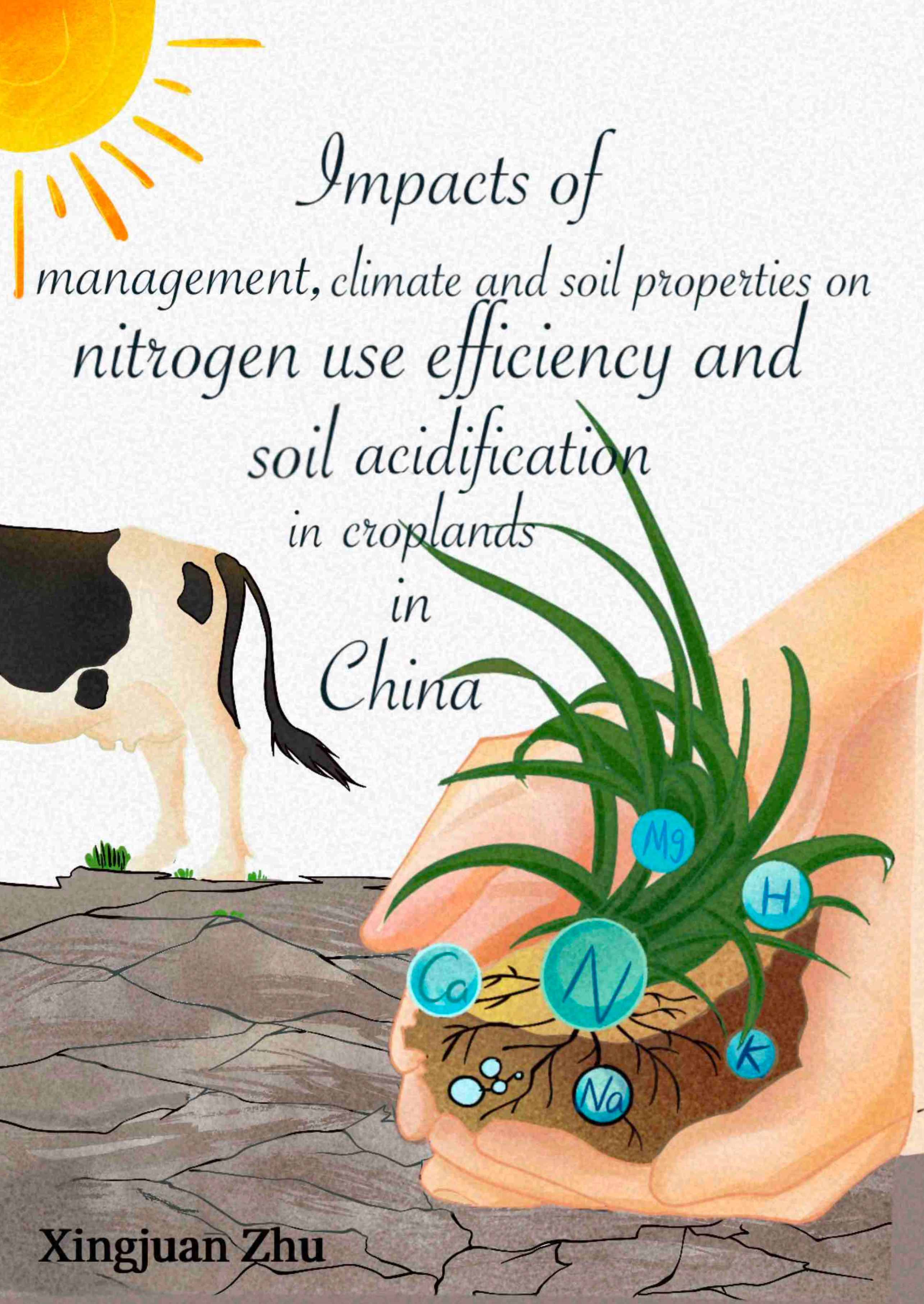
Impacts of management, climate and soil properties on nitrogen use efficiency and soil acidification in croplands in China



Xingjuan Zhu

Propositions

1. Data driven empirical models are an effective approach to assess effects of nutrient management strategies (this thesis).
2. Complete recycling of organic manure in China's croplands will cause adverse soil phosphorus accumulation (this thesis).
3. ChatGPT is a tool to improve the writing skills of non-native English speakers.
4. The development of comprehensive environmental models requires interdisciplinary thinking of modelers.
5. A world that is inundated with information is an opportunity for scientist but a challenge for citizens.
6. Implementing equitable dialogue in supervising doctoral students significantly benefits both scientific research and mental health.

Propositions belonging to the thesis, entitled

Impacts of management, climate and soil properties on nitrogen use efficiency and soil acidification in croplands in China

Xingjuan Zhu

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Impacts of management, climate and soil properties on nitrogen use efficiency and soil acidification in croplands in China

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Impacts of management, climate and soil properties on nitrogen use efficiency and soil acidification in croplands in China

Xingjuan Zhu

Thesis

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CHAPTER 1

General introduction

Enhanced nitrogen (N) losses due to high application rates of mineral N fertilizers is an important environmental problem globally, causing eutrophication of surface waters. High fertilizer N inputs, in combination with elevated levels of acid atmospheric deposition, also cause soil acidification due to increased leaching of base cations (BC, including exchangeable potassium, calcium, magnesium, and sodium ions, i.e., K^+, Ca^{2+}, Mg^{2+}, Na^+) in response to elevated nitrate (NO_3^-) leaching. Together these processes might lower the crop production when soil pH levels decline below the critical levels required for optimum crop growth. The adverse impacts of N fertilization on N losses and soil acidification are highly influenced by management and site conditions, including land use, climate, and soil quality. These factors not only affect the N use efficiency (NUE, the fraction of N input adsorbed by the crops), but also the acid neutralizing capacity to counteract the acidification induced by N fertilizers. Both nutrient losses and soil acidification can be counteracted by proper management including balanced fertilization, enhanced manure recycling replacing mineral fertilizer, and liming. Each of these aspects is introduced below, leading to three knowledge gaps being investigated in this thesis.

1.1 Mineral nitrogen fertilizer application and losses in croplands

1.1.1 Nitrogen fluxes and nitrogen use efficiency in China

Mineral N fertilizer is widely used in China to increase crop yield and meet the food demands of its growing population. China has become the largest consumer of N fertilizers in the world, accounting for about 30% of global N fertilizer consumption (Zhang et al., 2013a). For example, in 2015, the total N fertilizer use was 30 million tons per year, being about twice the amount of N taken up by crops (**Fig. 1.1**). The significant increase in mineral N fertilizer use over the last decades (from 12 million tons year^{-1} in 1980 to 31 million tons year^{-1} in 2015) has contributed to a considerable increase in crop production, but it has also led to environmental problems (Gu et al., 2015; Liang et al., 2017; Zhang et al., 2022). Excessive N application in China's croplands has been proven to accelerate N losses by leaching, runoff, and volatilization, resulting in soil acidification, eutrophication, and increased emissions of N_2O, being an important greenhouse gas (Castaldelli et al., 2019; Tian and Niu, 2015). In addition, the overuse of N fertilizer can lead to an acidification-induced reduction of directly available phosphorus (Olsen-P), but the potential effect on crop growth is limited due to an increase in moderately labile P (Mahmood et al., 2021), while the potential effect is further counteracted by P fertilization.

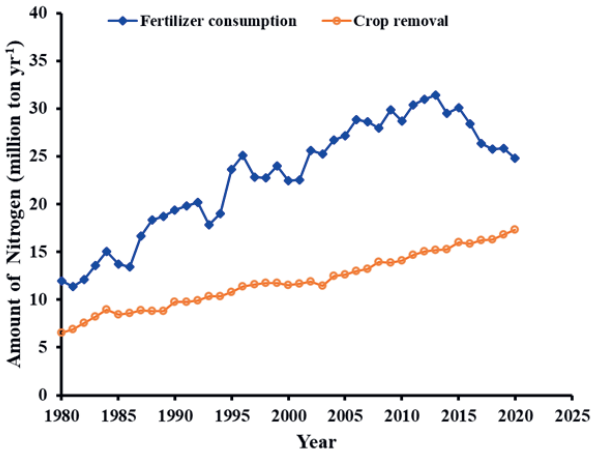

Figure 1.1 Mineral N fertilizer application rate and crop N remove in China croplands (Data from FAOSTAT, "crop nutrient balance". Apart from crop yields, so-called “Nitrogen Removal Coefficients” (kg N removed per ton crop produced) were given).

The NUE of N fertilizer application in crop production systems, defined as the ratio of N uptake by crops to the amount of N fertilizer applied (Ju et al., 2009), is about 35-45% in China. This is significantly lower than the global average NUE that ranges between 50 and 60% (Luis et al., 2014), implying that the majority of the added N is lost to the environment. One of the main reasons for the low NUE in China is the overuse of mineral N fertilizers. Farmers in China tend to use more N fertilizers than necessary to achieve higher yields, even though there is a marginal increase in yield with increasing fertilizer application rates while very high N inputs may even cause yield decline due to severe soil acidification (Chen et al., 2014). The overuse of N fertilizers not only leads to low NUE but also increases production costs for farmers. In addition, it can lead to substantial N losses to air (especially as ammonia, since most of the fertilizers are applied in the form of urea) and water (especially as nitrate) causing air and water pollution.

1.1.2 Factors affecting nitrogen use efficiency and nitrogen losses to water

Enhancing NUE has been identified as a main approach to reconcile crop production with acceptable N losses to air and water (Schulte-Uebbing and De Vries, 2021). NUE refers to the ability of crops to absorb and utilize N efficiently from the soil. It is influenced by a variety of factors. The NUE is specifically affected by nutrient management practices. The right fertilizer rate and right fertilizer type are two of the main fertilizer strategy components affecting NUE, together with application at the right time and the right place, known as the 4R's of nutrient management, further discussed in section 1.1.3. In addition, crop management practices (planting density weed control and pest control) and soil management practices (e.g. tillage) affects the NUE. The effects of management practices on NUE, depend further on-site conditions, including soil properties, land use (crop traits) and climate. First, soil properties, including soil texture, pH, soil organic matter (SOM) content, and nutrient availability other than nitrogen have been shown to affect the NUE (Ichami et al., 2019). For example, soils with low SOM content often require higher rates of N fertilizer to achieve the same crop yields compared to soils having more than 4% SOM (Oldfield et al., 2022) given the positive impact of SOM on nitrogen supply, water retention, root ability and diseases suppressiveness (Ros et al., 2022). This increase in crop yield implies a higher NUE. Conversely, soils with high nitrogen availability may lead to enhanced N losses due to denitrification under wet conditions and to leaching under upland conditions (Liu et al., 2003). Second, crop traits such as the type of crop, growth stage, and root system characteristics, also have a significant impact on NUE. For instance, crops with a deep root system can access N from deeper soil layers and are less susceptible to leaching losses, while shallow-rooted crops are more vulnerable to N losses (Ju et al., 2009). Moreover, some crop species, such as legumes, have the ability to fix atmospheric N, reducing their dependence on N fertilizer application. Third, climatic conditions, such as precipitation, temperature and moisture, together with irrigation, also affect NUE by affecting the capacity of soils to supply nitrogen on the one hand (Tan et al., 2018) and the pathways for N losses via denitrification, ammonification and leaching on the other (Ma et al., 2021; Rakotovololona et al., 2019). For example, high temperatures have been shown to increase denitrification losses by 42% (Tan et al., 2018), while soils under waterlogged conditions can increase N loss due to increased denitrification rates (Kemmann et al., 2022).

In short, apart from fertilizer and manure management, site conditions, including soil properties, land use/crop rotations and climatic conditions are essential in modulating the effectiveness of management strategies in reducing N losses. These factors can affect soil nutrient availability, soil retention capacity, and transport pathways, thereby influencing the fate of applied N in agricultural systems. Therefore, a comprehensive understanding of these site-specific conditions on the impacts of nutrient management practices is essential for developing site specific efficient strategies improving NUE and thus minimizing N losses and promoting sustainable agricultural production.

1.1.3 Strategies to increase NUE

There have been various efforts to promote more sustainable use of N fertilizer in China, such as the implementation of the "*Action Plan for Zero Growth of Chemical Fertilizers by 2020*" in 2015, which aims to reduce fertilizer use and improve fertilizer management practices (Jin and Zhou, 2018). In addition, there are also ongoing research efforts to develop more efficient N fertilizers and management practices that can reduce N losses and improve ecosystem health (Chen et al., 2014). In this context, the so-called 4R's of nutrient management, which stand for right, right rate, source, right time, and right place, is a main approach to guide farmers to improve the efficiency of the nitrogen applied. The use of high rates of N fertilizers can cause excessive vegetative growth, which reduces the efficiency of N uptake (of the edible part) and utilization by crops (Shao et al., 2022). Balanced fertilization in view of the expected crop yield is the main nutrient management strategy that can improve NUE and reduce N losses in China besides soil, crop, and water management. Balanced fertilization involves the application of N, P, and potassium (K) fertilizers in the right amounts and ratios to meet the crop's nutrient requirements. The balanced application of fertilizers can prevent nutrient imbalances in the soil and increase NUE, thereby reducing the N and P losses to the environment (Ren et al., 2022). Combining the use of organic manure and mineral fertilizers to improve soil fertility and crop yield has been proposed as management strategy to improve NUE and reduce N losses in China (Zhang et al., 2012) given its positive impact of manure on the SOM content, base saturation and soil nutrient availability (Zhang et al., 2020c). This approach can reduce the dependence on mineral N fertilizers, thereby reducing their environmental impact and production costs for farmers. Regarding fertilizer type, the use of slow-release fertilizers, such as urea with a urease inhibitor, can improve NUE by synchronizing N availability with crop demand as long as the N dose is adapted to the higher expected NUE (Abalos et al., 2014). Fertilizer practices optimising the best timing of fertilizer application (depending on the weather and seasonal conditions) and optimising the placement of fertilizers (banded or in the root zone) in view of field characteristics (e.g. soil type, soil nutrient status) are also known to improve the NUE (Ding et al., 2018; Liu et al., 2022; Zhu et al., 2020b).

1.1.4 Knowledge gaps

South China is the main producing area of cash crops and grain of China. However, excessive application of mineral nitrogen fertilizers has accelerated the occurrence of soil acidification, which may lead to reduced crop yield at low pH (Zhu et al., 2018). Improving soil fertility and NUE is critical to promoting agriculture's long-term sustainability.

Replacing part of the mineral N fertilizer with manure improves both yield and NUE (Cai et al., 2015; Meng et al., 2014), being supported by evidence from long-term field experiments across the region. However, the effectiveness by manure replacement in improving NUE and mitigating soil acidification depends on the type and application rate of manure. The manure type controls the nutrient composition as well the release rate of the organic N in the manure. For example, poultry manure is high in N and P and has a quick release rate, increasing the risk for nutrient losses throughout the growing season. In contrast, cattle manure has a slower release rate and lower N and P content. Research on the use of manure in double-cropping rice systems has demonstrated that when 20 to 40% of mineral N fertilizer is replaced by manure, rice yield is significantly increased (Xie et al., 2016b). The impact of this fertilizer strategy however is controlled by site conditions such as soil type, climate, and management. For instance, sandy soils have lower nutrient retention capacity and are more prone to nutrient leaching, while clay soils have higher nutrient retention but are more prone to compaction and erosion.

To maximize the benefits of manure as a fertilizer, it is key to have quantitative insights in the impact of site conditions on the NUE of manure, fertilizers, and combinations of them. Site-specific nutrient management practices that account for the variability in soil, climate, and crop requirements can increase NUE and minimize soil acidification. Identifying the main factors controlling both can help to improve the sustainability of agriculture, thereby increasing crop productivity and reducing soil acidification.

Several meta-analyses have been carried out, using published experimental data, to assess the effects of combined management practices on N uptake and N losses to air and water (Gu et al., 2023; You et al., 2023; Young et al., 2021) but the effects of site conditions on the NUE and/or N losses is mostly not included (Gu et al., 2023), or accounted very broadly (Young et al., 2021). There are only very few meta-analytical studies accountings for interactions between management practices and site conditions using a meta-regression model (You et al., 2023). In China, many long-term fertilization experiments with varying inputs of organic and mineral fertilizers have been caried out to assess the impacts on crop yields and the efficiency of nutrient application across farming systems that differ in site conditions (land use, soil properties and climate). However, a comprehensive overview of the modulating impact of site conditions, such as crop rotation, soil properties and climate on the effects of fertilizer and manure strategy on NUE is still lacking, being crucial for promoting site specific sustainable agricultural production.

1.2 Soil acidification in croplands

1.2.1 Soil acidification in China

Soil acidification, defined as a decrease in the acid neutralization capacity (ANC) of the soil (De Vries and Breeuwsma, 1987; Guo et al., 2010) is a major issue all around the world. In calcareous soils with a high buffer capacity due to dissolution of carbonates, the only concern is the decalcification rate and the time in which the carbonates are depleted. However, in non-calcareous soils with a low buffer capacity that are sensitive to acidification, especially sandy soils with low organic matter content, it may cause a relative fast pH to decline with related crop yield impacts below a critical pH. Soils with a relative low pH below 5.5 occur at 40% of the world's arable land (Kunhikrishnan et al., 2016), also widely spread across the provinces in China (Cai and Zhang, 2016). Early field research revealed that the soil pH of China's major farmlands declined by an average of 0.5 units between the 1980s and 2010s (Guo et al., 2010), particularly in southern China. This is partly related to the parent material where sandy acidic soils (being high in iron and aluminum) dominate. Together with the region's consistently high temperatures and humidity levels, the soils' acidity is enhanced by severe weathering and leaching. The awareness grows that farming practices, including the excess nitrogen inputs, might accelerate the acidification, thereby reducing the possibilities to increase crop yields.

Soil acidification affects nutrient availability through impacts on soil microorganisms affecting decomposition and on soil chemical processes, such as adsorption and desorption, which can have profound consequences for plant growth and health. The availability of essential nutrients such as P and calcium (Ca) is reduced at low pH, while concentrations of aluminum (Al) and other heavy metals might reach toxic levels for crop growth (**Fig. 1.2**). These effects can ultimately lead to decreased crop yield and quality (Kochian et al., 2015; Reeves and Liebig, 2016). Results from Zhu et al. (2019) showed that an average soil pH decline of about one unit can reduce the yield of wheat, maize and rice with 4% to 24% during the period 2010-2050. Avoiding and repairing soil acidification is therefore key to feed the growing population sustainably.

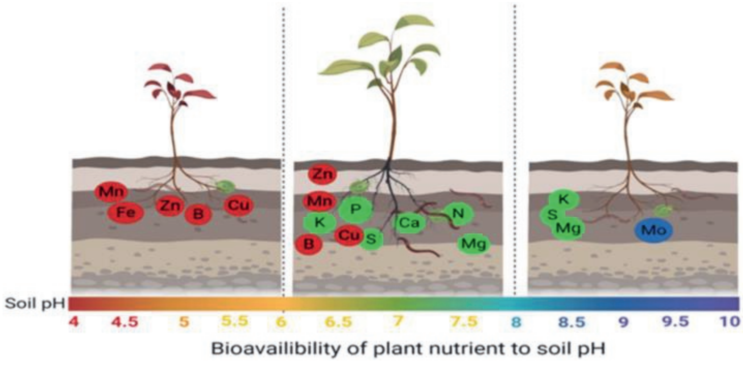

Figure 1.2 Plant nutrient availability in acidic, neutral, and basic soil pH ranges (Singh et al., 2020b). The major nutrients, i.e. N, P, K, Ca, Mg, and S, which are denoted in green colours, are most available in a soil pH range between 6.0 and 7.5, while B, Cu, Fe, Mn, Ni, and Zn are more available below a soil pH of 6. Most plant nutrients (especially micronutrients) tend to become less available at pH above 7.5, except Mo, which is abundant at moderately alkaline pH.

1.2.1 Factors affecting soil acidification

Factors involved in natural soil acidification

In natural ecosystems, soil acidification is mainly caused by the dissociation of CO_2 in both non-calcareous soils (soil pH lower than 6.5) and calcareous soils (soil pH higher than 6.5) (De Vries and Breeuwsma, 1987). The primary mechanism of natural soil acidification is the dissociation of carbonic and organic acids (**Fig. 1.3**), which leads to the leaching of bicarbonate (HCO_3^-) and organic acid anions ($RCOO^-$) (De Vries and Breeuwsma, 1986; Singh et al., 2020a; Ulrich, 1986). The amount of HCO_3^- leaching from soil to groundwater varies depending on the CO_2 pressure (P_{CO2}), soil pH and precipitation surplus (*PS*). High P_{CO2} in the soil increases the dissociation of CO_2 to HCO_3^-, and subsequently the leaching to groundwater, in particular for soils with pH levels above 5. This is because CO_2 reacts with water to form carbonic acid, which dissociates into H^+ and HCO_3^-. The HCO_3^- then leaches from the soil, leading to soil acidification (De Vries and Breeuwsma, 1986). Similarly, high precipitation surpluses can increase the movement of water through the soil profile, leading to greater leaching of HCO_3^- (Schindlbacher et al., 2019). However, dissociation of CO_2 does not occur in soils with pH values lower than 4.5 to 5. In these soils the leaching of $RCOO^-$ is the dominant cause of natural soil acidification (De Vries and Breeuwsma, 1986).

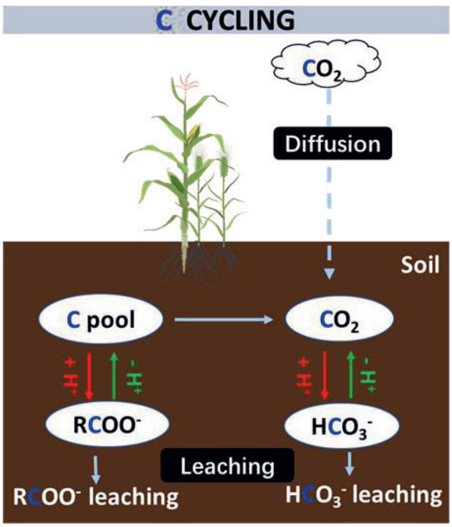

Figure 1.3 Natural soil acidification due to losses in the carbon cycle.

Factors involved in human induced soil acidification

Apart from natural soil acidification caused by HCO_3^- and/or $RCOO^-$ leaching as a result of the dissociation of carbonic and organic acids, the acidity production in managed agricultural systems is mainly induced by NO_3^- leaching, resulting from excessive N inputs by mineral fertilizer and organic manure application, together with enhanced acid deposition, as well as BC removal by crop uptake (**Fig. 1.4**).

Fertilizer management practices: Nitrogen inputs in croplands in China, mostly encountering double cropping, has reached 550-600 kg ha^{-1} yr^{-1} (Li et al., 2016) to ensure sufficient food production to feed the growing population. However, high mineral N fertilizer inputs has caused accelerated soil acidification and related pH decline (Guo et al., 2010; Wu et al., 2022; Zhang et al., 2020a; Zhang et al., 2022). For example, a 10-year pH monitoring study showed that the long-term application of N fertilizers increased the average acidification rate 7.5 times, leading to a decline in pH of about 0.08 units per year (Zhang et al., 2020a).

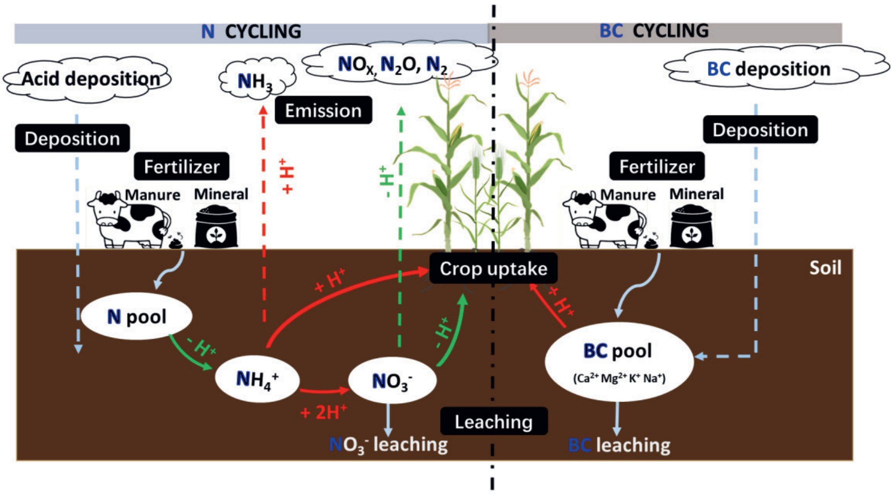

Figure 1.4 Overview of the linkage between acid (H^+) production by (i) NO_3^- leaching induced by N inputs by mineral fertilizer and manure and (ii) acid deposition (iii) BC uptake and leaching and H^+ consumption by exchange of H^+ against BC in agricultural soil.

Hence, increasing the NUE and reducing the N fertilizer inputs is a highly effective soil acidification mitigation measure. The effect of mineral fertilizer on soil acidification also varies with the mineral fertilizer type. During the transformation of organic N to ammonium (ammonification) and the transformation from NH_4^+ to NO_3^- by nitrification, H^+ is produced, leading to acidification unless NH_4^+ and NO_3^- are taken up by crops or NO_3^- is transformed to NO_x, N_2O and/or N_2 by denitrification. Net H^+ production in the soil thus only occurs when NO_3^- is leached, while the release of BC buffers the produced H^+. Associated BC leaching with NO_3^- reduces the acid buffering capacity, with related pH decline (De Vries et al., 1989; Dong et al., 2022; Zhang et al., 2017). In many studies it has thus been found that the pH of the soil treated with nitrate-N fertilizer application is higher than of soils treated with ammonium-N fertilizer (Silvertown et al., 2006).

Acid deposition: In addition to N fertilizer inputs substantial acidification occurs via the deposition of potential acids, being the sum of N and sulfur (S) deposition counteracted by BC deposition. The acid N and S deposition in China increased from 24 to 43 kg ha^{-1} from 1980 to 2014 (Yu et al., 2017). Both fossil fuel combustion and intensive agricultural practices have significantly contributed to the emission of sulfur dioxide (SO_2), nitrogen oxides (NO_x), and ammonia (NH_3), leading to acid deposition (Huang et al., 2021; Liu et al., 2013). With the rapid development of the economy, China has become the third-largest acid deposition area after Europe and the United States (Yu and Xu, 2009), especially in the southern region. Although sulfate ions (SO_4^{2-}) in precipitation in China have dropped significantly since the late 1990s due to policies to reduce SO_2 emissions and energy structure changes, the emission of NO_x and NH_3 has increased significantly (Liu et al., 2013).

Crop uptake is another major source of hydrogen production for soil acidification, mainly because the uptake of BC by crops exceeds the uptake of (acid) anions, including SO_4^{2+}, dihydrogen phosphate ($H_2PO_4^-$) and chloride (Cl^-). In this situation, the crop root secretes H^+ into the soil to maintain the charge balance. The amount of H^+ released is equal to the difference between the uptake of cations and anions by the crops. The uptake of cations and anions varies among crop types. According to research by Hao et al. (2022), rice produced more H^+ (2.2 $kmol_c$ ha^{-1}) from crop absorption than wheat (0.2 $kmol_c$ ha^{-1}) in a rice-wheat cropping system.

Acid consumption

Soil acidification, defined as a decrease in the ANC of the soil, occurs when H^+ production is buffered by a release of base cations, aluminum and or iron, although accumulation of acid anions may also cause H^+ consumption and a related ANC decrease. The acid consumption in soils refers to buffering substances in soil that consumes H^+ against soil pH changes. The buffer mechanism for the release of base cations, aluminum and or iron include the dissolution of calcium carbonate ($CaCO_3$) systems, silicate weathering exchange of base from clay or organic matter and dissolution of aluminum (hydr)oxides and iron (hydr)oxides (De Vries et al., 1989). The soil pH in the $CaCO_3$ buffer system is less affected by the H^+ produced by the soil, and generally the soil pH is relatively stable (Bowman et al., 2008; Slessarev et al., 2016). When soil pH decreases from 7 to 4, the most important buffer mechanism is generally the exchange of H^+ against BC. BC are easily exchanged by H^+ for leaching, resulting in a decrease in the ability of the soil to neutralize acid and depletion of the nutrient pool. And when soil pH further decreases (soil pH lower than 4), the soil enters the buffer system of aluminum (hydr)oxide of which Al^{3+} can be released to neutralize the H^+ production.

In conclusion, soil acidification is a dynamic process of H^+ production and consumption. In response to the net H^+ production in soil, the pH will change. The three main sources of H^+ production, include (i) N transformations (ii) crop uptake of cations over anions and (ii) HCO_3^- leaching. The produced H^+ is consumed by soil components buffering the released H, being $CaCO_3$ in calcareous soils and BC in non-calcareous soils. Adsorption of acid anions such as phosphate and sulphate also neutralize part of the H^+ production. The total H^+ produced and consumed can be quantified by a simple mass balance approach of all major cations and anions (De Vries and Breeuwsma, 1987; Hao et al., 2022; Van Breemen et al., 1984).

1.2.3 Strategies to mitigate acidification

There are several management strategies available to counteract these adverse impacts of intensive farming systems. Some effective management strategies include the optimisation of fertilizer dose and type, the replacement of mineral fertilizers with manure and liming.

Optimizing N fertilizer doses and type directly reduces the acidification potential by lower NO_3^- leaching losses and indirectly reduces the N deposition due to lower NH_3 losses (Zeng et al., 2017). Research showed that when applying 160 kg^{-1} ha^{-1} of N fertilizer, the acid production was 30 keq^{-1} ha^{-1} and when applying 320 kg^{-1} ha^{-1} of N fertilizer, it was 53 keq^{-1} ha^{-1}. Hence, adapting N fertilization to the actual crop demand (Lemaire et al., 2021) is a very effective mitigation measure to minimize the soil acidification. In addition, adapting N fertilizer types from ammonium-N to nitrate-N fertilizers can also be a useful strategy to counteract soil acidification as the acidity production by nitrification declines (Hao et al., 2020; Zamanian et al., 2024).

Replacing mineral N fertilizers with manure is another approach to mitigate soil acidification since manure contains base cation apart from nitrogen (Cai et al., 2020; Ye et al., 2019). Historical data of the experimental site of Qiyang showed that soil pH decreased when only mineral N fertilizer was applied while addition of manure stabilized or even increased the pH (Cai et al., 2015). Hence, manure plays an important role in avoiding severe acidification (Cai et al., 2018; Shi et al., 2019), as the alkalinity of manure following decarboxylation of organic anion and ammonification of organic N can avoid acidification and even reduce plant-toxic Al species through the formation of Al-organic matter complexes (Naramabuye and Haynes, 2007).

Liming is another strategy to mitigate soil acidification. Liming involves the application of alkaline materials such as limestone, dolomite, and quicklime to neutralize the acidity and raise the pH level. Liming has been shown to improve soil pH, increase nutrient availability, and enhance crop growth and productivity (Li et al., 2018). However, the effectiveness of liming depends on various factors, such as the type and amount of liming material applied, the soil properties, and the crop species. Over-liming can also lead to negative environmental impacts such as increased emissions of greenhouse gases (Wang et al., 2021). Therefore, proper liming management practices should be implemented.

1.2.4 Knowledge gaps

Soil acidification is a major issue in China, particularly in the south (Guo et al., 2010). This is due to the fact that, on the one hand, red soil is a typical acidic soil in this area, and, on the other hand, the overuse of mineral N fertilizer, especially NH_4^+- N fertilizer, has accelerated soil acidification. Soil acidification declines soil fertility, seriously restricting the agronomic yield potential.

Soil acidification in agricultural systems is a complex process, and the acidification rate can be quantified by the input-uptake balance of main nutrients, including N, P, K, Ca, Na, Mg, Na, S, and Cl. This approach has been applied to quantify the soil acidification rate for various cropping systems and fertilizer management options. For example, Hao et al. (2020) measured the input-output budgets of major elements for a wheat-maize rotation cropping system and found that ammonium-N fertilizers caused higher acidification rates than urea fertilizer. They also showed that BC removal by crop harvesting was a major source of H^+ production. In addition, the soil acidification rate varied among cropping systems where maize-wheat rotations had higher proton production rates than rice-fallow and rice-wheat rotation (Hao et al., 2022). Others showed that manure application mitigated soil acidification by increasing the BC inputs as illustrated for a 9-year maize field experiment in southern China (Cai et al., 2021).

In summary, soil acidification is influenced by site conditions, management and weather conditions. This includes the fertilizer dose, fertilizer type, crop type, precipitation surplus and the acid buffering capacity of soils. Quantifying soil acidification rate for farming systems that differ in fertilizer management, crop types and site conditions and understanding the interplay of these factors and their cumulative effects is essential for implementing effective soil management strategies that mitigate soil acidification. Long-term experimental sites are available in southern China, including data on nutrient inputs and crop yields and monitoring the influence of fertilizer and manure application on soil fertility, including available soil P levels and soil pH. However, data on nutrient leaching are lacking, while nutrient inputs and uptake are mostly limited to N, P and K, thus limiting the quantification and understanding of the contributions of natural and anthropogenic sources of soil acidification under diverse agricultural systems. By adding data on the inputs and uptake of base cations and applying methods to calculate nutrients leaching, soil acidification can be quantified fir those plots, enabling to unravel the interplay between factors controlling soil acidification and long-term fertiliser management.

1.3 Manure management to improve fertilizer use efficiency and counteract soil acidification in croplands

1.3.1 Manure production and recycling rate in China croplands

Over the past few decades, China has emerged as the world's leading livestock producer due to rapid economic growth and urbanization. In 2019, China produced over 4 billion tons of animal manure annually, accounting for approximately 40% of the global total production (National Bureau of Statistics of China, 2020). Part of the manure is excreted during grazing in pasture or by free ranging animals. However, only 40% of the manure N produced indoors is currently returned to croplands (Bai et al., 2017). Inadequate storage and management of livestock manure can lead to SOM decline, the release of NH_3, nitrous oxide (N_2O), and methane (CH_4) into the atmosphere, and loss of nutrients (particularly N and P) into water bodies, altogether causing air and water pollution, threatening human health and biodiversity. Substituting mineral N fertilizer with manure has been proposed as a potential solution to increase crop yield, enhance fertilizer use efficiency, and control soil acidification (Cai et al., 2015; Duan et al., 2011). Manure application counteracts soil acidification through alkaline substances, such as calcium carbonate ($CaCO_3$) and base cations (BC), which neutralize soil acidity and replenish BC removed during crop harvesting (Xu et al., 2023). This, in turn, increases the soil's acid buffering capacity, enhances soil fertility, and ultimately boosts crop yield. The shift from mineral fertilizer to manure has received considerable attention in recent years (Ye et al., 2019) and urgent measures are needed to enhance field manure recycling to croplands and reduce nutrient losses.

The application of manure in croplands improves soil's physical and chemical quality, boosts crop yield, and enhances agricultural product quality (Du et al., 2020). Additionally, manure usage enhances nutrient recycling and environmental protection, aligning with the principles of green agriculture. Consequently, the Chinese government has proposed policies like "*guiding farmers to fertilize rationally and encouraging increased manure utilization*." They have also implemented action plans, such as the "*Action Plan for Resource Utilization of Livestock and Poultry Manure (2017-2020)*" to promote green agricultural development. The enhanced replacement of mineral fertilizers by manure is becoming an inevitable trend in China's evolving fertilization practices. However, due to the high P/N ratio in the solid manure, which is mostly applied in cropland, it may also cause unwanted P accumulation. In addition, manure contains heavy metals, including Cd, and antibiotics which may cause environmental and health risks, which should be accounted for when assessing optimal manure application rates.

1.3.2 Factors affecting manure management to improve fertilizer use efficiency and counteract soil acidification all over China

The effectiveness of manure in enhancing NUE and mitigating soil acidification is contingent upon the specific type of manure used (Ren et al., 2023b; Van Dang et al., 2021). Different types of manure vary in their nutrient content and release rates, which directly influence their effects on NUE and soil acidification. For instance, poultry manure is rich in nitrogen and phosphorus with nutrients being but released rapidly, making it susceptible to enhanced leaching at high inputs (Kabelitz et al., 2021; Bolan et al., 2010). On the other hand, cattle manure exhibits a slower release rate but contains lower N and P content. Consequently, the utilization of poultry manure may lead to higher NUE but can also exacerbate soil acidification, whereas the use of cattle manure may result in reduced soil acidification but lower NUE.

Various site conditions, including soil type, climate, and management practices, further influence the efficacy of manure in enhancing NUE and combating soil acidification. Sandy soils, for instance, have lower nutrient retention capacity and are more susceptible to nutrient leaching, while clay soils possess higher nutrient retention capability but are prone to compaction and erosion (Tahir and Marschner, 2017). Additionally, the application rate and timing of manure significantly impact its effects on NUE and soil acidification. Research showed that substituting 50% synthetic N with manure increased maize yield by approximately 14% compared with use of either only manure or only synthetic fertilizer (Xie et al., 2016a). The pH of the soil can be maintained by replacing 30-40% of mineral fertilizer by manure Cai et al. (2021).

For optimal results in view of nitrogen use efficiency as well as soil acidification, it is essential to consider the specific characteristics of manure types and tailor their application based on site-specific conditions. Proper nutrient management practices and precise application strategies can help strike a balance between improved NUE and controlled soil acidification, thereby promoting sustainable agricultural practices.

1.3.3 Knowledge gaps

Unbalanced fertilizer management, causing low nitrogen and phosphorus use efficiency, enhances soil acidification and eutrophication of surface water in many provinces across China. In addition, the rapid development of livestock production in China has led to a strong increase in the amount of manure, combined with a low manure recycling rate to cropland, which has resulted results in large amounts of nutrients being released into the atmosphere and water bodies (Zhang et al., 2023). There is an urgent need for enhancing manure recycling all over China. However, manure is not only rich in SOM, N and base cations, but also in P and consequently manure should be used in appropriate amounts to avoid undesirable build-up of P for soils being rich in P and lowering the risk for P leaching to water (Cai et al., 2021).

Applying fertilizer (mineral fertilizer and manure) N and P based on crop nutrient demand and increasing manure recycling rate are ways to increase nutrients use efficiency and mitigate soil acidification. However, it is important to take into account the specific soil P supply (as determined via Olsen-P measurements) when developing strategies to address these problems. Phosphorus, unlike N, can be easily adsorbed in soil, resulting in soil P accumulation. For provinces with soils having high soil Olsen-P contents, full recycling of available manure may not be possible, implying that the replacement of mineral N fertilizers by manure is limited and lime application remains necessary to counteract soil acidification. There has been ample research in China on the impact of enhancing manure recycling on soil acidification (Cai et al., 2021) and on reducing N losses (Wang et al., 2019). However, there is yet limited research on assessing the spatial variation in the optimal application ratio of mineral N fertilizer and manure over China to simultaneously mitigate soil acidification and minimize N and P losses.

