c" and "ch", it are cattle manure and chicken manure.

uptake of cations than anions, varied between 6.3 and 29 ton ha^{-1} with no distinct patterns in calcareous or non-calcareous soils (Fig. 5) though the H^+ production tended to be higher in the calcareous soils. Higher crop yields generally increased the H^+ production, with the highest increase found in the upland soils (0.45 keq per ton yield increase) and the lowest one in the paddy soils (0.21 keq per ton yield increase), in particular in the calcareous soils. Differences between both paddy and upland soils were small in the non-calcareous soils.

3.2.1.4. HCO_3^- input. The main input of HCO_3^- came from the addition

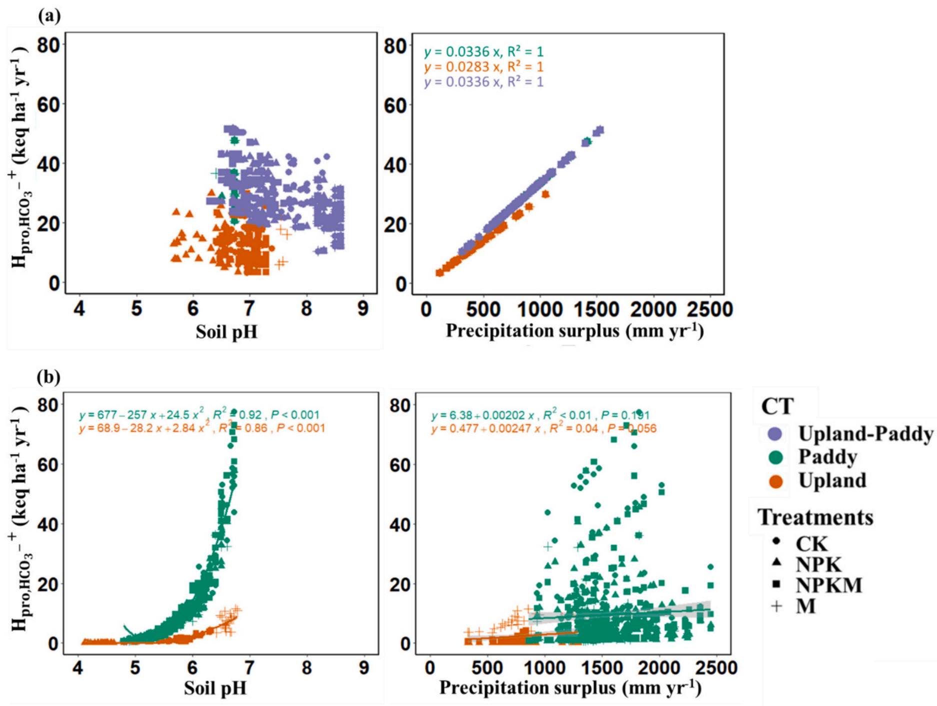

Fig. 3. Relationship between H^+ production rate by HCO_3^- leaching ($H_{pro,HCO_3^-}{}^+$) and soil pH (left), precipitation surplus (right), for different treatments (CK, NPK, NPKM and M) and land use types in calcareous soils (a) and non-calcareous soils (b).
Note: Land use types included: paddy soil (green, including continuous rice and rice); upland - paddy soil (purple, including rotations of wheat and rice crops); and upland soil (orange, including continuous maize, wheat and maize, and wheat and soybean rotations).

