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# 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 25–30% 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 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.

# 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 N use efficiency (NUE), being the fraction of the applied N that is taken up by crops (Zhang et al., 2008). Associated with enhanced air emissions of ammonia (NH<sub>3</sub>) (Shang et al., 2014), nitrous oxide (N<sub>2</sub>O) and nitrogen (di)oxides (NO<sub>x</sub>, NO<sub>2</sub>) (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 (Peter et al., 2019). Potential N 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 N availability under variable conditions. Classically, N fertilizer recommendations follow the theory of the "law of the minimum" developed by 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

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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 acidneutralizing 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<sup>+</sup> 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 calcium (Ca), magnesium (Mg), and potassium (K) ions, dented as BC), the 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 BC uptake (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 NH<sub>3</sub> 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 BC, thereby avoiding acidification (Cai et al., 2015). 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 N 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) (Da 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 (Duan et al., 2021), by crop type and variety (Cui et al., 2008), soil properties (Ye et al., 2007) and climate (Zhang et al., 2008). 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), 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; Cai et al., 2015). 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 and Shi, (2015) collected NUE values for these crops during 2004-2014 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 (SOM) 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 phosphorus (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 <sup>15</sup>N recovery by crops, associated with elevated SOM and soil P (P-Olsen) 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 P, 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 SOM, the N loss pathways and the crop yield. 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<sup>-1</sup> (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. Method and materials

#### 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 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) include Control (CK), combinations of inorganic N, P and K fertilizers (e.g., NP, NK, NPK), combinations of inorganic and organic fertilizers (e.g., NPM, NKM, 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<sup>-1</sup>, 75 kg P<sub>2</sub>O<sub>5</sub> ha<sup>-1</sup>, and 112.5 kg K<sub>2</sub>O ha<sup>-1</sup> per season. Organic fertilizer dose and timing varied per crop from 15 to 23 tonnes ha<sup>-1</sup>, often applied twice a year. Organic fertilizers included pig, cattle and chicken manure. Detailed information is given in Table 3.

#### 2.2. Data collection

Historical data regarding crop rotation, fertilizer input (type and dose), 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 (PRE), temperature (TEM) and sunshine hours (SSH) data were derived from the nearest meteorological station (http://data.cma.cn/).

Soil samples (0–20 cm 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

#### Table 2

Fertilizer and manure treatments used for different crop rotations in 13 longterm experiment sites of Southern China. Treatment descriptions, see legend Fig. 2.

Site No.	Crop type	Time Duration	Manure	Treatments
S1	Wheat- Soybean	1983–2018	Pig manure Cattle manure	CK, NPK, NPKM
S2	Rice-Rice	1981–2018	Pig manure	CK, N, NP, NK, NPK, 2NPK, NPKM
<b>S</b> 3	Rice-Rice	1981-2018	Pig manure	CK, NPK, M
S4	Wheat- Maize	1991–2012	Pig manure	CK, N, NP, NK, NPK, NPKM, M
<b>S</b> 5	Rice-Rice	1982–2015	Cattle manure	CK, NPK, PKM, NKM, NPM, NPKM, M
<b>S</b> 6	Maize	2010-2018	Cattle manure	CK, NPK, NPKM, M
S7	Rice-Wheat	1983–2015	Pig manure	CK, N, NP, NPK, M, NM, NPM, NPKM
S8	Rice-Wheat	1991–2018	Chicken manure	CK, N, NP, NK, NPK, NPKM
S9	Rice	2010-2018	Cattle manure	CK, NPK, NPKM, M
S10	Wheat-Rice	1981–2015	Pig manure	CK, N, NP, NPK, NM, NPM, NPKM
S11	Rice-Rice	1981-2007	Pig manure	CK, NP, NK, NPK, NKM
S12	Rice-Rice	1984-2017	Pig manure	CK, NP, NK, NPK, NPKM
S13	Rice-Rice	1984–2015	Cattle manure	CK, NPK, NPKM

(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)