1.4 Objectives and outline of these thesis

Overall scientific approach

The main objective of this thesis is to identify the optimal fertilizer and manure application strategy to increase nutrients use efficiency and counteract soil acidification all over China that help to make agricultural farming systems in southern China more sustainable. To achieve this objective, we selected a data-driven approach using data from 13 long-term experimental sites across southern China and combined this analysis with a mass balance approach on provincial level over China. First a systematic analysis is made of the long-term impacts of mineral fertilizer and manure on NUE and soil acidification rates at the experimental sites to gain insight in the effect of site conditions, i.e., different crop types, climatic conditions, and soil properties on NUE and soil acidification. Next, an assessment is made of the optimal rate of fertilizer and manure inputs across all 31 provinces in China in view of crop nutrient demands, target nutrients use efficiency (based on the systematic analysis of NUE before), while minimizing nutrients loss and mitigating soil acidification.

More specifically, the overall approach to solve the objectives (**Fig. 1.5**) includes:

1) quantification of interrelationships between agricultural management, climatic conditions, and soil properties in their ability to affect the NUE using a data driven empirical model approach (**Objective 1**).
2) integrative assessment of the nutrients balance to quantify and identify the main factors controlling the acid production and consumption rates in relation to site conditions (**Objective 2**).
3) assessment of optimal management strategies that differ in the use of mineral fertilizer and manure in their ability to increase the NUE, to reduce adverse P accumulation and to reduce soil acidification and related lime requirements across 31 provinces in China (**Objective 3**).

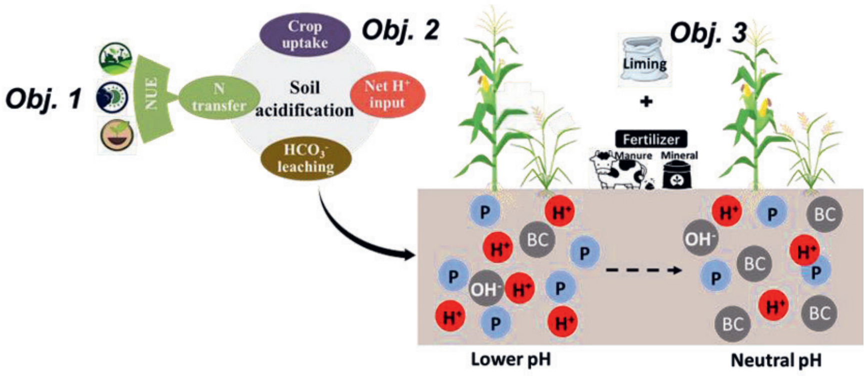

Figure 1.5 Overview of the three objectives addressed in this thesis within the conceptual framework.

The three objectives are described in the next chapters. First, I assess the long-term impact of site conditions on nitrogen use efficiency (**Chapter 2**). In this chapter, I assessed the impact of management (crop type, fertilizer rate, fertilizer type), climate (precipitation, temperature, and sunshine hours) and soil properties (contents of soil organic matter, available contents of N, P, and K) on the NUE using multi variate (non-linear) regression and machine learning algorithms using data from 13 long-term experiments in Southern China. This gives insights in the factors controlling NUE and helps to identify N fertilization strategies that are beneficial for crop yield and environment. The long-term experiments started between 1978 to 1994.

Second, in **Chapter 3**, I describe an assessment of impacts of management and site conditions on soil acidification rates. I used data from the same 13 long-term experimental sites in Southern China with variable crop types, fertilizer application (type and dose), climate and soil properties to quantify the inputs and outputs major element, specifically N, P, S, Ca, Mg, K, Na, Cl and C, and thereby the soil acidification rates. Data on fertilizer and manure use and crop harvests, which were used to assess inputs and uptake, were combining with model-based estimates of the leaching of those elements to quantify the rates and causes of soil acidification under different management practices. The causes were divided in natural soil acidification due to HCO_3^- leaching, and human induced causes, including fertilizer induced N transformations, crop uptake of cations over anions and acid consumption due to HCO_3^-

input, mainly originating from manure). By measuring the changes in soil carbonate contents (in case of calcareous soils) and exchangeable BC contents, we also estimated carbonate and BC loss rates to reflect soil ANC changes and to validate the estimated soil acidification rates. Next, we assessed the impact of management (fertilizer rate, fertilizer type), crop type, soil properties (e.g., SOC content, clay content) and climate (e.g., precipitation surplus, temperature) on soil acidification rates and their different drivers. This allows us to underpin the contribution of different drivers of soil acidification for different site conditions in Southern China.

Third, I identify optimal fertilizer and manure management practices to counteract soil acidification and minimize nutrient losses for cropland over provinces in China (**Chapter 4**). To do so, I first examined fertilizer use efficiency and soil acidification rates under current mineral and manure fertilization management across China for the year 2015. We then identified the optimal fertilizer and manure management in view of a simultaneous optimal reduction in nutrient surpluses and soil acidification rates (and thus liming requirements) for all provinces accounting for site conditions. This way, we can assess the efficacy of current policies and contribute to the development of nutrient management strategies to ensure food security in China while reducing nitrogen losses, adverse P accumulation and soil acidification. Finally, all the results in **Chapter 2-4** are integrated and discussed in **Chapter 5**.

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CHAPTER 2

Long-term impacts of mineral and organic fertilizer inputs on nitrogen use efficiency for different cropping systems and site conditions in Southern China

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Abstract

The application of nitrogen (N) fertilizer is key to realize high crop yields and ensure food security. Excessive N application and relatively low N use efficiency (NUE), however, have led to substantial N losses to air and water with related impacts on biodiversity and health. We used historical data from 13 long-term experiments to unravel how the NUE depends on fertilizer strategy and site conditions such as crop rotation, soil properties and climate. During nearly 40 years of fertilization, NUE decreased when crops were fertilized with N and potassium fertilizers only, while the NUE increased when multi-nutrient or organic fertilizers were used. The highest NUE was found when 25 to 30% of the total N input was supplied in organic form. Among the site conditions analysed, soil pH was the most important factor controlling NUE with an optimum pH around 6. In addition to soil acidity, phosphorus availability increased NUE. Crop rotation, soil properties and fertilizer management together explained 49 to 84% of the variation in NUE, depending on the statistical model used, allowing site specific fertilizer strategies to be developed boosting NUE. Current NUE equalled on average 30% in paddy soils, 39% in upland soils and 42% in paddy upland soils. Optimizing all fertilizer inputs and soil nutrient levels might increase the NUE up to 40-47% in paddy soils, up to 40-77% in upland soils and even up to 40-87% in a paddy upland soils.

Key words

Nitrogen use efficiency, Long-term experiments, Southern China, Nitrogen fertilizer, Manure, Site condition

2.1 Introduction

Nitrogen (N) is a major limiting factor for sustainable and profitable crop production. As a result, N fertilizers are usually applied to increase crop production (Robertson and Vitousek, 2009). However, excessive application of N fertilizer leads to a low nitrogen use efficiency (NUE), being the fraction of the applied N that is taken up by crops (Yang et al., 2017; Zhang et al., 2008). Associated with enhanced air emissions of ammonia (NH_3) (Shang et al., 2014), nitrous oxide (N_2O) and nitrogen (di)oxides (NO_x, NO_2) (Zou et al., 2009; Nayak et al., 2015) and N leaching and runoff to water (Heumann et al., 2013), since N accumulation in soils is limited in the long-term (Omara et al., 2019). Potential nitrogen loss leads to a range of environmental problems, including reduced terrestrial biodiversity (Midolo et al., 2018), enhanced climate change (Nayak et al., 2015), declined microbial activity (Du et al., 2018) and enhanced soil acidification (Guo et al., 2010). Therefore, effective use of N fertilizers is key to boost the sustainability of agriculture on both the short and long-term (Norse and Ju, 2015).

In order to optimize N fertilizer inputs given crop requirements, one needs to understand the crop response to nitrogen availability under variable conditions. Classically, N fertilizer recommendations follow the theory of the “law of the minimum” developed by von Liebig (1855) and Mitscherlich (1925) where the rate of the crop yield response to the availability of N is unaffected by the availability of other factors. Though Liebscher (1895) already came with a new “law of the optimum”, his insights remained largely ignored and yield curves, in response to increased N application rates following the approach of Liebig and Mitscherlich, have been the basis for agronomy research during the last 100 years (Lemaire et al., 2021). It is now well accepted that the law of the minimum fails to capture the interactions among nutrients and the soil properties controlling the release of nutrients. The uncertainty in average response curves derived from field experiments have led farmers to often apply fertilizers in excess to avoid any yield reduction (Lemaire et al., 2021) with undesirable effects on soil quality and environment. Understanding the factors controlling the rate of crop yield change given the availability of N (being the Nitrogen Use Efficiency) is key to improve the efficient use of N in agriculture.

For example, soil acidification, defined as a net decrease of the acid-neutralizing capacity (ANC), has greatly accelerated by excessive N inputs over the last decades, especially in southern China (Guo et al., 2010; Cai et al., 2015), the main producing area for cash crops (for example, rapeseed, sugarcane and peanuts) and food (mainly rice). After N fertilizer application H+ is produced in soil during nitrification, resulting in the soil become more acidic unless the nitrate is taken up by crop. However, when nitrate is leached, accompanied base cations (including K+, Ca^{2+}, Na^{+}, Mg^{2+}, dented as BC), the acid neutralizing capacity is reduced, implying soil acidification (De Vries et al., 1989; Dong et al., 2022). The acidification risk is enhanced when only N fertilizers are applied, since the associated increase in crop yield also leads to an enhanced base cation uptake (Nohrstedt 2001; Bai et al., 2010; Lucas et al., 2011). Current measures mitigating acidification include therefore strategies for N fertilization (prevent pH decline) as well as liming (repair pH decline). Optimizing the N fertilizer dose directly reduces the acidification potential by lowering nitrate leaching and indirectly reduces the N deposition due to lower ammonia emissions (Zeng et al., 2017). Hence, adapting N fertilization to the actual crop demand (Lemaire et al., 2021) is a very effective mitigation measure to minimize the soil acidification and to increase the NUE of agricultural systems. One simple approach is to replace ammonium-N by nitrate-N, declining the acidity production by nitrification. Silvertown et al (2006) for example found that after more than 150 years of fertilization, the pH of the soil fertilized with nitrate-N was higher than that of the soils fertilized with ammonium-N. Replacing inorganic N fertilizers by manure is another approach as it adds additional base cations (BC), such as calcium, magnesium, and potassium, thereby avoiding acidification (Cai et al., 2015; Meng et al., 2012; Dai et al., 2017). However, organic manure might also increase soil acidification via mineralization (Zhou, 2015) complicating the design of sustainable fertilizer strategies.

The acidification potential of inorganic and manure increase with a decrease in NUE, as this determined the N surplus, being defined as the nitrogen input not taken up by crops, and thereby the potential N leaching and thus the N-induced acidification rate (Zhang et al., 2015). In general, NUE decreases with N input, in particular when the N input exceeds crop N uptake, which is calculated by multiplying the crop N concentration with the crop yield (sum of grain and straw biomass) (Jiang et al., 2019;

De Silva et al., 2020; Duan et al., 2021; Zhang et al., 2015). The increase in crop N uptake with crop yield is not linear, and consequently the additional N uptake per unit of additional biomass declines during crop growing season (Briat et al., 2020; Lemaire et al., 2008). Due to the asymptotic nature of the crop yield response curve to N inputs, the NUE declines as the crop N nutrition becomes less limiting. The NUE is not only affected by N fertilizer dose but also by crop yield (Lemaire et al., 2021), fertilizer type (Zhao et al., 2007; Duan et al., 2021), by crop type and variety (Cui et al., 2008), soil properties (Ye et al., 2007; Su et al., 2020) and climate (Zhang et al., 2008; Yang et al., 2017). This shows that fertilizer recommendations based on unified crop response curves alone cannot be confidently generalized to conditions beyond the experiments done. Understanding factors controlling the rate of N uptake given N inputs via the aforementioned factors is key.

Fertilizer type impacts NUE since the plant uptake differs with N species, in particular when fertilizers are compared with manure. Urea, as one of the most widely used fertilizer, has a fast hydrolysis rate while manure-N is released slowly, thereby affecting N losses. Though the N release of manure-N outside the growing season theoretically would result in lower NUE (Kirchmann et al., 2007; Schönfeldt et al., 2014), field experimental data in China suggests that NUE in manure fertilized croplands can be higher than those fertilized with inorganic fertilizers. This higher NUE has been explained by the fact that manure includes organic matter and all macro, meso and micronutrients, thereby counteracting acidification and enhancing crop productivity (e.g., Shi et al., 2019; Diacono and Montemurro 2011; Cai et al., 2015; Dai et al., 2017). For example, Yan et al. (2011) found that long-term application of manure enhanced the NUE, and yield compared to treatments using fertilizers only. Similarly, Wang et al. (2010) showed that the NUE of slow-release fertilizer applied under summer maize was 4–5% higher than urea. However, the relation between fertilizer type and NUE is not straightforward since Gai et al. (2018) found higher NUE in mineral fertilizer treatments due to their higher plant availability.

Besides fertilizer type, NUE varies among different crops (Li et al., 2011; Yu and Shi, 2015). Rice, wheat, maize and soybean are key crops in China. Yu et al. (2015) collected NUE values for these crops during 2004 to 2014 and showed that they ranged from 29% for rice up to 39% for wheat. This also shows that most of the N added is lost to the environment. In addition, legume-based cropping systems are known to reduce carbon and nitrogen losses (Miao et al., 2011) thereby improving NUE. Crop diversification and diverse crop rotation schemes have the potential to increase crop N uptake (Vandermeer, 1989). As the crop N response varies by N dose, fertilizer type and inputs of macronutrients other than N, the final impact of cropping systems on NUE depends on the interplay between soil fertility, fertilizer strategy and crop sequence. Site factors, such as nutrient availability, clay content, soil organic matter content, pH, and weather conditions also affect NUE given their impact on crop development. Focusing on soil conditions, crop yield response to N is not only affected by the availability of nutrients (available P, K, Ca, Mg and soil pH) but also by soil properties controlling the availability of water, such as the SOM and texture (Tao et al., 2018). For example, Hua et al. (2020) found that application of manure combined with NPK fertilizers resulted in higher ^{15}N recovery by crops, associated with elevated soil organic matter (SOM) and soil phosphorus (Olsen P) levels. Duan et al. (2011) also found an increase in NUE from 20% to 45% by increasing soil available P, in particular for regions where P deficiencies are limiting crop production. Apart from soil available P, the soil pH can play an important role due to its impact on the availability of K, Ca and Mg (Ichami et al., 2019). Based on an analysis of 90 yield survey districts and 10 long-term field experiments, Kirchmann et al. (2020) found that crop yields in Sweden were significantly affected by soil pH, SOM and plant-available soil phosphorus, while plant available K and Mg had limited impact. In addition, sandy soils are often much more vulnerable for N leaching losses than clay soils (Pardon et al. 2017).

Lastly, weather conditions also affect NUE since temperature and water availability control both the decomposition of soil organic matter, the N loss pathways, and the crop yield (Halford, 2009). Elevated global temperature and CO_2 levels as well as changing rainfall patterns require therefore optimized fertilizer strategies favouring high NUE. For example, Liang et al. (2018) showed that the NUE would decrease by 15% due to altered rainfall and temperature regimes enhancing leaching, surface runoff (Zhang et al., 2016) and volatilization pathways (Parry et al., 2004).

Up to now, a systematic assessment how the NUE differs given N fertilizer strategy (dose, type, timing) and site conditions (soil properties, crop rotation type and climate variables) is lacking, in particular for situations on the long-term. We aim to unravel this interplay among aforementioned factors using 13 long-term experiments from Southern China. We hypothesized that the NUE increases with a decrease in N input, that it varies by crop type, an increase with available soil P and pH up to situations where each soil property does not further affect crop yield, i.e. a P-Olsen level around 20 mg kg^{-1} (Bai et al., 2013) and a soil pH around 6 (Zhu et al., 2020), and with an increase in SOM and clay content. High number of excessive rainfall events as well as sites with high precipitation surpluses are expected to have lower NUE values due to increased leaching risks.

2.2 Method and materials

2.2.1 Experimental Locations

Data were retrieved from 13 long-term experimental sites in Southern China where crop type, fertilizer strategy (type and dose), climate variables (precipitation, temperature, and sunshine hours data during growing season) and soil properties (available nutrients, soil texture, soil organic carbon, pH) were recorded. The experiments started from 1978 to 1994 and were designed to investigate the effects of inorganic and organic fertilizers on soil fertility and crop yield. The sites were in the provinces Anhui, Jiangxi, Hunan, Guizhou, Sichuan, Chongqing, Hubei and Fujian. Relevant experimental details are given in **Table 2.1**.

The 13 experiments cover the main cropping rotations present in Southern China, including "Wheat-Soybean", "Wheat-Maize", "Maize-Maize", "Maize", " Rice-Wheat", "Wheat-Rice", "Rice-Rice" and "Rice". The experimental treatments (**Table 2.2**) include Control (CK), combinations of inorganic N, P and K fertilizers (NPK), combinations of inorganic and organic fertilizers (e.g., NPKM), and organic fertilizer (M) only. The main inorganic fertilizers used were urea, calcium phosphate and potassium chloride. Generally, the fertilizer dose was 150 kg N ha^{-1}, 75 kg P_2O_5 ha^{-1}, and 112.5 kg K_2O ha^{-1} per season. Organic fertilizer dose and timing varied per crop from 15 to 23 tonnes ha^{-1}, often applied twice a year. Organic fertilizers included pig, cattle and chicken manure. Detailed information on N inputs is given in **Table 2.3** and on P and K inputs in **Table S2.1 and S2.2**, respectively.

2.2.2 Data collection

Historical data regarding crop rotation, fertilizer input (type and rate), soil properties (texture, SOC, available nutrients, and pH) and crop (crop yield and contents of N, P, K in grain and straw), were collected. Climate data for precipitation, temperature and sunshine hours data were derived from the nearest meteorological station (http://data.cma.cn/).

Soil samples (0-20cm depth) were collected each year and analysed for clay content, pH, SOC and available N, P and K contents (Bao, 1999). Soil texture was classified according to the United Nations Food and Agriculture Organization (FAO) soil classification system. The dichromate oxidation method was used to measure SOC. Available nitrogen (AN) was determined by the alkali diffusion method, whereas available phosphorus (AP) was determined by sodium bicarbonate extraction. Available potassium (AK) was determined by ammonium acetate extraction. Soil pH was determined with a pH combination electrode in a 1:2.5 soil/distilled water suspension (Cai et al., 2015).

Plant samples, including both crop grains and straw were collected at harvest. The biomass of crop grain and straw was recorded separately every year, and the sum was taken as the crop yield. Total nitrogen (TN) content of crop straw and grain was determined by Kjeldahl extraction (Bao, 1999), total phosphorus (TP) by H_2SO_4-H_2O_2 desaturation – molybdenum - antimony colorimetric method (Bao, 1999), and total potassium (TK) was determined by H_2SO_4-H_2O_2 desaturation - flame photometer method (Bao 1999). The C, N, P and K content of organic fertilizers were analysed similarly. Missing data were replaced by using an average of the adjacent two years.

Table 2.1 Location, initial soil conditions and climate of 13 long-term experimental sites in Southern China.

Site No.	Site name	Location	Start Year	SOC[a] (g kg^{-1})	Initial pH	Total (g kg^{-1}) N	P	K	Available (mg kg^{-1}) N	P	K	Soil type (FAO)	PRE[b] (mm)	TEM[b] (°C)	SSH[b] (h)
S1	Anhui-Mengcheng	33°13' N 116°37'E	1982	6.0	7.4	1.0	0.3	-	85	10	125	Calcic Kastanozems	872	15	2352
S2	Jiangxi-Jinxian	28°35'N 116°17'E	1981	16	6.9	1.5	0.5	13	144	9.5	81	Eutric Cambisol	1537	18	1950
S3	Jiangxi-Jinxian	28°35'N 116°17'E	1981	16	6.9	1.7	0.5	15	144	10	125	Eutric Cambisol	1537	18	1950
S4	Hunan-Qiyang	26°45'N 111°52'E	1990	6.7	5.7	1.1	0.5	14	79	14	104	Eutric Cambisol	1255	18	1610
S5	Hunan-Qiyang	26°45'N 111°52'E	1982	12	6.0	1.5	0.5	14	158	9.6	66	Eutric Cambisol	1255	18	1610
S6	Guizhou-Guiyang	26°11' N 106°07' E	1993	26	7.0	2.0	2.4	16	167	17	109	Ferralosols	1071	15	1354
S7	Sichuan-Suining	30°10'N 105°03'E	1982	9.2	8.6	1.1	0.6	22	66	3.9	108	Regosols	927	19	1042-1412
S8	Chongqing-Beipei	30°26´N 106°26´E	1991	14	7.7	1.3	0.7	21	93	4.3	88	Regosols	1105	18	1294
S9	Guizhou-Guiyang	26°11'N 106°07'E	1994	18	6.6	1.8	2.3	14	134	21	158	Ferralosols	1100-1200	15	1354
S10	Hubei-Wuchang	30°28'N 114°25'E	1981	16	6.3	1.8	1.0	30	151	5.0	99	Albic Luvisol	1300	17	2080
S11	Hunan-Wangcheng	28°37'N 112°80'E	1981	20	6.6	2.1	0.7	14	151	10	62	Eutric Cambisol	1370	17	1610
S12	Jiangxi-Nanchang	28°57' N 115°94'E	1984	15	6.5	1.4	0.5	-	82	21	35	Ultisols	1600	18	1610
S13	Fujian-Minhou	26°13'N 119°04'E	1983	13	5.0	1.5	0.3	16	141	12	41	Fe-leachi-Stagnic	1351	20	1813

[a] SOC, soil organic carbon.

[b] PRE, mean precipitation of each year; TEM, mean temperature of each year; SSD, mean sunshine hours of each year.

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Table 2.2 Fertilizer and manure treatments used for different crop rotations in 13 long-term experiment sites of Southern China.

Site No.	Crop type	Site name	Time Duration	Manure	Treatments
S1	Wheat-Soybean	Anhui-Mengcheng	1983-2018	Pig manure Cattle manure	CK, NPK, NPKM
S2	Rice-Rice	Jiangxi-Jinxian	1981-2018	Pig manure	CK, N, NP, NK, NPK, 2NPK, NPKM
S3	Rice-Rice	Jiangxi-Jinxian	1981-2018	Pig manure	CK, NPK, M
S4	Wheat-Maize	Hunan-Qiyang	1991-2012	Pig manure	CK, N, NP, NK, NPK, NPKM, M
S5	Rice-Rice	Hunan-Qiyang	1982-2015	Cattle manure	CK, NPK, PKM, NKM, NPM, NPKM, M
S6	Maize	Guizhou-Guiyang	2010-2018	Cattle manure	CK, NPK, NPKM, M
S7	Rice-Wheat	Sichuan-Suining	1983-2015	Pig manure	CK, N, NP, NPK, M, NM, NPM, NPKM
S8	Rice-Wheat	Chongqing-Beibei	1991-2018	Chicken manure	CK, N, NP, NK, NPK, NPKM
S9	Rice	Guizhou-Guiyang	2010-2018	Cattle manure	CK, NPK, NPKM, M
S10	Wheat-Rice	Hubei-Wuchang	1981-2015	Pig manure	CK, N, NP, NPK, NM, NPM, NPKM
S11	Rice-Rice	Hunan-Wangcheng	1981-2007	Pig manure	CK, NP, NK, NPK, NKM
S12	Rice-Rice	Jiangxi-Nanchang	1984-2017	Pig manure	CK, NP, NK, NPK, NPKM
S13	Rice-Rice	Fujian-Minhou	1984-2015	Cattle manure	CK, NPK, NPKM

Table 2.3 Total N inputs (kg N ha^{-1} yr^{-1}) from inorganic and organic sources in 13 long-term experiments.

Sitename	N	M	NM	NK	NKM	NP	NPM	NPK NPK	2NPK	NPKM NPKM	1.5NPKM
S1	--	--	--	--	--	--	--	180	--	(180-210) +95# (180-210) +77※	-
S2	180	--	--	180	--	180	--	180	360	180+276※	--
S3	--	144-199★ 299-247※★	--	--	--	--	--	180-228	--	--	--
S4	300	196-458※	--	300	--	300	--	300	--	90+(137-320) ※	135+(206-420) ※
S5	--	109-217#	--	--	290+217# 145+109#	--	290+217# 145+109#	73-145	--	290+217# 145+109#	-
S6	--	61	--	--	--	--	--	165	--	124+(15-68) #	--
S9	--	61-271#	--	--	-	--	-	99	--	74+(15-68) #	--
S7	240	106-135※	240+(106-135) ※	--	--	240	240+(106-135) ※	240	--	240+(106-135) ※	--
S8	285-300	13-65※	--	285-300	--	285-300	--	285-300	--	(285-300) +(12-221) ※	(427-450) +(13-65) ※
S10	150	53-113※	150+(53-113)※	--	--	150	150+(53-113)※	150	--	150+(53-189) ※	--
S11	--	--	--	150	150+414※	150	--	150	--	--	--
S12	--	--	--	329	--	329	--	329	--	(100-232) + (98-230) ※	--
S13	--	--	--	--	--	--	--	103- 207	--	(103-207) +(56-112）#	--

※ pig manure; # cattle manure; ★green fertilizer, Astragalus sinicus.

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2.2.3 Data analysis

Calculation of the NUE

The agronomic NUE (sometimes also referred as Apparent Nitrogen Recovery) was calculated as the fertilizer induced change in crop N uptake divided by the total N input as:

$$NUE(\%) = \frac{\left(N_{\text{up,fer}} - N_{\text{up,ck}}\right)}{TNI} \times 100$$

with $N_{up,fer}$ and $N_{up,ck}$ being the crop N uptake (removal) of the fertilized and the non N-fertilized control plot (kg N ha^{-1}) and TNI being the total N input (kg N ha^{-1}), originating from organic (ONI, kg ha^{-1}) and inorganic (TNI, kg ha^{-1}) fertilizers. The crop N uptake was determined by the total N removal by grain and straw, was calculated by multiplying crop yield with nutrients concentration in crop grain and straw. The organic N input was calculated by multiplying the amount of added manure with the N content in the manure. The use of the agronomic NUE also avoids the classic limitations of the approaches of von Liebig and Mitscherlich, since all site properties controlling crop yield are equal for both the unfertilized and fertilized treatments per experiment, allowing the search for site properties controlling the crop yield response to the availability of N.

Included management and site factors affecting the NUE

Management and site factors affecting the NUE include fertilizer and crop management, soil properties and climate variables. Fertilizer management include annual inputs for total carbon, nitrogen, phosphorus and potassium and the relative proportion of organic N input (Ratio: calculated by ONI/TNI) as well as the duration of the experiment (Ysn, in years). As with nitrogen, the total carbon input (TCI, kg C ha^{-1}), phosphorus input (TPI, kg P ha^{-1}) and potassium input (TKI, kg K ha^{-1}) were calculated by multiplying the manure dose with the C, P or K contents in the manure, respectively and adding the P or K input by mineral fertilizers.

The total carbon and nutrient inputs varied from 61-615 kg ha^{-1} for TNI, 0-525 kg ha^{-1} for TPI, 0-940 kg ha^{-1} for TKI and 0-12.991 kg ha^{-1} for TCI with ratio of organic to total nitrogen fertilizer input varying from 3-78% with the highest inputs occurring in the combined fertilizer treatments (**Fig. S2.1**).

Crop management reflects the crop rotation type and included paddy soil (including continuous rice and rice); paddy-upland soil (including rotations of wheat and rice crops); and upland soil (including continuous maize, wheat and maize, and wheat and soybean rotations). The clay content varied between 19 and 65%, the silt content between 25 and 46% and the sand content between 7 and 45%. Available nitrogen ranged from 10 to 464 mg N kg^{-1}, available phosphorus from 0.1 to 347 mg P kg^{-1} and available potassium from 20 to 988 mg K kg^{-1}. There was also a substantial variation in soil organic matter levels and soil acidity with SOC levels ranging between 6 and 39 g kg^{-1} and the pH varying between 3.5 and 8.6 (**Fig. S2.2**). Climatic variables include the mean temperature (TEM), the total number of sunshine hours (SSH) and the cumulative precipitation (PRE) during the growing season as well as the number of heavy rain events where the daily precipitation exceeds the 25mm (daynumber). The mean temperature varied from 14 to 28 °C and the total sunshine hours from 417 up to 3.202 hours. The precipitation ranged from 266 up to 4868 mm whereas the number of extreme precipitation events could range from 2 up to 65 days (**Fig. S2.3**).

Statistical approaches to evaluate the impact of site factors affecting the NUE

All data corresponded to a normal distribution after natural log transformation. Data were subsequently scaled to unit variance. Pearson rank correlation tests were used to evaluate the relationships between individual variables. ANOVA tests were done to assess the impact of fertilizer treatments on NUE.

To evaluate the integrative impact of fertilizer strategy, crop rotation, soil properties, and climate variables on NUE, we applied both generalized linear (regression) modelling (GLM) and gradient boosted tree (XGBoost) regression modelling. Both main and interaction effects were included for the GLM models. Where linear regression assumes that the target variable can be expressed as a linear combination of the independent variables (plus error), gradient boosted trees are nonparametric. Linear regression models are strong for finding global patterns and relationships among NUE, soil and nutrient input variables, but struggle with the assumption of homoscedasticity due to a clustering of soil properties and treatments across long-term experimental sites. Gradient boosting refers to a class of ensemble machine learning algorithms where ensembles are constructed from decision tree models (Rokach and Maimon, 2008). Trees are added one at a time to the ensemble and fit to correct the prediction errors made by prior models. This is a type of ensemble machine learning model referred to as boosting. Models are fit using any arbitrary differentiable loss function and gradient descent optimization algorithm. This gives the technique its name, "gradient boosting," as the loss gradient is minimized as the model is fit, much like a neural network. Gradient boosted regression trees are likely to include site specific clusters in the data better and might also capture non-linear relations though they are prone to overfitting and are less appropriate for extrapolating beyond the variation found in the data. So, we combined both approaches to unravel the impact of site conditions on NUE.

Model performance was tested on randomly selected observations (an independent set of 20%) that was left out of the model calibration. The importance of site factors was evaluated based on a permutation-based approach (as being implemented in DALEX), determining the root mean square error (RMSE) loss after permutation of each individual variable. Model performance was evaluated using the percentage explained variance (R^2) as well as the RMSE, defined as the square root of the average of squared differences between predicted and observed target variables. The calibrated and validated models were subsequently used to estimate the maximum change in NUE given the potential variation in controlling variables by estimating the impact of 1-2 units' pH change, a variable N fertilizer strategy (varying in N dose and the ratio organic versus inorganic fertilizer type) and improved soil quality by elevating SOC and soil P levels to an optimum level. All statistics have been done in R (R Code Team, 2013) using the R packages XGBoost (Chen and Guestrin, 2016), mlr3 (Lang et al., 2019) and supporting packages for tuning, measures, learners, and hyperband optimisation.

2.3. Results

2.3.1 Nitrogen use efficiency, crop yield and crop nitrogen uptake changes under long-term fertilization strategies

The agronomic NUE across the 13 experimental sites ranged from -6% to 127% with a mean value of 36%, crop yield ranged from 0 to 30 t ha^{-1} with a mean value of 16 t ha^{-1}, and N uptake of the cropping system ranged from 0 to 461 kg ha^{-1} with a mean value of 172 kg ha^{-1} (**Fig. 2.1**). As expected, a strong relationship was found between NUE and crop yield (**Fig. S2.4**). Highest values of NUE, yield and N uptake were found in Wangcheng, Wuchang and Jinxian, while lowest values were all found in Qiyang (**Fig. S2.5**). Using the long-term observations, the observed long-term average NUE varied from 30% up to 71% in paddy soils, from 42 up to 69% in paddy upland soils and from 39 up to 83% in upland soils (with the highest value representing the 95% quantile) (data not shown).

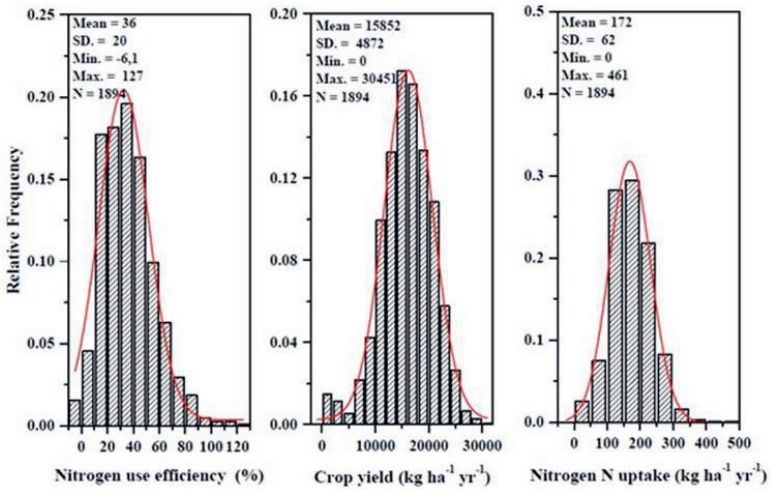

Figure 2.1 Frequency distributions of nitrogen use efficiency (NUE), crop yield and crop N uptake.

Long-term impacts of fertilizer inputs caused a substantial variation in NUE (**Fig. S2.5**). When only inorganic fertilizers were applied for N and K, the NUE decreased from 29 to 15% (only N applied) and from 54% to 22% (when both N and K were applied) ($P < 0.05$). When also phosphorus fertilizer was applied, the NUE did not change significantly, and the average NUE was around 40%. In the three treatments receiving organic manure (NM, NKM, and NPM) the NUE was not significantly altered, whereas the NPKM and M treatments showed that the NUE might increase up to 47% ($P < 0.05$).

Differences in fertilizer inputs and fertilizer types had a significant impact on the mean NUE, yield and N uptake over the period 1981 to 2018 (**Fig. 2.2**). The lowest NUE was found when only inorganic N fertilizers were applied and in the combined NKM treatment: the NUE was on average below 20%. The highest NUE values were found in treatments receiving organic manure besides the inorganic fertilizers (NM, NPM, NPK and NPKM treatments) with a mean NUE ranging between 41 and 44%. Compared with N fertilizer application, the addition of manure (treatments M and NM) significantly increased NUE ($P < 0.01$). Surprisingly, the opposite was found when manure was added to the K treatment: the NKM treatment was 24% lower in NUE than the NK treatment. Differences between NP and NPM, NPK and NPKM treatments were not significant.

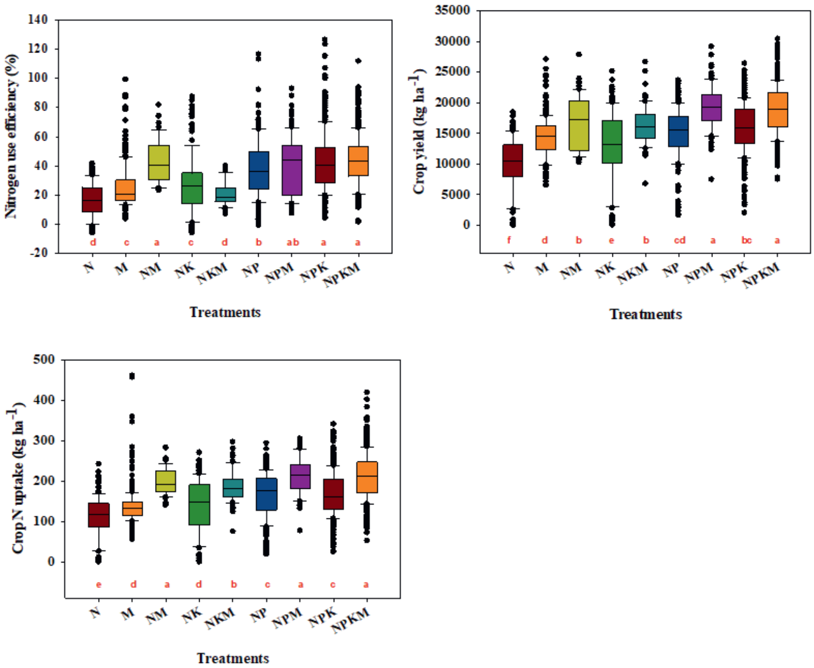

Figure 2.2 Mean NUE, crop yield and crop N uptake over the period 1981-2018 for different long-term fertilization treatments.

In line with the NUE, the lowest crop yield and N uptake was found when only N fertilizers were applied, with a crop production of 10 t ha^{-1} and an N uptake of 113 kg ha^{-1}. The highest yield was found in the NPM and NPKM treatments (about 19 t ha^{-1}) whereas the highest N uptake was found in the NM, NPM and NPKM treatments (about 208 kg ha^{-1}) (**Fig. 2.2**). As expected, the NUE was positively correlated with crop yield ($r = 0.6$) and N uptake ($r = 0.7$) (**Fig. S2.6**).

2.3.2 Relationship of nitrogen use efficiency with management and site factors

The NUE showed a direct negative relationship with total N fertilizer input (TNI) and the relative proportion of organic N input (ratio, a fraction of the total N input) whereas it positively correlated with the total K input. Among the soil properties, NUE tended to increase with the silt content ($r = 0.2$), pH ($r = 0.4$) and the available nutrients ($0.2 <$

r < 0.4). Clay content had a negligible impact on NUE (r = 0.1). Among the climate variables, NUE was only weakly positively correlated with the number of sunshine hours (SSH) and weakly negatively correlated with the mean temperature (TEM), precipitation (PRE) and the number of extreme rain events during the growing season (**Fig. S2.6**).