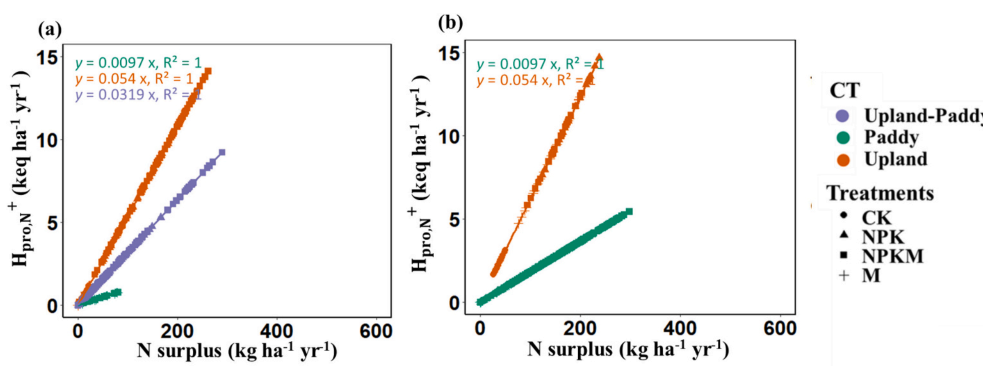

Fig. 4. Relationship between H^+ production rate by N transformation ($H_{pro,N}{}^+$) and nitrogen surplus (N surplus) for different fertilizer treatments (CK, NPK, NPKM and M) and land use types in calcareous soils (a) and non-calcareous soils (b).
Note: Land use types included: paddy soil (green, including continuous rice and rice); upland - paddy soil (purple, including rotations of wheat and rice crops); and upland soil (orange, including continuous maize, wheat and maize, and wheat and soybean rotations).

of manure. The input rate exhibited a positive relationship with the rate of manure application (Fig. 6 a). There was an input of 0.30 keq ha^{-1} yr^{-1} HCO_3^- per ton manure ha^{-1} yr^{-1}. The variation of HCO_3^- input rate across sites and treatments dependents on the manure types as well the weather conditions across different years.

3.2.2. Soil acid consumption rates

3.2.2.1. BC release. The soil acid consumption was highly controlled by the $BC_{release}$ and partly by the sorption of anions. As the amount of fertilizer application increased, the net release of soil BC decreased by 0.38 keq ha^{-1} yr^{-1} per ton manure ha^{-1} yr^{-1} input (Fig. 6). This was caused by more BC inputs through mineral fertilizer (Ca^{2+} input from superphosphate) and/or manure (Fig. S2 a), supplementing the soil BC pool.

3.2.2.2. Phosphorus accumulation. Though the impact of P accumulation on acid consumption was much smaller than that of BC release (Tables S10 and S11), the total P input of fertilizers and manure was strongly driven H^+ consumption (Fig. S2 b). Therefore, a linear increase in H^+ consumption by 0.08 keq per ton manure added was found (Fig. 6 c).

3.3. Relationships between soil pH change, buffering capacity change and acid production rates

The measured BC pool change was positively associated to the predicted BC pool change in non-calcareous sites (not shown), implying that the mass balance approach was able to simulate the main acidification processes in long-term experiments that differ in soil properties, climatic conditions, crops, and fertilizer management. Situations with a

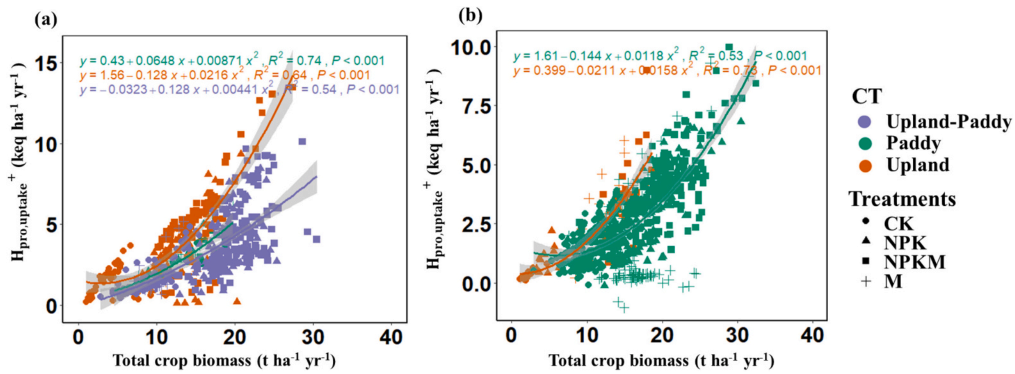

Fig. 5. Relationship between H^+ production rate by crop and straw removal ($H_{pro,uptake}{}^+$) and total crop biomass for different treatments (CK, NPK, NPKM and M) and land use types in calcareous soils (a) and non-calcareous soils (b).
Note: Land use types included: paddy soil (green, including continuous rice and rice); upland - paddy soil (purple, including rotations of wheat and rice crops); and upland soil (orange, including continuous maize, wheat and maize, and wheat and soybean rotations).