#### Table 1

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

Site	Site name	e name Location	Start	SOC <sup>a</sup>	Initial pH	Total	Total (g/kg)		Available (mg/kg)		/kg)	Soil type	PRE <sup>b</sup>	TEM <sup>b</sup>	SSH <sup>b</sup>
No.			Year	(g/ kg)		N	Р	К	N	Р	К	(FAO)	(mm)	(°C)	(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	1.1	13	150	9.5	98	Eutric Cambisol	1537	18	1950
S3	Jiangxi-Jinxian	28°35'N 116°17'E	1981	16	6.9	1.0	1.0	15	144	10	125	Eutric Cambisol	1537	18	1950
S4	Hunan-Qiyang	26°45'N 111°52'E	1990	7.9	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	1227
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	1150	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	169	18	41	Fe-leachi-Stagnic	1351	20	1813

<sup>a</sup> SOC, soil organic carbon.

<sup>b</sup> PRE, mean precipitation of each year; TEM, mean temperature of each year; SSH, mean sunshine hours of each year.

Site No	N	М	NM	NK	NKM	NP	NPM	NPK		NPKM	
								NPK	2NPK	NPKM	1.5NPKM
S1	I	1	1	I	1	I	1	180	I	(180-210)+95#(180-210)+77%	-
S2	180	1	I	180	I	180	1	180	360	180 + 276 %	I
S3	I	144-199☆ 299-247 ※☆	I	I	I	I	1	180 - 228	I	1	1
S4	300	196-458 ※	I	300	I	300	1	300	I	$90 + (137 - 320) \approx$	$135 + (206-420) \approx$
S5	I	109–217#	I	I	290 + 217 # 145 + 109 #	I	290 + 217 # 145 + 109 #	73-145	I	290 + 217 # 145 + 109 #	1
S6	I	61	I	I	I	I	1	165	I	124 + (15-68) #	1
S9	I	61-271#	I	I	1	I	1	66	I	74 + (15-68) #	1
S7	240	106-135 %	240 + (106 - 135) %	I	I	240	$240 + (106 - 135) \approx$	240	I	240 + (106 - 135) %	I
S8	285-300	13-65 %	I	285-300	I	285-300	1	285-300	I	$(285-300) + (12-221) \approx$	(427-450) + (13-65)
S10	150	53-113 **	150+(53-113)	I	I	150	150 + (53 - 113) %	150	I	150 + (53-189)	1
S11	I	1	I	150	150 + 414 %	150	1	150	I	1	1
S12	I	1	I	329	I	329	1	329	I	$(100-232) + (98-230) \approx$	I
S13	I	1	I	I	I	I	1	103-207	ı	(103-207) + (56-112)#	I

Table :

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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.

### 2.3. Data analysis

### 2.3.1. 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:

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

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<sup>-1</sup>) and TNI being the total N input (kg N ha<sup>-1</sup>), originating from organic (ONI, kg ha<sup>-1</sup>) and inorganic (INI, kg ha<sup>-1</sup>) 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.

## 2.3.2. 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<sup>-1</sup>), phosphorus input (TPI, kg P ha<sup>-1</sup>) and potassium input (TKI, kg K ha<sup>-1</sup>) 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 to 615 kg ha<sup>-1</sup> for TNI, 0–525 kg ha<sup>-1</sup> for TPI, 0–940 kg ha<sup>-1</sup> for TKI and 0–13 kg ha<sup>-1</sup> for TCI with ratio of organic to total nitrogen fertilizer input varying from 3% to 78% with the highest inputs occurring in the combined fertilizer treatments (Fig. S1).

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%. AN ranged from 10 to 464 mg N kg<sup>-1</sup>, AP from 0.1 to 347 mg P kg<sup>-1</sup> and  $\widetilde{AK}$  from 20 to 988 mg K kg<sup>-1</sup>. There was also a substantial variation in soil organic matter levels and soil acidity with SOC levels ranging between 6 and  $39 \text{ g kg}^{-1}$  and the pH varying between 3.5 and 8.6 (Fig. S2). Climatic variables include the mean TEM, SSH and PRE during the growing season as well as the number of heavy rain events where the daily precipitation exceeds the 25 mm (daynumber). The mean TEM varied from 14° to 28°C and the SSH from 417 up to 3202h. The PRE ranged from 266 up to 4868 mm whereas the number of extreme precipitation events could range from 2 up to 65 days (Fig. S3).