To unravel the interactive impact of fertilizer management, soil properties and climatic variables, we assessed their impact on the NUE assuming a linear or nonlinear response to a change in these variables. In total 49% of the variation in NUE could be explained with the GLM model (**Fig. 2.3, right; Fig. S2.7, S2.8 and S2.9**). Using the GLM model, there was a substantial impact of crop rotation with the highest NUE found in paddy-upland crop rotations and the lowest in paddy soils (**Table 2.4**). Increasing the total N dose led to a strong decline in NUE, where the negative impact increased over time, likely due to enhanced acidification, considering the strong negative impact of soil pH on the NUE, in particular when the pH drops down below 5. The clay content had a negative impact on NUE (correlated with temperature as well) whereas the total Carbon content was positively related to the NUE. Interestingly, there was a positive response of the NUE to a change in available P in soil whereas the total P input was negatively correlated to the NUE. The NUE declined with the total precipitation surplus. Analysing the feature importance showed that soil pH, total N and P input as well as the clay content, the precipitation and the crop rotation had the highest impact on NUE whereas the duration of the experiment, the ratio organic versus total N input (the Norg fraction) and the level of available P had the lowest impact (**Fig. 2.3**, left GLM model). Other site variables had no relevant impact on NUE when using linear relations and their interactions only. Using a partial dependency analysis for a paddy soil for illustration, we found that the NUE increased from less than 10% at low pH up to 30% at a pH level of 6 after which it remained stable or slightly declined (**Fig. 2.4**). In addition, the NUE strongly declined with total N inputs, from >50% at low N rates (below 10 kg N ha^{-1}) down to 20% when total N inputs increased to 400 kg N ha^{-1}. The optimum N input via organic manure was found around 25%, whereas the NUE slightly declined at ratios above 40%. The NUE increased with more than 20% up to a soil available P level of 100 mg P kg^{-1} after which it gradually increased up to 35% at P levels above 150 mg P kg^{-1}.

Table 2.4 Multi-linear model (GLM) of the effects of site factors on the NUE

Overall site factors	**Site factors**	**Coefficient value**
Crop rotation type	Paddy soil	-0.32
	Paddy-upland soil	0.86
	Upland soil	0.63
Nutrient management	TNI	-0.38
(N, P inputs)	Norg-fraction^2	-0.16
	TPI	0.31
	TPI^2	-0.04
	duration	-0.14
Soil properties	Clay	-0.38
	pH	-0.44
	pH^2	-0.11
	pH^3	0.26
	Ln(SOC)	0.27
	Ln(AP)	0.25
Climatic variables	Ln(PREg)	-0.19

Note: some variables are ln-transformed and all are scaled to unit variance. Impact of these variables are all significant (P<0.01). pH2 and pH3 denotes the pH to power 2 and 3 respectively whereas the ratio between organic and inorganic N inputs (Norg-fraction) and total P input are also squared (Norg-fraction2 and TPI2). "ln" variables were ln-transformed. The function thus reads:

$$\ln(NUE) = cropsystem_i - 0.38 * TNI - 0.16 * Norgfraction^2 + 0.31 * TPI - 0.04 * TPI^2 - 0.14 * duration - 0.38 * clay - 0.44 * pH - 0.11 * pH^2 + 0.26 * pH^3 + 0.27 * \ln(SOC) + 0.25 * \ln(AP) - 0.19 * \ln(PREg)$$

with a cropping system dependent intercept being -0.32 for paddy soils, 0.86 for paddy upland soils, and 0.63 for upland soils.

Using a gradient boosted tree regression on all variables potentially controlling the NUE, the variation in NUE could be explained for 84% by site conditions and fertilizer inputs (when tested on a random selection of NUE observations**; Fig. 2.3, right**). The most important factors controlling the variation in NUE include soil pH, total P input, and experimental duration, with mean root mean square error (RMSE) loss values (the higher the number, the more important the variable) being higher than 20% (**Fig. 2.3,**

left). This reflected the influence of the main properties of the experimental site as well the related acidification rate (since pH is declining over time similar as NUE).

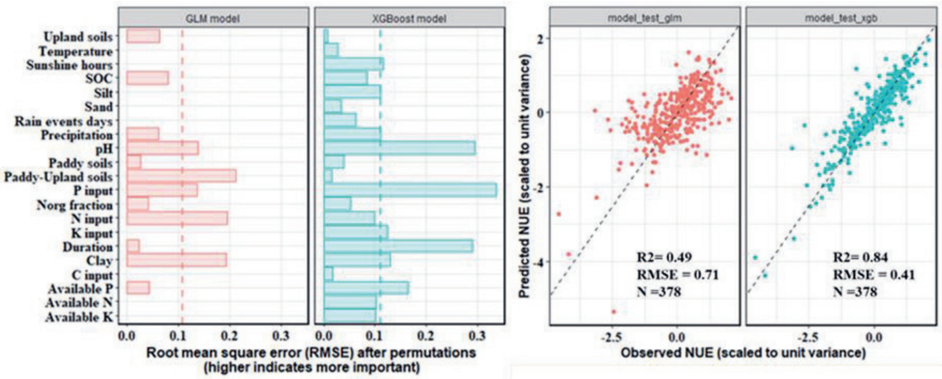

Figure 2.3 Feature importance in predicting NUE of GLM and XGBoost models (left) and model performance in terms of predicted vs measured NUE with these two models (right).

Of slightly lower importance was the available phosphorus in soil, showing that N uptake is substantially affected by both the input and availability of phosphorus. Crop rotation had less impact; only the paddy upland soils showed distinct different patterns than the other crop rotations. Climate variables had limited impact on the NUE, probably due to the strong interaction with other site related properties. When analysing the impact of main features affecting NUE (**Fig. 2.4a-c**), the NUE increased with pH up to a pH value around 5, increased with TPI up to a phosphorus dose of 100 kg P ha^{-1} and soil available P levels up to 80 mg P kg^{-1}. Although not being a main driver of variation in NUE (**Fig. 2.3**), we found that NUE is affected by N input, where the highest NUE was found when TNI varied between 180 to 220 kg N ha^{-1} (**Fig. 2.4d**). The ratio of organic to inorganic nitrogen (ONI/TNI) had very limited impact on the NUE (**Fig. 2.4e**).

Using a bootstrapping approach using normal distributed variables extending the properties of the long-term trials, the possibilities to improve the NUE with soil and fertilizer management was evaluated. Here, a clear distinct pattern was observed between both regression techniques. Using the underlying relationships from the GLM, the NUE could be improved from 30 to 42% in the paddy soils, from 39 to 65% in the upland soils and from 42 to 67% in the mixed paddy upland soils, with the upper values being the 95% quantile of the predicted NUE (data not shown). The ratio organic versus inorganic fertilization was less important. Using the same approach with the XGBoost model to explain the interactive impacts among site properties, weather conditions and fertilizer inputs, the NUE could be improved from 30 to 38% in the paddy soils, whereas the NUE in both upland and mixed soils could not be elevated above the 45% (data not shown).

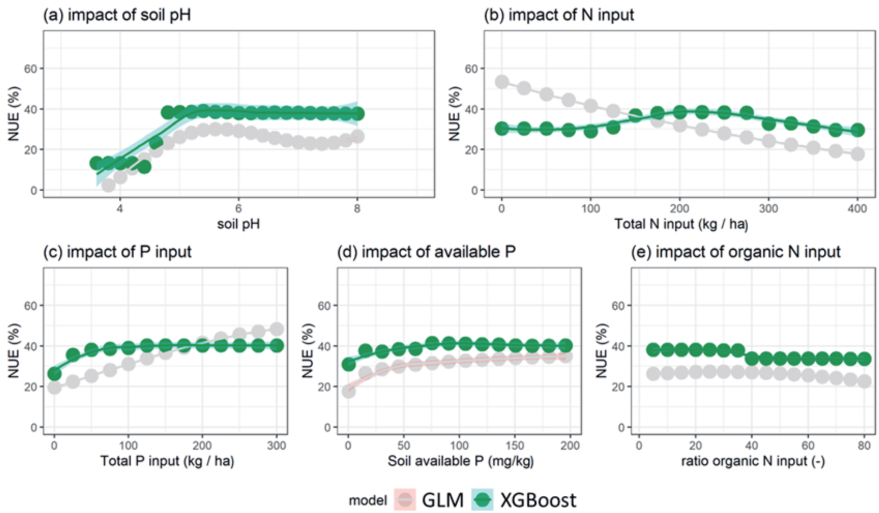

Figure 2.4 Predicted illustrative changes in NUE for an averaged location with variation in pH (a), TNI (b), TPI (c), soil available P (d), and Ratio of ONI/TNI (e) on the nitrogen use efficiency (NUE) in Paddy System using the XGBoost (green) and GLM regression models (gray).

2.4. Discussion

2.4.1 The use of NUE to optimize N management

Global food production must increase considerably if we are to feed the growing population in a sustainable way. Increasing agricultural crop production can be achieved in two ways: by increasing the agricultural area or by enhancing productivity to close yield gaps on existing agricultural lands (Tilman et al., 2011). Closing yield gaps usually requires increasing inputs, such as water, N and other nutrients. Two major options exist to remain within 'safe boundaries' for N losses without reducing (or even while increasing) crop yields (Schulte-Uebbing & De Vries, 2021). First, by spatially redistributing crop and animal production and associated N inputs and losses one can avoid high nitrogen losses due high N surpluses. Second, by improving N use efficiency

(NUE) the N losses can be reduced while maintaining high productivity levels. The NUE of cropping systems can be increased by better matching N inputs with crop demand through improved fertilizer technologies and practices or by using improved crop varieties or crop rotations. Comparing the NUE of averaged farmers with best-performing farmers showed that the NUE for grains in China can increase from 40 up to 68-80%. The observations in the long-term experiments show that the long-term NUE can vary from 30 up to 83% depending on crop type. When total nutrient inputs as well as the soil available nutrients are optimized to increase NUE, then the NUE can increase with at maximum 25%. Most important factors controlling this change are related to the soil pH as well as the availability of phosphorus. Given the large heterogeneity in agricultural systems, fertilizer strategies to increase NUE should at least account for both site conditions as well as the form of the nitrogen added.

Our statistical analysis of long-term experiments gave additional proof for the law of the optimum proposed by Liebscher (1895) that "*all nutrients are used most efficiently when the availability of the nutrient that is most limiting is increased near its optimum*" where the NUE is not constant but variable by site factors controlling N uptake. In contrast to Lemaire et al. (2021), who left the classic agronomic approach and proposed a more diagnosis approach using the in-site crop nutrient status, our data suggests that data driven approaches might be applicable to relate crop N responses to N fertilizers accounting for site properties controlling the crop N response. This is line with results given by Kirchmann et al. (2020) who showed that crop yields can be derived from soil and climatic variables. Coulibali et al. (2020) also showed that optimum N doses for potato in Eastern Canada varies as a function of weather, soil and land management variables, as derived from machine learning models calibrated on 273 field experiments. And Qin et al. (2018) showed that the Economic Optimum N Rate for maize can be derived from weather and soil data. Nevertheless, since data driven models are not expected to be applied outside the calibrated range, a systematic and open data analysis approach across countries is required to find generalized and broadly applicable relationships that account for nitrogen-nutrient and nitrogen-water interactions.

Optimising the soil conditions and fertilizer inputs allows one to increase the NUE. Though both GLM and XGBoost were able to describe the observed variation in NUE

(**Fig. 2.3; Fig. S2.7**) and to identify the same site properties controlling NUE (**Fig. 2.3, Fig. S2.8**), the potential increase in NUE was substantially higher for GLM than for XGBoost. This shows that observed linear relationships between NUE and the site conditions are only limited valid outside the observed range of site conditions of the long-term field experiments. This is confirmed by the strong negative impact of clay and total N input on NUE of the GLM (**Fig. 2.4, Fig. S2.8**), the observed maxima of 40-45% in the partial dependency plots for XGBoost (**Fig. 2.4**) as well by the limited improvement of NUE when all site conditions are optimized to find the highest NUE (data not shown). More important however is the fact that the long-term field trials were not designed to identify the conditions under which the NUE can be maximized; they reflect the search for optimized combinations of fertilizer type and nutrient interactions. Additional field evidence with more variation in N inputs (e.g. half or double the agronomic optimum effective N dose) and including all aspects of nutrient stewardship (right time, right dose, right location and right type) might help to explore the full potential of fertilizer (and manure) strategies to enhance NUE in cropping systems.

2.4.2 Methodological aspects

Knowing that soil type, soil properties, geohydrology, weather, crop and fertilizer management affect the NUE, we used the apparent N recovery as indicator for the rate of crop yield response to the availability of nitrogen. Using this approach, all site properties controlling crop yield have been equal., and sufficient nutrients other than nitrogen have been applied to ensure that those are not limiting the crop response. Using this approach over multiple years allows one to derive average response curves required to obtain optimum yields. However, as shown by the strong variation across sites, these average curves do not account for specific climate or soil conditions that occur in individual farmers fields in a given cropping year, thus limiting their use in fertilizer recommendations systems (Lemaire et al., 2021). Adding site specific covariates are needed to support appropriate fertilizer decision in arable cropping systems. Combining this with classic prognosis approaches where the crop N requirement is estimated as the difference between crop N requirement (derived by crop yield and desired protein content) and soil N supply, allows one to avoid huge overfertilization and associated decline in soil health and environmental quality.

Quantifying the impact of site properties on NUE using long term experiments from multiple sites is challenging when factors controlling N uptake and N losses show a high dependency with the location of the experiment. We used both linear regression (GLM) and clustering algorithms (XGBoost) to unravel the factors controlling NUE knowing that both approaches have their own advantages and disadvantages (as explained in 2.3). Both approaches confirm a positive relationship between NUE and pH, available P and the use of organic N inputs whereas precipitation, clay, soil organic matter and total N input showed a negative impact on NUE (**Fig. S2.9**). The actual impact of site factors controlling NUE differs due to the fact that GLM assumes continuous linear or non-linear relationships between site factors and NUE, while interactions were found to be insignificant) across the experimental locations, where this was not the case for XGBoost. In addition, linear model handles collinearity differently, focussing on the most important site factor, whereas clustering algorithms value correlated factors similarly. As a consequence, XGBoost accounts in a more appropriate way for site factors controlling NUE at site level, being pH, P input, K availability and the duration of the experiment (likely reflecting the long-term impact of acidification, being site dependent) than linear models in which the impact of these factors was limited. In contrast, the linear model identifies site factors that strongly relates to differences between locations, such as the crop type and clay content, being more important than the variation in site factors within an experimental location. We used both approaches to unravel the relevance of site properties, knowing that the use of these models in fertilizer recommendations systems might require independent validation on actual field trials done.

2.4.3 Impacts of fertilizer management on nitrogen use efficiency

Application of fertilizer is an important practice in achieving high yield in crop production and low nitrogen losses, since sufficient and timely nutrient supply affects both crop grain formation and soil fertility. Nitrogen fertilizers play an important role in increasing crop production. However, in this research, adding N fertilizers alone without mitigation of soil acidification declines crop yield, crop N uptake and NUE substantially (**Fig. 2.2**), with the NUE significantly decreasing over the 40 years of the experiment. This may also be the result from nutrient depletion given the net removal of phosphorus, potassium, and certain micronutrients and micronutrients from the soil.

More important, however, seems the negative feedbacks originating from soil acidification. The NUE sharply declined at low pH values, in particular for fields being fertilized with inorganic N fertilizers only. Soil acidification has been proven to have a negative effect on nutrients supply and associated crop yield and soil fertility decline (Guo et al., 2010; Cai et al., 2019; Zhu et al., 2020). Compared with the fertilizer treatments receiving N and K, the application of P fertilizer had a positive effect on both crop yield and NUE (**Fig. 2.2**) being consistent with earlier observations by Duan et al. (2014). An adequate supply of P enhances crop yield given the impact of P on photosynthesis, flowering, and development of seed (Ziadi et al., 2008). The positive impact of soil available P and P inputs can be attributed to the high P retention capacities of the investigated soils. The experimental sites in this study are all located in the southern region with red soil as the main soil type. Red soil is a typical acidic soil with low parent phosphorus content, characterized by relatively high retention capacities due to high iron oxide and aluminium levels (Dari et al., 2015; Chang & Jackson, 1957). In addition to the P input, additional calcium was added in those treatments receiving P from superphosphate (where the extra calcium partly mitigates the acidification from the N inputs).

Fertilizing soils with organic manure is a traditional and effective method to maintain soil productivity because this improves not only the physical and chemical characteristics of the soil but also regulates the quality of the soil organic matter, promote the growth and reproduction of microorganisms, and improves the NUE (Liang et al., 2009). We showed that adding organic manure indeed enhanced crop growth as well as the NUE in all sites whereas the NUE decreased when only inorganic N, and N and K were applied (**Fig. 2.2**). On the long term however, we showed that the effect of soil amendment with organic manure on the NUE varied a lot (**Fig. 2.S5**). Similar findings have been shown for a wheat-maize rotation over 33 years, by Yang et al. (2015b), who concluded that organic fertilizers enhance the capacity of soils to supply nitrogen (by increasing the mineralizable N pool) and that the actual release depends on manure history and weather conditions (Yadav et al., 2000; Cai et al., 2019). Considering the serious soil acidification problems in southern China, adding manure will have a positive impact for crop growth, which helps to increased NUE indirectly, since that the addition of base cations to soil prevents acidification (Hao et al., 2022).

The optional ratio of organic N fertilizer and total N fertilizer input was around 30 to 40% (**Fig. 2.4**). When the applied chemical fertilizer was completely replaced by manure (M treatment), the crop yield and NUE declined, likely to a lower N efficiency of the manure, as compared to fertilizer, during the crop growing season (**Fig. 2.2**). Optimizing the fertilizer strategies by smart combinations of inorganic and organic fertilizers and the right dose of each of them might thus boost both crop yield, NUE and minimize N losses to the environment (Ren et al., 2022).

Apart from fertilizer type, the fertilize dose can affect NUE directly. Generally, with the increase of N fertilizer application dose, the observed crop yield and nitrogen uptake increased up to a total N input level around 200 kg N ha^{-1} (data not shown). Adding more N resulted in a decline of NUE (**Fig. 2.4**) showing that fertilizing a crop above a critical threshold will result in adverse environmental impacts on both the short and long-term. Total nitrogen input had indeed a positive correlation with crop yield while NUE declines (**Fig. S2.5**). Finding the lowest N dose with an optimum ratio of manure and inorganic fertilizers was however hampered by the experimental design of the 13 long-term experiments. Where the fertilizer dose was derived from agronomic recommended N doses, the total effective N input was not adapted when manure-N was added. This automatically leads to overfertilization with N in all cases that receive both inorganic fertilizers and manure. The observed impact of the combined treatments on the NUE might therefore be higher than estimated in our study.

2.4.4 Impacts of site factors on nitrogen use efficiency

The variation of NUE was determined by crop type, soil properties and climate variables (Cui et al., 2008; Yang et al., 2017). From the soil properties evaluated, the soil pH and available P and K were the most important ones affecting the NUE. The soil pH was positive correlated with NUE and identified as one of the most important soil properties controlling NUE, confirming its relevance for crop production in acid soils (Bolan et al., 2003). Liming soils is therefore a prerequisite to boost NUE for farmlands in southern China (Guo et al., 2010). The soil pH has been known to affect both chemical and biochemical processes, affecting the form, transformation, and availability of almost all essential nutrients. In addition, the loss of base cations (calcium, magnesium, potassium) via leaching increases at lower soil pH (Fenn et al., 2006). Furthermore, very low soil pH values (below 4-4.5) will also affect crop yields negatively due to potential toxic effects of aluminium, manganese, and heavy metals. Lastly, at low pH values below 4 the soil pH will also result in a decline in the capacity of soils to supply nitrogen. All these processes result in a negative impact on crop yield and associated NUE (Zhu et al., 2020). Balanced fertilization with multi-nutrient fertilizers and manure therefore not only supplement all desired nutrients for crop growth, but also avoid base cation depletion and severe acidification (Cai et al., 2015; Meng et al., 2012; Dai et al., 2017). The benefit of organic matter via manure increases with the dose applied (Duan et al., 2021). As total P fertilizer input and soil available phosphorus and potassium contents were among the most important variables affecting NUE, bringing the soil nutrient status to an optimal status for crop development is key to enhance NUE. Soils with high clay and SOC levels are usually less susceptible for N leaching losses and are characterized by higher chemical and biological soil fertility, enhancing crop growth and NUE. Data from the long-term trials supports this hypothesis, but this could not be confirmed by strong evidence for clay due to a strong site clustering of these properties. SOC had a clear positive impact on NUE, whereas the GLM approach found a negative one for clay content (partly confounded by precipitation effects) whereas XGBoost suggested only a minor (though negative) impact of clay content on NUE (**Fig. S2.9**).

Furthermore, the efficiency of N uptake varies among crop types. The nitrogen uptake and NUE of urea fertilized rice is generally low compared with upland crops, mainly because paddy soil is an anaerobic system under flooding, where the applied N fertilizer is rapidly lost through denitrification. In general, upland plants such as maize and wheat prefer nitrate, while rice prefers ammonium under flooded conditions (Zhang et al, 2018). Ju et al. (2009) showed for an upland wheat-maize rotation in North China Plain that 27% of the added N was taken up by the crop whereas 23% was lost due to volatilisation, 18% due to nitrate leaching and 2% via denitrification. Actually, comparable increases in NUE could be achieved for the paddy soils as well as the upland soils, and occurred under similar conditions: a higher pH, relatively low N inputs, sufficient P inputs and a high soil P fertility status. The main reason for the higher NUE in mixed paddy upland soils was caused by high pH (0.5 pH unit higher), high available N and P levels in soil (> 100 mg P kg^{-1}), and relatively low total N inputs (< 125 kg N ha^{-1}) and high P inputs (> 100 kg P ha^{-1}). The high relevance of total P inputs can be explained by both the P requirement as well as the calcium input given via the P fertilizers, compensating the N induced acidification. Furthermore, frequent alternation of upland and paddy also breaks the water-stable aggregate structure and increases the contact between microorganisms and organic matter, which improves the mineralization of soil organic nitrogen. Since the NUE declines with the total N availability from both soil mineralization and fertilizer inputs, a higher soil N supply will often lead to lower NUE in arable cropping systems. Adapting the N dose to the crop requirement given the natural soil N supply via mineralization is therefore key to minimize losses to the environment.

Nitrogen transformations in soil are strongly affected by climate conditions. Many studies involving mineralization of organic N in soil have been undertaken since the early studies in 1972 by Stanford and Smith, who demonstrated that net N mineralization followed first order kinetics with the rate doubling for each 10 °C increase in temperature. In addition, the optimal moisture content for nitrogen mineralization was found to vary between 80% and 100% of field capacity (Guntiñas et al., 2012). Compared with crop management and soil properties, climatic variables throughout the growing season had little effect on the variation in annual NUE across the experimental sites (**Fig. 2.3**). This can partly be explained by the fact that all experimental sites are in the subtropical monsoon climate region, limiting the spatial variation in mean temperature (TEM), precipitation (PRE), and evaporation. Both SSH and TEM showed however a positive relationship with crop yield and a negative relationship with NUE, showing that loss pathways for N are affected by the variation in weather conditions. This is supported by earlier research in southern China where Cai et al. (2016) found that an increase of temperature led to higher ammonification losses (Fan et al., 2011). In addition, high PRE can disperse soil particle structure and increase the nutrient concentration of surface water and runoff, and consequently sites with high PRE have higher risks for leaching and runoff. Consequently, sites with higher PRE had indeed lower NUE.

2.5 Conclusion

A systematic analysis was done for 13 long-term experiment sites to quantify the effect of long-term fertilizer inputs, soil properties and climatic variables on the NUE. The NUE of cropland systems in Southern China showed a high variation with values ranging from -6% to 127%. Lowest NUE was found in cases where crops were fertilized with chemical N fertilizers only, and the NUE increased when multi-nutrients or organic manures were applied. The soil, climatic and fertilizer inputs explained 49% of the variation in NUE with a generalized linear regression (GLM) model while 84% of the variation could be explained with a gradient boosted tree regression model. The main variables controlling NUE across the sites were the pH, total P inputs, available P and K and the duration of the fertilizer regimes applied. In line with our hypothesis, soil pH had an optimum pH around 6, with lower values being associated with reduced nutrient availability for P, Ca, Mg and K availability. In addition to soil acidity, NUE increased with available soil P (AP) reaching a plateau at an AP near 50 to 100 mg kg^{-1}, being much higher than the common optimum P-Olsen thresholds for P deficiencies near 20 mg kg^{-1}. Using generalized linear regression modelling, we found that the NUE decreased with an increase in N input, in line with our hypothesis, but this effect was less evident when applying gradient boosted tree regression models. Soil organic carbon had a positive impact on NUE, whereas the evidence was less clear for the impact of clay. Sites with higher precipitation rates had lower NUE values, whereas NUE increased with temperature. Furthermore, we found that the optimum NUE was found when 30 to 40% of the N input is given as manure. Using empirical models trained on data from the long-term experiments, we found that the NUE can increase from 30-42% up to 42-67% by altering the soil nutrient levels and the N dose and fertilizer type. Additional field evidence is needed to explore the full potential of fertilizer strategies to enhance NUE.

Acknowledgements

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CHAPTER 3

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

Zhu, X., Ros, G. H., Xu, M., Xu, D., Cai, Z., Sun, N., Duan, Y. & de Vries, W. (2024). The contribution of natural and anthropogenic causes to soil acidification rates under different fertilization practices and site conditions in southern China. Submitted.

Abstract

Excessive application of mineral fertilizers has accelerated soil acidification in China, threatening the future of crop production. However, the distinct contributions of natural and anthropogenic causes of soil acidification under variable fertilizer management strategies are not well quantified, in particular considering the impact of land use, climate, and soil properties buffering the pH. This study quantifies soil acidification rates using an input-output budget of major cations and anions for 13 long-term experimental sites in southern China. The acidification rates strongly varied among fertilizer treatments and with the addition of animal manure. In non-calcareous upland soils, the main driver of soil acidification was the overuse of nitrogen (N) and associated nitrate leaching. 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 upland soils. Natural bicarbonate leaching was the dominant acid production process in all 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 total acid production rate, respectively. The calcareous soils were strongly buffered, and acidification led to a decline in calcium carbonate levels but with no or a limited decline in pH. In contrast, N transformations were the most important driver for soil acidification in upland crops on non-calcareous soils, accounting for 72% of total acid production rate of 8.4 keq ha^{-1} yr^{-1}. In these soils, the soil pH considerably decreased being accompanied by a substantial decline in exchangeable base cation. 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.

Keywords

Mineral fertilizer, manure, acid production, acid consumption, acidification

3.1 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 (Fenn et al., 2006; Kochian et al., 2015; Zhang et al., 2020c; 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., 2020a). 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). However, it 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 (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., 2018a; 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 ANC. 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 texture, soil fertility, soil organic matter, crop rotation and crop species (Fageria and Baligar, 2008), insight in those factors is needed to select appropriate management, including liming rates and intervals 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. Using a mass balance approach, we quantified all relevant input and output fluxes for major cations and anions and assessed the impacts of management strategies on these fluxes. 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 pH will vary near linearly in response to the acidification rates in non-calcareous soils with the variation being affected by the soil cation exchange capacity.

3.2 Method and materials

3.2.1 Study sites

The 13 long-term experimental sites in southern China started from 1981 to 1993 and 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 3.1. 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 (P_2O_5, 12%) and potassium chloride (K_2O, 50%). The annual fertilizer input was on average 150 kg N ha^{-1}, 75 kg P_2O_5 ha^{-1}, and 112.5 kg K_2O ha^{-1} per season for all fertilized treatments. Manure inputs varied per cropping system and varied between 15 to 23 tonnes ha^{-1}, often applied twice a year. Manure types include pig, cattle, and chicken manure.

3.2.2 Basic soil properties and climate data

Soil samples (0-20cm) were collected and analysed for soil basic soil properties, including soil mineralogy (clay, sand, and silt), soil bulk density (BD), soil organic carbon (SOC) content and soil pH (Bao, 1999). 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 BD. 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 ($CaCO_3$) in calcareous soils was measured for selected long-term sites and years in 2021 (**Table S3.1**). 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, 1999).

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 3.2**.

3.2.3 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 losses 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 chlorine (Cl^-).

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3.2.3.1 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):

$$H_{pro,total}{}^+ = H_{pro,HCO_3^-}{}^+ + H_{pro,N}{}^+ + H_{pro,uptake}{}^+ + H_{pro,H}{}^+ \quad (3\text{-}1)$$

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:

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

where HCO_{3le}^- represent the leaching of HCO_3^-.

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

$$H_{pro,N}{}^+ = (\mathrm{NH_4}_{\mathrm{in}}{}^+ - \mathrm{NH_4}_{\mathrm{le}}{}^+) + (\mathrm{NO_3}_{\mathrm{le}}{}^- - \mathrm{NO_3}_{\mathrm{in}}{}^-) \quad (3\text{-}3)$$

Table 3.1 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 3.2 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 (%)	$CaCO_3$ (%)	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 pH7 ($mmol\ kg^{-1}$) was calculated based on the measured data of 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.

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where NH4in+ and NO3in- 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:

$$ {H_{pro,uptake}}^{+} = \mathrm{BC}_{\mathrm{uptake}} - An_{\mathrm{uptake}} \tag{3-4} $$

where BC_{uptake} represents the uptake of Ca^{2+}, Mg^{2+}, Na^+, and K^+ 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. 3.1, 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:

$$ {H_{pro,H}}^{+} = {H_{in}}^{+} - {H_{le}}^{+} \tag{3-5} $$

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 3.2.4).

The total proton production by natural and anthropogenic causes can, however, be counteracted due to HCO_3^- input ($HCO3_{in}^{-}$), mainly due to by input of manure. The total $HCO3_{in}^{-}$ (keq ha^{-1}) is calculated as the difference in cations and anions inputs (following charge balance principles) as follows:

$$ {H_{con,HCO_3^-}}^{+} = {HCO_3}_{in}^{-} = H_{in}^{+} + {NH_4}_{in}^{+} + BC_{in} - {SO_4}_{in}^{2-} - {H_2PO_4}_{in}^{-} - Cl_{in}^{-} - {NO_3}_{in}^{-} \tag{3-6} $$

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:

$$ {H_{pro,net}}^{+} = {H_{pro,total}}^{+} - {H_{con,HCO_3^-}}^{+} \tag{3-7} $$

3.2.3.2 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:

$$BC_{release} = BC_{uptake} + BC_{le} - BC_{in} - BC_{we} \quad (3\text{-}8)$$

where BC_{uptake}, BC_{le}, BC_{in} and BC_{we} represent the BC removed by crop harvests, lost by leaching, 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 S3.1 and Fig. S3.1**)) and this was calculated as:

$$An_{accumulation} = ({H_2PO_4}_{in}^{-} - {H_2PO_4}_{le}^{-} - {H_2PO_4}_{uptake}^{-}) + ({\mathrm{SO}_4}_{\mathrm{in}}^{2-} - {\mathrm{SO}_4}_{\mathrm{le}}^{2-} - {\mathrm{SO}_4}_{\mathrm{uptake}}^{2-}) \quad (3\text{-}9)$$

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:

$$P_{accumulation} = An_{accumulation} = {H_2PO_4}_{in}^{-} - {H_2PO_4}_{uptake}^{-} \quad (3\text{-}10)$$

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

$$H_{con,total} = BC_{release} + P_{accumulation} \quad (3\text{-}11)$$

3.2.4 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 S3.2**, including inputs by mineral fertilizer, manure, deposition, fixation (only for N), and output data by crop uptake, and leaching. The detailed N input rate under different treatments of each site was given on **Table S3.2**. 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 S3.4**.

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 S3.5**). 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).

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, 2011b; 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^-.

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}). Crop yield and major element (N, P, K) concentration in crop were measured annually. Element concentration of Ca, Mg, Na, Cl and S were determined for both grain and straw samples in 2021 using crop 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 are missing, default element per crop type were extracted from literature (Zhu et al., 2018) (**Table S3.6**).

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 is only in form of nitrate. The leaching of nitrate (${NO_3}_{le}^{-}$) was calculated as:

$$ {NO_3}_{le}^{-} = \left(N_{in} - N_{uptake} - N_{\text{amonia emission}}\right) \times fr_{le} \qquad (3\text{-}12)$$

where N_{in}, N_{uptake} and $N_{\text{ammonia emission}}$ 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 S3.2**. 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 S3.3**.

The leaching of H^+ and $HCO3_{in}^-$ to groundwater and surface water was calculated by multiplying the precipitation surplus (mm) with H^+ and the $HCO3_{in}^-$ concentration (mmol L^{-1}) in soil solution via

$$ {H_{le}}^{+} = [H^{+}] \times PS \times 10 \qquad (3\text{-}13)$$

$$HCO_{3_{le}}^{-} = [HCO_3^-] \times PS \times 10 \qquad (3\text{-}14)$$

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 (BD), 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 S3.7**, 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:

$$\log([HCO_3^-]) = -1.94 + log(P_{CO2})/3 \qquad (3\text{-}15)$$

where P_{CO2} 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 are given in **Text S3.4**).

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:

$$[HCO_3^-] = (KCO_2 * pCO_2)/[H] \tag{3-16}$$

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 P_{CO2} 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:

$$BC_{le} = {NO_3}_{le}{}^- + Cl_{le}{}^- + {SO_4}_{le}{}^{2-} + H_2{PO_4}_{le}{}^- + {HCO_3}_{le}{}^- - H_{le}{}^+ \tag{3-17}$$

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 he 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.

3.3 Results

3.3.1 Mean acid production and consumption rates and their drivers

3.3.1.1 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. 3.1, Table S3.8 and S3.9**). 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 differences in HCO_3^- leaching caused by differences in CO_2 pressure and low N transformation rates 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 and

1.6 for non-calcareous soils and 28 and 13 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%). The net soil acid production rate of the mineral fertilizer treatment (NPK) was higher than those 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.

3.3.1.2 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. 3.2, Table S3.8 and S3.9**). 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 non-calcareous soils, BC release also dominated in treatments without organic manure (CK and NPK). In manure-treated plots, however, (NPKM and M in Jinxian, Qiyang and Minhou), there can be even base cation accumulation due to high BC inputs and here P accumulation became the most dominant H^+ consumption process.

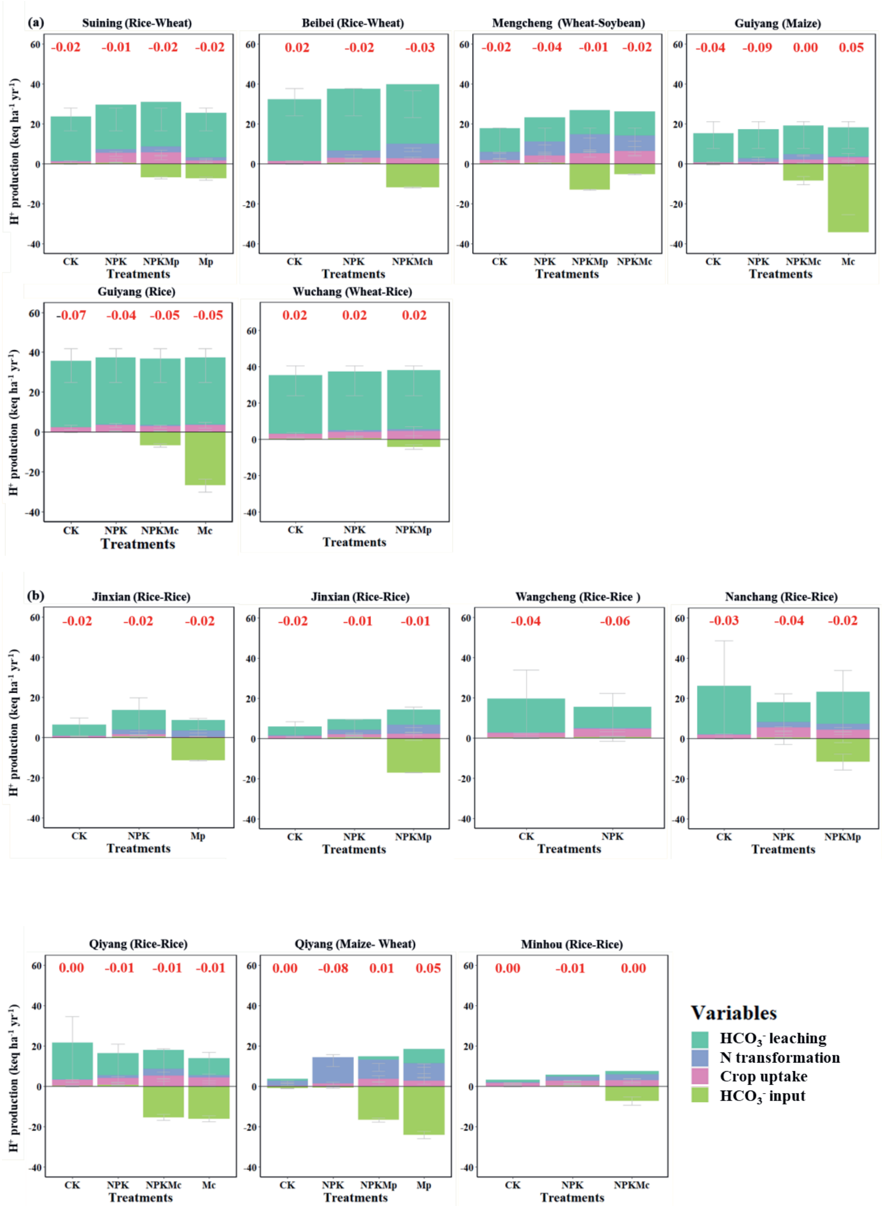

Figure 3.1 The net H+ production by different source under long-term fertilization for calcareous soils (a) and non-calcareous soils (b). Red numbers represent the mean soil pH change during the experimental trial. Note: Error bars denote standard deviation.