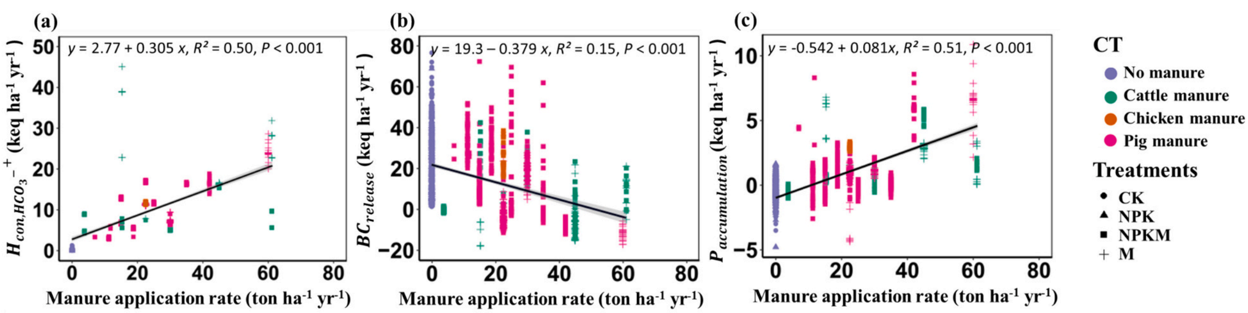

Fig. 6. Correlation between H^+ consumption rate by HCO_3^- input ($H_{con,HCO_3^-}{}^+$), BC $_{release}$ and P $_{accumulation}$ and manure application rate for different treatments (CK, NPK, NPKM, M) and manure types (no, cattle, chicken, and pig manure).

positive BC pool change were on average correlated to situations with higher BC input, BC surplus and HCO_3^- leaching. High BC leaching occurred simultaneously with high nitrate losses ($r = 0.89$) showing the importance of nitrate loss in driving acidification rates in soil (Fig. S3).

Averaged values over the experimental sites and treatments showed a clear pattern in the relationship of net acid production between (i) soil $CaCO_3$ change in calcareous soils; (ii) soil BC pool change in non-calcareous soils and (iii) observed pH changes in both types of soil (Fig. 7). In calcareous soils there was a clear distinction between cropping systems. The cropping systems with wheat, maize or soybean had a pH decline or $CaCO_3$ loss when there was net acid production. In contrast, rice dominated cropping systems showed an increase in soil pH even when the net acid production was positive. For non-calcareous soils the changes in soil pH, and associated BC pool changes increased with the net acid production. Cropping systems with positive net acid production showed a decline in soil pH or BC pool whereas systems with negative acid production were characterized by an increase in pH or BC pool. Note that observed changes in soil pH were usually lower in calcareous soils than in non-calcareous soils with a same net H^+ production.

4. Discussion

4.1. Adequacy of the experimental sites to study soil acidification

In this study, we used data from 13 long-term experimental sites to quantify soil acidification rates and unravel the impacts of natural and anthropogenic causes of acidification by assessing the input and output of major nutrients. At the sites, observations were made of element inputs and uptake but not of element leaching which had to be estimated. In this context, the leaching of nitrate is one of the most uncertain parameters in the mass balance approach, while it has strong impacts on the estimated H^+ production. The updated Velthof - Gao method (Gao et al., 2016; Velthof et al., 2009), which we used to estimate the nitrate leaching fraction seems appropriate for use in China but further validation via field experiments is warranted. The diverse fertilizer management strategies at the experiment sites were evaluated to gain observation-based insights on their acidifying impacts though these experiments were originally designed to assess the impacts of fertilization on soil fertility, nutrient use efficiency and crop yields. The choice of the sites hampers a thorough assessment of impact of fertilizer management on soil pH due to the fact that the majority of the sites is calcareous and/or under paddy land use. In calcareous soils, changes in soil acidification rates hardly affect changes in soil pH given the strong buffer capacity by carbonate dissolution. In the non-calcareous paddy soils, the wet circumstances cause high denitrification and thus low relatively soil acidification. Overall, there was only one experimental site with a well-drained upland soil (Qiyang wheat-maize) where an NPK treatment caused a soil pH decrease from 5.7 to 4.1 after 25 years. Despite its limitations, the set of 13 experiments with substantial variation in treatments, soil types and climate zones gives long-term insights in the effects of fertilizer and manure management under diverse circumstances and how long a soil can effectively buffer incoming acidity.