2.3.3. Statistical approaches to evaluate the impact of site factors affecting the NUE  $% \mathcal{A}_{\mathrm{S}}$ 

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 et al., 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 permutationbased 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 ( $\mathbb{R}^2$ ) 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.

# 3. Results

# 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 -6-127% with a mean value of 36%, crop yield ranged from 0 to 30 t ha<sup>-1</sup> with a mean value of 16 t ha<sup>-1</sup>, and N uptake of the cropping system ranged from 0 to 461 kg ha<sup>-1</sup> with a mean value of 172 kg ha<sup>-1</sup> (Fig. 1). As expected, a strong relationship was found between NUE and crop yield (Fig. S4). Highest values of NUE, yield and N uptake were found in Wangcheng, Wuchang and Jinxian, while lowest values were all found in Qiyang (Fig. S5). 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).

Long-term impacts of fertilizer inputs caused a substantial variation in NUE (Fig. S5). 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 P 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 1981–2018 (Fig. 2). The lowest NUE was found when only inorganic N fertilizers



Fig. 1. Frequency distributions of nitrogen use efficiency (NUE), crop yield and crop N uptake (N<sub>uptake</sub>).



Fig. 2. Mean NUE, crop yield and crop N uptake (Nuptake) over the period 1981-2018 for different long-term fertilization treatments.

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.

In line with the NUE, the lowest crop yield and N uptake was found when only inorganic N fertilizers were applied, with a crop production of 10 t ha<sup>-1</sup> and an N uptake of 113 kg ha<sup>-1</sup>. The highest yield was found in the NPM and NPKM treatments (about 19 t ha<sup>-1</sup>) whereas the highest N uptake was found in the NM, NPM and NPKM treatments (about 208 kg ha<sup>-1</sup>) (Fig. 2). As expected, the NUE was positively correlated with crop yield (r = 0.6) and N uptake (r = 0.7) (Fig. S6).

# 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 (TKI). 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).

#### Table 4

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Multi-linear model (GLM) of the effects of site factors on the NUE.
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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 <sup>2</sup>	-0.16
	TPI	0.31
	TPI <sup>2</sup>	-0.04
	duration	-0.14
Soil properties	Clay	-0.38
	pH	-0.44
	pH <sup>2</sup>	-0.11
	pH <sup>3</sup>	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). pH<sup>2</sup> and pH<sup>3</sup> denotes the pH to power 2 and 3 respectively whereas the ratio between organic and inorganic N inputs (N<sub>org</sub>-fraction) and TPI are also squared (N<sub>org</sub>-fraction<sup>2</sup> and TPI<sup>2</sup>). "In" variables were In-transformed. The

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

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



Fig. 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).

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. S6).

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. 3, right; Fig S7, S8 and S9). 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 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 TEM 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 (TPI) 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 PRE and the crop rotation had the highest impact on NUE whereas the duration of the experiment, the ratio organic versus TNI (the Norg fraction) and the level of available P had the lowest impact (Fig. 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. 4). In addition, the NUE strongly declined with TNI, from > 50% at low N does (below 10 kg N ha<sup>-1</sup>) down to 20% when TNI increased to 400 kg N ha<sup>-1</sup>. 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<sup>-1</sup> after which it gradually increased up to 35% at P levels above 150 mg P kg $^{-1}$ .

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. 3, right). The most important factors controlling the variation in NUE include soil pH, TPI, 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. 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). Of slightly lower importance was the available P in soil, showing that N uptake is substantially affected by both the input and availability of P. 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. 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<sup>-1</sup> and soil available P levels up to 80 mg P kg<sup>-1</sup>. Although not being a main driver of variation in NUE (Fig. 3), we found that NUE is affected by N input, where the highest NUE was found when TNI varied between 180 and 220 kg N ha<sup>-1</sup> (Fig. 4d). The ratio of organic to inorganic nitrogen (ONI/TNI) had very limited impact on the NUE (Fig. 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



Fig. 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).