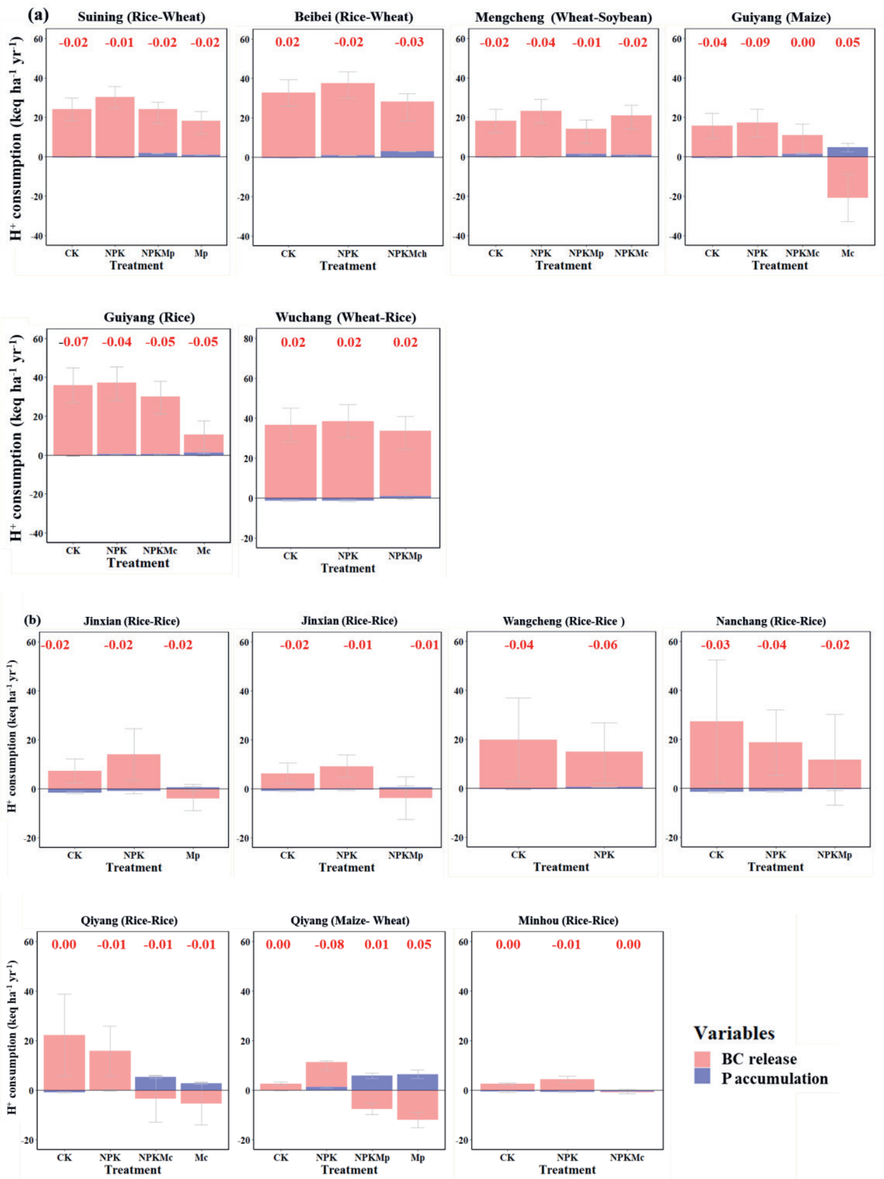

Figure 3.2 The soil H^+ consumption by different source under long-term fertilization for calcareous soils (a) and non-calcareous soils (b). Red numbers represent the mean soil pH change during the experimental trial. Note: Error bars denote standard deviation.

3.3.2 Impacts of management and site conditions

3.3.2.1 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 produce rate of the mainly processes (the acid produced by net H^+ input was neglected in our research given its low contribution as shown in **Table S3.8 and S3.9**) versus site properties including soil pH, and precipitation surplus (**Fig. 3.3**), the nitrogen surplus (**Fig. 3.4**), crop yield (**Fig. 3.5**) and land use types (paddy, upland and their combination) in both 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. 3.6**).

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. 3.3 and S3.1**).

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} 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. 3.3a**). 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. 3.3b**).

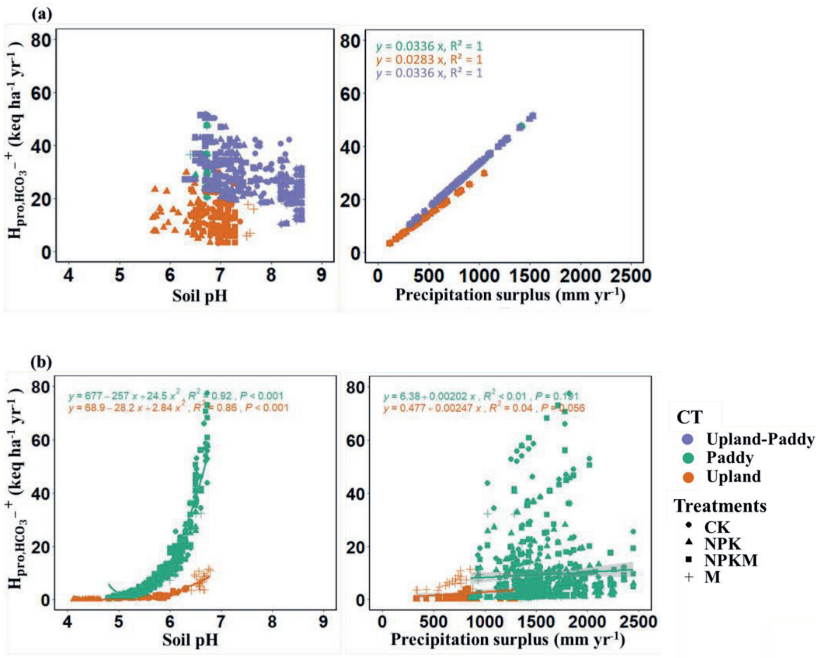

Figure 3.3 Relationship between H^+ production rate by HCO3- leaching ($H_{pro,HCO_3^-}{}^{+}$) and soil pH (left), precipitation surplus (right), for different treatments (CK, NPK, NPKM and M) and land use types in calcareous soils (a) and non-calcareous soils (b). Note: Land use types included: paddy 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).

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. 3.4**). 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. 3.4**) 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) due to higher denitrification rates in waterlogged soils. 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.

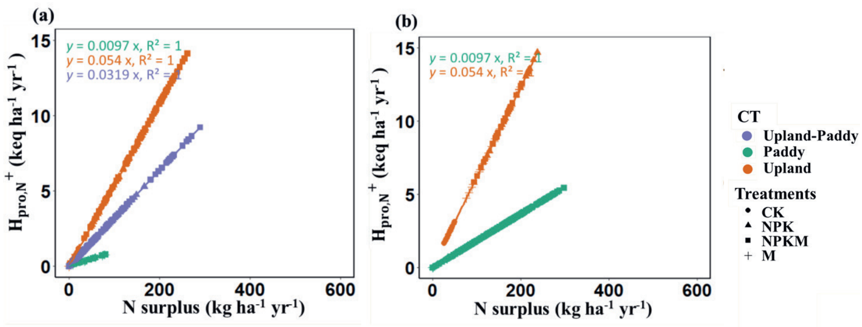

Figure 3.4 Relationship between H^+ production rate by N transformation ($H_{pro,N}{}^+$) and nitrogen surplus (N surplus) for different fertilizer treatments (CK, NPK, NPKM and M) and land use types in calcareous soils (a) and non-calcareous soils (b). Note: Land use types included: paddy soil (green, 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).

Crop uptake

The total crop biomass, producing H^+ via excess uptake of cations than anions, varied between 6.3 to 29 ton ha^{-1} with no distinct patterns in calcareous or non-calcareous soils (**Fig. 3.5**) though the H^+ production tended to be higher in the calcareous soils. A change in crop yield resulted therefore in more H^+ production in the calcareous soils than in the non-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.

HCO_3^- input

The main input of HCO_3^- came from the addition of manure. The input rate exhibited a positive relationship with the rate of manure application (**Fig. 3.6a**). There was an input of 0.30 keq ha^{-1} yr^{-1} HCO_3^- per ton manure ha^{-1} yr^{-1}. The variation across sites and treatments dependent on the manure type as well the weather conditions across different years.

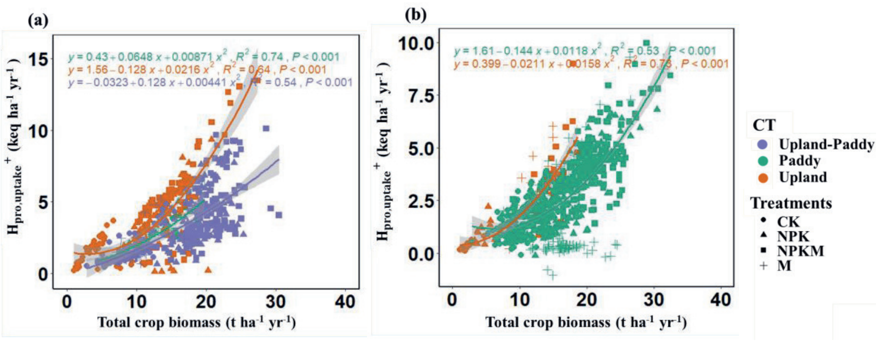

Figure 3.5 Relationship between H+ production rate by crop and straw removal ($H_{pro,uptake}{}^{+}$) and total crop biomass for different treatments (CK, NPK, NPKM and M) and land use types in calcareous soils (a) and non-calcareous soils (b). Note: Land use types included: paddy soil (green, including 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).

3.3.3.2 Soil acid consumption rates

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 release of soil BC decreased by 0.38 keq ha^{-1} yr^{-1} per ton manure ha^{-1} yr^{-1} input (**Fig. 3.6b**). This was caused by more BC inputs through mineral fertilizer (Ca^{2+} input from superphosphate) and/or manure (**Fig. S3.2a**), supplementing the soil BC pool.

Though the impact of P accumulation on acid consumption was much smaller than that of BC release (**Table S3.8 and S3.9**), the total P input of fertilizers and manure was strongly driven H^+ consumption (**Fig. S3.2b**). Therefore, a linear increase in H^+ consumption by 0.08 keq per ton manure added was found (**Fig. 3.6c**).

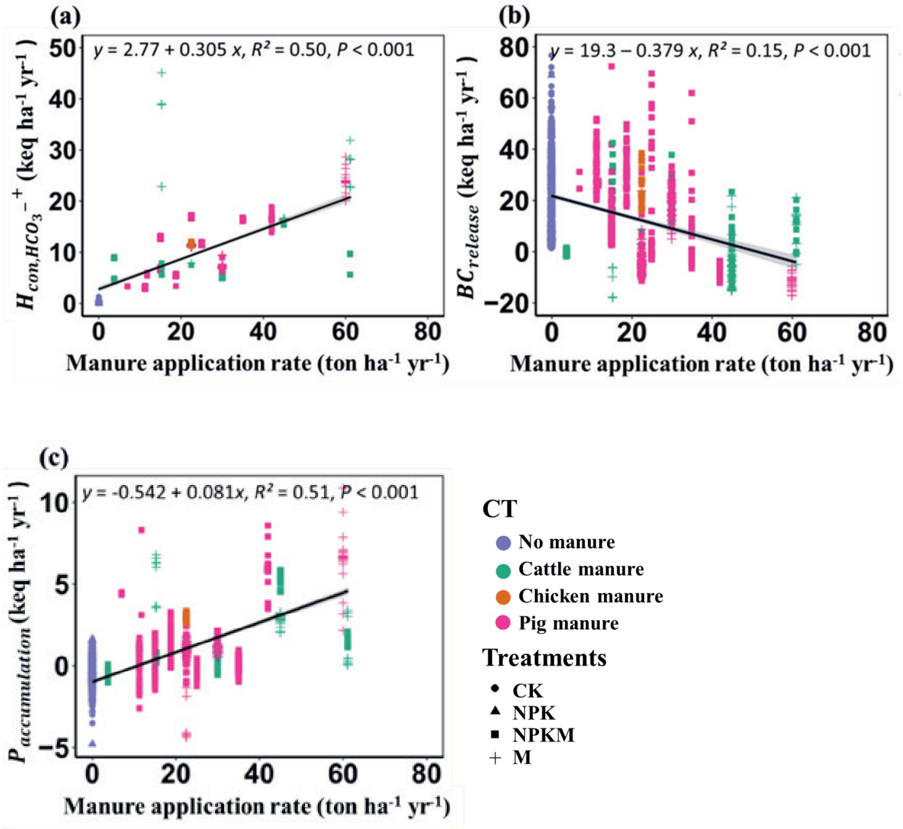

Figure 3.6 Correlation between H^+ consumption rate by HCO_3^- input ($H_{con,HCO_3^-}{}^{+}$), BC $_{release}$ and P $_{accumulation}$ and manure application rate for different treatments (CK, NPK, NPKM, M) and manure types (no, cattle, chicken, and pig manure).

Phosphorus accumulation

3.3.3 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 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. S3.3**).

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. 3.7**). 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 net acid production was also negatively correlated to the changes in soil pH, and associated BC pool changes. 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.

3.4 Discussion

3.4.1 Adequacy of the experimental sites to study soil acidification

Using a mass balance approach in which he inputs and outputs of all relevant cations and anions are quantified allows one to unravel the natural and anthropogenic sources of soil acidification. Zhu et al. (2018) thus assessed the variation in soil acidification rates over China by modelling the inputs and outputs of major cations and anions as a function of land use, soil properties, and climate. Unravelling the contribution of natural and anthropogenic drivers is key to understand the current occurrence of soil acidification and adverse impacts on crop yield, the efficiency of liming activities and to estimate how soil pH will evolve over time given climate change, and management programs affecting crop biodiversity and fertilizer strategies. An observation-based assessment of the effect of site conditions, including land use, climate, and soil properties, on the acidifying impact of fertilizer and crop management is, therefore of crucial importance to guide farmers and policy makers in the identification of appropriate measures to avoid adverse acidification impacts on crop yield.

In this study, we thus 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. The diverse fertilizer management strategies at these sites were evaluated to gain observation-based insights on their acidifying impacts as a function of site conditions. The sites were, however, originally designed to focus on the impacts of fertilization on soil fertility, nutrients 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 is calcareous. Changes in soil acidification rates are difficult to detect by changes in soil pH given the strong buffer capacity by carbonate dissolution. In the non-calcareous soils, our study calculated base cations leaching as the sum of anions leaching while neglecting aluminium as this hardly occurs in soils with pH levels above pH 4.5 - 5.0. In our study pH values below 5.0 only occurred in the Minhou and Qiyang sites.

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. Despite its limitations, the set of 13 experiments with substantial variation in treatments, soil types and climate zones give long-term insight in the effects of fertilizer and manure management under diverse circumstances and how long a soil can effectively buffer incoming acidity.

3.4.2. Main drivers of soil acidification in croplands of China

The mass balance approach allows to quantify 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 processes Include the release of base cations or the retention of anions, including phosphate and sulphate, as discussed below.

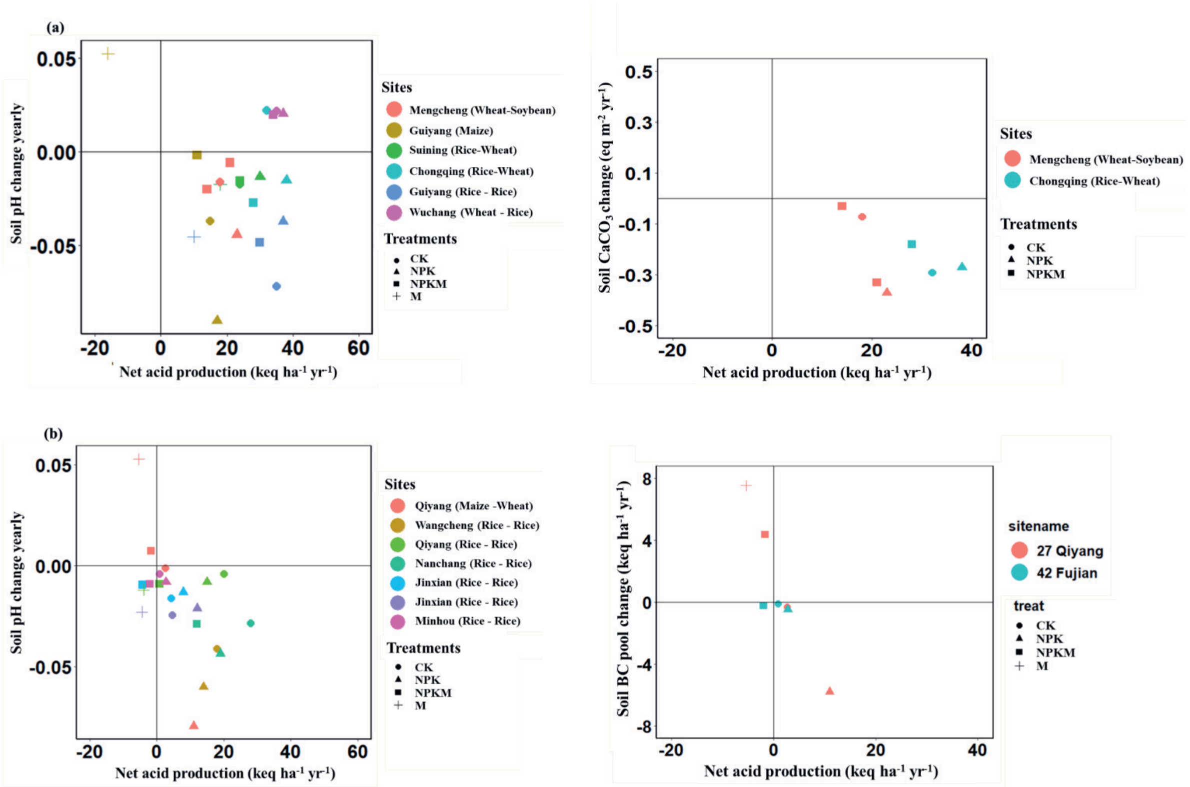

Figure 3.7 Scatter plot of the relationship between net acid production and soil pH yearly change (left), soil acid buffering capacity change (right) ($CaCO_3$ in calcareous soil and BC in non-calcareous soil) for calcareous soils (a) and non-calcareous soils (b).

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), high pH and the existence of $CaCO_3$. 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 input 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. 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 (**Fig. 3.3**). More than 30% of N surplus was leached in upland soil, supporting the hypothesis that nitrate leaching is the main pathway driving acid production. 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 farmer's practice (Hao et al., 2020). In calcareous soils the dissolution of $CaCO_3$ is the main acid buffering substance (**Table S3.8**). 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 P_{CO2}).

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. 3.2**). 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 S3.1**). 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.

3.4.3 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 decrease in soil pH of 0.03 units only. The net acid production rate was 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. 3.7**), being more sensitive to changes in acidity inputs (De Vries et al., 1989). Therefore, in non-calcareous 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 it (Xu et al., 2022), particularly in acidic soils. Conversely, in soils with excessively high pH and base saturation, management strategies may involve using appropriate soil amendments such as manure to promote soil buffering capacity (Cai et al., 2021; Xu et al., 2023).

3.4.4 Mitigation strategies of soil acidification in croplands

Given the diverse drivers of soil acidification across various soil types, land use types, soil properties and fertilization practices in the long-term experiments, developing soil or crop specific mitigation strategies is crucial for sustaining soil pH of croplands. 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. 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.

3.5 Conclusions

In this study, we quantified the rate of acid production and consumption in 13 long-term experiments in southern China by calculating the balance of major nutrients in response to fertilizer treatments, climate, and site conditions. Net acid production varied from -16 up to 38 keq ha^{-1} yr^{-1}. 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 acidification risks due to the excess phosphorus input causing accumulation in soils at most sites.

Main drivers of soil acidification varied across soil types and land use. Natural acidification by HCO_3^- leaching was the primary cause of acid production in calcareous soils (accounting for 80% of total acid production rate), followed by crop uptake (accounting for 11% of total acid production rate), while the impact of N transformations was limited. Soil pH changes in calcareous soils were limited, even in situations of high net acid production rates due to carbonate buffering. As with calcareous soils, HCO_3^- leaching was the main driver of acid production paddy rice on non-calcareous soils, due to the high CO_2 pressure and high denitrification losses caused by the anaerobic conditions in those systems. In contrast, N transformations were the most important driver for soil acidification in upland crops on non-calcareous soils (accounting for 72% of total acid production rate). In these soils, the soil pH considerably decreased being accompanied by a substantial BC pool decline.

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 derivation of an optimum strategy of on regional scale warrants further study.

Acknowledgements

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CHAPTER 4

Spatial variation in optimal fertilizer and manure application to minimize nutrient losses and counteract soil acidification in China

In preparation

Abstract

The application of nitrogen (N) and phosphorous (P) fertilizers in excess of crop demand, combined with low manure recycling, has led to low N and P use efficiencies (NUE and PUE) with associated N and P losses causing surface water eutrophication and soil acidification in China. By a combination of balanced fertilization and enhanced manure recycling, fertilizer inputs can strongly be reduced and soil acidification can be mitigated due to elevated base cation inputs by manure. However, enhanced manure input can also cause undesired soil P accumulation, in particular in soils with a high soil P status. In this research, we quantified the optimal fertilizer and manure inputs for all provinces in China, based on the crop nutrient demand and accounting for the soil P status as well the lime requirements to neutralize soil acidification. Optimising the fertilizer and manure use reduced the total nutrient inputs with 48% for N and 70% for P. The NUE increased from 33 to 68% while the PUE increased from 30% to 109%, implying net mining of soil P. The optimal manure recycling percentage increased from 37% to 69%. Manure was the main P source under optimal management, accounting for 81% of the P input. Soil acidification rates also decreased by 86% and the dominating acid production process changed from N transformation to crop uptake. Provinces where cropland manure can be fully recycled include Anhui, Gansu, Hebei, Henan, Inner Mongolia, Jiangsu, Ningxia, Shaanxi, Shanxi and Xinjiang. In other provinces, manure needs to be exported, implying the need for an improved manure market chain. When manure is properly distributed, no P fertilizer is needed and even then part of the manure need to be exported to avoid adverse impacts of P accumulation.

Keywords

Fertilizer strategy, manure recycling rate, crop nutrients demand, soil acidification

4.1 Introduction

Nitrogen (N) and phosphorus (P) are two of the most essential macronutrients required for crop growth. Their availability in soil can significantly increase agricultural productivity. In China, high application of mineral N and P fertilizers, in many cases coupled with poor management practices, has led to low N and P fertilizer use efficiency, which is defined as the ratio of nutrient uptake by crops to the amount of fertilizer applied (Zhang et al., 2011). Studies have shown that the average N use efficiency (NUE) in China ranges from 30% to 40%, while the P use efficiency (PUE) ranges from 20% to 30% (Wang et al., 2018b; Zhang et al., 2019). These low fertilizer use efficiency values indicate that a substantial portion of the N and P fertilizers applied are either lost to air (N only) and water (N and P) or immobilized and accumulated in the soil (mainly P), leading to a series of environmental problems, including N and P induced eutrophication of surface water, and soil acidification induced by enhanced nitrate leaching (Liu et al., 2013; Mao et al., 2017; Schindler, 1974).

Soil acidification is a key issue in intensive Chinese agriculture systems. From the 1980s to the 2000s, the soil pH of major farmlands in China dropped by 0.5 units (Guo et al., 2010). The rapid and great increase in mineral fertilization exceed crop demands, especially N fertilizers, accelerates soil acidification by enhanced nitrate (NO_3^-) leaching, unless H^+ production by ammonification and nitrification is countered by crop N uptake and/or N losses to air via NH_3 and N_2/N_2O (denitrification). The country averaged proton (acid) production rates induced by N transformation have increased from 4.7 keq ha^{-1} in 1980 to 11.0 keq ha^{-1} in 1996, stabilizing at 8.6 keq ha^{-1} in the years after 2000 (Zhu et al., 2018). Soil acidification results in the decrease of soil pH and the depletion of essential base cation nutrients (BC), including potassium (K^+), calcium (Ca^{2+}) and magnesium (Mg^{2+}), and the increase in the solubility and mobility of toxic elements, such as aluminium (Al^{3+}) and manganese (Mn^{3+}), which can negatively impact soil health and crop production (Kochian et al., 2015; Ning et al., 2017; Zhu et al., 2020a). In addition, acidic conditions result in the sequestration of certain nutrients like P, causing it to be insoluble through binding with cations (Sharma et al., 2013), further decreasing the PUE. Soil acidification is a widespread problem in China, where its occurrence depends on several agro-ecological site conditions such as soil types, climate, and agricultural practices.

Manure is a valuable alternative for fertilizers that can be used to increase FUE and minimize soil acidification (Li et al., 2011b; Ye et al., 2019). This is because manure is not only rich in N and P, but also in K and trace elements, which can help supplement nutrient deficiencies, thereby reducing the need for mineral fertilizer (Ye et al., 2019). Furthermore, manure adds organic carbon, which may reduce the leaching loss of NO_3^- by which soil acidification is mitigated. More important the application of manure also helps to counteract soil acidification by the addition of base cations, such as Ca^{2+} and Mg^{2+}, which can neutralize the acid production in the soil and replenish the base cations removed by crop harvesting (Shi et al., 2019). Research on the use of farmyard manure for double-cropping rice shows that rice yields can substantially increase when mineral fertilizers are replaced by farmyard manure (Xie et al., 2016b). However, while manure application reduces soil acidification, it may cause an additional P input that is in excess of the required P input in view of crop demand. For example, Cai et al. (2021) found that manure application to a red soil in China reduced soil acidification, but simultaneously increased soil P status, thereby increasing the risk for runoff and leaching of P.

Manure should thus be used in appropriate amounts to avoid build-up of P at high soil Olsen-P levels in the soil, since more than 70% of P in manure is inorganic, which can be used by plants (Eghball et al., 2002). At high soil P levels, adding P above crop P demand will cause P accumulation in soil without enhancing production (Bai et al., 2013; Tang et al., 2008). To prevent environmental P losses without risks for P deficiency, the P input should thus be adapted to the soil P status, using a so-called build-up and maintenance approach (Li et al., 2011a). This implies that P input is equal to crop P demand if the soil is an adequate P status (maintenance) while more P is applied at low soil P status (build-up) and less at high soil P status (mining). Similarly, manure N input should not exceed the required N input, which can be determined from the crop N demand divided by the NUE of the added (organic) manure, taken into account unavoidable N losses. The optimal amount of manure can be derived as the minimum needed in view of crop N or P requirement or BC demand to counteract soil acidification. If the optimum dose to meet the N and/or P requirement fails to meet BC demand, extra lime has to be applied. Liming is a common and effective measure to mitigate soil acidification and increasing crop yield (Goulding, 2016). A meta-analysis study found that liming significantly reduced toxic Al content (75%) and increased cation exchange capacity (14%) under field conditions (Li et al., 2018). Lime can also promote the mineralization of soil organic matter (SOM), thereby releasing N, P and other mineral nutrients, promoting crop uptake (Holland et al., 2018) and ultimately increasing the fertilizer use efficiency.

Over the past decades, China has emerged as the world's leading livestock producer due to rapid economic growth and urbanization. In 2019, China produced over 4 billion tons of animal manure annually, accounting for approximately 40% of the global total (National Bureau of

Statistics of China, 2020). However, only about 40% of the manure is returned to croplands. There has been ample research in China on the impact of enhancing manure recycling on soil acidification (Cai et al., 2021) and on reducing N losses (Wang et al., 2019). However, there is yet limited research on assessing the optimal percentage of mineral N fertilizer, manure, and, if necessary, liming application to simultaneously mitigate soil acidification and minimize N and P losses. Given the agronomic and environmental challenges agriculture has to face, the nutrients use efficiency in China has to increase. Optimizing manure, fertilizer and lime has certainly potential as illustrated for a long-term experiment (Xu et al., 2023).

The goal of this study is to assess the optimal rate of fertilizer and manure inputs across all 31 provinces in China in view of crop nutrient demands, while minimizing P losses considering the soil P status (soil fertility), N losses to air and water (air and water quality) and soil acidification (soil quality). To that end, we first examined fertilizer use efficiency and soil acidification under current nutrient management (mineral fertilizer and manure) in 2015. The optimal amount is then derived by calculating the required P, N and BC input to fulfil the crop P, N and BC demand, while accounting for the (i) needed extra P or less P depending on the soil P status, (ii) extra N based due to unavoidable N losses at an optimal NUE and (iii) extra BC to counteract BC leaching induced by enhanced NO_3- leaching and the leaching of sulphate (SO_4^{2-}) and bicarbonate (HCO_3^-). By comparing both situations, we assessed the potential for improved nutrient management strategies that ensure food security while preventing soil acidification and environmental quality.

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4.2 Method and Materials

4.2.1 Overall framework to assess impacts of current and optimal fertilizer management on nutrient losses and soil acidification rates

The study area in this research included 31 provinces of China. Impacts of current fertilizer and manure management on nutrients (N and P) losses and soil acidification rates, was calculated from the balance of the elements ammonium (NH_4^+), nitrate (NO_3^-), base cations (BC: Ca^{2+}, Mg^{2+}, Na^+, K^+), bicarbonate (HCO_3^-), sulphate (SO_4^{2-}), phosphate ($H_2PO_4^-$) and chloride (Cl^-) by assessing the inputs by fertilizer and manure, atmospheric deposition, fixation (only for N), and the outputs by crop uptake, soil accumulation and leaching to groundwater, as described in detail in 4.2.2 and all the data for the calculation is given in **Table 4.1**. In the current situation (year 2015, indicated as business as usual, BAU), the inputs by fertilizer and manure were based on national statistics, with the amount of manure that being recycled set at 30% of the total production of manure in each province, except for the provinces with many grazing animals, i.e.

Xizang, Inner Monglia, Qinghai, Xinjiang, Gansu and Ningxia where it has been set at 10% (Zhu, 2018).

The optimal manure allocation, in combination with mineral fertilizer, was derived by assessing (i) P inputs that are appropriate in view of the soil P status (e.g. being equal to crop demand at medium soil P status, implying no soil P surplus), (ii) N inputs that are balanced with the crop N demand while using an optimized NUE (thus limiting N losses to water) and (iii) BC inputs that avoid soil acidification. More specifically, nutrient inputs and surpluses and soil acidification rates at optimal fertilizer and manure application management in each province in China were calculated as follows:

1. *Quantify the optimal P input by manure and fertilizer in different provinces*
   The optimal total P input was calculated on the basis of the crop P demand multiplied by a factor that depended on the soil P status, based on the soil Olsen-P concentration. The used fractions (frP_{demand}) were derived as a function of the soil Olsen-P status, distinguishing five P status classes, varying from "Very high" for Olsen-P values > 40 mg kg^{-1} to "Very low" for Olsen-P values < 7 mg kg^{-1}, based on the approach of Li et al. (2011a), as given in **Table S4.1**. Based on data (N = 222,907) on the spatial variation in soil Olsen-P over China, we assessed the fraction of sites in the various P status classes, in each province by assuming that each site represents a similar area. Results of the average frP_{demand} for each province thus calculated is given in **Table 4.2**. We used manure P to fulfil the P requirement and only applied P fertilizer when the potential amount of manure P, assuming 100% recycling, could not meet the required P input in each province. Manure import or export to and from provinces was not included.
2. *Quantify the optimal N input by mineral fertilizer in different provinces*
   The optimal fertilizer N input for crop was estimated based on the crop N demand, corrected by the effective N input by non-fertilizer inputs (inputs by biological N fixation, atmospheric N deposition and manure N input times its availability for N uptake), divided by the NUE of N fertilizer, according to:
   $$N_{fert,opt} = (N_{req} - N_{fix} \times NUE_{fix} - N_{env} \times NUE_{env} - N_{man} \times NUE_{man})/NUE_{opt} \quad (4\text{-}1)$$
   where $N_{fert,opt}$ is optimal fertilizer N input rate (kg ha^{-1}), N_{req} is crop demand N (kg ha^{-1}) estimated based on current yields and N content of different crops; N_{env} and N_{man} is the N input (kg ha^{-1}) from environment (including biological fixation, atmospheric deposition, irrigation, seed) and manure, respectively.

Table 4.1 Available data sources used to assess element inputs and outputs.

Data	Data source
Area cropland per province	National Bureau of Statistics of China (NBSC, http://data.stats.gov.cn/)
N, P, K fertilizer input data per province	National Bureau of Statistics of China (NBSC, http://data.stats.gov.cn/)
Fertilizer composition (N, P, K, Ca, Mg, S, Cl) content	Zhang and Zhang, 2013
Livestock number per province	National Bureau of Statistics of China (NBSC, http://data.stats.gov.cn/)
Excretion rates per animal category for whole of China	Li and Jin, 2011; Jia, 2014
Animal manure recycling ratio (%)	Zhu, 2018
N fixation rates per crop for whole of China	Li and Jin, 2011; Smil, 1999; Giller, 2001; Herridge et al., 2008
Seeding rates per crop for whole of China	Price Office of National Development and Reform Commission
N, P and K inputs by Irrigation per province	Li and Jin, 2011
Area of effective irrigation per province	National Bureau of Statistics of China (NBSC, http://data.stats.gov.cn/)
Deposition per province	Zhu, 2018
Crop sown area and crop yields per province	National Bureau of Statistics of China (NBSC, http://data.stats.gov.cn/)
Element contents N, P, K, Ca, Mg, Na, S, Cl in grains (also used for seeds) and straw per crop for whole of China	Canter for Disease Control and Prevention and Food Security of China (2009); U.S. and International Nutrient Databases (http://www.foodhealth.info/); National Agricultural Technical Extension and Service Centre (1999)
Element contents N, P, K, Ca, Mg, Na, S, Cl, C in manure for whole of China	Zhu, 2018
Ratio of harvest to residue per crop for whole of China	Bi, 2010
NH3 emission fractions per province	Derived from Wang et al., 2021
N leaching fractions per province	Derived from Gao et al., 2016 and Velthof et al., 2009
CO2 pressure	De Vries and Breeuwsma, 1986; Greenway et al., 2006
Precipitation and potential evapotranspiration	RESDC (Resource and Environment Science and Data Center)
P-Olsen content	Zhu, 2018
SOM content	RESDC (Resource and Environmental Science and Data Center)
Clay content	RESDC (Resource and Environmental Science and Data Center)

Table 4.2 Average soil properties (SOM, P-Olsen and clay content), precipitation surplus (PS), CO_2 pressure (pCO2) and parameters affecting, N losses to air and water ($fr_{NH3\ emission}$ and $fr_{N\ leaching}$), soil acidification ($fr_{calcareous\ soil}$ and fr_{paddy}) and required P inputs ($fr_{Pdemand}$) for 31 provinces in China. Note that the soil properties are averages per province and detailed information on the variation within a province is used to assess the fraction of SOM, P-Olsen and clay in different classes (see SI4).

Province	SOM	Olsen-P	clay	PS	*p* CO2	*fr* NH_3 emission	*fr* N leaching	*fr* calcareous soil	*fr* *paddy*	*fr* P_{demand}
	$g\ kg^{-1}$	$mg\ kg^{-1}$	%	mm	mbar			-		
Anhui	17	17	24	1125	24	0.05	0.65	0.47	0.26	1.2
Beijing	17	59	18	81	15	0.14	0.56	0.97	0.00	0.34
Chongqing	21	12	24	1004	22	0.06	0.63	0.40	0.20	1.0
Fujian	29	44	33	1012	29	0.32	0.44	0.05	0.41	0.72
Gansu	14	16	20	41	15	0.03	0.60	1.00	0.00	0.99
Guangdong	35	26	28	973	30	0.19	0.38	0.02	0.43	0.63
Guangxi	34	19	32	1035	26	0.10	0.48	0.21	0.31	0.98
Guizhou	37	17	30	880	20	0.06	0.50	0.32	0.13	1.1
Hainan	18	8.8	27	1020	27	0.20	0.47	0.02	0.35	1.2
Hebei	19	15	19	86	15	0.04	0.60	0.95	0.01	0.99
Heilongjiang	34	25	23	422	24	0.03	0.34	0.28	0.26	0.59
Henan	18	15	23	280	16	0.07	0.67	0.73	0.04	1.1
Hubei	21	13	24	1236	26	0.07	0.59	0.46	0.30	1.1
Hunan	35	20	28	1372	33	0.07	0.43	0.28	0.51	1.1
Inner Mongolia	17	12	21	578	15	0.04	0.72	0.81	0.01	0.92
Jiangsu	22	20	31	1329	25	0.12	0.60	0.71	0.29	0.95
Jiangxi	27	18	22	634	37	0.03	0.38	0.06	0.62	0.73
Jilin	21	16	22	292	20	0.04	0.54	0.45	0.13	0.68
Liaoning	17	23	19	133	19	0.03	0.37	0.40	0.11	1.1
Ningxia	12	13	18	85	17	0.04	0.60	1.00	0.07	1.0
Qinghai	20	0.0	13	104	15	0.02	0.45	1.00	0.00	1.4
Shaanxi	14	16	19	182	16	0.07	0.60	0.90	0.03	1.1
Shandong	16	25	20	215	15	0.05	0.60	0.70	0.01	0.64
Shanghai	23	46	22	1045	26	0.05	0.48	0.63	0.31	0.35
Shanxi	11	8.5	20	79	15	0.03	0.59	1.00	0.00	1.3
Sichuan	20	11	20	715	22	0.03	0.54	0.59	0.20	1.1
Tianjin	19	29	19	127	17	0.08	0.64	0.98	0.05	0.72
Xinjiang	14	11	16	29	16	0.03	0.64	1.00	0.01	1.3
Xizang	24	13	13	299	15	0.03	0.44	0.93	0.00	1.1
Yunnan	31	17	29	478	20	0.08	0.52	0.29	0.13	1.0
Zhejiang	23	33	30	1158	26	0.12	0.49	0.21	0.32	0.73

NUE_{fix}, NUE_{env}, NUE_{man} and NUE_{opt} is the nitrogen use efficiency (%) of N fixation, other environment input (atmospheric deposition, irrigation, seed), organic manure and mineral fertilizer, respectively, which was assumed to be 90%, 75%, 65% and 65% respectively. The NUE values for deposition and fixation are based on De Vries et al. (2022), while the value for manure and fertilizer are based on Zhu et al. (2023) for upland paddy crops, assuming optimal management practices.

3. *Quantify the soil acidification and liming requirements under optimal N and P input for provinces*

   The soil acidification rate (net H^+ production rate) was quantified by an input-output budget of all relevant cations and anions, including N, P and BC as elaborated in 2.2. based on the current fertilizer and manure inputs (BAU, year 2015) and the optimized inputs (OPT). The calculated soil acidification rates are set equal to required liming rates assuming the application of quicklime (containing 99% CaO) (Xu et al., 2023).

4.2.2 Net soil acidification rates calculation

Net soil acidification rate (net H^+ production rate) was quantified via a mass balance approach where inputs and losses are quantified for all relevant cations and anions, including ammonium, nitrate, BC, bicarbonate, sulphate, phosphate and chloride. The net H^+ production was divided over various driving process including HCO_3^- leaching, N transformation, crop uptake and net H^+ input, counteracted by H^+ consumed by HCO_3^- input, mainly by manure application, according to (Zhu et al., 2024, Chapter 3):

$$H_{pro,net}{}^{+} = H_{pro,total} = H_{pro,HCO_3}{}^{-+} + H_{pro,N}{}^{+} + H_{pro,uptake}{}^{+} + H_{pro,H}{}^{+} - H_{con,HCO_3}{}^{-+} \quad (4\text{-}2)$$

Natural acidification

The H^+ production by natural soil acidification due to *HCO_3^-* leaching ($H_{pro,\ HCO3-}{}^{+}$) was calculated as:

$$H_{pro,HCO_3}{}^{-+} = HCO_{3_{le}}{}^{-} \quad (4\text{-}3)$$

where $HCO_{3_{le}}{}^{-}$ represent the leaching of HCO_3^-.