4.2. Main drivers of soil acidification in croplands of China

The mass balance approach allows quantifying the main acid production and consumption processes at field scale as a function of fertilizer management, and site conditions, including land use, climatic conditions, and soil properties. The net acid production includes bicarbonate leaching, N transformations, base cation removal by crop harvesting and bicarbonate input, while the soil acid consumption

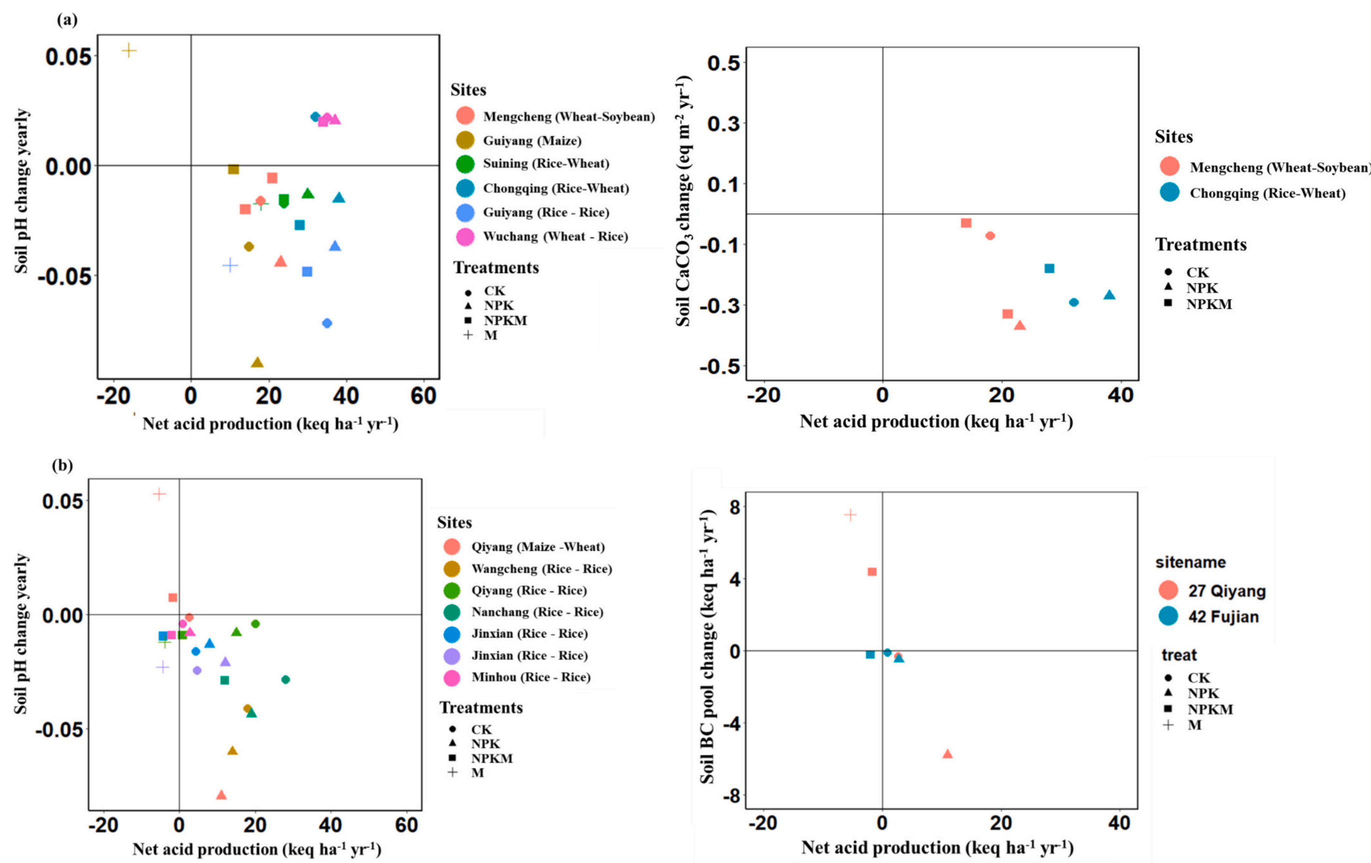

Fig. 7. Scatter plot of the relationship between net acid production and soil pH yearly change (left), soil acid buffering capacity change (right) ($CaCO_3$ in calcareous soil and BC in non-calcareous soil) for calcareous soils (a) and non-calcareous soils (b).

processes Include the release of base cations or the retention of anions, including phosphate and sulphate, as discussed below.