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).

## 4. Discussion

#### 4.1. The use of nitrogen use efficiency 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 and de Vries, 2021). First, by spatially redistributing crop and animal production and associated N inputs and losses one can avoid high N 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. 3, Fig S6) and to identify the same site properties controlling NUE (Fig. 3, Fig S8), 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. 4, Fig S8), the observed maxima of 40–45% in the partial dependency plots for XGBoost (Fig. 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.

# 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 N. Using this approach, all site properties controlling crop yield have been equal, and sufficient nutrients other than N 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. S9). 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.

# 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 N losses, since sufficient and timely nutrient supply affects both crop grain formation and soil fertility. N 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), 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 P, K, 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) 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 P content, characterized by relatively high retention capacities due to high iron oxide and aluminium levels (Chang and Jackson, 1957). In addition to the P input, additional Ca 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). On the long term however, we showed that the effect of soil amendment with organic manure on the NUE varied a lot (Fig. 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 N (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 BC to soil prevents acidification (Hao et al., 2022). The optional ratio of organic N fertilizer and total N fertilizer input was around 30-40% (Fig. 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). 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 N uptake increased up to a total N input level around 200 kg N ha<sup>-1</sup> (data not shown). Adding more N resulted in a decline of NUE (Fig. 4) showing that fertilizing a crop above a critical threshold will result in adverse environmental impacts on both the short and long-term. Total N input had indeed a positive correlation with crop yield while NUE declines (Fig. S5). 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.

# 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). 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 BC 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 N. 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 BC depletion and severe acidification (Cai et al., 2015). The benefit of organic matter via manure increases with the dose applied (Duan et al., 2021). As total P fertilizer input and soil available P and K 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. S9).

Furthermore, the efficiency of N uptake varies among crop types. The N 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<sup>-1</sup>), and relatively low total N inputs ( $< 125 \text{ kg N ha}^{-1}$ ) and high P inputs (>100 kg P ha<sup>-1</sup>). 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.

N 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 (1972), 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 N 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. 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, precipitation, and evaporation. Both sunshine hours and temperature 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. In addition, high precipitation can disperse soil particle structure and increase the nutrient concentration of surface water and runoff, and consequently sites with high precipitation have higher risks for leaching and runoff. Consequently, sites with higher precipitation had indeed lower NUE.

#### 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 -6-127%. Lowest NUE was found in cases where crops were fertilized with inorganic N fertilizers only, and the NUE increased when multi-nutrients or organic manures were applied. The soil, climatic and fertilizer inputs together explained 46-85% of the variation in NUE. 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 50–100 mg kg<sup>-1</sup>, being much higher than the common optimum POLSEN thresholds for P deficiencies near 20 mg kg<sup>-1</sup>. Using generalized linear regression modelling, we found that the NUE decreases 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 30-40% 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% to 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.

#### CRediT authorship contribution statement

Xingjuan Zhu: Methodology, Data analysis, Writing – review & editing. Gerard Ros: Conceptualization, Data analysis, Writing – review & editing. Wim de Vries: Conceptualization, Methodology, Writing – review & editing. Minggang Xu: Conceptualization, Methodology, Review, Data supporting. Zejiang Cai: Methodology and Data supporting. Nan Sun: Data supporting. Yinghua Duan: Data supporting.

# **Declaration of Competing Interest**

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

#### **Data Availability**

The authors do not have permission to share data.

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## Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.eja.2023.126797.