N transformations

The total H^+ production from N transformations ($H_{pro,\ N}{}^{+}$) was calculated as the difference between the inputs and the leaching of NH_4^+ and NO_3^+ (De Vries et al., 1987):

$$H_{pro,N}{}^{+} = (\mathrm{NH}_{4_{\mathrm{in}}}{}^{+} - \mathrm{NH}_{4_{\mathrm{le}}}{}^{+}) + (\mathrm{NO}_{3_{\mathrm{le}}}{}^{-} - \mathrm{NO}_{3_{\mathrm{in}}}{}^{-}) \quad (4\text{-}4)$$

where, NH_{4in}^+ and NO_{3in}^- represents the input of ammonium and nitrate from fertilizer and manure, atmospheric deposition and biological fixation, and NH_{4le}^+ and NO_{3le}^- represents the leaching flux outside the rooting zone. To gain insight in the role of N fertilizers and manure, a distinction was made by the input of and derived leaching of both N compounds from mineral fertilizer and manure. Assuming full nitrification, NH_{4le}^+ can be neglected, while in case of manure application, the acidification induced by N application can be simplified to manure N induced NO_3^- leaching since the input of NH_4^+ and NO_3^- does not need to be accounted (N enters the soil as organic N).

Crop uptake

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

$$H_{pro,uptake}{}^{+} = \mathrm{BC}_{\mathrm{uptake}} - An_{\mathrm{uptake}} \tag{4-5}$$

where BC_{uptake} represents the uptake of Ca^{2+}, Mg^{2+}, K^+ and Na^+ and the removal of major anions (An) 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 are assumed to be negligible (Xu et al., 2021).

Net H^+ input

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

$$H_{pro,H}{}^{+} = H_{in}{}^{+} - H_{le}{}^{+} \tag{4-6}$$

where H_{in}^+ and H_{le}^+ represent the input and leaching of H^+, respectively. The input of H^+ was neglected. The total leaching of H^+ was estimated based on soil pH (see details in 2.4.2).

HCO_3^- input

The proton production by natural and anthropogenic causes can, however, be counteracted due to, mainly human induced, HCO_3^- input (HCO_{3in}^-). Atmospheric deposition of HCO_{3in}^- is mostly negligible, but substantial HCO_{3in}^- inputs can come from manure and from alkaline mineral fertilizers, such as calcium phosphate.. The total HCO_{3in}^- was derived from the difference of cations and anions inputs (following charge balance principles) as:

$$H_{con,HCO_3^-}{}^{+} = HCO_{3}{}_{in}^{-} = H_{in}^{+} + NH_{4}{}_{in}^{+} + BC_{in} - SO_{4}{}_{in}^{2-} - H_2PO_{4}{}_{in}^{-} - Cl_{in}^{-} - NO_{3}{}_{in}^{-} \tag{4-7}$$

When manure is the dominant HCO_3^- input and then the equation can be simplified since (i) the input of NH_4^+ and NO_3^- does not need to be accounted for since N enters the soil as organic N and (ii) the H+ input by manure is negligible due to the high pH, implying that:

$$H_{con,HCO_3^-}^{+} = HCO_{3\,in}^{-} = BC_{in} - SO_{4\,in}^{2-} - H_2PO_{4\,in}^{-} - Cl_{in}^{-} \quad (4\text{-}8)$$

4.2.3 Data needs and data sources for assessing elements input and output

All data required for use in the calculation are given in **Table 4.1**, including data to asses inputs by fertilizer and manure, fixation, deposition, irrigation, and seeds and outputs by crop uptake and leaching, including climate data and soil properties. 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 S4.2**.

4.2.3.1 Element inputs

Element inputs include mineral fertilizer, manure, fixation (N only), atmospheric deposition, irrigation and seeds as discussed below.

Mineral fertilizer

The data of N, P and K fertilizer consumption in each province in 2015 came from the National Bureau of Statistics of China (NBSC, http://data.stats.gov.cn/), splitting NPK compound fertilizers into N, P_2O_5, K_2O using a ratio of 1:1:1 (Liu, 2017). The total ion input was calculated based on the consumption rate and composition of mineral fertilizers (Zhang and Zhang, 2013**)**. For mineral N fertilizer, the fertilizer type for NH_4^+ and NO_3^- input including NO_3^--N, NH_4^+-N and Urea. We split Urea-N into 50% NH_4^+ and 50% NO_3^- (Zeng et al., 2017). For K fertilizers, we assumed that all K was applied as potassium chloride (KCl), which accounts for more than 95% of the total K consumption (Wang, 2009). For other ions input by mineral fertilizer, sulphate, calcium, magnesium, bicarbonate and chloride inputs were calculated from the rates of N and P and K fertilizers per fertilizer type; SO_4^{2-}, HCO_3^- and Cl^- inputs by fertilizer were derived from fractions of $(NH_4)_2SO_4$, NH_4HCO_3, NH_4Cl and KCl combined with the total N ***and K consumption. The same approach was used for Ca and Mg in P fertilizer.***

Manure

In this study, only animal manure was considered as organic nutrient source, so excluding human excreta and other plant derived organic products. The nutrient input by animal manure ($X_{m,input}$) was calculated by:

$$X_{m,iuput} = \sum F_m \times N_j \times (X_u \times U_{u,j} \times T_j + X_f \times D_{f,j} \times T_j) \quad (4\text{-}9)$$

where, F_m is the proportion of animal manure applied to the farmland; N is the number of animals; j represents the type of animals (this paper only considers beef and dairy cattle, sheep, pigs and poultry); U_u and D_f represent the daily urine and feces emissions; T is the animal breeding period; X_u and X_f represent the nutrient concentrations of urine and feces, respectively. Here, the number of pigs, cattle, and poultry is the slaughtered number. See **Table S4.3** and **Table S4.4** for the breeding cycles, element concentrations and urine dejection rates.

The potential manure input to cropland was calculated similar to Eq. (4-9) but here the value of F_m was replaced by Fh being the proportion of animal manure produced in housing systems, thus excluding the fraction that is deposited on either grassland or other land uses by free ranging or grazing animals. An average fraction left on soils (pasture) for each animal category for the whole of China was based on FAOSTAT data for N in manure excreted, N manure left on soils/pasture, and the remaining fraction being available for application for cropland. This fraction was higher for grazing animals, i.e. beef and dairy cattle (0.43 on average, varying from 0.23 for dairy cattle up to 0.73 for beef cattle) and sheep (0.83) than for poultry (0.15), and pigs (0; all indoors). Note that the numbers for non-grazing animals refer to free grazing animals. The fraction left on soils (pasture) outside the housing system in each province was assessed by multiplying the China average fraction, with a correction (weight) fraction based on the fraction grassland, which is linked to the probability for grazing (See Table S4.5 for the fractions per province for cattle, sheep, poultry and pigs). For N, we accounted for a 20% loss of the excreted N in housing and manure storage systems, being 15% for NH_3, and 5% for N_2, N_2O and NO_x (Bai et al., 2016). Actually, Bai et al (2016) assume NH_3 emission fractions of 30% for traditional housing systems and 10% for industrial systems, but we used 15% as an attainable value for the future. We assumed no losses for all other nutrients.

N fixation

The N fixation data was collected from published literature and varied with crop type. For soybean, the N fixation amount was set at 80 kg ha^{-1} yr^{-1} (Li and Jin, 2011a; Smil, 1999), for rice at 25 kg ha^{-1} yr^{-1} (Giller, 2001), and for maize and other upland at 5 kg ha^{-1} yr^{-1} (Herridge et al., 2008; Smil, 1999). The amount of N fixation per province can be calculated by multiplying the crop area with the N fixation rate:

$$X_{fix,i} = \sum N_{f,k} \times A_{y,k} \quad (4\text{-}10)$$

where N_f is the amount of N fixed per unit area of crops; k and y represent the crop type and year, respectively; A represents the crop planting area (NBSC).

Atmospheric deposition, irrigation and seeds

The atmospheric deposition was from published literature at provincial level (Zhu et al., 2018). Nutrient inputs by irrigation were only included for N, P and K, while Ca, Mg and S were neglected due to data limitation. Element inputs by irrigation were based on Li and Jin (2011), where N inputs by irrigation in 2008 varied from 2.7 to 4.8 kg N ha^{-1} yr^{-1}, and P and K varied from 0.13 to 0.26 kg P ha^{-1} yr^{-1} and 2.7 to 5.0 kg K ha^{-1} yr^{-1} across provinces. Nutrient inputs by seeds were included by multiplying seeding rates per crop, which are available for the whole of China (see **Table 4.1**), with nutrients element (N, P, K, Ca, Mg and S) concentrations in seeds.

4.2.3.2 Element outputs

Element outputs include crop uptake and losses by NH3 emissions and leaching of bicarbonate, nitrate and of other elements, requiring climate data and soil properties for their assessment as given in **Table 4.2**.

4

Crop uptake

The crop removal of N, P, K, Ca, Mg, Na, Cl and S by harvesting was assessed by multiplying the yield of crop grain and straw (kg ha^{-1} yr^{-1}) with the element concentrations (g kg^{-1}). The yield for main crops were downloaded from NSSC. The used nutrient contents, water contents, and grass-to-grain ratios of each part of the crops are given in **Table S4.6**.

Bicarbonate leaching

The leaching flux of bicarbonate (${HCO_3}_{le}{}^{-}$) was calculated by multiplying the precipitation surplus with an estimated HCO_3^- concentration ($[{HCO_3}^-]$) in non-calcareous and calcareous soil. In non-calcareous soil (soil pH lower than 6.5), HCO_3^- in the soil solution is generated by the dissociation of CO_2 according to:

$$CO_2 + H_2O \rightleftarrows HCO_3^- + H^+ \tag{4-11}$$

The bicarbonate concentration can be calculated from the H^+ concentrations ($[H^+]$) (De Vries and Breeuwsma, 1986) according to:

$$[{HCO_3}^-] = (KCO2 * \ pCO2)/[H^+] \tag{4-12}$$

where KCO_2 is the product of Henry's law constant for the equilibrium between CO_2 in soil water and soil air, and the first dissociation constant of HCO_3^- is set at $10^{-7.8}$ mol^2 l^{-2} bar^{-1} and pCO_2 is the partial CO_2 pressure in the soil.

The $[H^+]$ concentration was calculated by the soil pH. We have spatial distribution soil pH value of all provinces (N = 222,907). We assume that sites with a pH value above 6.5 are calcareous and each sampling point represents a similar area. The ratio that number of points with pH higher than 6.5 and total number of points is then the fraction of calcareous soils in each province and the remainder is the fraction non-calcareous soils (*frca*lcareous soil). The bicarbonate concentration in non-calcareous soil of each province was the mean $[HCO_3^-]$ of all the non-calcareous points. The *pCO2* used in the calculations was derived from the fraction of paddy field and upland field since this value varied in paddy and upland soil. In this study, we set *pCO2* 15 mbar for upland and 50 mbar for paddy soils (De Vries and Breeuwsma, 1986; Greenway et al., 2006). The rice area and the total cropland area of each province was downloaded from NBSC. The ratio that rice area and total cropland area is then the percentage of paddy field (fr_{paddy}) in each province and the remainder is the fraction upland field (fr_{upland}).

Then the *pCO2* for each province was calculated:

$$p_{CO2} = (p_{CO2_{paddy}} * fr_{paddy} + P_{CO2_{upland}} * fr_{upland})/100 \tag{4-13}$$

In calcareous soil, HCO_3^- was produced by dissociation of CO_2 and the dissolution of calcium carbonate ($CaCO_3$) according to:

$$CaCO_3 + CO_2 + H_2O \rightleftarrows 2HCO_3^- + Ca^{2+} \tag{4-14}$$

The $[HCO_3^-]$ was here calculated as (De Vries and Breeuwsma, 1986):

$$\log([HCO_3^-]) = -1.94 + log(pCO2)/3\ ) \tag{4-15}$$

Nitrate leaching

Nitrate leaching ($NO_3^-{}_{le}$) was calculated as a fraction of soil N surplus, defined as the difference between the N inputs (fertilizer, deposition and fixation) and output (crop uptake and ammonium emission). We assumed that soil ammonium N is completely nitrified in croplands, and that thus all leached N is NO_3^-. $NO_3^-{}_{le}$ was calculated as：

$$NO_{3_{le}}^{\ -} = \left(N_{in} - N_{uptake} - N_{\text{ammonia emission}}\right) \times fr_{le} \tag{4-16}$$

where, N_{in}, N_{uptake} and $N_{\text{ammonia emission}}$ represent total N input (fertilizer and manure, deposition and fixation), N removed by crop harvests, and N loss by ammonia emission, respectively. fr_{le} is the fraction of N leaching from N surplus.

The ammonia emission rate ($N_{\text{ammonia emission}}$) was calculated as function of the total N application rate, clay content and mean annual temperature following the procedure from Wang et al. (2021). The data on soil clay content were taken from RESDC (Resource and

Environmental Science and Data Center) at a resolution of 30 arc-second (about 1 km×1 km at the equator). The mean clay content per province was set equal to the mean of all data points within each province. More details are given in the supplementary Text. The ammonia emission fractions per province thus derived are given in **Table 4.2.**

The fraction of N leaching, $frN_{leaching}$, was calculated as function of soil properties (clay, Soil Organic Carbon), climate data (temperature, precipitation) and irrigation for each provinces, based on an approach developed by Velthof et al. (2009) and adapted based on Gao et al. (2016) for observed N leaching rates in China. More details are given in the supplementary Text. The N leaching fractions per province thus derived are given in **Table 4.2**.

Leaching of other elements

$H_2PO_4^-{}_{le}$ was neglected due to strong $H_2PO_4^-$ adsorption to the soil (Hao et al., 2022; Hao et al., 2018). $SO_4^{2-}{}_{le}$ was calculated by SO_4^{2-} input minus SO_4^{2-} uptake, as we assumed negligible SO_4^{2-} adsorption. And we assumed that there was no Cl^- adsorption in the soil (Hao et al., 2022), which means $Cl^-{}_{le}$ is equal to the surplus of Cl^-, being the difference between Cl^- input and Cl^- uptake.

Based on the charge balance, BC_{le} is calculated by the total anions minus H^+ in the leachate:

$$BC_{le} = {NO_3}_{le}^{\ -} + Cl_{le}^{\ -} + {SO_4}_{le}^{\ 2-} + H_2{PO_4}_{le}^{\ -} + {HCO_3}_{le}^{\ -} - H_{le}^{\ +} \quad (4\text{-}17)$$

where H^+ leaching ($H_{le}^{\ +}$) was calculated by multiplying H^+ concentrations ([H]) in leachates, which was estimated based on soil pH and the precipitation surplus.

The precipitation surplus (PS), being the water flux leaving the rootzone (in $m^3\ ha^{-1}\ yr^{-1}$) was calculated as the sum of precipitation (P) and irrigation (I) minus and actual evapotranspiration, ET (surface runoff was ignored):

$$PS = P + I - ET \quad (4\text{-}18)$$

where actual evapotranspiration (ET) stands for the sum of interception (Ei), soil evaporation (Es) and transpiration (Et), and calculated according to the procedures outlined in Zhang et al. (2001) after De Vries & McLaughlin (2013). These authors developed the following relationship between the actual evapotranspiration at catchment scales and both precipitation and potential evapotranspiration:

$$ET/P = (1 + w \cdot Eo/P)/(1 + w \cdot Eo/P + (Eo/P)^{-1}) \quad (4\text{-}19)$$

where Eo stands for potential evapotranspiration, and w is a fitted plant available water coefficient, which represents the difference in the way in which plants turn rainfall into evapotranspiration. The w was set with 0.8 for crops (Zhang et al., 2001). Data of precipitation (P, mm) and potential evapotranspiration (Eo, mm) were downloaded from Resource and

Environment Science and Data Center (https://www.resdc.cn). We used a fixed irrigation values for the paddy soils, the mean irrigation amounts were 1026 and 736 mm in the northern and southern China, respectively (He et al., 2020).

4.3 Results

4.3.1 Current and optimal manure and fertilizer nutrient inputs, and related lime requirements for China

The nutrients inputs of N, P and base cations input from mineral fertilizer, manure and the lime requirements under current and optimal management for the whole of China are shown in **Table 4.3**. The calculated current total N input by fertilizer and manure for China is 35 Mton N yr^{-1}, of which 89% is fertilizer (31 Mton N yr^{-1}) and 11% is manure (3.8 Mton N yr^{-1}). For P, the total input is 7.9 Mton P yr^{-1}, of which 87% is fertilizer (6.9 Mton P yr^{-1}) and 13% is manure (1.0 Mton P yr^{-1}). Balanced fertilization, combined with an optimized fertilizer and manure input could reduce the total inputs with 48% for N and with 70% for P, while increasing the BC input with 12% on average, due to a change in the ratio of fertilizer and manure. The N, P, and BC input rates from mineral fertilizers decreased by 61%, 93% and 71% respectively, while the N, P, and BC input from manure increased by 37%, 46%, and 46% respectively. Using a total cropland area for China of 167 Mha, the average current P input over China was calculated as 47 kg P ha^{-1}, divided over 41 kg P ha^{-1} mineral P fertilizer and 6.2 kg P ha^{-1} manure while this was 15 kg P ha^{-1}, divided over 2.8 kg P ha^{-1} mineral P fertilizer and 12 kg P ha^{-1} manure in the optimal situation (**Table S4.7**). The average current N input over China was calculated to be 236 kg N ha^{-1}, divided over 203 kg N ha^{-1} mineral N fertilizer and 33 kg N ha^{-1} manure while this was 93 kg N ha^{-1}, divided over 58 kg N ha^{-1} mineral N fertilizer and 35 kg N ha^{-1} manure in the optimal situation (**Table S4.8**).

The potential production of manure N and manure P after correction for gaseous N losses in China was around 1.4 times higher than the required N and P for crop production, implying an optimal manure recycling percentage near 69% as compared to a current value near 37% when all manure would be available for cropland application (see **Table 4.3 and S4.7**). When corrected for manure deposited outside the stable and even if the full P demand is fulfilled with manure, approximately 30% of the manure cannot be recycled if one wants to avoid unwanted P accumulation. To avoid soil acidification in the whole of China there remains a need for 2664 kton lime yr^{-1}. Compared with the current situation, the lime requirement reduced by 85%.

Table 4.3 Nitrogen (N), phosphorus (P) and base cation (BC) input from mineral fertilizer, manure, and lime under current and optimal management for the whole of China (kton yr^{-1} for N and P and 106 keq yr^{-1} for BC) and the potential N and P available as manure for cropland, accounting for grazing.

Fertilizer	N input		Potential	P input		Potential	BC input		Lime input	
Types	Current	Optimal	manure N	Current	Optimal	manure P	Current	Optimal	Current	Optimal
	kton yr^{-1}						10^6 keq yr^{-1}		kton yr^{-1}	
Mineral Fertilizer	30868	11944	-	6847	460	-	342	100	-	-
Manure[1]	3054	6033	7641	1035	1922	2788	403	750	-	-
Lime	-	-	-	-	-	-	-	-	17959	2664
Total	33922	17977		7882	2382		745	850	17959	2664

Note: The calculated manure recycling percentages equal 40% for N and 37% for P for the current situation and 79% for N and 69% for P for the optimal situation. The difference in N and P is due to different N/P ratios in the recycled manure. These inputs per hectare can be derived by using a total cropland area for China of 166829 kha. This means that all numbers need to be divided by approximately 167 Mha to get input data per ha and year.

4

4.3.2 Variation in current and optimal manure and fertilizer nutrient inputs among provinces

Phosphorus The phosphorus input from fertilizer and manure, and crop P demand based on soil Olsen P for each province of China in current and optimal situation are shown in **Fig. 4.1** and **Table S4.7**.

Under current situation (BAU), total P input by mineral fertilizer and manure ranged from 17 to 78 kg ha^{-1}, of which mineral P fertilizer accounted for 84%. Most provinces had P fertilizer input ranging between 20-60 kg ha^{-1}, mainly occurring in Central South China. The lowest P fertilizer input was found in Guizhou (< 20 kg P ha^{-1}) while substantially higher fertilizer P inputs were found in Xinjiang, Henan, Hainan, and Fujian (60 – 80 kg P ha^{-1}). The highest manure P input was found in Xizang, with doses higher than 40 kg ha^{-1}, since the manure P production was 475 kton yr^{-1} and the cropland area was only about 230 kha. For other provinces, manure P input was lower than 20 kg ha^{-1}. Under current fertilizer P input, the mean P surplus and P use efficiency (equal to P uptake/P input) was about 36 kg ha^{-1} and 30%.

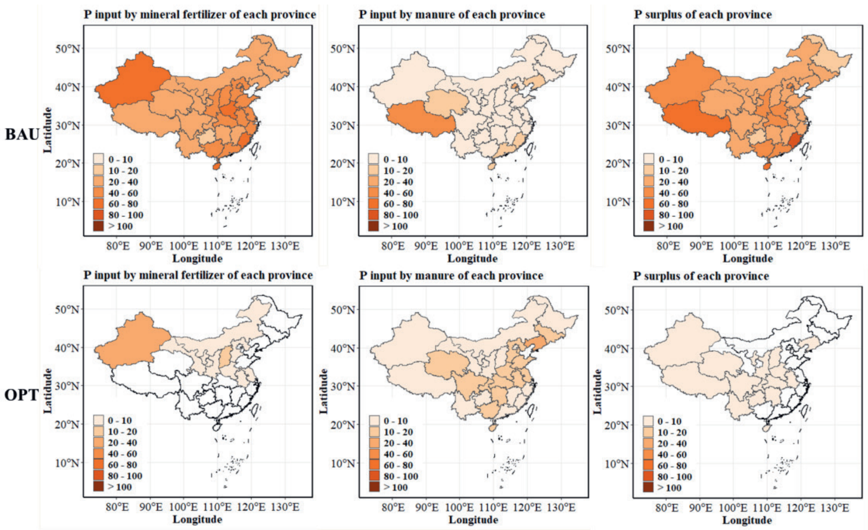

Figure 4.1 Spatial distributions of total phosphorus input by mineral fertilizer, manure and the P surplus (in kg P ha^{-1}) across China under current fertilizer management in 2015 (BAU, top); and optimal fertilizer management (OPT, bottom).

Compared with BAU, total P input via manure and fertilizers of all 31 provinces under optimal situation (OPT) ranged from 4.8 to 27 kg ha^{-1}, of which mineral fertilizer only accounted for 15%. For most provinces, no extra P fertilizer was needed, except for the provinces Anhui, Gansu, Hebei, Henan, Jiangsu, Inner Mongolia, Ningxia, Shaanxi, Shanxi and Xinjiang, where the potential manure P production was not enough for crop demand given the soil P status. Manure P input increased for most provinces except for Beijing, Fujian, Guangdong and Xizang, because of their high soil P status (> 26 mg kg^{-1}) and current high manure P inputs. The decline in fertilizer use resulted in lower P surplus, which ranged from -16 to 7.2 kg ha^{-1}, a negative mean P surplus of -1.3 kg ha^{-1} and a mean PUE of 109%. Provinces with PUE higher than 100% were characterized by soils having high soil Olsen-P contents, implying mining of the soil. For example, the mean soil Olsen-P in Beijing was 59 g kg^{-1} and the calculated PUE was 297%.

Nitrogen The N fertilizer input from fertilizer and manure, and crop N demand in each province of China in current and optimal situation are shown in **Fig. 4.2** and **Table S4.8**.

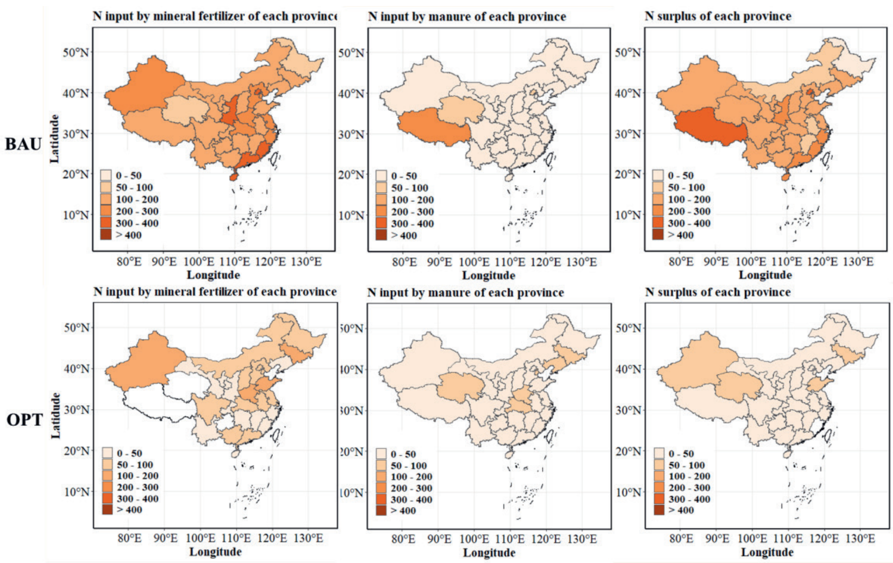

Figure 4.2 Spatial distributions of total nitrogen input by mineral fertilizer, manure and the N surplus (in kg N ha^{-1}) across China under current fertilizer management in 2015 (BAU, top); and optimal fertilizer management (OPT, bottom).

Under current situation (BAU), total N input by mineral fertilizer and manure for all provinces ranged from 88 to 439 kg ha^{-1}, of which mineral N fertilizer accounted for

86%. The highest N fertilizer input was found in provinces Beijing, Fujian, Guangdong, Hainan and Shaanxi with N inputs ranging between 300 and 400 kg N ha^{-1}, while the lowest N inputs were found in Qinghai and Heilongjiang (with doses <100 kg N ha^{-1}). In line with manure P input, the highest manure N input was found in Xizang (200-300 kg ha^{-1}), followed by Qinghai and Beijing (50-100 kg ha^{-1}). In all other provinces the N manure dose was lower than 50 kg N ha^{-1}. High fertilizer N input resulted high N surplus. The N surplus ranged from 26 to 330 kg ha^{-1}, with a mean N surplus of 161 kg ha^{-1} and a mean NUE (equal to N uptake/N input) of 33%.

When optimizing the manure and fertilizer input (OPT), the total N input ranged from 71 to 211 kg ha^{-1}, of which mineral fertilizer accounted for 58%. The fertilizer N input was calculated to match the difference between crop demand and effective manure N inputs. We found that no N fertilizers were needed in provinces Guiyang, Qinghai, and Xizang, indicating that all crop demand can be supplied by manure. Under OPT, the N surplus ranged from -4.7 to 75 kg ha^{-1}, with a mean N surplus of 33 kg ha^{-1} and a mean NUE of 68%.

Base cations: The BC input from mineral fertilizer and manure, and the BC surplus in each province for current and optimal situation are shown in **Fig. 4.3** and **Table S4.9**.

Under current situation (BAU), total BC input by fertilizers and manure ranged from 2.2 to 20 keq ha^{-1}, of which mineral BC fertilizer accounted for 44%. For most provinces, the BC input via fertilizers was lower than 2 keq ha^{-1}, expect for provinces Beijing, Fujian, Guangdong, Guangxi, Hainan, Henan and Shaanxi where 2 to 6 keq BC ha^{-1} were supplied. Similar to the situation for the nutrients, the highest manure BC input was found in Xizang (19 keq BC ha^{-1}), followed by Beijing, Fujian, Qinghai, and Hainan (4-12 keq BC ha^{-1}). The BC surplus ranged from -2.9 to 20 keq ha^{-1} and a mean BC surplus of 3.3 keq ha^{-1}. On average about 48% of the BC inputs were taken up by crops.

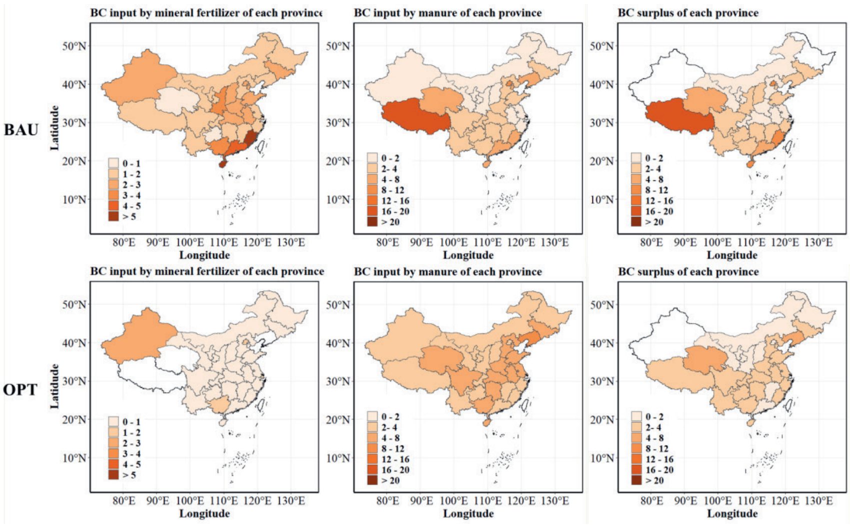

Figure 4.3 Spatial distributions of base cations (BC) input by mineral fertilizer, manure and BC surplus (in keq BC ha-1) across China under current fertilizer management in 2015 (BAU, top); and optimal fertilizer management (OPT, bottom).

Under optimal situation, total BC input by fertilizer and manure of all provinces ranged from 2.3 keq ha^{-1} to 8.5 keq ha^{-1}, of which mineral fertilizer accounted for 14 %. The BC input via fertilizers was lower than 1 keq ha^{-1} in most provinces except for Xinjiang (2.0 keq ha^{-1}) or even zero in the provinces Liaoning, Qinghai and Xizang. The provinces with manure BC input higher than 4 keq ha^{-1} were mainly found in Southern and Central South China. Under OPT, the BC surplus ranged from -1.8 keq to 5.7 keq ha^{-1} and a mean BC surplus of 2.4 keq ha^{-1}. Approximately 64% of the added BC was taken up by crop.

4.3.3 Variation in current and optimal lime requirements and manure recycling rate among provinces

The soil acidification rates and desired lime applications in each province of China for the current and optimal situation are shown in **Fig. 4.4** and **Table S4.10**. Under current situation, net soil acidification ranged from -2.6 to 16 keq ha^{-1} yr^{-1}, with a mean value of 9.3 keq ha^{-1} yr^{-1}. A negative acid production rate was found only in Xizang, and the highest net acid production rate was found in Shaanxi. Most provinces had a net acid rate between 5 and 15 keq ha^{-1} yr^{-1}. The dominating acid producing process was N transformation, accounting for 74% of net acid production rate, followed by crop uptake

(19%) and bicarbonate leaching (8.5%). The lime needed to counteract this soil acidification rate ranged between 0.0 and 188 kg ha^{-1}, with a mean value of 109 kg ha^{-1}. Under optimal situation, net soil acidification ranged from -2.6 to 5.0 keq ha^{-1} yr^{-1}, with a mean value of 1.3 keq ha^{-1} yr^{-1}. There was deacidification in 8 provinces, including Fujian, Hainan, Liaoning, Qinghai and Xizang. Under OPT, crop uptake was the dominated H^+ producing process, accounting for 43% of net acid production rate, followed by N transformations (41%) and bicarbonate leaching (19%). The lime needed to counteract soil acidification ranged from 0 to 57 kg ha^{-1}, with a mean value of 18 kg ha^{-1}.

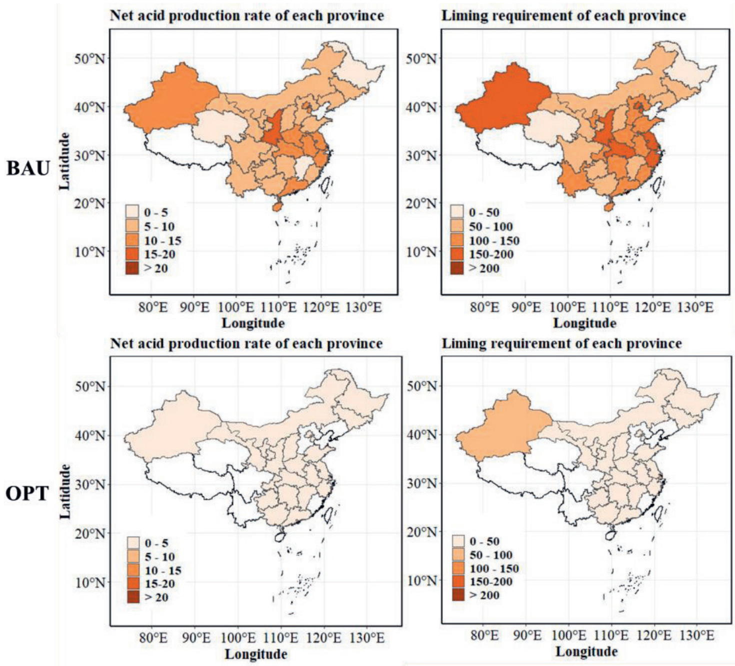

Figure 4.4 Spatial distributions of net acid production rate (in keq ha^{-1}) and lime requirements (in kg ha^{-1}) across China under current fertilizer management in 2015 (BAU, top); and optimal fertilizer management (OPT, bottom).

The variation in optimal manure recycling percentage over the provinces, as compared to the current percentage, rate is given in **Fig. 4.5** (see also **Table S4.7**). After updating the fertilizer and manure management, manure recycling almost doubled for most provinces, from 37% to 69%. In 10 provinces, all the manure needs to be recycled, including Anhui, Gansu, Hebei, Henan, Inner Mongolia, Jiangsu, Ningxia, Shaanxi, Shanxi and Xinjiang.

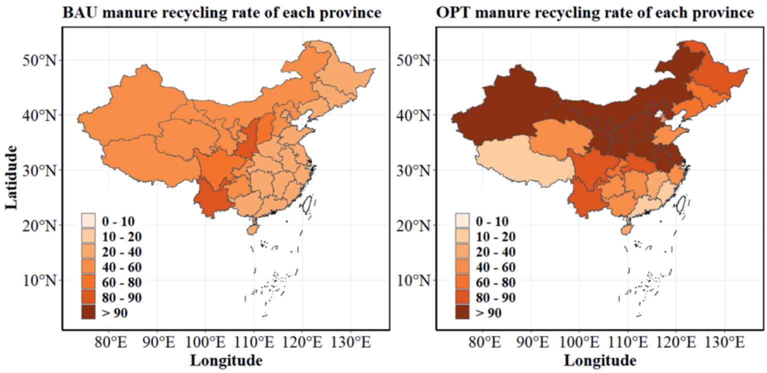

Figure 4.5 Spatial distributions of current and optimal manure recycling percentages (%) across China under current fertilizer management in 2015 (BAU, top); and optimal fertilizer management (OPT, bottom). The manure recycling is expressed as percentage of manure that potentially can be applied on cropland (see Table S7 and S8).

4.4 Discussion

4.4.1 Optimization of manure and fertilizer inputs in China

China is the largest producer and consumer of mineral fertilizers in the world (Zhang et al., 2013b). In 2015, N fertilizer input in cropland was calculated in this study at about 31 million tons, being approximately 30% of the global fertilizer input in 2015 (estimated at 98 million tons for the period 2011-2015) (Zhang et al., 2021). This number for China compares very well with a benchmark estimate made by Zhang et al. (2021) for the year 2015, who estimated the total N fertilizer use at 31 million tons based on 13 different N budget datasets covering 115 countries. The calculated N manure input to cropland of 3.8 million tons was however significantly lower than the benchmark value of 4.8 million tons by Zhang et al (2021) but in terms of total N inputs our calculated value is within 3% of the benchmark (34.7 vs 35.8 million tons). In our calculations, N fertilizer accounted for 89% of total N inputs from fertilizer and manure while the benchmark data by Zhang et al. (2021) lead to 87%. Mineral P fertilizer input in cropland was calculated at 6.8 million tons, accounted for 87% of total P inputs (**Table 4.3**) and being 37% of the global P fertilizer consumption in 2015 (estimate by the International Fertilizer Association). The current N and P use efficiencies were only

33% and 30%, respectively (**Table S4.11**). This implies an excessive fertilizer rate compared to crop nutrient demands, leading to a substantial loss of nutrients to the environment and soil acidification (Dong et al., 2021).

Adapting current nutrient management based on crop nutrient demand and soil properties (balanced fertilization), reduced those N and P inputs by 48% and 70%, respectively (**Table 4.3**). Since surplus N inputs are easily leached into groundwater (Tian and Niu, 2015), improving the balance between crop N demand and input is key to improve the NUE and reduce N losses to air and water (Oscar et al., 2021). The mean NUE increased from 33 to 68% (**Table S4.11**) under optimal fertilizer management. Different from N fertilizer, P is easily fixed in the soil to form insoluble substances, causing less P can be uptake by crops, especially in soils where high levels of aluminium and iron oxides stimulate P adsorption. However, long-term excessive P fertilizer input increases the soluble and plant available P concentration in soil (Li et al., 2011b), increasing the risk of soil P loss to water bodies via surface runoff and leaching (De Vries et al., 2023; Schindler, 2012). Therefore, when adapting the P management given a build-up and maintenance approach, undesired P accumulation is avoided whereas the soil P status remains sufficient to deliver all required P for crop growth (Li et al., 2013; Zhang et al., 2011). When the manure and fertilizer inputs are optimized given soil P status and crop P requirement, China's average PUE is calculated to increase from the current 30% to 109%, implying net mining of soil P. This is largely due to a few provinces (e.g. Beijing) being characterized by excessive soil Olsen-P content (**Table S4.17**).