4.2.1. Net acid production rates

Bicarbonate leaching: The most important driver of soil acidification across all cropping systems in calcareous soils and non-calcareous paddy soils is bicarbonate leaching triggered by high CO_2 pressure (in paddy soils), and by the high pH and the availability of $CaCO_3$ in calcareous soils. An exception was the paddy soils in Minhou site where the pH remained around 5 over the whole duration of the experiment across all treatments. The reason that high inputs of manure did not affect soil pH in Minhou site was probably due to the high CEC of the soil, implying a high buffering capacity.

Note that the underlying processes controlling bicarbonate leaching strongly differs between calcareous and non-calcareous soils. Besides the precipitation surplus, the HCO_3^- leaching in non-calcareous soil is mainly affected by the CO_2 partial pressure and soil pH (Kindler et al., 2011) and in calcareous soils by the CO_2 pressure alone (De Vries and Breeuwsma, 1987). The CO_2 partial pressure varied from 50 bar in paddy soils to 15 bar in upland soils (Greenway et al., 2006), with high values in paddy soils being due to the flooded conditions (and associated higher water surplus) that also stimulates denitrification, thus causing limited nitrate leaching (Bolan et al., 2003). Adding manure (with associated bicarbonate inputs) might replenish part of the bicarbonate leaching, thereby neutralizing part of the acids produced (Materechera and Mkhabela, 2002), as further discussed below.

Nitrogen transformations: In non-calcareous upland cropping systems, N transformations induced by excessive N inputs to crop demand are mainly driving soil acidification, implying that optimizing the N fertilizer management is key to avoid or minimize adverse impacts of soil acidification. Higher N surpluses are linearly correlated to higher nitrate leaching losses, being observed in north China Plain and subtropical areas (Dong et al., 2021; Huang et al., 2017) as well as west-European countries such as Denmark and the Netherlands (De Notaris et al., 2018; De Vries et al., 2023). On average, an increase of 1.0 kg ha^{-1} in N surplus (after correction for gaseous losses) produced 54 eq H^+ per hectare in upland soils and 10 eq H^+ per hectare in paddy soils (Fig. 4) due to higher denitrification rates in waterlogged soils, counteraction N induced acidifications. The contribution of N transformations triggered by the N fertilizer strategy was therefore higher in upland cropping systems than in the paddy and upland-paddy cropping systems. If the total N surplus would be leached, it would lead to an acid production of 71 eq H^+ per ha per 1.0 kg N surplus. The calculated N leaching fraction, based on the approach by Velthof et al. (2009) and the Gao et al. (2016) was on average 0.76 in upland soils and 0.14 in paddy soils leading to the values of 54 to 10 eq H^+ per kg N surplus. Since > 70 % of the N surplus was calculated to be leached in upland soil, nitrate leaching (N transformations) was the main driver of acid production in those soils. Note that the observed N surplus declined when manure was applied, partly due to the higher NH_3 emissions (Velthof et al., 2009). Recently Wu et al. (2019) showed that adding manure also improved the structure of the soil, enhances the microbial activity, and balances the changes in soil pH by addition of additional cations, implying that manure addition has benefits for both soil health and crop production. In addition, many others have shown that the risk of nitrate leaching from manure, compost and crop residues is lower than that of mineral fertilizers (Fageria et al., 2003), thereby reducing the associated acidity production (Hao et al., 2018; Zhu et al., 2018a).

Crop uptake: Regardless of soil types or land use types, crop uptake was the second primary acidogenic process. Acid production induced by crop removal resulted from the excess of cations over anions, affected by crop yield and crop type changes. Adding manure increases not only the

BC inputs but also the crop yield and associated uptake of BC, leading to differences among the land use types studied. Upland crops tended to have higher H^+ production rates than rice, being in line with earlier studies showing that the excess uptake of cations is smaller for rice than for other crops (Dong et al., 2021).