#### References

- Bai, Z., Li, H., Yang, X., Zhou, B., Shi, X., Wang, B., Li, D., Shen, J., Chen, Q., Qin, W., Oenema, O., Zhang, F., 2013. The critical soil p levels for crop yield, soil fertility and environmental safety in different soil types. Plant Soil. Int. J. Plant Soil. Relatsh. 372 (1–2), 27–37. https://doi.org/10.1007/s11104-013-1696-y.
- Bao, S. (1999). Soil and agricultural chemistry analysis. Beijing: China Agricultural Press. (In Chinese).
- Bolan, N.S., Adriano, D.C., Curtin, D., 2003. Soil acidification and liming interactions with nutrient and heavy metal transformation and bioavailability. Adv. Agron. 78, 216–272. https://doi.org/10.1016/S0065-2113(02)78006-1.
- Briat, J.-F., Gojon, A., Plassard, C., Rouached, H., Lemaire, G., 2020. Reappraisal of the central role of soil nutrient availability in nutrient management in light of recent advances in plant nutrition at crop and molecular levels. Eur. J. Agron. 116. https:// doi.org/10.1016/j.eja.2020.126069.
- Cai, A., Xu, M., Wang, B., Zhang, W., Liang, G., Hou, E., Luo, Y., 2019. Manure acts as a better fertilizer for increasing crop yields than synthetic fertilizer does by improving soil fertility. Soil Tillage Res. 189, 168–175. https://doi.org/10.1016/j. still.2018.12.022.
- Cai, C., Yin, X., He, S., Jiang, W., Si, C., Struik, P.C., Luo, W., Li, G., Xie, Y., Xiong, Y., Pan, G., 2016. Responses of wheat and rice to factorial combinations of ambient and elevated CO<sub>2</sub> and temperature in FACE experiments. Glob. Change Biol. 22 (2), 856–874. https://doi.org/10.1111/gcb.13065.
- Cai, Z., Wang, B., Xu, M., Zhang, H., He, X., Zhang, L., Gao, S., 2015. Intensified soil acidification from chemical n fertilization and prevention by manure in an 18-year field experiment in the red soil of southern China. J. Soils Sediment. 15 (2), 260–270. https://doi.org/10.1007/s11368-014-0989-y.
- Chang, S.C., Jackson, M.L., 1957. Fractionation of soil phosphorus. Soil Sci. 84 (2), 133–144. https://doi.org/10.1097/00010694-195708000-00005.
- Chen, T., Guestrin, C., 2016. XGBoost: a scalable tree boosting system. Proceedings of the 22nd ACM SIGKDD International Conference on Knowledge Discovery and Data Mining (KDD '16). Association for Computing Machinery, New York, NY, USA, pp. 785–794. https://doi.org/10.1145/2939672.2939785.
- Coulibali, Z., Cambouris, A.N., Parent, S.-É., 2020. Site-specific machine learning predictive fertilization models for potato crops in eastern canada. Plos One 15 (8), 0230888. https://doi.org/10.1371/journal.pone.0230888.
- Cui, Z., Zhang, F., Chen, X., Miao, Y., Li, J., Shi, L., Xu, J., Ye, Y., Liu, C., Yang, Z., zhang, Q., Huang, S., Bao, D., 2008. On-farm evaluation of an in-season nitrogen management strategy based on soil N min test. Field Crops Res. 105 (1), 48–55. https://doi.org/10.1016/j.fcr.2007.07.008.
- Da Silva, J.M., Fontes, P.C.R., Milagres, C., do, C., de Abreu, J.A.A., 2020. Yield and nitrogen use efficiency of bell pepper grown in slab fertigated with different nitrogen rates. J. Plant Nutr. 43 (18), 2833–2843. https://doi.org/10.1080/ 01904167.2020.1783297.
- De Vries, W., Posch, M., Kämäri, J., 1989. Simulation of the long-term soil response to acid deposition in various buffer ranges. Water, Air, Soil Pollut.: Int. J. Environ. Pollut. 48 (3–4), 349–390. https://doi.org/10.1007/BF00283336.
- Dong, Y., Yang, J.-L., Zhao, X.-R., Yang, S.-H., Mulder, J., Dörsch, P., Peng, X.-H., Zhang, G.-L., 2022. Soil acidification and loss of base cations in a subtropical agricultural watershed. Sci. Total Environ. 827. https://doi.org/10.1016/j. scitotenv.2022.154338.
- Du, Y., Niu, W., Zhang, Q., Cui, B., Gu, X., Guo, L., Liang, B., 2018. Effects of nitrogen on soil microbial abundance, enzyme activity, and nitrogen use efficiency in greenhouse celery under aerated irrigation. Soil Sci. Soc. Am. J. 82 (3), 606–613. https://doi. org/10.2136/sssaj2017.11.0377.
- Duan, Y., Xu, M., Wang, B., Yang, X., Huang, S., Gao, S., 2011. Long-term evaluation of manure application on maize yield and nitrogen use efficiency in China. Soil Sci. Soc. Am. J. 75 (4), 1562–1573. https://doi.org/10.2136/sssaj2010.0315.
- Duan, Y., Yang, H., Shi, T., Zhang, W., Xu, M., Gao, S., 2021. Long-term manure application to improve soil macroaggregates and plant-available nitrogen in a mollisol. Soil Tillage Res. 211. https://doi.org/10.1016/j.still.2021.105035.
- Duan, Y., Xu, M., Gao, S., Yang, X., Huang, S., Liu, H., Wang, B., 2014. Nitrogen use efficiency in a wheat-corn cropping system from 15 years of manure and fertilizer