Considering the much lower P fertilizer requirement based on balanced P demand combined with build-up and maintenance approach, not even all potentially available manure for cropland can be recycled, but only up to 69% (**Table 4.3**). By reducing fertilizer input based on current crop nutrients demand and soil properties of China,

The total manure production of China in 2015 was 3.8 million tons. Due to grazing and free ranging animals, only 70% of that manure is available for application at croplands (**Table S4.7 and S4.8**). High grazing rates are found in several provinces (e.g., Inner Mongolia and Xizang) implying that a large part of the produced manure is left to pasture. Manure has been promoted as a viable alternative to mineral fertilizers. Manure can help supplement nutrient shortages brought on by soil acidity, leading to improved crop yields and soil quality (Cai et al., 2021; Naramabuye and Haynes, 2007; Ye et al., 2019). Replacing fertilizers with manure increased crop yields by 4.4% on average, where this increase was even higher (13%) when contribution of manure to the crop nutrient supply increased up to 50-75% (Xia et al., 2017). Currently, about 37% of the available manure, correcting for grazing, returns to the cropland. This low manure recycling percentage, combined with excessive P inputs in croplands have led to large N leaching losses and to the accumulation of soil P with related P leaching and runoff, which constitutes an eutrophication risk for surface water across China. The spatial variation of optimum P inputs across China reflects the historic P accumulation in soil given the followed build-up and maintenance approach. In the optimized scenario, the manure recycling percentage increased from 37% to 69% (**Fig. 4.5;** see also footnote in **Table 4.3 and Table S4.7 and S4.8**) and fertilizer P is only added where the manure P supply is lower than crop P demand.

4.4.2 Spatial variation in current and optimal nutrient inputs

Phosphorus The long-term application of mineral P fertilizers has resulted in substantial soil P accumulation in some regions of China. Mean soil Olsen-P content of 31 provinces was about 20 mg kg^{-1} (**Table S4.7**), and the highest soil Olsen-P content was found in Beijing (59 mg kg^{-1}). The P fertilizer input rate under BAU varied among 31 provinces, and mineral fertilizer was the main P input, except for Xizang that has a low cropland area, resulting in a high manure application rate of 41 kg P ha^{-1} exceeding the mineral P fertilizer application rate of 36 kg P ha^{-1} (**Fig. 4.1 and Table S4.7**). High fertilizer input was found mainly in Central Southern China, where croplands were characterized by high P surpluses (36 kg ha^{-1}) and low PUE (30%). High P surpluses over the 31 provinces poses a serious threat for aquatic systems, especially for the provinces Beijing, Fujian, Shanghai with soil P contents higher than 44 mg kg^{-1} (**Table S4.7**). The optimal manure recycling percentage, following the build-up and maintenance approach (Bai et al., 2013), varied from 9.4 to 100%, while currently varied from 32 to 71% (Table S7). For most provinces, manure P could fully meet crop P demand except for Anhui, Gansu, Hebei, Henan, Inner Mongolia, Jiangsu, Ningxia, Shaanxi, Shanxi and Xinjiang (**Table S4.7**). Thus, in these 10 provinces, manure are fully recycling under OPT situation. And actually, the mineral P fertilizer in these 10 provinces was lower than 21 kg ha^{-1}. This amount of P fertilizer can be supplied by manure P fertilizer form the nearest provinces.

Nitrogen Excessive N fertilizer application beyond crop demand is a major problem given its impact on air quality, water quality, biodiversity and soil acidification. The N surplus reflects the N input-output balance and has been used to evaluate environmental risks associated with N fertilization (Oenema et al., 2003). In the current situation, the mean total N input across China was about 236 kg ha^{-1} but can increase to values higher than 439 kg ha^{-1} (e.g. in Beijing, **Table S4.8**). Given the averaged N uptake of 92 kg N ha^{-1}, this implies that more than half of the added N was lost to the environment. Optimizing the N dose to crop demand is an effective approach to reduce the N losses. We showed that the optimum total N input decreased to 91 kg ha^{-1} and N surplus decreased to 33 kg ha^{-1}. Furthermore, applying manure to fulfil P requirement increased the manure recycling rate thereby increasing the N inputs up to the crop N demand. In addition to the N supply via fixation and deposition, there was no need for N fertilized in a few provinces, including Guizhou, Qinghai, and Xizang.

Base cations Base cations are the main acid buffering elements when soil pH range between 4 and 7 (Ulrich, 1983). Increasing soil BC content is an effective way to counteract N induced soil acidification (Tian and Niu, 2015). When the manure dose is optimized given crop N and P demand, the total BC input by manure increased from 57 to 64%.

4.4.3 Optimization of lime inputs by reducing sources of soil acidification current and optimal liming rates

After changing the fertilizer and manure inputs, the soil acidification rate decreased and the dominant acid production process changed from N transformations to crop uptake (**Fig. 4.4 and Table S4.10, S4.12, and S4.13**). In the current situation, the mean net soil acidification rate was 9.3 keq ha^{-1} yr^{-1}, where the rate ranged from -0.26 to 16 keq ha^{-1} yr^{-1}. The dominant acid production process was N transformation, accounting for 74% of the total acidification rate, being consistent with previous studies in China (Guo et al., 2010; Wang et al., 2023). The highest acidification rate was found in North and Central South part of China, where N induced leaching is the main pathway driving soil acidification. A negative net acid production rate was found in Xizang due to the high manure inputs.

Many studies have shown that applying appropriate rate and type of N fertilizer is the most effective strategy for reducing soil acidification (Hao et al., 2020; Tian and Niu, 2015; Van Dang et al., 2021). For example, Cai et al. (2021) found that soil acidification was prevented when 40% of the total N input originated from manure. Hence, the combined use of manure N in combination with N fertilizers is an effective strategy to mitigate acidification. This effect can be attributed to the numerous positive effects of manure, since organic matter buffers and stabilises pH (Ye et al., 2019); contains alkaline constituents such as calcium and magnesium, mitigating the acidification processes (Cai et al., 2015); supplies nutrients needed for plant growth, and stimulates microbial activity (Shen et al., 2018; Xiang et al., 2021).

High manure inputs however can also have adverse impacts on the environment in particular when applied on the surface. Nevertheless, with optimum manure recycling rates, soil acidification remains and varied from -2.6 to 5.0 keq ha^{-1}. This implies that liming remains needed to apply to counteract soil acidification. Liming is the most common practice used to neutralize soil acidification by adding carbonates (Goulding, 2016). However, considering the cost for lime application and the negative effect from lime application, for example, soil compaction and nutrient imbalances (Xu et al., 2018), lime was only applied where needed after we optimized manure application rate.

4.5 Conclusions

A systematic analysis was conducted to investigate optimal fertilizer and manure management strategies addressing in view of reducing soil acidification and nutrient (N and P) surpluses over 31 provinces in China. After optimizing manure recycling and using a balanced N and P input approach, accounting for the soil P status, total N and P fertilizer input to cropland over China decreased by 48% and 70% respectively. Most of the nutrient requirement can be fulfilled by manure, thereby reducing the contribution of N fertilizer from 89 to 66% and of P fertilizer use from 87 to 19%. In addition, the average soil acidification rate would decline from 9.3 to 1.3 keq ha^{-1} yr^{-1}, as well the required liming rate. Changing the manure and fertilizer inputs changed the dominant acidification process from nitrogen transformation to crop uptake, indicating that matching N fertilizer inputs with crop N demand is an efficient way to decrease the soil N surplus and associated acid production and to increase the NUE of croplands.

The calculated manure recycling rate increased from a current value near 37% to an optimal value near 69% where the maximum P dose was limited by the crop P demand and soil P status This implies that manure production alone can fulfil crop P demand based on the build-up and maintenance approach, even requiring manure treatment when P demand is leading. Especially in provinces with a high percentage of livestock compared to cropland, the manure needs to be treated and exported to other provinces to avoid adverse environmental impacts of P accumulation. Improving the manure market chain across provinces might theoretically lead to a situation where P fertilizers are abandoned.

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CHAPTER 5

Synthesis

5.1 Background

Excessive nitrogen (N) fertilizer input beyond crop demands leads to low nitrogen use efficiency (NUE) and high soil N surplus, as well as high risk of high leaching of NO_3^- generated by nitrification. Nitrate leaching is one of the main factors driving accelerated soil acidification in China croplands (Guo et al., 2010), along with the leaching of base cations (BC), including exchangeable potassium, calcium, magnesium, and sodium ions (Huang et al., 2015).

Replacing mineral N fertilizer with manure helps in increasing NUE and counteract soil acidification. On the one hand, combining manure and mineral fertilizers can boost crop uptake of inorganic N due to improved soil fertility and crop yields and subsequently improve the NUE. As a result, accumulation and leaching loss of NO_3^- in the soil is reduced, as is the generation of hydrogen ions (H^+) in acidic soil, and soil acidification is mitigated. Manure, on the other hand contains significant amounts of BC, supplying BC to crops and reducing soil acidification. However, the N input by manure can also increase soil acidification by producing H^+ during the mineralization-nitrification chain, and the ultimate effect depends on the BC/N ratio in manure and the fate of added N (how much of it is leached as nitrate). In addition, the input of phosphorus (P) by the application of manure may also causes a P surplus (input in excess of uptake) and in soils with a high Olsen-P content, this increases the risk of eutrophication in water bodies by enhanced P runoff (Materechera and Mkhabela, 2002). Furthermore, the higher crop yield often observed after the addition of manure might decrease the capacity of soils to buffer pH changes given the elevated BC uptake.

Thus, in order to resolve the conflict between food security and environment security, it is necessary to establish efficient combinations of fertilizer and manure management that enhance the N and P use efficiency and reduce the N and P surpluses and losses, thereby also reducing soil acidification. The effect of optimization strategies in practice varies depending on crop types, soil properties, and climate, which means that integration of N fertilizer management with the crop-soil-climate system is expected to enhance NUE and mitigate soil acidification.

For this aim, the main factors affecting NUE and the driving factors of soil acidification were identified through modelling work and input-output budget calculations, using and historical data from 13 long-term experiment sites. To quantify soil acidification rates, inputs and outputs of all major cations and anions were assessed while historical data sets were limited to N, P and K. Consequently, additional data on the composition of C, Ca, Mg, S and Cl in manure and in crops were gathered as well as changes in base cation amounts in the soils. Since, data on nutrient leaching were also lacking in the experiments, a model-based approach was use to estimate those fluxes. The budgets thus derived are used to quantify soil acidification and the contributions of natural and anthropogenic sources under diverse agricultural systems. The work was then expanded to 31 Chinese provinces to assess the impact of current fertilizer management with a focus on nutrient surpluses and soil acidification. My research addresses the following three objectives:

Objective 1: To assess the long-term impact of mineral and organic fertilizer inputs on nitrogen use efficiency for different cropping systems and site conditions (climate: precipitation, temperature and sunshine hours; soil properties: e.g., soil type, contents of soil organic matter, available contents of N, P, and K) in Southern China (Chapter 2)

Objective 2: To quantify soil acidification rates under different fertilization practices and site conditions in Southern China, as well as the contribution of natural and anthropogenic causes (Chapter 3)

Objective 3: To optimize fertilizer, manure and lime management practices to counteract soil acidification and minimize nutrient loss from croplands over China (Chapter 4)

In this synthesis chapter, I summarize the main findings related to each objective, as shown in **Fig 5.1** and discuss the methods employed to answer the scientific questions.

5.2 Nitrogen use efficiency in response to fertilizer management and site conditions

5.2.1 Main finding

In Chapter 2, I used generalized linear regression modelling and clustering algorithms to analyse the effect of fertilizer strategy and site conditions such as crop land use types, soil properties and climate variables on NUE and quantify their importance. NUE exhibited variation under different fertilizer treatments across 13 long-term experiment sites. Lowest NUE was found when only mineral fertilizer was applied.

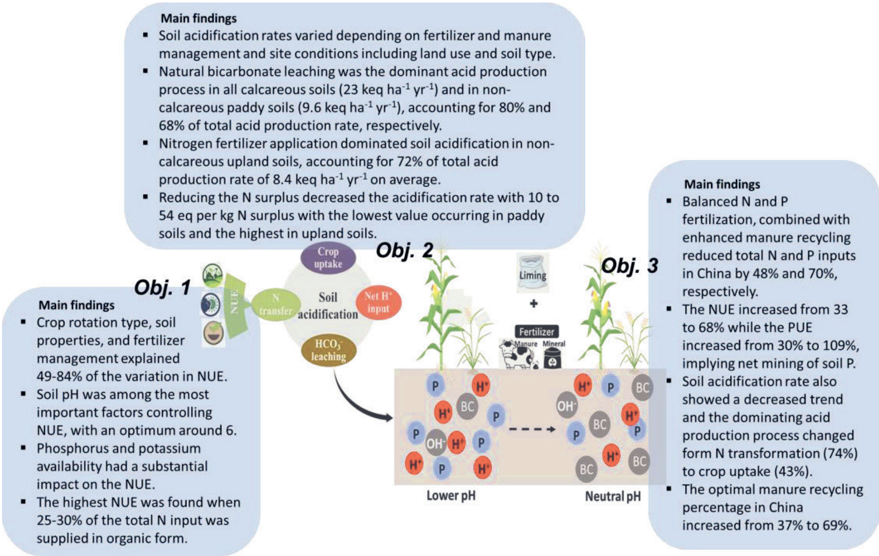

Figure 5.1 Summary of the main finding of this thesis related to the three objectives.

Although there was no significant difference in mean NUE between NPK and NPKM fertilization over nearly 40 years, the NUE under NPKM displayed a significant upward trend. This finding underscores the efficacy of incorporating manure into fertilizer strategies for improving NUE outcomes.

In total 49% of the variation in NUE could be explained with a generalized linear regression model while 84% of the variation in NUE could be explained with a gradient boosted tree regression models by accounting for the variation in crop type, N and P fertilizer inputs, soil properties and climate variables. The main variables controlling NUE across the sites were the pH, total P inputs, available P and K and the duration of the fertilizer regimes applied. The GLM model can easily be used to optimize fertilizer management when one knows the variables included. Hence, the variation in NUE can be estimated via:

$$\begin{aligned}\ln(NUE) = {} & cropsystem_i - 0.38 * TNI - 0.16 * Norgfraction^2 + 0.31 * TPI \\ & - 0.04 * TPI^2 - 0.14 * duration - 0.38 * clay - 0.44 * pH - 0.11 \\ & * pH^2 + 0.26 * pH^3 + 0.27 * \ln(SOC) + 0.25 * \ln(AP) - 0.19 \\ & * \ln(PREg)\end{aligned}$$

with a cropping system dependent intercept being -0.32 for paddy soils, 0.86 for paddy upland soils, and 0.63 for upland soils, where *TNI* is total N input (kg N ha^{-1} yr^{-1}), *Norg fraction* is the ratio of organic N to total N input, *TPI* is total P input (kg P ha^{-1} yr^{-1}), duration is the time period over which the experiment was carried out (years) of, clay is soil clay content (%), SOC is soil organic carbon content (g kg^{-1}), AP is available phosphorus content (mg kg^{-1}), PRE_g is the cumulative precipitation (PRE) during the growing season (mm). Data used in this model were scaled to unit variance. By measuring soil basic information (for example, soil pH, soil available P) and land use, the fertilizer input rate can be calculated for a target NUE by using the equation. The results show that apart from fertilizer inputs and the ratio of organic to total N, the clay content, soil pH and phosphorus availability have a substantial impact on the NUE. The highest NUE was found when 25-30% of the total N input was supplied in organic form.

5.2.2 Drivers of the spatial variation in nitrogen use efficiency over China

The NUE is affected by variables related to land use (crop systems), nutrient management (N and P fertilizer application rate, fertilizer types), soil properties (clay content, soil pH and soil available P content) and climate (precipitation).

Crop systems

Crop rotation affects soil N transformation, as different crops have different preferences for N forms. Paddy crops rice mainly absorbs ammonium nitrogen and absorbs very little nitrate nitrogen, due to limited nitrification under flooded conditions, while upland crops such as wheat and wheat mainly absorb nitrate nitrogen. NUE of rice in this research was generally low compared with upland crops (-0.32 SD units for paddy soils in the equation above), mainly because paddy soil is an anaerobic system under flooding, where the applied N fertilizer is rapidly lost through denitrification.

Nutrient management

NUE is related to N fertilizer application rate, which usually decreases with the increase of NUE. Research conducted at Rothamsted in the long-term so-called “Broadbalk experiment” showed that when the N application rate was increased from 96 kg ha^{-1} to 240 kg ha^{-1}, the NUE of crops decreased from 96% to 69% (Brentrup and Palliere, 2010). Long-term application of N fertilizer leads to the increase of N surplus in cropland, but after exceeding the crop demand and the fixation capacity of soil, the excess N in the soil will be leached, which will reduce the NUE and cause a series of environmental issues, for example soil acidification (Zhang et al., 2022). In other side, when crop N demand is not meet by N input, this implies the risk of soil N mining, and this may result in declining soil fertility and crop yield. Mixed manure and mineral fertilizer application has been proven to be an effective measure to maintain soil fertility and increase crop yield, as well as NUE (Duan et al., 2014; Lu et al., 2020; Ye et al., 2019). A study in west south China found that replacing 75% of mineral fertilizers with manure in short-term trials increased NUE in winter wheat-summer maize crops by about 6% compared to mineral fertilizer alone (Lv et al., 2020). In our research, the highest NUE was found when manure replace 25-30% of mineral fertilizer. The ratio of manure to mineral fertilizer depends on manure types and the experiment duration. At the beginning of experiment (from year 1981 to 1985), the mean NUE under NPKM treatment was lower than the NUE under NPK treatment, while there was no significant difference between NPKM and NPK after 22-38 years experiment (**Chapter 2, Fig. S2.4**).

Soil properties

Except crop management, soil properties also play important role in the change of NUE. The first is the clay content. NUE was negative related to clay content, since soils with high clay tend to have low soil microporosity and poor gas exchange capacity, reducing nutrient use efficiency (Franzluebbers, 2002; You et al., 2023). The results of all experiment show that the NUE increases with an increase in pH up to a pH value around 6 after which its impact stabilized (**Chapter 2, Fig. 2.4a**). Soil pH plays a pivotal role in influencing crop growth by affecting soil health, nutrient availability, and microbial activity (Miller and Kissel, 2010), then directly effect crop growth, as well as crop N uptake and NUE. The experiment sites in this research are all located in southern China, where with the typical red acid soil. The soil here has become more acid due to the excessive N fertilizer application (Cai et al., 2015).

The results also showed that the NUE increased with an increase in soil available P, in particular when the Olsen-P values remain below 30 mg P kg^{-1} (**Chapter 2, Fig. 2.4d**). This positive impact of P availability on NUE emphasizes the interconnection of nutrient dynamics in the soil, especially in southern China with low available soil P contents. Soil available P is easily fixed by Fe, Al oxide in the red acid soil (Dari et al., 2015). P fertilizer application in this research increased soil available P content, this is why there was a higher NUE under treatments with P fertilizer than N fertilizer alone.

Climate

The effect of climate (e.g. precipitation, temperature) on NUE was less than crop management and soil properties. The climate affected NUE by influencing soil N transformation and crop growth. The negative coefficient value (-0.19 SD units) of precipitation in our research implied that NUE decreased with increased precipitation, which is consistent with other studies (Ren et al., 2023a). Temperature is the key factor in regulating the process of soil physicochemical reactions, however, there was no significant influence of temperature on NUE in our research, as these long-term experiment sites are all located in south China with a similar temperature.

5.3 Soil acidification in response to fertilizer management and site conditions

5.3.1 Main findings

In Chapter 3, I used an input-output budget calculation method to quantify the main acid production and consumption processes of soil acidification, then to unravel how the soil acidification rate depends on fertilizer strategy and site conditions such as crop types, with a main difference in (wet) paddy soils and (well-drained) upland soils, soil properties such as clay and SOC content affecting the NUE and N loss fractions and climate variables affecting the precipitation surplus and thereby leaching losses.

Compared with mineral fertilizer application, lower soil acidification rate were found under manure application as expected. However, the dominated soil acid production process varied among soil types (calcareous or non-calcareous) and land use types (paddy or upland). In non-calcareous upland soil, the main driver of soil acidification was the nitrogen (N) transformations driven by the overuse of N and associated nitrate (and bicarbonate) leaching, accounting for 72% of total acid production rate. Reducing the N surplus decreased the acidification rate with 54 eq per kg N surplus in non-calcareous upland soil. In calcareous soil and in non-calcareous paddy soil, the natural bicarbonate leaching was the dominated acid production process, accounting for 80% and 68% of total acid production rate.

5.3.2 Factors affecting soil acidification rates and their implications for crop systems in China

Soil acidification has become more serious due to excessive mineral N fertilizer application (Guo et al., 2010; Zhang et al., 2022), and manure application helped to mitigate soil acidification due to the addition of acid buffering materials (Cai et al., 2020). Our analysis of long-term experiments confirmed higher acidification rate under mineral fertilizer application than treatments with manure (NPKM and M). However, the main acid production process was not always N transformation. The dominated acid produce process varied among soil types and land use types.

In **Table 5.1**, I illustrate how the factors mentioned in section 5.3.1 affect the main acid production processes for different combinations of land use (paddy and upland soils), soils (calcareous and non-calcareous) and N management (recommended N inputs level vs farmers practices) on their contribution to soil acidification rates by (i) natural acidification by HCO_3^-, (ii) N transformation due to N inputs and (iii) crop uptake. The related site conditions include: a rice-rice rotation for paddy soil and a wheat-maize rotation for upland soil; with a precipitation surplus of 500 mm in paddy soils (irrigated) and 250 mm in upland soils (not irrigated); recommended mineral N fertilizer inputs (200 kg N ha^{-1} from Urea) and farmer practices (300 kg N ha^{-1} from Urea) and CO_2 pressures depending on drainage status (15 mbar in upland soils and 50 mbar in paddy soils); we set the target yield per year for paddy soil (rice–rice rotation) at 10 tons yr^{-1} and 13 tons yr^{-1} for upland soil (wheat-maize rotation) including grain and crop residues and used N contents in the harvest parts of rice, wheat and maize according to **Chapter 3, Table S3.6**. This leads to a net crop N removal of 86 kg N ha^{-1} yr^{-1} for rice-rice and 93 kg N ha^{-1} yr^{-1} for wheat-maize, being in line with the average crop N demand in China (see Chapter 4, Table S8). In the calculation, I assumed complete nitrification and the N leaching fraction, determining the fraction of the N surplus that is leached as NO_3^-, is related to soil properties. The N leaching fractions thus derived are 0.14 for the paddy soil and 0.76 for the upland soil based on the updated Velthof and Gao method, described in **Chapter 3** (Gao et al., 2016; Velthof et al., 2009)..

In calcareous soils, the dominant acid production process varied between paddy soil and upland soil. Natural acidification process by bicarbonate (HCO_3^-) leaching was the mainly H^+ production process, accounting for higher than 80% of total acid production rate, in the paddy (rice-rice) crop system. While N transformation was the dominated acid production process in upland (wheat-maize rotation) crop system, accounting for 46% of total acid production rate at an N input of 200 kg N ha^{-1} yr^{-1} and even 59% at an N input of 300 kg N ha^{-1} yr^{-1}. The much higher acid production rate induced by N transformations (nitrification of N followed by nitrate leaching) at higher N inputs is because the additional N is assumed to cause the same crop yield (just unnecessary high N input). The higher acid production due to HCO_3^- leaching in paddy soils as compared to the upland soil is caused by the higher CO_2 pressure (50 vs 15 mbar) and the higher precipitation surplus (500 vs 250 mm), while the lower higher acid production due to N transformation in paddy crop system is due to lower N leaching fraction in paddy soils. This is caused by the wetter circumstances in these soils, due to irrigation, thus favoring denitrification in paddy soil. There was a higher acid production rate by N transformation under farmer practice, due to the higher N application rate with the same crop yield.

Table 5.1 The acid production rate of different processes under given site information in the text.

Crop system	**Soil types**	**N input**	**HCO_3^- leaching**	**N transformations**	**BC uptake**	**Total**
		kg ha^{-1}		**keq ha^{-1}**		
Paddy	Calcareous	200	21	1.9	1.6	25
		300	21	2.8	1.6	25
Upland	Calcareous	200	7.1	7.9	2.0	17
		300	7.1	13	2.0	22
Paddy	Non-calcareous	200	1.3	11	1.6	14
		300	1.3	15	1.6	18
Upland	Non-calcareous	200	0.2	7.9	2.0	10
		300	0.2	13	2.0	15

In non-calcareous soils, N transformation was the main acid production process, accounting for about 80% of total acid production rate under recommended N fertilization and even 85% under farmer practice, due to the higher N application rate with the same crop yield. The low HCO_3^- leaching in non-calcareous soils is mainly because of the lower soil pH (**Chapter 3**), and because the soil acid buffering system changed form calcium carbonate ($CaCO_3$) to base cation exchange (Ulrich, 1983).

5.4 Optimal combinations of manure, fertilizer and lime application rates to reduce nutrient surpluses and soil acidification

5.4.1 Main findings

Chapter 4 predicted the impacts of different fertilizer and manure management options on N and P surpluses and on soil acidification rate to assess the optimal ratio of manure and fertilizer combinations over 31 provinces in China.

Under current fertilizer management in 2015, the high fertilizer input and low manure recycling rate resulted in high soil nutrients surplus and low nutrients use efficiency. By optimizing manure recycling and using a balanced N and P input approach, total N and P fertilizer input to cropland over China decreased by 48% and 70% respectively, and the NUE increased from 33 to 68% and PUE increased from 30 to 109%. The calculated manure recycling rate increased from a current value near 37% to an optimal value near 69%. In addition, the average soil acidification declined from 9.3 to 1.3 keq ha^{-1} yr^{-1}, with a related reduction in required liming rate.

Changing the manure and fertilizer inputs changed the dominant acidification process from nitrogen transformation to crop uptake, indicating that matching N fertilizer inputs with crop N demand is an efficient way to decrease the soil N, P surplus and associated acid production and to increase the nutrients use efficiency of croplands. In this research, we only consider the positive role of manure in mitigating soil acidification and preventing soil P accumulation, the negative side of manure application, for example, the heavy metal input by manure needs also to be considered when apply manure to the soil.

5.4.2 Mitigation strategies to reduce nutrient losses and soil acidification

Mitigation strategies to reduced nutrient losses and soil acidification include management options to increase the NUE, enhanced manure recycling to reduce acidification and addition of lime when manure is not enough. Each come with their own challenges as discussed below.

Challenges to increase the nitrogen use efficiency in China

Optimizing N fertilizer management is the key to improving NUE and reducing N loss. Optimal fertilizer management refers to the application of N fertilizer in balance with crop N demand, using the appropriate amount of N fertilizer, while selecting the appropriate type of N fertilizer, applying the appropriate N fertilizer at the appropriate time, and applying it in the right position, which is internationally known as the '4Rs' method (Snyder et al., 2014). Although the application of available 4R technologies have already made large gains, new technological developments may be needed, since the technology and management practices required to attain the 4Rs differ geographically depending on the local agricultural systems, soil types, climate. From Chapter 4, there were significant differences in NUE among 31 provinces in China, ranged from 15 to 121% (**Chapter 4, Table S4.11**). The highest value was found in Heilongjiang, with fertile soil. NUE higher than 100% means crop uptake N from soil, associated with decreased soil fertility. More N fertilizer needs to apply in this province to keep soil N pool stable. For other province with low NUE, fertilizer N application rate need to decrease to reduce environmental risks.

Challenges to increase manure recycling in China

Combining application of mineral fertilizer and manure in arable farming is an effective way to increase crop yield (Xie et al., 2016b), soil fertility (Du et al., 2020), and mitigate ongoing soil acidification (Cai et al., 2015) and achieve agricultural sustainability due to higher base cation and other nutrients input, reduced fertilizer use and nutrient losses (Bai et al., 2022) and improved plant growth and soil health (Zhang et al., 2020b). The rapid development of livestock has made China the world's largest producer of manure. But the average manure recycling rate in 2015 in China is less than 40%, indicating that more than half of the manure nutrients are lost to the environment. Therefore, the government has released a strategy to improve manure utilization and replace mineral fertilizers with manure,

Due to the large distances between livestock farms and arable farms, mostly being small farms in China, there is a large challenge to enhance manure recycling. On the one hand, relocation of livestock is an option, and it has been estimated to require the relocation of 10 billion animals in China (Bai et al., 2022). The gradual transfer from small holder farm to large holder farm is also a way to increase manure recycling rate in China. On the other hand, improved utilization of manure resources including improved manure storage, manure treatment, and subsidies for the transport of manure is an option to improving the recycling rate of manure. However, at present, farmers prefer to apply manure directly to the soil, ignoring the nutrient loss of manure resources in the process of storage and processing, which is not conducive to the management of manure resources.

Challenges to apply lime in China

When organic manure application does not fully counteract acidification, lime application rate regular intervals is needed to ensure that acidification is not limiting crop production. Liming is a long-established practice to ameliorate soil acidity and improve crop yields (Fageria and Baligar, 2008; Holland et al., 2021) and it is widely used in Europe and the US but its application has rarely been adopted in China and other developing countries (Hijbeek et al., 2021), for both logistic and economic reasons. Ensuring the application of lime thus implies the need for farmer education regarding its benefits and where needed the use of subsidies to ensure proper acidification management.

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Summary

Summary

Excessive nitrogen (N) fertilizer application in China's croplands has led to low nitrogen use efficiency (NUE), leading to enhanced nitrate leaching which is accompanied by soil acidification unless enough base cations are added by manure and/or lime. The use of manure, which contains base cations and HCO_3^-, mitigates the acidifying impact of N fertilizer inputs, but the input of phosphorus (P) may cause unwanted accumulation in soils with a high soil P status.

To assess optimal fertilizer, manure and/or lime management practices in China croplands, it is necessary to quantify how NUEs and soil acidifications rates are affected by different fertilizer and manure management practices under different site conditions. In this thesis, I thus investigated the impacts of nutrient management on NUE and soil acidification rates, accounting for differences in land use, soil properties and climate, followed by an assessment of optimal fertilizer, manure and lime management practices across China. The thesis aims to answer three questions:

1. What are long-term impacts of different mineral fertilizer and manure application practices on the NUE of different cropping systems as a function of site conditions?
2. What is the contribution of natural and human-induced causes of soil acidification rates under different fertilization practices for different site conditions and cropping systems?
3. What is optimal fertilizer, manure and lime management practices to improve NUE and mitigate soil acidification across China?

The thesis contains five chapters:

Chapter 1: General Introduction

In this chapter, I outline the impacts of excessive nitrogen fertilization in China and explain why it leads to low nitrogen use efficiency and enhanced soil acidifications rates, with related adverse impacts on air, soil and water quality. I present a review of current research on the impacts of fertilization on NUE and soil acidifications rates and

identify knowledge gaps for these two topics. Then I elaborate on the main research objectives of my thesis in view of these knowledge gaps.

Chapter2: Long-term impacts of mineral and organic fertilizer inputs on nitrogen use efficiency for different cropping systems and site conditions in Southern China (Published in European Journal of Agronomy)

In this chapter, I analyse historical data from 13 long-term experiment sites with different fertilizer and manure application rates to unravel how the NUE depends on fertilizer and manure application rates and site conditions, including crop rotation, soil properties and climate. Results showed that, the highest NUE was found when 25 to 30% of the total N input was supplied in organic form. Among the site conditions analysed, soil pH was the most important factor controlling NUE with an optimum pH around 6. In addition to pH, an increase in phosphorus availability increased NUE. Crop rotation, soil properties and fertilizer management together explained 46 to 85% of the variation in NUE. Current NUE equalled on average 30% in paddy soils, 39% in upland soils and 42% in paddy upland soils. Optimizing all fertilizer inputs and soil nutrient levels might increase the NUE up to 40-47% in paddy soils, up to 40-77% in upland soils and even up to 40-87% in a paddy upland soils.

Chapter 3: The contribution of natural and anthropogenic causes of on soil acidification rates under different fertilization practices and site conditions (Submitted to Science of The Total Environment)

In this chapter, I use data from the same 13 long-term experimental sites in Southern China to quantify soil acidification rates based on the inputs and outputs of main nutrients, specifically ammonium, nitrate, calcium, magnesium, potassium, sodium, bicarbonate, sulphate, phosphate and chloride by assessing the inputs by fertilizer and manure, atmospheric deposition, fixation, and the outputs by crop uptake, soil accumulation and leaching to groundwater. Combining observation-based estimates of nutrient inputs and nutrient uptake, with model-based estimates of the leaching of those elements, the rates and causes of soil acidification under different management practices (fertilizer rate, types) were quantified. Furthermore, an assessment was made of the impact of management, crop type, soil properties (e.g., soil organic carbon content and clay content) and climate (e.g., precipitation surplus, temperature) on soil acidification rates. The contribution of different causes to total acid production is quantified, including acid production by (i) natural HCO_3^- leaching (ii) human induced N transformations and (iii) crop uptake of cations over anions. The net acid production is quantified by subtracting human induced base cation inputs (mainly by manure) and the resulting soil acidification rate is quantified in terms of soil buffering by base cation release and P adsorption.

Results showed that natural bicarbonate leaching was the dominant acid production process in all calcareous soils (on average 23 keq ha^{-1} yr^{-1}) and in non-calcareous paddy soils (on average 9.6 keq ha^{-1} yr^{-1}), accounting for 80% and 68% of total acid production rate. N transformation was the main driver of soil acidification in non-calcareous upland soils, accounting for 72% of total acid production rate of 8.4 keq ha^{-1} yr^{-1}.

Chapter 4: Variations in optimal fertilizer, manure, and lime management practices to counteract soil acidification and minimize nutrient losses for cropland over China (In preparation)

In this chapter, I present a study in which nutrient (N and P) surpluses and soil acidification rates under current fertilizer and manure management (year 2015) are compared with optimal fertilizer and manure management practices across 31 provinces of China. The optimal fertilizer management was based on balancing the N and P input in view of crop N and P demand while accounting for the soil P status and minimizing soil acidification rates based on crop base cation (BC) demand, while using available manure to satisfy this demand up to a maximum defined by the acceptable P input.

Results showed that under optimal fertilization management, the need for total fertilizer and manure N and P inputs in China decreased by 49% and 70% respectively. More specifically, the N and P inputs from mineral fertilizers decreased by 65% and 93%, respectively, while the N and P inputs from manure increased by 44% and 46%, respectively. The manure recycling percentage increased from 40 to 67%. The reduced nitrate leaching combined with enhanced BC inputs by manure reduced soil acidification rates by 84%, while the dominating acid production process changed from N transformation to crop uptake. Provinces where cropland manure can be fully recycled include Anhui, Henan, Jiangsu, Shaanxi, Shanxi and Xinjiang, requiring manure transport to other provinces, implying the need for an improved manure market chain.

Chapter 5: Synthesis

In this chapter, I summarize the main findings and conclusions of the thesis. I further discussed the impact of site conditions, including crop type, soil properties and climate on NUE and on soil acidification rates, based on the results obtained in the Chapters 2 and 3, respectively. Finally, I discuss the options to increase the NUE and mitigate soil acidification by improved farming practices, including balanced fertilization, and the challenges to enhance manure recycling in China, considering the long distances between livestock farms and cropland.

Supplementary Information

Supplementary information for Chapter 2

The amount of P and K fertilizer inputs is given in following tables.

Table S2.1 Total P inputs (kg N ha^{-1} yr^{-1}) from inorganic and organic sources in 13 long-term experiments.

Sitename	N	M	NM	NK	NKM	NP	NPM	NPK NPK	2NPK	NPKM NPKM	1.5NPKM
S1	--	--	--	--	--	--	--	39	--	39 +50 # 39 +40 ※	--
S2	0	--	--	0	--	39	--	39	79	39 +36 ※	--
S3	--	26 ★ 122 ※★	--	--	--	--	--	46	--	--	--
S4	0	96-365 ※	--	0	--	52	--	52	--	52+(86-256) ※	79 +(129-383) ※
S5	--	128 #	--	--	128 #	--	100+128 #	49	--	100+128 #	--
S6	--	135-231 #	--	--	--	--	--	36	--	27+(34-58) #	--
S7	0	40-52 ※	40-52 ※	--	--	53	53+(40-52) ※	53	--	53+(40-52) ※	--
S8	0	1-13 ※	--	0	--	52-65	--	52-65	--	(52-65) +63 ※	(79-98) + (1-13) ※
S9	--	25-135 #	--	--	-	--	-	36	--	27+(6-34) #	--
S10	0	73-165 ※	73-165 ※	--	--	33	33+(73-165) ※	33	--	33+(73-165) ※	--
S11	--	--	--	0	465 ※	40	--	40	--	--	--
S12	--	--	--	0	--	52	--	52	--	(17-37) + (35-58) ※	--
S13	--	--	--	--	--	--	--	12-24	--	(12-24) +(11-21）#	--

※ pig manure; # cattle manure; ★green fertilizer, Astragalus sinicus.

Table S2.2 Total K inputs (kg K ha^{-1} yr^{-1}) from inorganic and organic sources in 13 long-term experiments.

Sitename	N	M	NM	NK	NKM	NP	NPM	NPK		NPK,	
								NPK	2NPK	NPKM	1.5NPKM
S1	--	--	--	--	--	--	--	112	--	112 +47 # 112 +35 ※	-
S2	0	--	--	125	--	0	--	125	249	125+106 ※	--
S3	--	0-112 ★ 73-185 ※★	--	--	--	--	--	62-174	--	--	--
S4	0	135-313 ※	--	100	--	0	--	100	--	100 +(94-219) ※	150 +(142-328) ※
S5	--	135 #	--	--	176+135 #	--	135 #	88	--	176+135 #	-
S6	--	461-787 #	--	--	--	--	--	68	--	(115-197) #	--
S7	0	118-189 ※	118-189 ※	--	--	0	118-189 ※	100	--	100 +(118-189) ※	--
S8	0	11-229 ※	--	100-125	--	0	--	100-125	--	(100-125) +109 ※	(149-187) +(11-229) ※
S9	--	115-461 #	--	--	-	--	-	69	--	29-115 #	--
S10	0	47-116 ※	47-116 ※	--	--	0	47-116 ※	124	--	124+(47-116) ※	--
S11	--	--	--	100	100+267 ※	0	--	100	--	--	--
S12	--	--	--	249	--	0	--	249	--	(59-162) + (106-247) ※	--
S13	--	--	--	--	--	--	--	112-224	--	(112-224) +(28-56） #	--

※ pig manure; # cattle manure; ★green fertilizer, Astragalus sinicus.

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Frequency distributions of all variables motioned in this paper. The fitted curve is an estimated by Gaussian distribution. The mean, standard error, and the number of observations of each variable are noted. Note the different scales among the graphs.