Bicarbonate input: Bicarbonate input via deposition is often minor while the input substantially increases when ammonium bicarbonate or organic manure is added as fertilizer. Adding manure has multiple benefits in ameliorating soil acidification (Ye et al., 2019), confirming previous findings (Shi et al., 2019), and fits in an integrative management approach to increase the overall sustainability of agriculture. In non-calcareous soil, optimizing nutrient and lime management is key and includes an optimum balance between nitrogen inputs and crop requirement, sufficient use of manure (being rich in base cations replacing mineral fertilizers and compensating acidity production) and extra lime applications where needed. For example, adapting the N fertilizer type and dose to crop requirements in maize-wheat cropping systems could reduce the H^+ production by 80 % compared to farmers' practice (Hao et al., 2020). In calcareous soils the dissolution of $CaCO_3$ is the main acid buffering substance (Table S10). Although adding manure can restore some of the dissolved $CaCO_3$, these inputs usually do not compensate the leaching loss of bicarbonate, especially in paddy soil (high water flux and high pCO_2).

4.2.2. Soil acid consumption rates

BC release: The release of BC was the dominant acid consumption process in both calcareous and non-calcareous soils under most of the fertilizer and manure treatments (Fig. 2). The BC release consumes −21 to 39 keq ha^{-1} yr^{-1} in calcareous soils and − 12 to 27 keq ha^{-1} yr^{-1} in non-calcareous soils. Adding fertilizers increased the release of BC from soil to compensate the nitrate leaching and BC uptake whereas extra BC inputs via manure partly compensates this BC loss (Shi et al., 2019; Ye et al., 2019).

P accumulation: The contribution of P accumulation was on average 0.7 keq ha^{-1} yr^{-1}, being generally small except in the treatments with manure, where the P accumulation can be as high as 6.5 keq ha^{-1} yr^{-1}. The high P accumulation often occurred in typical red soils having high iron oxide and aluminium levels with high sorption capacity (Zhu et al., 2023).

Sulphate adsorption is an important process that regulates the concentration of sulphate in the soil solution and to minimize acidification, thereby affecting SO_4^{2-} leaching together with BC. However, sulphate adsorption only became significant when soil pH is as low as 4.0 or when high concentrations of Fe or Al oxides occur (Gustafsson et al., 2015). Our uncertainty analysis showed that 95 % to 99 % of the sulphur surplus was lost via leaching in Qiyang site (Text S1). Therefore, sulphate leaching is likely negligible in soils with a relatively high pH. Further experiments can be helpful to quantify the potential S sorption as a function of soil properties and sulphate concentrations.

4.3. Effects of soil acidification on soil pH

The decline in soil pH happens when net H production exceeds the acid buffering capacity. In global acid addition experiments, the soil pH significantly decreased when the H^+ addition rate exceeded 5.0 kmol ha^{-1} yr^{-1} (Meng et al., 2019). In our research, we observed a mean annual decrease in soil pH of 0.03 units only. The net acid production rate was, however, 23 keq ha^{-1} yr^{-1} in calcareous soil and 7.5 keq ha^{-1} yr^{-1} in non-calcareous soil. This variation was due to the soil's acid buffering capacity. In calcareous soils, H^+ is buffered by calcium carbonate, of which the buffering capacity is 1500 keq H^+ per 1.0 % of calcium carbonate, while in non-calcareous soils, the main acid buffering process is BC exchange, which is determined by the cation exchange capacity (CEC) (Ulrich, 1983). The assumed relationship between base saturation and soil pH within the pH range of 4.4 to 6.6 implies a pH buffer capacity of 0.44 CEC per unit pH (Magdoff and Bartlett, 1985). This explains why non-calcareous soils showed a larger change in soil pH under similar acid production (Fig. 7), being more sensitive to changes in acidity inputs (De Vries et al., 1989). Overall, our results indicate that soil acidification rates and pH decline is limited in the non-calcareous soils except for the NPK treatment in the upland site (Qiyang), where soil pH decreased from 5.7 to 4.1 after 25 years. The reason for this is that all non-calcareous sites, except for Qiyang, were paddy soils where the wet circumstances cause high denitrification and thus low relatively soil acidification. In China, almost 50 % of the croplands are cultivated on upland soils, implying that soil acidification is a potential threat to crop yield when liming is not properly practiced.