#### X. Zhu et al.

applications. Field Crops Res. 157, 47–56. https://doi.org/10.1016/j. fcr.2013.12.012.

Fenn, Mark, E., Huntington, T.G., McLaughlin, S.B., Eager, C., Gomez, A., Cook, R.B., 2006. Status of soil acidification in North America. J. For. Sci. 52, 3–13. https://doi. org/10.17221/10152-JFS.

- Gai, X., Liu, H., Liu, J., Zhai, L., Yang, B., Wu, S., Ren, T., Lei, Q., Wang, H., 2018. Longterm benefits of combining chemical fertilizer and manure applications on crop yields and soil carbon and nitrogen stocks in north china plain. Agric. Water Manag. 208, 384–392. https://doi.org/10.1016/j.agwat.2018.07.002.
- Guntiñas, M.E., Leirós, M.C., Trasar-Cepeda, C., Gil-Sotres, F., 2012. Effects of moisture and temperature on net soil nitrogen mineralization: a laboratory study. Eur. J. Soil Biol. 48, 73–80. https://doi.org/10.1016/j.ejsobi.2011.07.015.
- Guo, J., Liu, X., Zhang, Y., Shen, J., Han, W., Zhang, W., Christie, P., Goulding, K., Vitousek, P., Zhang, F., 2010. Significant acidification in major Chinese croplands. Science 327 (5968), 1008–1010. (http://www.jstor.org/stable/40509964).
- Hao, T., Liu, X., Zhu, Q., Zeng, M., Chen, X., Yang, L., Shen, J., Shi, X., Zhang, F., de Vries, W., 2022. Quantifying drivers of soil acidification in three chinese cropping systems. Soil Tillage Res. 215. https://doi.org/10.1016/j.still.2021.105230.
- Heumann, S., Fier, A., Haßdenteufel, M., Höper, Heinrich, Schäfer, Walter, Eiler, T., Böttcher, Jurgen, 2013. Minimizing nitrate leaching while maintaining crop yields: insights by simulating net n mineralization. Nutr. Cycl. Agroecosystems: (Former. Fertil. Res. ) 95 (3), 395–408. https://doi.org/10.1007/s10705-013-9572-y.
- Hua, W., Luo, P., An, N., Cai, F., Zhang, S., Chen, K., Yang, J., Han, X., 2020. Manure application increased crop yields by promoting nitrogen use efficiency in the soils of 40-year soybean-maize rotation. Sci. Rep. 10 (1) https://doi.org/10.1038/s41598-020-71932-9.
- Ichami, S.M., Shepherd, K.D., Sila, A.M., Stoorvogel, J.J., Hoffland, E., 2019. Fertilizer response and nitrogen use efficiency in african smallholder maize farms. Nutr. Cycl. Agroecosyst. 113 (1), 1–19. https://doi.org/10.1007/s10705-018-9958-y.
- Ju, X., Xing, G., Chen, X., Zhang, S., Zhang, L., Liu, X., Cui, Z., Yin, B., Christie, P., Zhu, Z., Zhang, F., Tilman, G.D., 2009. Reducing environmental risk by improving n management in intensive Chinese agricultural systems. Proc. Natl. Acad. Sci. USA 106 (9), 3041–3046. (http://www.jstor.org/stable/40443266).
- Kirchmann, H., Ryan, M.H., Bergström, L., 2007. Plant nutrient use efficiency in organic farming - consequences of exclusive use of organic manures and untreated minerals. Cab. Rev. Perspect. Agric., Vet. Sci., Nutr. Nat. Resour. 2 (076), 12. https://doi.org/ 10.1079/PAVSNNR20072076.
- Kirchmann, H., Borjesson, G., Bolinder, M.A., Katterer, T., Djodjic, F., 2020. Soil properties currently limiting crop yields in swedish agriculture - an analysis of 90 yield survey districts and 10 long-term field experiments. Eur. J. Agron. 120. https:// doi.org/10.1016/j.eja.2020.126132.