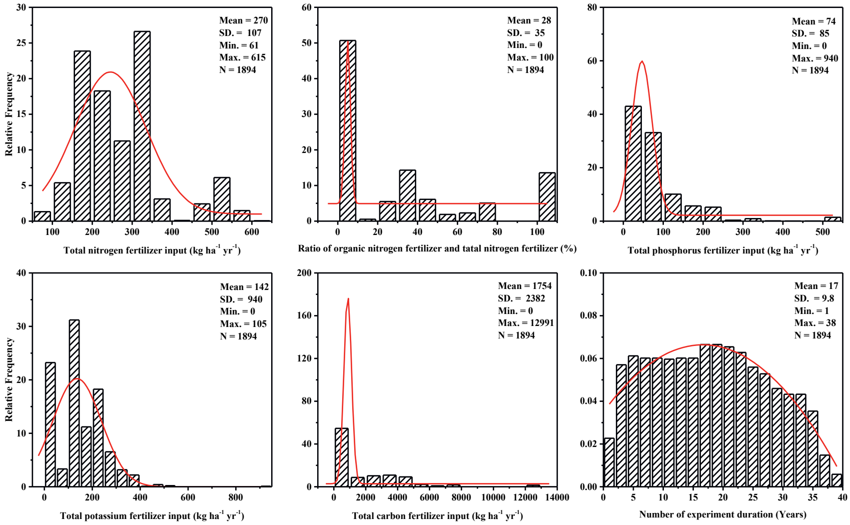

Figure S2.1 Frequency distributions of management factors, including yearly total nitrogen fertilizer input (TNI), ratio of organic to total nitrogen fertilizer input (Ratio), yearly total phosphorus fertilizer input (TPI), yearly total potassium fertilizer input (TKI), yearly total carbon fertilizer input (TCI) and experiment duration (Ysn).

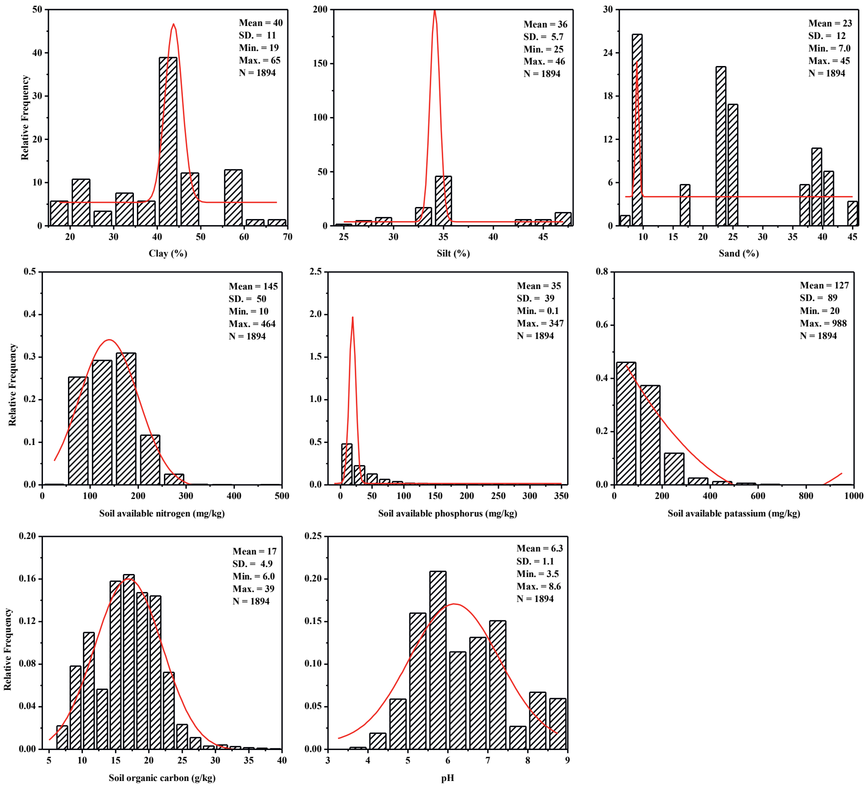

Figure S2.2 Frequency distributions of soil properties, including soil texture (Clay, Silt and Sand content), soil available nitrogen (AN), available phosphorus (AP), available potassium (AK) soil organic carbon (SOC) content and pH.

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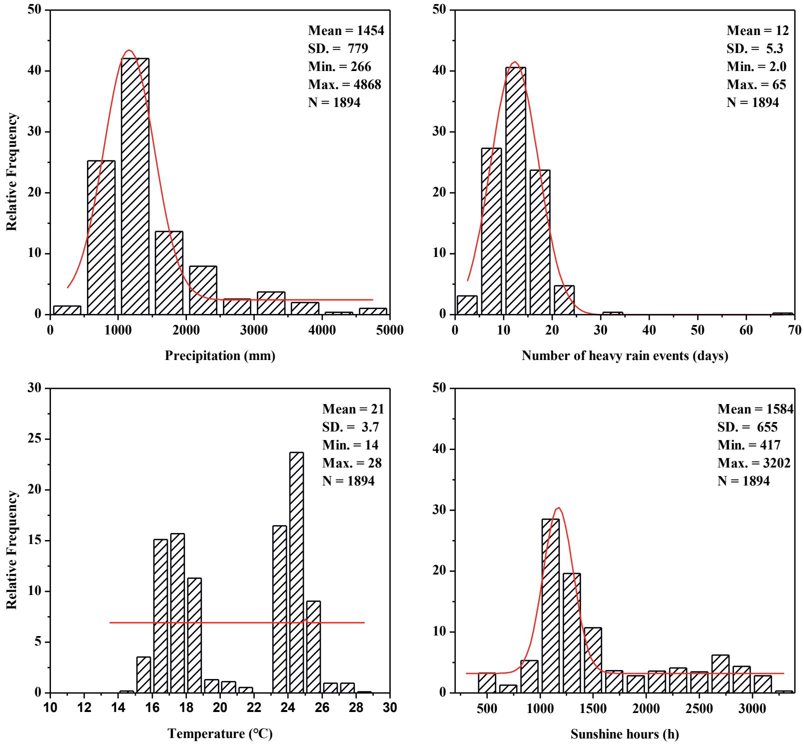

Figure S2.3 Frequency distributions of climate variables, including precipitation (PRE), number of heavy rain events (Daynumber), temperature (TEM) and sunshine hours (SSH) during crop growing season.

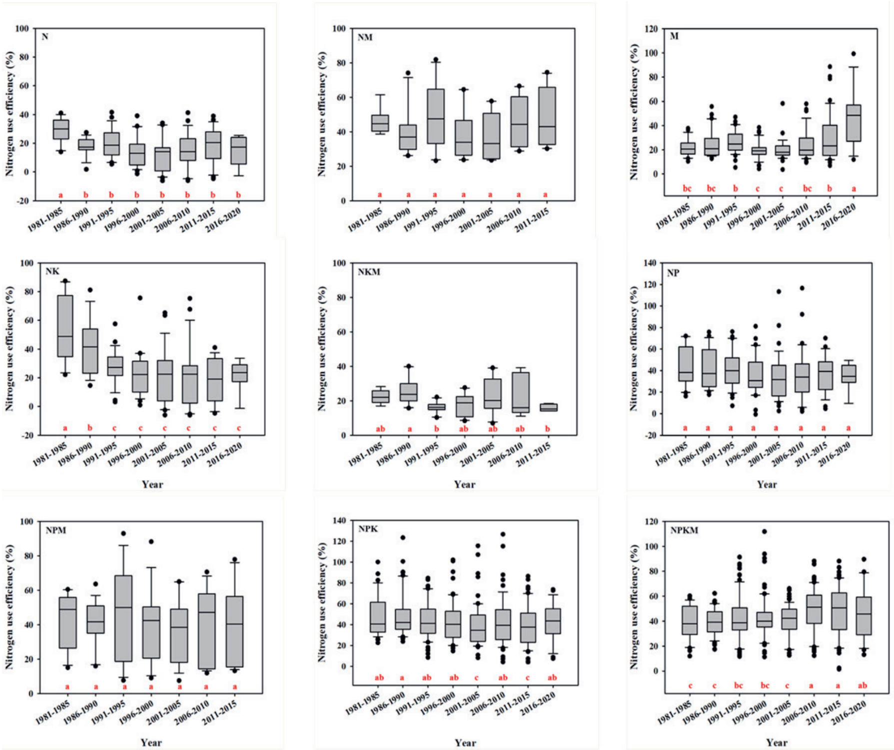

Figure S2.4 Scatterplot of NUE and crop yield under long-term fertilization treatments consisting of combinations of NPKM, where N = nitrogen; P = phosphorus, K = potassium and M = manure for 13 long-term experiment sites.

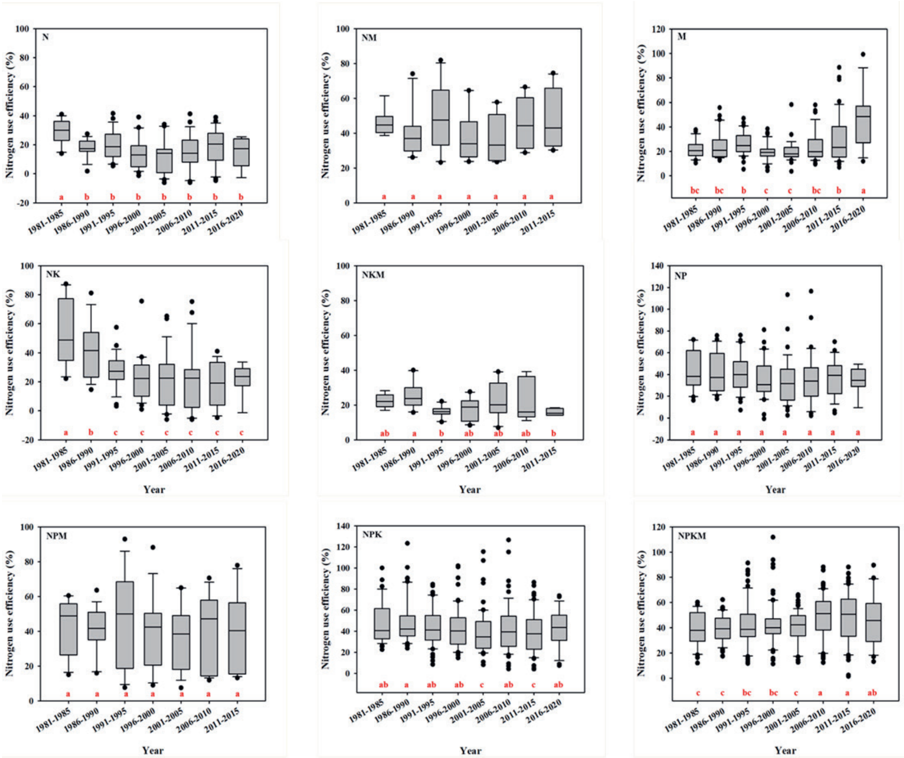

Figure S2.5 Changes in NUE between 1981-2018 under long-term fertilization treatments consisting of combinations of NPKM, where N = nitrogen; P = phosphorus, K = potassium and M = manure.

Figure S2.6 Pearson correlation coefficient matrix of nitrogen use efficiency (NUE), crop yield, crop nitrogen and all site conditions potentially affecting NUE. Abbreviations include precipitation (ln_PRE), sunshine hours (SSH), N uptake (Noutput), the NUE (ln_NUE), the available K (ln_AK) and P (ln_AP), the duration of the experiment (in number of years, Ysn), the available N (ln_AN), the soil organic carbon level (ln_SOC), mean temperature (TEM), the number of days with excessive rainfall during the growing season (Daynumber) and the total inputs via fertilizer and manure for K (TKI), N (TNI) and P (TPI) and the organic N fraction of the total N input (Ratio). Variables that are ln-transformed have a prefix "ln_".

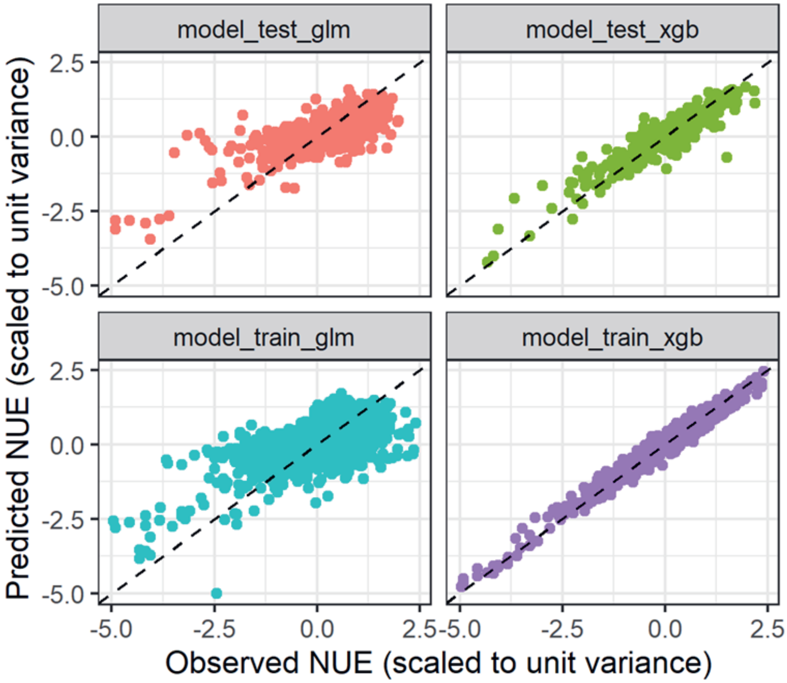

Figure S2.7 Predicted versus observed NUE for for the training (80% of the data, bottom) and the independent test set (20% of the data, top) for both the generalized linear regression model (left) as the XGBoost regression model (right).

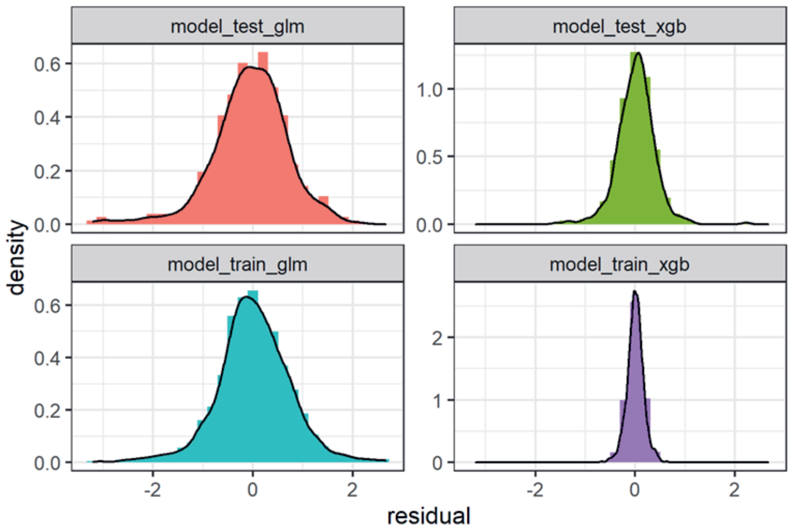

Figure S2.8 Residual histograms for both the generalized linear regression model (left) as the XGBoost regression model (right), applied for the training set (80% of the data, bottom, calibration) and the independent test set (20% of the data, top, validation).

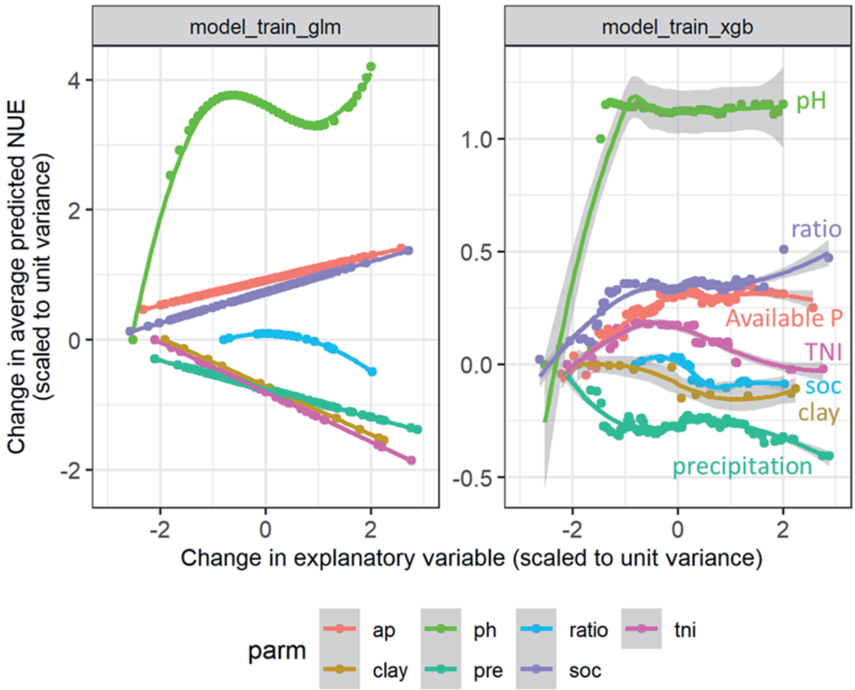

Figure S2.9 Accumulated Local Effect Plots showing the change in average predicted NUE (scaled to unit variance) by a change in one of the top-7 most important variables controlling the NUE (also scaled to unit variance) for both the generalized linear regression (left) and the XGBoost regression model (right).

Summary information for Chapter 3

Supplementary text

Text S3.1 Calculation of sulphate adsorption with an example in Qiyang site

Text S3.2 Calculation of nitrogen leaching fraction

Text S3.3 Calculation of NH_3 emission

Text S3.4 Calculation of HCO_3^- concentration in calcareous soils

Supplementary tables

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Table S3.5 Element contents for different manure type (dry mass)

Table S3.6 Element contents in grain and straw of different crop types

Table S3.7 Annual fluxes for precipitation, evaporation and precipitation surplus for 13 long-term experiment sites

Table S3.8 H^+ production and consumption rate (keq ha^{-1} yr^{-1}) by different source under long-term fertilizer treatments for calcareous experiment

Table S3.9 H^+ production and consumption rate (keq ha^{-1} yr^{-1}) by different source under long-term fertilizer treatments for non-calcareous experiment sites

Supplementary figures

Figure S3.1 The percent of leaching SO_4^{2-} to S surplus in Österström, Risfallet and Tärnsjö sites.

Figure S3.2 Correlation between BC input rate (a) and P input (b) with manure application rate for different manure types and treatments

Figure S3.3 Frequency distribution histograms and scatter-plot matrix of BC fluxes (input, surplus and leaching), other leaching factors and measured soil BC pool change in non-calcareous sites

Supplementary text

Text S3.1: Sulphate adsorption

Sulphate (SO_4^{2-}) adsorption is an important H^+ consumption processes, while due to the lacking observed value, we estimated it based on its input and crop uptake fluxes and the soil properties for different experiments. Firstly, we assumed that the SO_4^{2-} concentration in the soil solution at the beginning of the experiment was in equilibrium with the deposition (without crop grown):

$$[SO_4^{2-}]_{ini} = SO_4^{2-}{}_{,dep} / PS /2000$$

$[SO_4^{2-}]_{ini}$ is the equilibrium SO_4^{2-} concentration (mol L^{-1}), $SO_4^{2-}{}_{,dep}$ is the atmospheric deposition at the beginning of the experiment (eq m^{-2}), PS is precipitation surplus (m) and 2000 is the conversion factor from eq m^{-3} to mol L^{-1} (1 mol SO_4^{2-} equal to 2 eq). Note that this can be lower if the history of S deposition was lower, but the inverse is true when it was higher.

Then, the initial SO_4^{2-} adsorption (Q_0, mol kg^{-1}) was estimated based on an extended Freundlich equation, assuming logarithm of Q is linear correlated with a function of SO_4^{2-} concentration and soil pH (Gustafsson et al., 2015):

$$\log Q_0 = \log K_F + \mathrm{m} \cdot \left(\log[SO_4{}^{2-}]_{ini} \; - \; \mathrm{n} \cdot \mathrm{pH}\right)$$

where K_F is termed the Freundlich coefficient, m and n are non-ideality parameters and pH_{ini} is the initial soil pH, implying that a plot of log Q against $\log[SO_4] \; - \; n \cdot pH$ leads to a straight line with the slope m and the intercept $\log K_F$.

Next, in the following years, the equilibrium SO_4^{2-} concentration was then estimated based on the S surplus (total input minus crop uptake):

$$[SO_4{}^{2-}]_i = (SO_{4,dep,i}^{2-} \; + \; SO_{4,fer,i}^{2-} - \; SO_{4,up,i}^{2-}) / PS_i /2000$$

Where i is the number (≥1) of year after the beginning of the experiment, $_{fer}$ and $_{upt}$ is the fertilizer inputs and crop uptake (eq m^{-2}), respectively. SO_4^{2-} adsorption in year i was then calculated as follows:

$$\log Q_i = \log K_F + \mathrm{m} \cdot \left(\log[SO_4{}^{2-}]_i \; - \; \mathrm{n} \cdot pH_i\right)$$

Finally, the leached S in year i was thus calculated as:

$$SO_{4,le,i}^{2-} = \left(SO_{4,fer,i}^{2-} + SO_{4,dep,i}^{2-} - \; SO_{4,up,i}^{2-}\right) - (Q_i - Q_{i-1}) \times \rho_i \times T \times 2$$

Where ρ_i is soil bulk density (kg m^3) and T is the thickness of soil layer (m), 2 is the conversion factor from mol m^{-2} to eq m^{-2}.

Taking the NPK treatment in Qiyang experiment, Hunan province as an example, we tested the above calculation based on the K_F, m and n values reported by Gustafsson et al. (2015) in Österström, Risfallet and Tärnsjö sites, with similar aluminium oxalate contents (120-265 mmol kg^{-1}) and iron oxalate contents (46-115 mmol kg^{-1}), respectively, since these two properties mainly affect the S adsorption. The results showed that, on average, 95~99% of S surplus was leached among the years (see Figure S3.1). Values >100% indicate that the soil released S due to a decreased adsorption capability with declining pH). Based on these results, we assumed SO_4^{2-} leaching is equal to S (SO_4^{2-}) surplus and that SO_4^{2-} adsorption can be neglected over the whole

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period.

Text S3.2: Calculation of nitrogen leaching fractions

As with MITERRA-EUROPE, the value of nitrogen leaching fraction (frle), is calculated from a maximal leaching fraction and a set of reduction fractions according to Velthof et al. (2019), where the fractions for land use and precipitation surplus have (slightly) been adapted:

f_le= f_(le.max)*f_lu*min(f_p,f_t,f_c)

fle,max = maximum leaching fraction for different soil types

flu = reduction fraction for land use

fp = reduction fraction for precipitation and irrigation

ft = reduction fraction for temperature

fc = reduction fraction for soil organic carbon content

However, the various reduction functions used by Velthof et al. (2009), being applied in many scientific publications on N flows in China (Ma et al., 2010) have been adapted, based on data relationships derived by Gao et al. (2016) for observed N leaching rates in China and site properties.

The following soil type dependent maximum leaching fractions fle,max are used (Gao et al., 2016):

Texture class 1 (Clay <18%): fle,max_{sand} = 1.0

Texture class 2 (18 < Clay <35%): $fle,max_{light\ clay}$ = 0.75

Texture class 3 (>35%): $fle,max_{heavy\ clay}$ = 0.50

Based on Fig. 3 (f) of Gao et al. (2016), we assumed that the higher LR fraction for clay content below 40.8% relates to <18% and make this 1. The lower value LR fraction for clay contents 40.8%, being about 50% of the higher value, was assumed to be linked to 35% clay and we interpolated in between.

The reduction fraction for land use, flu, was set at is 1 for upland, 0.8 for upland-paddy and 0.6 for paddy based on Gao et al. (2016).

Based on Fig. 3 (d) of Gao et al. (2016), the LR fraction for Upland is almost 5 times higher than rice. Assuming that the highest LR fraction for Upland is 1, the value of rice (paddy) would become 0.2, but this seems too low and we made it thus 0.6, while interpolating it for upland-paddy.

Denitrification increases and thus leaching decreases at lower precipitation surplus due to longer residence times allowing enhanced denitrification The reduction fraction for precipitation surplus, fp, is adapted from Velthof et al. based on data on precipitation plus irrigation (P+I) by Gao et al, 2016 according to:

P +I < 500 mm: fp = 0.5

500 mm ≤ P+I < 1500 mm: fp = 0.5 + (P+I-500)*0.0005

P +I ≥ 1500 mm: fp = 1

In Fig. 3 (f) of Gao et al. (2016), the data for P+I were divided into two groups based on P+I higher or lower than 360. This value seems odd. After data collecting from the articles used in Gao et al. (2016). We found the range of P+I >360 mm is 370 to 1850 mm (not including all the lab leaching experiment data). Thus, we assumed that the highest LR fraction for P+I>360 mm relates to > 1500mm, make it 1, below 360 mm is assumed to be linked to 500 mm and this is about 50% of the higher value. And we interpolated in between.

Denitrification increases with increasing temperature and thus leaching decreases. The following reduction fractions for temperature, ft is used, assuming that denitrification at 15 °C is twice as high as at 5 °C: a general effect of temperature on microbial activity, after Gao yet all (2016):

Temperature < 5 °C: ft = 0.50

5°C < Temperature < 15 °C: ft = 0.75

Temperature > 15 °C: ft = 1.0

The temperature range in Gao et al. (2016) varies from 2-22°C. We assumed that the highest LR fraction for Temperature >7.16°C relates to > 15 °C: and make this 1. The value below 7.16 is assumed to be linked to 5 °C and this is about 50% of the higher value, and we interpolate in between.

Denitrification increases with increasing total soil organic carbon (SOC) content and thus leaching decreases. Based on Gao et al. (2016), 5he following reduction fractions for SOC content, fc, are used:

SOC < 1.5%: fc = 1.0

1.5 < SOC < 3.5%: fc = 0.7

SOC > 3.5%: fc = 0.35

In Gao et al. (216), the leaching rate below SOC is 3.46% (3.5%) is more nearly thrice as high as the leaching rate above SOC is 3.46%. The value below 3.46% is assumed to be linked to 1.5% and above 3.46% it is linked to 3.5% and we interpolate in between.

Text S3.3: Calculation of NH_3 emission

Based on Wang et al. (2021), we applied empirical model 1 to calculate the N_$_{NH3\ emission}$. The functional forms of the fitted model were expressed as below:

$$Ln(Y) = 0.009\, N_{rate} + 0.048\, Clay + 0.038\, Temperature - 1.129$$

where Y represents accumulated ammonia emissions per hectare (N $_{NH3\ emission}$, kg NH_3 ha^{-1}), N $_{rate}$ stands for the N input by fertilizer (mineral N fertilizer and manure N) of each province, and the Clay and Temperature are the mean value of each province.

Text S3.4: Calculation of HCO_3^- concentration in calcareous soils

In calcareous soil (soil $CaCO_3$ content higher than 0.3% and/or soil pH higher than 6.5), HCO_3^- is produced by dissociation of CO_2 and by the equilibrium dissolution of $CaCO_3$ (carbonate buffer range) according to:

$$CaCO_3 + CO_2 + H_2O \rightleftarrows 2HCO_3^- + Ca^{2+}$$

The concentration of Ca and HCO_3 is thus derived as:

$$[Ca^{2+}] + [HCO_3^-]^2 = K_{carb} * pCO2$$

Assuming that$[Ca^{2+}] = [HCO_3^-]$ gives

$$[HCO_3^-]^3 = K_{carb} * pCO2$$

This leads to

$$log[HCO_3^-] = logK_{carb}/3 + log(\,pCO2)\,/3$$

Considering that log K_{carb} = 5.83 gives

$log[HCO_3^-] = -1.94 + log(\,pCO2)\,/3$

Supplementary tables

Table S3.1 Information about soil samples for soil calcium carbonate and base cations measurement.

Soil properties	Selected sites of soil sample	Selected year of soil sample
Calcium carbonate	Mengcheng (Wheat-Soybean)	2012
	Beibei (Rice-Wheat)	1990, 2005, 2013
Base cations	Qiyang (Wheat-Maize)	1990, 2000, 2012, 2019
	Minhou (Rice-Rice)	1991, 2005, 2013, 2019

Table S3.2 Data sources to assess major elements input and outputs and soil pool changes in 13 long-term experiment sites.

Items	Data source of sites
Nutrient input	
By Mineral fertilizers	
• Fertilizer application amount	LTES[1]
• N, P, K, Ca, Cl, S content of fertilizers	LTES
By Organic fertilizers	
• Fertilizer application amount	LTES
• N, P, K, C content of fertilizers	LTES
• Other elements (S, Ca, Mg, Na, Cl) content of fertilizers	Measured
N bio fixation	Smil, 1999; Giller, 2001; Herridge et al., 2008; Li and Jin et al, 2011
By atmospheric deposition	
• N	Zhu et al. (2018)
• S	Zhu et al. (2018)
• BC	Zhu et al. (2018)
• Cl and P	Zhu et al. (2018)
Nutrient output	
Crop uptake	
• Crop yield	LTES
• N, P, K Nutrient content	LTES
• Other elements (C, S, BC, Cl) content	Measured, Zhu et al. (2018), Xu et al. (2022)
Ammonia volatilization	LTES, Wang et al. (2021)
Nutrient leaching	
• **NO3-**	Calculated
• **HCO_3^-**	Calculated
• **$H_2PO_4^-$**	-
• **$SO4^{2-}$, Cl^-**	-
• **BC**	Calculated
Nutrient in soil (soil pool change)	
• **N, P, K**	LTES
• **BC**	Measured
• **CaCO3**	Measured

[1] LTES mean historical measurement by each long-term experiment sites.

Table S3.3 Total N inputs (kg N ha^{-1} yr^{-1}) from mineral fertilizer and manure in 13 long-term experiments.

Site	CK	NPK		NPKM		M
		NPK	2NPK	NPKM	1.5NPKM	
Suining	0	99	--	74+(15-68) ※	--	61-271 ※
Beibei	0	240	--	240+(106-135) *	--	106-135*
Mengcheng	0	180	--	(180-210) +95# (180-210) +77※	--	--
Guiyang	0	165	--	124+(15-68) #	--	61
Guiyang	0	285-300	--	(285-300)+(12-221) #	(427-450)+(13-65) #	13-65#
Wuchang	0	150	--	150+(53-189) ※	--	53-113※
Jinxian	0	180-228	--	--	--	299-247※
Jinxian	0	180	360	180+276※	--	--
Wangcheng	0	150	--	--	--	--
Nanchang	0	329	--	(100-232)+ (98-230) ※	--	--
Qiyang	0	300	--	90+(137-320) ※	135+(206-420) ※	196-458※
Qiyang	0	73-145	--	290+217# 145+109#	-	109-217#
Minhou	0	103-207	--	(103-207)+(56-112) #	--	--

※ pig manure; * chicken manure; # cattle manure

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Table S3.4 Calculations of cations/anions from kg ha-1 yr-1 to keq ha^{-1} yr^{-1}.

Cations/Anions	kg ha^{-1} yr^{-1}	keq ha^{-1} yr^{-1}
NH_4^+	1	1/14
NO_3^-	1	1/14
$H_2PO_4^-$	1	1/31
Ca^{2+}	1	1/40×2
Mg^{2+}	1	1/24×2
Na^+	1	1/23
K^+	1	1/39
SO_4^{2-}	1	1/32×2
HCO_3^-	1	1/12
Cl^-	1	1/35.5

Table S3.5 Element contents in different manure type (dry mass).

Manure type	Element contents in organic fertilizer (Dry mass, g/kg)					pH
	Ca	Na	Mg	S	Cl	
Pig Manure	18.0	2.78	7.44	3.46	2.05	8.02
Cattle Manure	18.4	2.37	4.66	3.13	2.37	7.98
Chicken manure	28.2	0.39	7.51	4.37	3.51	7.84

Table S3.6 Element contents in grain and straw of different crop types.

	Nutrients	Crop type			
		Rice	Wheat	Maize	Soybean
Element concentration in harvested part (g/kg) [a]	N	11.8	19	13.9	56
	P	1.1	3.25	2.18	4.65
	K	1.03	2.89	3.00	15
	Ca	0.13	0.34	0.14	1.91
	Mg	0.34	0.04	0.96	1.99
	Na	0.04	0.07	0.03	0.02
	S	0.3	0.9	0.83	0.3
	Cl	0.2	0.2	0.4	0.1
Element concentration in crop residues (g/kg) [a]	N	9.1	6.5	9.2	18.1
	P	1.3	0.8	1.52	1.96
	K	18.9	10.5	11.8	11.7
	Ca	6.1	5.2	5.4	17.1
	Mg	2.24	1.65	2.24	4.8
	Na	0.12	0.29	0.39	1
	S	1.38	0.96	0.94	2.1
	Cl	8.6	5.7	7.5	3.4
W% [b]		14	12.5	14	13
RRH [c]		0.9	1.1	1.2	1.6

[a] The concentration in harvest parts for different crops are fresh weight based, while the concentration in crop residues are dry weight based, date from Zhu et al. (2018) and Xu et al. (2022).
[b] W% denotes water concentration in harvest parts (%), data from Zhu et al. (2018).
[c] $R_{RH \text{ denotes}}$ the ratio of crop residue to harvest part, data from https://wenku.baidu.com/view/41ee87a7770bf78a64295422.html.

Table S3.7 Annual fluxes for precipitation (P), irrigation (I), evapotranspiration (Ev), and precipitation surplus (PS), for 13 long-term experiment sites in mm per year.

Site	Crop type	P	I	Ev	PS
		mm yr-1			
Suining	Rice-Wheat	927	368	634	661
Beibei	Rice-Wheat	1105	368	548	926
Mengcheng	Wheat-Soybean	872	-	458	414
Guiyang	Maize-Bare	1071	-	578	493
Guiyang	Rice-Bare	1150	368	544	974
Wuchang	Wheat-Rice	1300	368	698	971
Jinxian	Rice-Rice	1537	736	680	1593
Jinxian	Rice-Rice	1537	736	680	1593
Wangcheng	Rice-Rice	1370	736	664	1442
Nanchang	Rice-Rice	1600	736	559	1777
Qiyang	Rice-Rice	1255	736	660	1331
Qiyang	Wheat-Maize	1255	-	521	734
Minhou	Rice-Rice	1351	736	599	1488

Table S3.8 H^+ production and consumption rate (keq ha^{-1} yr^{-1}) by different source under long-term fertilizer treatments for calcareous long-term experiment site.

Sites	Treatment	Total H^+ production				H^+ consumption	Soil H^+ consumption		Net H^+ production = Soil H^+ consumption
		HCO_3^- leaching	N transformation	Crop uptake	Net H^+ input	HCO_3^- input	Ca^{2+} release	P accumulation	
Suining (Rice-Wheat)	CK	22	0.18	1.0	0.00	-0.28	24	-0.36	24
	NPK	22	1.8	5.1	0.00	-0.47	30	-0.53	30
	NPKMp	22	3.0	5.7	0.00	6.8	22	1.9	24
	Mp	22	1.6	1.8	0.00	7.3	17	1.00	18
Beibei (Rice-Wheat)	CK	31	0.02	1.3	0.00	-0.08	33	-0.39	32
	NPK	31	3.7	2.5	-0.01	-0.48	37	0.89	38
	NPKMch	30	7.2	2.9	-0.01	12	25	3.0	28
Mengcheng (Wheat-Soybean)	CK	12	4.0	1.7	-0.01	-0.25	18	-0.36	18
	NPK	12	7.1	3.6	-0.03	-0.53	23	0.09	23
	NPKMc	12	7.9	6.4	0.00	5.2	20	1.0	21
	NPKMp	12	9.7	5.3	-0.01	13	13	1.5	14
Guiyang (Maize)	CK	14	0.05	0.75	-0.01	0.01	16	-0.50	15
	NPK	14	1.9	0.93	-0.02	-0.08	17	0.25	17
	NPKMc	14	2.6	2.1	0.00	8.3	9.4	1.5	11
	Mc	14	0.54	3.3	0.00	34	-21	4.8	-16
Guiyang (Rice)	CK	33	0.05	2.3	-0.02	0.18	36	-0.46	35
	NPK	33	0.45	3.3	-0.02	-0.08	37	0.50	37
	NPKMc	33	0.49	2.9	-0.02	6.6	30	0.53	30
	Mc	33	0.31	3.6	-0.02	27	9.2	1.2	10
Wuchang (Wheat-Rice)	CK	32	0.04	2.7	-0.01	-0.36	37	-1.3	35
	NPK	32	1.0	3.5	-0.01	-0.60	39	-1.2	37
	NPKMp	32	1.1	4.6	-0.01	4.2	33	1.1	34

Table S3.9 H^+ production and consumption rate (keq ha^{-1} yr^{-1}) by different source under long-term fertilizer treatments for non-calcareous long-term experiment sites.