4.4. Mitigation strategies of soil acidification in croplands

An observation-based assessment of the effect of drivers of soil acidification across various soil types, land use types, soil properties and fertilization practices in the long-term experiments, is of crucial importance to identify appropriate mitigation measures for sustaining soil pH and avoid adverse acidification impacts on crop yields. In calcareous soils, where natural acidification by HCO_3^- leaching dominates, mitigation strategies are not needed in a short term, while frequent monitoring for the carbonate content is useful. Moreover, exploring strategies to enhance calcium carbonate preservation or replenishment could be beneficial. When soil calcium carbonate content is lower than 0.3 % or pH drops below 6.5, it transitions to non-calcareous soil. In non-calcareous soils, especially those associated with upland areas, the decline in soil pH poses a significant challenge. Here N transformation dominates the acid production process. In those soils, maintaining or increasing the base saturation by extra BC inputs is essential to mitigate soil acidification. Agricultural practices, such as the application of lime, can be employed to achieve this (Xu et al., 2022), particularly in acidic soils, but appropriate soil amendments such as biochar, and enhanced recycling of crop residues and of manure also mitigates soil acidification (Cai et al., 2021; Xu et al., 2023). Combining manure and mineral N fertilizer in view of the crop N demand is an effective way to mitigate soil acidification. However, considering the potential negative effects of a high manure recycling rate, such as soil phosphate accumulation, especially in areas with high soil P content, adjustments to the manure recycling rate are needed based on soil properties and crop nutrient demands. If the manure input is not enough to counteract net acid production, extra lime will be required.

5. Conclusions

In this study, we quantified the rate of acid production and consumption in 13 long-term experiments in southern China, differing in land use (paddy versus upland soils), soil type (calcareous versus non-calcareous soils) and site conditions by calculating the balance of major nutrients in response to fertilizer and manure treatments. For a given N input, treatments with manure application caused lower acidification rate compared to mineral fertilizer treatments since manure also contains base cations, associated with HCO_3^- input and lower soil BC release. However, manure application also increased phosphorus accumulation in soils at most sites with related eutrophication risks.

In line with our hypothesis, natural acidification by HCO_3^- leaching was the primary cause of acid production at 6 experimental sites on calcareous soils (accounting for 80 % of total acid production rate) and soil pH changes in calcareous soils were limited, even in situations of high net acid production rates due to carbonate buffering. However, unlike our hypothesis, HCO_3^- leaching was also the main driver of acid production in 6 of the 7 non-calcareous soils, where land use was paddy rice, due to the high CO_2 pressure and high denitrification losses caused by the anaerobic conditions in those systems. In line with our hypothesis, N transformation was the only most important driver for soil acidification in one site with upland crops (Wheat-Maize) on a non-calcareous soil (accounting for 72 % of total acid production rate). At this site, the soil pH considerably decreased being accompanied by a substantial BC pool decline. In China the percentage of non-calcareous upland soils is about 30 % (Hao et al., 2020), and here acidification is a potential threat to crop yield when liming is not properly practiced, which often occurs at small holder farms due to high labour intensity.

We conclude that mitigation strategies of soil acidification require different focus considering soil type and land use. In calcareous soils, mitigating soil acidification by adding manure is not necessary given the high buffering capacity of the soil. In non-calcareous soil, the manure recycling rate need to be adjusted to the required crop P demand to compensate for the acidity produced while avoiding P accumulation when P is not limiting crop yield anymore. If those manure inputs do not fully compensate for the acid production rate, lime application is needed to compensate the soil acidification. The optimal combination of fertilizers and manure for controlling soil acidification and preventing soil P accumulation in China's cropland, considering the variation in soil P status affecting crop P demand, warrants further study.

CRediT authorship contribution statement

Xingjuan Zhu: Writing – review & editing, Writing – original draft, Methodology, Data curation. **Gerard H. Ros:** Writing – review & editing, Data curation, Conceptualization. **Minggang Xu:** Supervision, Funding acquisition, Data curation, Conceptualization. **Donghao Xu:** Writing – review & editing, Data curation. **Zejiang Cai:** Data curation. **Nan Sun:** Data curation. **Yinghua Duan:** Data curation. **Wim de Vries:** Writing – review & editing, Writing – original draft, Supervision, Methodology, Formal analysis, Data curation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The authors do not have permission to share data.

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Appendix A. Supplementary data

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