- Lang, M., Binder, M., Richter, J., Schratz, P., Pfisterer, F., Coors, S., Au, Q., Casalicchio, G., Kotthoff, L., Bischl, B., 2019. mlr3: A modern object-oriented machine learning framework in R. J. Open-Source Softw. https://doi.org/10.21105/ joss.01903.
- Lemaire, G., Jeuffroy, M.-H., Gastal, F., 2008. Diagnosis tool for plant and crop n status in vegetative stage: theory and practices for crop n management. Eur. J. Agron. 28 (4), 614–624. https://doi.org/10.1016/j.eja.2008.01.005.
  Lemaire, G., Tang, L., Bélanger, Gilles, Zhu, Y., Jeuffroy, Marie-Hélène, 2021. Forward
- Lemaire, G., Tang, L., Bélanger, Gilles, Zhu, Y., Jeuffroy, Marie-Hélène, 2021. Forward new paradigms for crop mineral nutrition and fertilization towards sustainable agriculture. Eur. J. Agron. 125 https://doi.org/10.1016/j.eja.2021.126248.
- Li, C.-J., Li, Y.-Y., Yu, C.-B., Sun, J.-H., Christie, P., An, M., Zhang, F.-S., Li, L., 2011. Crop nitrogen use and soil mineral nitrogen accumulation under different crop combinations and patterns of strip intercropping in northwest china. Plant Soil.: Int. J. Plant-Soil. Relatsh. 342 (1–2), 221–231. https://doi.org/10.1007/s11104-010-0686-6.
- Liang, S., Li, Y., Zhang, X., Sun, Z., Sun, N., Duan, Y., Xu, M., Wu, L., 2018. Response of crop yield and nitrogen use efficiency for wheat-maize cropping system to future climate change in northern China. Agric. For. Meteorol. 262, 310–321. https://doi. org/10.1016/j.agrformet.2018.07.019.
- Liang, W., Lou, Y., Qi, L.I., Zhong, S., Zhang, X., Wang, J., 2009. Nematode faunal response to long-term application of nitrogen fertilizer and organic manure in Northeast China. Soil Biol. Biochem. 41, 883–890. https://doi.org/10.1016/j. soilbio.2008.06.018.
- Liebig, J. von, 1855. Die grundsätze der agricultur-chemie mit rücksicht auf die in england angestellten untersuchungen (2. durch einen Nachtrag verm. Aufl). Agric. For. Meteorol. 250, 202–208. https://doi.org/10.1016/j.agrformet.2017.12.254.
- Liebscher, G., 1895. Untersuchungen über die Bestimmung des Düngerbedürfnisses der Ackerböden und Kulturpflanzen. J. für Landwirtsch. 43, 49–125.
- Lucas, R.W., Klaminder, J., Futter, M.N., Bishop, K.H., Egnell, G., Laudon, H., Högberg, P., 2011. A meta-analysis of the effects of nitrogen additions on base cations: implications for plants, soils, and streams. For. Ecol. Manag. 262 (2), 95–104. https://doi.org/10.1016/j.foreco.2011.03.018.
- Miao, Y., Stewart, B.A., Zhang, F., 2011. Long-term experiments for sustainable nutrient management in china. a review. Agron. Sustain. Dev.: Off. J. Inst. Natl. De. La Rech. Agron. Inra 31 (2), 397–414. https://doi.org/10.1051/agro/2010034.
- Midolo, G., Alkemade, R., Schipper, A.M., Benítez-López, A., Perring, M.P., de Vries, W., 2018. Impacts of nitrogen addition on plant species richness and abundance: a global meta-analysis. Glob. Ecol. Biogeogr. https://doi.org/10.1111/geb.12856.
- Mitscherlich, E.A. (1925). Die Bestimmung des Düngerbedürfnisses des Bodens. P. Parey. Nayak, D., Saetnan, E., Cheng, K., Wang, W., Koslowski, F., Cheng, Y., Zhu, W., Wang, J., Liu, J., Moran, D., Yan, X., Cardenas, L., Newbold, J., Pan, G., Lu, Y., Smith, P., 2015.
- Management opportunities to mitigate greenhouse gas emissions from chinese agriculture. Agric, Ecosyst. Environ. 209, 108–124. https://doi.org/10.1016/j. agee.2015.04.035.