Sites	Treatment	Total H^+ production				H^+ consumption	Soil H^+ consumption		Net H^+ production
		HCO_3^- leaching	N transformation	Crop uptake	Net H^+ input	HCO_3^- input	BC release	P accumulation	= Soil H^+ consumption
Jinxian (Rice-Rice)	CK	4.5	0.45	0.99	-0.67	-0.20	6.3	-0.86	5.4
	NPK	5.2	2.4	1.6	-0.60	-0.48	9.2	-0.22	9.0
	NPKMp	7.5	4.4	2.4	-0.52	17	-3.7	0.65	-3.1
Jinxian (Rice-Rice)	CK	5.5	0.27	0.58	-0.66	-0.20	7.4	-1.5	5.9
	NPK	9.7	2.4	1.1	-0.65	-0.53	14	-0.93	13
	Mp	5.2	3.2	0.30	-0.62	11	-3.9	0.69	-3.2
Wangcheng (Rice-Rice)	CK	17	0.35	2.1	-0.21	-0.37	20	-0.37	20
	NPK	10	0.55	4.0	-0.47	-0.66	14	0.57	15
Nanchang (Rice-Rice)	CK	27	0.11	1.8	-0.30	-0.19	27	-1.4	26
	NPK	12	2.9	4.9	-0.61	-0.57	19	-1.2	18
	NPKMp	18	2.9	4.4	-0.30	12	12	-0.29	11
Qiyang (Rice-Rice)	CK	18	0.15	2.9	-0.14	-0.37	22	-0.83	21
	NPK	11	1.4	3.5	-0.53	-0.72	16	0.05	16
	NPKMc	9.4	3.3	5.4	-0.65	15	-3.3	5.4	2.1
	Mc	8.4	1.1	4.5	-0.60	16	-5.5	2.9	-2.6
Qiyang (Maize-Wheat)	CK	0.98	2.4	0.35	-0.16	0.92	2.6	-0.01	2.6
	NPK	0.09	13	1.4	-2.5	0.54	10	1.3	11
	NPKMp	1.5	9.5	3.8	-0.10	17	-7.6	5.9	-1.7
	Mp	7.1	8.8	2.8	-0.02	24	-12	6.5	-5.4
Minhou (Rice-Rice)	CK	1.3	0.49	1.4	-1.4	-0.17	2.6	-0.56	2.0
	NPK	0.94	2.1	2.4	-1.8	-0.31	4.5	-0.58	3.9
	NPKMc	1.5	2.9	3.0	-1.1	7.2	-0.45	-0.42	-0.87

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Supplementary figures

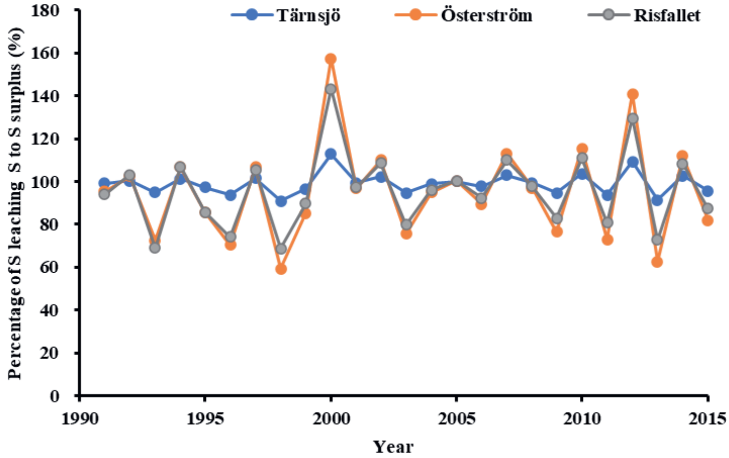

Figure S3.1 The percent of leaching SO_4^{2-} to S surplus in Österström, Risfallet and Tärnsjö sites.

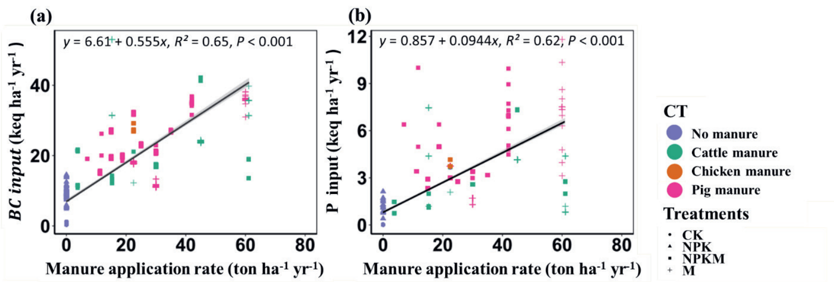

Figure S3.2 Correlation between BC input rate (a) and P input (b) with manure application rate for different manure types and treatments.

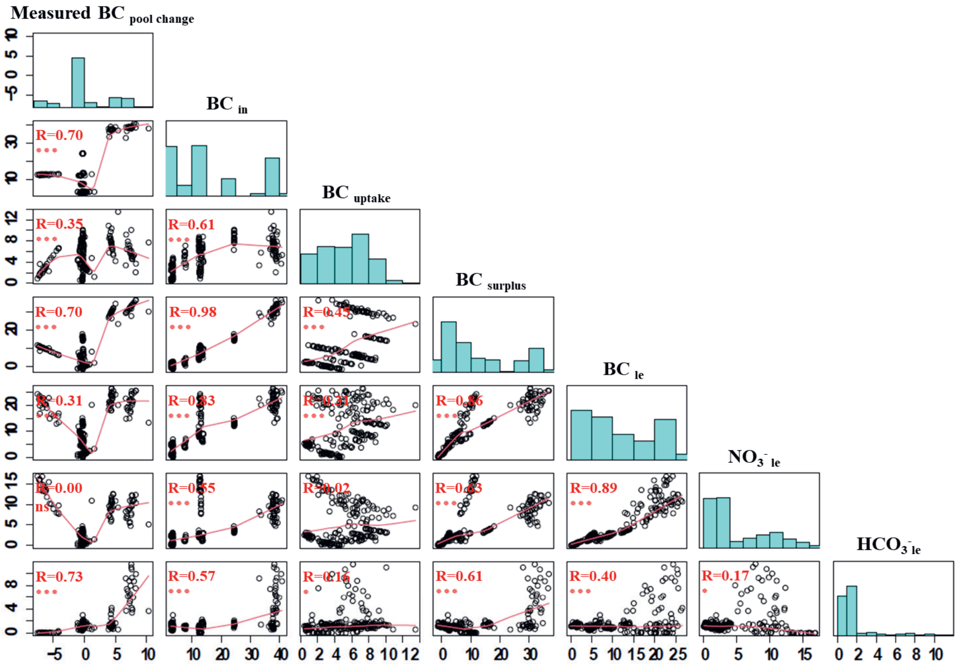

Figure S3.3 Frequency distribution histograms and scatter-plot matrix of BC fluxes (input, surplus and leaching), other leaching factors and measured soil BC pool change in non-calcareous sites. Pearson correlation values between each pair of variables are indicated in the upper left corner of the scatterplots (ns non-significant, * significant at p<0.05, *** significant at p<0.001).

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Table S4.13 H^+ production and consumption rate (keq ha^{-1} yr^{-1}) by different source under optimal fertilizer management

Supplementary Text Assessment of nitrogen losses by NH_3 emission and NO_3^- leaching

Based on Wang et al. (2021), we applied empirical model 1 to calculate the $N\_{NH3\ emission}$ according to:

$$Ln(Y) = 0.009\, N_{rate} + 0.048\, Clay + 0.038\, Temperature - 1.129$$

where *Y* represents accumulated ammonia emissions per hectare ($N_{NH3\ emission}$, kg NH3 ha^{-1}), N_{rate} stands for the N input by fertilizer (mineral N fertilizer and manure N) of each province, and the Clay and Temperature are the mean value of each province. The value of the NH_3 emission fraction per province (*fr*NH_3 emission; See Table 2) was derived by dividing the NH3 emission thus obtained by the total N input.

The value of nitrogen leaching fraction ($frN_{leaching}$), is calculated from a maximal leaching fraction and a set of reduction fractions according to *Velthof et al.* (2019), where the fractions for land use and precipitation surplus have (slightly) been adapted:

$$fr_{Nleaching} = f_{le.max} * f_{lu} * min(f_p, f_t, f_c)$$

$f_{le,max}$	=	maximum leaching fraction for different soil types
f_{lu}	=	reduction fraction for land use
f_p	=	reduction fraction for precipitation and irrigation
f_t	=	reduction fraction for temperature
f_c	=	reduction fraction for soil organic carbon content

However, the various reduction functions used by *Velthof et al*. (2009), being applied in scientific publications on N flows in China (e.g. Ma et al., 2010), have been adapted, based on data relationships derived by *Gao et al.* (2016) for observed N leaching rates in China and site properties.

The following soil type dependent maximum leaching fractions $f_{le,max}$ are used (Gao et al., 2016):

Texture class 1 (Clay <18%): $f_{le,max,sand} = 1.0$
Texture class 2 (18 < Clay <35%): $f_{le,max,light\ clay} = 0.75$
Texture class 3 (>35%): $f_{le,max,heavy\ clay} = 0.50$

The reduction fraction for land use, f_{lu}, was set at is 1 for upland, 0.8 for upland-paddy and 0.6 for paddy based on Gao et al. (2016).

Denitrification increases and thus leaching decreases at lower precipitation surplus due to longer residence times allowing enhanced denitrification The reduction fraction for precipitation surplus, fp, is adapted from Velthof et al. (2009) based on data on precipitation plus irrigation (P+I) by Gao et al, (2016) according to:

P +I < 500 mm: $f_p = 0.5$
500 mm ≤ P+I < 1500 mm: $f_p = 0.5 + (P+I-500) *0.0005$
P +I ≥ 1500 mm: $f_p = 1$

Denitrification increases with increasing temperature and thus leaching decreases. The following reduction fractions for temperature, ft is used, assuming that denitrification at 15 ºC is twice as high as at 5 ºC: a general effect of temperature on microbial activity, after Gao yet all (2016):

Temperature < 5 ºC: $f_t = 0.50$
5 < Temperature < 15 ºC: $f_t = 0.75$
Temperature > 15 ºC: $f_t = 1.0$

Denitrification increases with increasing total soil organic carbon (SOC) content and thus leaching decreases. Based on Gao et al. (2016), 5he following reduction fractions for SOC content, fc, are used:

SOC < 1.5%: $f_c = 1.0$
1.5 < SOC < 3.5%: $f_c = 0.7$
SOC > 3.5%: $f_c = 0.35$

Data sources used for the assessment of input data to derive NH_3 emission and N loss fractions are the *RESDC (Resource and Environmental Science and Data Center)* for clay, precipitation, and temperature; Zhu (2018) for SOC content; He et al (2020) for irrigation.

Supplementary tables on data for phosphorus input and soil acidification rate calculations

Table S4.1 Phosphorus fertilizer recommendations based on "Building-up and maintenance method".

Soil fertility class	Soil Olsen-P ($mg\ kg^{-1}$)	Recommend P rate ($kg\ P\ ha^{-1}$)
Very high	>40	0
High	30-40	0.5 crop P demand
Medium	14-30	1.0 Crop P demand
Low	7-14	1.4 crop P demand
Very low	<7	1.7 crop P demand

Table S4.2 Calculations of cations/anions from $kg\ ha^{-1}\ yr^{-1}$ to $keq\ ha^{-1}\ yr^{-1}$

Cations/Anions	$kg\ ha^{-1}\ yr^{-1}$	$keq\ ha^{-1}\ yr^{-1}$
NH_4^+	1	1/14
NO_3^-	1	1/14
$H_2PO_4^-$	1	1/31
Ca^{2+}	1	1/40×2
Mg^{2+}	1	1/24×2
Na^+	1	1/23
K^+	1	1/39
SO_4^{2-}	1	1/32×2
HCO_3^-	1	1/12
Cl^-	1	1/35.5

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Table S4.3 Element concentrations in urine and faeces for different animal manure (%).

Items	Element	Pig	Sheep	Poultry	Cattle
Urine	N	0.17	0.59	-	0.50
	P	0.02	0.02	-	0.02
	K	0.16	0.70	-	0.91
	Ca	0.01	0.69	-	0.06
	Mg	0.01	0.18	-	0.05
	Na	0.05	0.02	-	0.06
	S	0.02	0.24	-	0.04
Faeces	N	0.55	1.01	0.76	0.38
	P	0.25	0.22	0.33	0.10
	K	0.29	0.53	0.59	0.23
	Ca	0.49	1.31	1.66	0.43
	Mg	0.22	0.25	0.24	0.11
	Na	0.08	0.06	0.20	0.04
	S	0.10	0.15	0.15	0.07

Data from National Agricultural Technical Extension and Service Center (NATESC), 1999

Table S4.4 Parameters used in the calculation of animal excretion.

Animals	Breeding days per cycle (d)	Urination rate (kg d^{-1})	Defecation rate (kg d^{-1})
Pig	199	3.0	2.0
Dairy Cattle/Farm cattle	365	8.5	37
Beef cattle	300	4.7	18
Sheep	243	0.50	1.5
Poultry	210	0.00	0.13

Data from Li and Jin, 2011; Jia 2014.

Table S4.5 Grazing fractions per animal category and province (%).

Province	Cattle	Sheep	Poultry	Pig
Anhui	9	68	8	0
Beijing	9	68	8	0
Chongqing	36	83	12	0
Fujian	36	83	12	0
Gansu	82	99	23	0
Guangdong	9	68	8	0
Guangxi	9	68	8	0
Guizhou	36	83	12	0
Hainan	9	68	8	0
Hebei	36	83	12	0
Heilongjiang	9	68	8	0
Henan	9	68	8	0
Hubei	9	68	8	0
Hunan	9	68	8	0
Inner Mongolia	82	99	23	0
Jiangsu	9	68	8	0
Jiangxi	9	68	8	0
Jilin	9	68	8	0
Liaoning	9	68	8	0
Ningxia	82	99	23	0
Qinghai	82	99	23	0
Shaanxi	82	99	23	0
Shandong	9	68	8	0
Shanghai	9	68	8	0
Shanxi	82	99	23	0
Sichuan	82	99	23	0
Tianjin	9	68	8	0
Xinjiang	82	99	23	0
Xizang	82	99	23	0
Yunnan	82	99	23	0
Zhejiang	9	68	8	0

Table S4.6 Element concentrations in crop harvest, crop residues and related parameters in crop removal calculation.

Crops	Element concentration in harvested part [a] (g/kg)							Element concentration in crop residues [a] (g/kg)							W[b] (%)
	N	P	K	Ca	Mg	Na	S	N	P	K	Ca	Mg	Na	S	
Rice	12	1.1	1.0	0.13	0.34	0.04	0.30	9.1	1.3	19	6.1	2.2	0.1	1.4	14
Wheat	19	3.3	2.9	0.34	0.04	0.07	0.90	6.5	0.8	11	5.2	1.7	0.3	0.96	13
Maize	14	2.2	3.0	0.14	0.96	0.03	0.83	9.2	1.5	12	5.4	2.2	0.4	0.94	14
Chinese sorghum	17	3.3	2.8	0.22	1.3	0.06	1.0	13	1.5	14	4.6	1.9	0.4	0.94	14
Millet	14	2.3	2.8	0.41	1.1	0.04	2.0	8.2	1.0	18	4.8	4.5	0.3	1.1	14
Potato	3.2	0.4	3.4	0.08	0.23	0.03	0.26	27	2.7	40	30	5.8	1.0	3.7	75
Sweet Potato	2.0	0.43	1.5	0.24	0.15	0.43	0.26	24	2.8	31	21	4.6	1.0	3.0	75
Soybean	56	4.7	15	1.9	2.0	0.02	0.3	18	2.0	12	17	4.8	1.0	2.1	13
Peanut	38	3.2	5.9	0.39	1.8	0.04	1.7	18	1.6	11	18	5.6	1.0	1.4	15
Sunflower	38	2.4	5.6	0.72	2.6	0.06	2.0	8.2	1.1	18	16	3.1	1.0	1.7	12
Rape seeds	46	5.6	7.2	3.4	2.9	0.37	6.4	8.7	1.4	19	15	2.5	1.0	4.4	8
Cotton	24	3.3	12	2.2	1.6	0.23	0.80	12	1.5	10	8.5	2.8	1.0	1.7	12
Hemp	6.0	0.5	7.0	6.0	1.5	0.25	0.50	13	0.6	5.0	31	4.5	1.0	0.50	14
Sugar cane	16	1.4	16	3.3	1.8	0.14	0.35	11	1.4	11	8.8	2.1	0.4	0.63	70
Sugar beet	14	1	16	2.6	3.9	3.9	0.85	10	2.9	12	9.4	7.7	17	2.6	75
Tobacco	21	2.3	16	23	2.8	0.26	4.5	14	1.7	19	15	1.9	1.0	2.7	17
Vegetables	1.7	0.79	1.5	0.29	0.14	0.32	0.32	30	3.8	28	15	5.0	0.0	3.2	90
Water melons	1.0	0.09	0.87	0.08	0.08	0.03	0.09	26	2.3	20	46	8.3	1.0	2.4	95
Other melons	0.77	0.13	1.4	0.13	0.13	0.11	0.09	24	4.8	22	46	8.3	1.0	2.4	95
Tea	55	1.9	17	3.3	2.0	0.28	4.5	-	-	-	-	-		-	-
Apple	0.32	0.12	1.2	0.04	0.04	0.02	0.00	-	-	-	-	-	-	-	-
Pear	0.64	0.14	0.92	0.09	0.08	0.02	0.04	-	-	-	-	-	-	-	-
Banana	2.2	0.28	2.6	0.07	0.43	0.01	2.1	-	-	-	-	-	-	-	-
Orange	1.1	0.18	1.5	0.35	0.11	0.01	0.08	-	-	-	-	-	-	-	-
Grape	0.80	0.13	1.0	0.05	0.08	0.01	0.75	-	-	-	-	-	-	-	-

[a] The concentration in harvested parts for different crops are fresh weight based, while the concentration in crop residues are dry weighed based. Data from the Center for Disease Control and Prevention and Food Security of China (2009); U.S. and International Nutrient Databases (http://www.foodhealth.info/).

[b] w% denotes water concentration in harvested parts (%), data from Bi, 2010.

Table S4.7 Phosphorus (P) input from mineral fertilizer, manure under current and optimal management for 31 provinces of China and China as a whole.

Province	Soil Olsen-P	fr P demand	P uptake	P demand	P env	P require	BAU P input mineral	BAU P input manure	OPT P input mineral	OPT P input manure	P potential manure excreted	P potential manure available for cropland	Cropland area	Percentage BAU [a]	Percentage OPT [a]
	mg kg-1	%	kg ha-1								k ton	k ton	k ha	%	
Anhui	17	1.2	16	19	0.9	18	41	4.4	4.7	13	140	128	9598	33	100
Beijing	59	0.3	24	8.0	1.8	6.2	54	22	0.0	6.2	13	11	172	33	9
Chongqing	12	1.0	11	11	0.8	10	34	5.9	0.0	10	65	52	3311	38	67
Fujian	44	0.7	15	11	0.9	10	78	18	0.0	9.9	98	85	1617	34	19
Gansu	16.0	1.0	13	13	1.3	12	34	2.4	5.9	6.1	90	23	3768	39	100
Guangdong	26	0.6	14	8.6	1.0	7.6	53	12	0.0	7.6	173	162	4195	32	20
Guangxi	19	1.0	14	13	1.4	12	45	9.2	0.0	12	187	173	6079	32	42
Guizhou	17	1.1	8.1	8.8	0.9	7.9	17	6.1	0.0	7.9	113	81	5533	42	54
Hainan	8.8	1.2	11	14	1.2	12	67	13	0.0	12	32	30	758	33	32
Hebei	15	1.0	23	23	1.1	22	43	6.6	5.4	16	186	138	8458	40	100
Heilongjiang	25	0.6	14	8.4	0.9	7.5	23	2.6	0.0	7.5	131	118	14812	33	95
Henan	15	1.1	21	23	1.0	22	63	5.9	3.7	18	294	266	14880	33	100
Hubei	13	1.1	14	16	0.8	16	52	5.9	0.0	16	156	144	7983	32	87
Hunan	20	1.1	12	13	0.6	12	27	6.5	0.0	12	182	168	8355	32	60
Inner Mongolia	20	0.9	14	13	1.0	12	34	2.0	7.8	4.4	171	37	8424	47	100
Jiangsu	18	1.0	19	18	0.9	17	42	4.4	3.5	13	112	103	7694	33	100
Jiangxi	16	0.7	9.7	7.1	0.7	6.5	32	6.5	0.0	6.5	123	115	5688	32	32
Jilin	23	0.7	20	14	0.9	13	39	6.7	0.0	13	134	122	5998	33	63
Liaoning	12	1.1	20	22	1.0	21	33	11	0.0	21	158	144	4335	33	65
Ningxia	13.0	1.0	13	13	1.1	12	37	2.2	6.8	4.8	25	5.5	1132	45	100
Qinghai	0.0	1.4	10	15	1.2	14	24	13	0.0	14	73	14	558	54	56
Shaanxi	25.0	1.1	14	15	1.3	14	54	3.6	7.8	5.7	49	23	4050	64	100
Shandong	46	0.6	24	16	1.0	15	47	8.9	0.0	15	337	301	11381	34	55
Shanghai	8.5	0.4	17	5.8	1.0	4.8	25	4.9	0.0	4.8	6	5.4	351	32	32
Shanxi	16	1.3	14	18	1.3	17	43	3.3	11.2	5.7	40	20	3613	58	100
Sichuan	11	1.1	14	15	0.9	14	32	9.4	0.0	14	298	152	9451	59	87
Tianjin	29	0.7	23	16	1.2	15	56	11	0.0	15	16	15	433	33	44
Xinjiang	11.0	1.3	21	28	1.0	27	70	2.1	22.9	4.5	107	23	5175	46	100
Xizang	13	1.1	8.8	10	1.4	8.6	36	41	0.0	8.6	94	17	230	56	12
Yunnan	17	1.0	10	11	1.1	9.5	34	8.2	0.0	9.5	187	79	6819	71	82
Zhejiang	33	0.7	14	10	1.0	9.4	40	5.2	0.0	9.4	35	32	1978	32	58
Mean China	-	-	16	15	1.0	14	41	6.2	2.8	12	-	-	-	37	69
Sum China (kton)	-	-	2672	2540	160	2380	6847	1035	460	1922	3824	2788	166829	-	-

[a] The Percentage is the manure recycling rate, calculated as $P_{input\ manure}$ times the cropland area/1000 dived by the crop land manure input x 100%. A value of 100 under OPT indicates the necessity of applying mineral fertilizer. Conversely, percentage below 100 under OPT signify that the P content in manure is sufficient to meet the crop's demand, eliminating the need for additional mineral P fertilizer.

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Table S4.8 Nitrogen (N) input from mineral fertilizer, manure under current and optimal management for 31 provinces of China and China as a whole.

Province	N uptake	N demand	N env	N required	BAU N input mineral	BAU N input manure	OPT N input mineral	OPT N input manure	N potential manure excreted	N potential manure available for cropland	Cropland area	Percentage BAU [a]	Percentage OPT [a]
					kg ha-1				kton	kton	kha	%	
Anhui	111	111	38	79	169	13	89	32	428	305	9598	34	100
Beijing	105	105	65	55	370	70	64	20	40	28	172	34	12
Chongqing	66	66	33	39	175	21	22	38	233	137	3311	41	91
Fujian	79	79	45	42	364	49	38	27	267	181	1617	35	24
Gansu	75	75	47	39	134	11	41	19	433	73	3768	48	100
Guangdong	86	86	45	49	309	37	52	23	518	386	4195	32	25
Guangxi	108	108	43	72	175	32	71	41	640	470	6079	33	53
Guizhou	51	51	37	21	113	27	0.0	35	496	270	5533	44	72
Hainan	69	69	48	29	302	45	2	43	113	82	758	33	40
Hebei	120	120	36	92	220	25	96	45	708	383	8458	44	100
Heilongjiang	107	107	49	67	77	11	76	27	560	396	14812	34	100
Henan	128	128	34	100	227	23	101	54	1139	807	14880	34	100
Hubei	96	96	36	67	217	21	53	50	551	400	7983	33	100
Hunan	82	82	34	54	152	24	39	44	672	486	8355	33	76
Inner Mongolia	95	95	43	61	145	10	80	14	836	116	8424	58	100
Jiangsu	113	113	36	83	252	12	99	28	307	218	7694	34	100
Jiangxi	79	79	39	46	108	23	48	23	438	325	5688	32	40
Jilin	132	132	41	100	193	27	103	51	530	382	5998	33	80
Liaoning	113	113	42	79	199	39	46	76	556	399	4335	33	82
Ningxia	69	69	42	37	199	11	41	16	120	18	1132	54	100
Qinghai	34	34	42	1.8	97	66	0.0	69	369	52	558	56	73
Shaanxi	79	79	48	41	310	15	49	14	204	58	4050	84	100
Shandong	135	135	35	106	198	29	115	48	1111	771	11381	35	71
Shanghai	84	84	40	51	178	15	64	15	18	13	351	33	40
Shanxi	81	81	47	45	147	13	55	13	154	48	3613	76	100
Sichuan	88	88	36	59	152	37	51	39	1172	373	9451	75	100
Tianjin	114	114	42	81	286	38	73	51	55	39	433	33	56
Xinjiang	142	142	32	116	245	10	165	14	523	72	5175	58	100
Xizang	49	49	49	12	122	207	0.0	44	475	67	230	57	15
Yunnan	71	71	39	40	197	35	30	31	798	211	6819	91	100
Zhejiang	79	79	48	41	275	15	36	27	98	72	1978	33	73
Mean China	102	102	39	70	185	23	72	36	-	-	-	50	79
Sum China (kton)	16964	16964	6567	11640	30868	3817	11944	6033	14562	7641	166829	-	-

[a] The Percentage is the optional manure recycling rate, calculated as Ninput manure OPT times the cropland area/1000 dived by the crop land manure input x 100%. A value of 100 indicates the necessity of applying mineral N fertilizer. Conversely, ratios below 100 signify that the N content in manure is sufficient to meet the crop's demand, eliminating the need for additional mineral N fertilizer. The difference of the ratio value in table S7 and S8 was caused by the variation of nutrients content among animal types and provinces.

Table S4.9 Base cations (BC) input from mineral fertilizer, manure under current and optimal management for 31 provinces of China and China as a whole.

Province	BC uptake	BC demand	BC env	BC require	BAU BC input mineral	BAU BC input manure	OPT BC input mineral	OPT BC input manure
	keq ha^{-1}							
Anhui	3.6	3.6	0.7	2.9	2.2	1.6	0.7	5.0
Beijing	3.7	3.7	2.0	1.7	2.9	8.1	1.2	2.3
Chongqing	2.4	2.4	0.8	1.6	1.1	2.2	0.2	3.9
Fujian	2.9	2.9	1.0	2.0	5.3	6.5	0.8	3.6
Gansu	2.8	2.8	1.4	1.5	1.3	1.1	0.1	2.7
Guangdong	3.1	3.1	0.9	2.1	4.3	4.5	1.0	2.8
Guangxi	4.4	4.4	1.1	3.3	3.5	3.5	1.4	4.5
Guizhou	2.0	2.0	0.9	1.0	0.9	2.5	0.0	3.3
Hainan	2.6	2.6	1.2	1.4	5.2	4.9	0.4	4.8
Hebei	4.2	4.2	0.9	3.3	2.0	2.6	0.6	6.5
Heilongjiang	3.1	3.1	0.7	2.4	1.1	1.1	0.6	3.1
Henan	4.2	4.2	0.6	3.6	2.8	2.3	0.3	7.0
Hubei	3.3	3.3	0.7	2.6	2.1	2.2	0.2	5.8
Hunan	2.7	2.7	0.6	2.1	1.9	2.4	0.3	4.4
Inner Mongolia	3.2	3.2	1.0	2.1	1.3	1.0	0.9	2.1
Jiangsu	3.6	3.6	0.7	2.9	1.7	1.5	1.0	4.7
Jiangxi	2.4	2.4	0.6	1.8	1.8	2.4	0.6	2.4
Jilin	4.0	4.0	0.8	3.2	2.5	2.7	0.6	5.3
Liaoning	3.6	3.6	0.8	2.8	1.9	4.3	0.0	8.5
Ningxia	2.4	2.4	1.2	1.2	1.8	1.0	0.1	2.2
Qinghai	2.6	2.6	1.3	1.3	0.8	6.1	0.0	6.3
Shaanxi	2.8	2.8	1.3	1.5	3.4	1.5	0.8	2.3
Shandong	4.6	4.6	0.8	3.9	2.5	3.5	0.9	5.7
Shanghai	2.8	2.8	1.0	1.8	1.2	1.6	1.0	1.6
Shanxi	2.7	2.7	1.3	1.4	2.1	1.3	0.9	2.2
Sichuan	3.1	3.1	0.8	2.2	1.1	3.7	0.1	5.5
Tianjin	4.0	4.0	1.2	2.8	2.3	4.2	0.7	5.7
Xinjiang	6.8	6.8	0.8	5.9	2.1	1.0	2.0	2.1
Xizang	1.8	1.8	1.0	0.9	1.5	18.9	0.0	4.0
Yunnan	2.8	2.8	1.1	1.7	1.6	3.3	0.3	3.9
Zhejiang	2.7	2.7	1.1	1.6	1.9	1.7	0.7	3.1
Mean China	3.5	3.5	0.8	2.6	2.0	2.4	0.6	4.5
Sum China (kton)	582	582	140	440	342	403	99	750

Table S4.10 Net soil acid production and lime requirement under current and optimal management for 31 provinces of China and China as a whole.

Province	BAU		OPT	
	Net acid production keq ha^{-1}	**Lime requirement kg ha^{-1}**	**Net acid production keq ha^{-1}**	**Lime requirement kg ha^{-1}**
Anhui	12	143	4.2	49
Beijing	14	163	1.7	20
Chongqing	10	122	1.2	13
Fujian	8.9	104	-1.0	9
Gansu	7.1	83	0.7	20
Guangdong	11	123	1.7	13
Guangxi	8.5	99	1.2	8.9
Guizhou	6.0	70	0.8	0
Hainan	11	123	-1.3	10
Hebei	10	118	-0.1	6
Heilongjiang	3.8	44	0.9	27
Henan	12	136	0.5	33
Hubei	13	156	2.4	23
Hunan	8.9	104	2.8	30
Inner Mongolia	8.2	96	2.0	14
Jiangsu	14	160	2.6	6
Jiangxi	4.8	56	1.3	10
Jilin	7.7	89	0.5	15
Liaoning	5.8	67	-2.6	12
Ningxia	10	119	0.9	55
Qinghai	2.8	32	-1.6	18
Shaanxi	16	188	1.3	0.0
Shandong	8.7	101	1.0	6
Shanghai	11	130	4.8	57
Shanxi	8	98	1.5	0.0
Sichuan	6.9	80	-0.1	23
Tianjin	14	161	0.5	49
Xinjiang	14	159	5.0	20
Xizang	-2.6	0.0	-0.7	13
Yunnan	8.6	101	0.0	9
Zhejiang	14	157	2.0	20
Mean	9.2	108	1.3	18
Sum China (M keq)	1543	17965	214	307

Table S4.11 Phosphorus (P), nitrogen (N), and base cations (BC) use efficiency under current and optimal management for 31 provinces of China and China as a whole.

Province	**BAU(%)**			**OPT (%)**		
	NUE	**PUE**	**BCUE**	**NUE**	**PUE**	**BCUE**
Anhui	60	35	70	69	86	61
Beijing	24	31	30	70	297	69
Chongqing	34	27	59	71	98	55
Fujian	19	16	22	72	140	61
Gansu	52	36	73	71	101	78
Guangdong	25	21	30	72	158	69
Guangxi	53	24	52	70	102	67
Guizhou	36	34	45	71	92	52
Hainan	20	14	22	74	84	48
Hebei	49	45	73	68	101	59
Heilongjiang	121	53	98	71	168	71
Henan	51	30	65	68	93	59
Hubei	41	25	61	69	87	56
Hunan	47	35	52	70	94	59
Inner Mongolia	62	39	88	70	109	78
Jiangsu	43	39	87	69	105	63
Jiangxi	60	25	48	72	137	70
Jilin	60	43	59	68	146	64
Liaoning	47	45	51	69	90	45
Ningxia	33	31	56	71	99	80
Qinghai	21	27	34	31	69	38
Shaanxi	24	24	40	71	95	67
Shandong	59	43	65	68	156	67
Shanghai	43	54	76	70	286	80
Shanxi	51	30	53	70	79	64
Sichuan	47	32	57	70	92	55
Tianjin	35	33	52	68	139	59
Xinjiang	55	29	147	67	75	118
Xizang	15	11	9.4	53	88	42
Yunnan	31	24	46	71	97	58
Zhejiang	27	31	56	72	137	61
Mean	33	30	48	68	109	62

Table S4.12 Acid production and consumption rate (keq ha^{-1} yr^{-1}) by different source under current fertilizer management for 31 provinces of China and China as a whole.

Province	Total H+ production				H+ consumption	Net H+ production[1]
	N transformation	Crop uptake	Net H^+ input	HCO_3^- leaching	HCO_3^- input	
Anhui	7.6	2.5	-0.1	3.4	1.2	12
Beijing	20	2.3	0.0	0.0	8.0	14
Chongqing	9.9	1.6	-0.2	1.5	2.3	10
Fujian	14	2.0	-0.7	1.0	7.1	8.9
Gansu	7.1	1.9	0.0	0.0	1.9	7.1
Guangdong	12	2.3	-0.3	2.3	5.6	11
Guangxi	7.1	3.6	-0.3	1.9	3.8	8.5
Guizhou	6.1	1.3	-0.2	1.3	2.5	6.0
Hainan	14	1.9	-0.6	1.5	5.9	11
Hebei	10	2.8	0.0	0.0	3.0	10
Heilongjiang	2.0	2.2	-0.1	0.9	1.3	3.8
Henan	11	2.9	0.0	0.3	2.1	12
Hubei	11	2.2	-0.1	2.9	2.1	13
Hunan	6.2	1.9	-0.3	3.8	2.6	8.9
inner Mongolia	7.4	2.3	0.0	0.5	1.9	8.2
Jiangsu	11	2.5	-0.1	2.2	1.9	14
Jiangxi	4.3	1.7	-0.4	1.1	1.9	4.8
Jilin	7.9	2.8	-0.1	0.4	3.4	7.7
Liaoning	7.7	2.4	0.0	0.2	4.4	5.8
Ningxia	11	1.6	0.0	0.0	2.4	10
Qinghai	7.1	1.6	0.0	0.0	6.0	2.8
Shaanxi	17	1.9	0.0	0.1	2.9	16
Shandong	8.4	3.1	0.0	0.2	3.0	8.7
Shanghai	7.9	1.8	0.0	2.4	0.8	11
Shanxi	7.7	1.8	0.0	0.0	1.0	8.5
Sichuan	7.7	2.1	-0.1	0.9	3.8	6.9
Tianjin	15	2.6	0.0	0.1	4.1	14
Xinjiang	11	5.4	0.0	0.0	2.3	14
Xizang	12	1.2	0.0	0.2	16	-2.6
Yunnan	10	2.1	-0.1	0.8	4.3	8.6
Zhejiang	12	1.8	-0.5	1.8	2.1	14
Mean	8.4	2.4	-0.1	1.2	2.6	9.3

Note: Net H^+ production equals to Total H+ production minus H^+ consumption by HCO_3^- input.

Table S4.13 Acid production and consumption rate (keq ha^{-1} yr^{-1}) by different source under optimal fertilizer management for 31 provinces of China and China as a whole.

Province	Total H+ production				H+ consumption	Net H+ production[1]
	N transformation	Crop uptake	Net H^+ input	HCO_3^- leaching	HCO_3^- input	
Anhui	3.5	2.5	-0.07	3.4	5.0	4.2
Beijing	2.1	2.3	0.0	0.05	2.7	1.7
Chongqing	1.4	1.6	-0.21	1.5	3.1	1.2
Fujian	0.53	2.0	-0.73	1.0	3.8	-1.01
Gansu	1.9	1.9	0.0	0.02	3.1	0.7
Guangdong	1.3	2.3	-0.33	2.3	3.8	1.7
Guangxi	2.3	3.6	-0.34	1.9	6.4	1.2
Guizhou	0.59	1.3	-0.21	1.3	2.2	0.77
Hainan	0.24	1.9	-0.61	1.5	4.4	-1.3
Hebei	3.8	2.8	0.0	0.05	6.7	-0.09
Heilongjiang	2.3	2.2	-0.06	0.93	4.5	0.9
Henan	4.1	2.9	-0.01	0.29	6.8	0.5
Hubei	2.4	2.2	-0.13	2.9	5.0	2.4
Hunan	1.5	1.9	-0.28	3.8	4.1	2.8
inner Mongolia	3.3	2.3	-0.01	0.53	4.0	2.00
Jiangsu	3.2	2.5	-0.06	2.20	5.2	2.6
Jiangxi	1.6	1.7	-0.37	1.1	2.8	1.3
Jilin	3.9	2.8	-0.06	0.36	6.5	0.5
Liaoning	2.0	2.4	-0.03	0.19	7.1	-2.6
Ningxia	1.8	1.6	0.0	0.04	2.6	0.9
Qinghai	2.4	1.6	0.0	0.05	5.7	-1.6
Shaanxi	1.9	1.9	0.0	0.14	2.7	1.3
Shandong	4.4	3.1	-0.02	0.18	6.6	1.0
Shanghai	2.2	1.8	-0.05	2.4	1.5	4.8
Shanxi	2.3	1.8	0.00	0.04	2.6	1.5
Sichuan	2.2	2.1	-0.10	0.93	5.2	-0.07
Tianjin	3.1	2.6	0.0	0.08	5.3	0.5
Xinjiang	5.8	5.4	0.0	0.01	6.2	5.0
Xizang	1.3	1.2	0.0	0.20	3.3	-0.66
Yunnan	1.3	2.1	-0.11	0.80	4.1	-0.04
Zhejiang	1.3	1.8	-0.46	1.8	2.4	2.0
Mean	2.7	2.4	-0.1	1.2	4.9	1.3

Note: Net H^+ production equals to Total H+ production minus H^+ consumption by HCO_3^- input.

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About the author

Xingjuan Zhu was born on 24 August 1991 in Shandong, China. In 2011, she started to study Environmental Science at Jinan University in Jinan, the capital city of Shandong province. After four years' bachelor study, she started the MSc program in Environmental Engineering at Huazhong Agricultural University of China in Wuhan, Hubei Province. In September 2018, she joined the National Engineering Laboratory for Improving Quality of Arable Land group of Chinese Academy of Agricultural Sciences to start her PhD study under the project "Wageningen University-CAAS joint PhD program". In March 2019, she came to the Environmental Systems Analysis group, now merged with Water Systems and Global Change group, the new group name is Earth Systems and Global Change group at Wageningen University. During her PhD, she worked on the impacts of fertilizer management, climate and soil properties on nitrogen use efficiency and soil acidification in croplands in China, the results about this research are presented in this thesis.

List of publications

This thesis

Zhu, X., Ros, G. H., Xu, M., Cai, Z., Sun, N., Duan, Y., & de Vries, W. (2023). Long-term impacts of mineral and organic fertilizer inputs on nitrogen use efficiency for different cropping systems and site conditions in southern China. European Journal of Agronomy, 146. https://doi.org/10.1016/j.eja.2023.126797

Zhu, X., Ros, G. H., Xu, M., Xu, D., Cai, Z., Sun, N., Duan, Y. & de Vries, W. (2024). The contribution of natural and anthropogenic causes to soil acidification rates under different fertilization practices and site conditions in southern China. Submitted.

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Oral Presentations

- *Long-term impacts of mineral and organic fertilizer inputs on nitrogen use efficiency for different cropping systems and site conditions in Southern China.* AGD symposium, 29 June - 1 July 2022, Wageningen, the Netherlands
- *Long-term impacts of mineral and organic fertilizer inputs on nitrogen use efficiency for different cropping systems and site conditions in Southern China.* NAC conference, 5 - 6 September 2022, Utrecht, the Netherlands

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