- Norse, D., Ju, X., 2015. Environmental costs of china's food security. Agric., Ecosyst. Environ. 209, 5–14. https://doi.org/10.1016/j.agee.2015.02.014.
- Pardon, Le, Huth, N.I., Nelson, P.N., Banabas, M., Gabrielle, B., Bessou, C., 2017. Yield and nitrogen losses in oil palm plantations: main drivers and management trade-offs determined using simulation. Field Crops Res. 210, 20–32. https://doi.org/10.1016/ j.fcr.2017.05.016.
- Parry, M.L., Rosenzweig, C., Iglesias, A., Livermore, M., Fischer, G., 2004. Effects of climate change on global food production under sres emissions and socio-economic scenarios. Glob. Environ. Change 14 (1), 53–67. https://doi.org/10.1016/j. gloenycha.2003.10.008.
- Peter, O., Lawrence, A., William, R.R., 2019. Nitrogen uptake efficiency and total soil nitrogen accumulation in long-term beef manure and inorganic fertilizer application. Int. J. Agron. 2019. https://doi.org/10.1155/2019/9594369.
- Qin, Z., Myers, D.B., Ransom, C.J., Kitchen, N.R., Liang, S.-Z., Camberato, J.J., Carter, P. R., Ferguson, R.B., Fernandez, F.G., Franzen, D.W., Laboski, C.A.M., Malone, B.D., Nafziger, E.D., Sawyer, J.E., Shanahan, J.F., 2018. Application of machine learning methodologies for predicting corn economic optimal nitrogen rate. Agron. J. 110 (6), 2596–2607. https://doi.org/10.2134/agronj2018.03.0222.
- Ren, K., Xu, M., Li, R., Zheng, L., Liu, S., Reis, S., Wang, H., Lu, C., Zhang, W., Gao, H., Duan, Y., Gu, B., 2022. Optimizing nitrogen fertilizer use for more grain and less pollution. J. Clean. Prod. 360. https://doi.org/10.1016/j.jclepro.2022.132180.
- Robertson, G.P., Vitousek, P.M., 2009. Nitrogen in agriculture: balancing the cost of an essential resource. Annu. Rev. Environ. Resour. 34 (1), 97–125. https://doi.org/ 10.1146/annurev.environ.032108.105046.
- Rokach, L., Maimon, O.Z., & Maimon, O. (2008). Data mining with decision trees: theory and applications (Ser. Series in machine perception and artificial intelligence, v. 69). World Scientific.
- Schulte-Uebbing, L., de Vries, W., 2021. Reconciling food production and environmental boundaries for nitrogen in the european union. Sci. Total Environ. 786. https://doi. org/10.1016/j.scitotenv.2021.147427.
- Shang, Q., Gao, C., Yang, X., Wu, P., Ling, N., Shen, Q., Guo, S., 2014. Ammonia volatilization in chinese double rice-cropping systems: a 3-year field measurement in long-term fertilizer experiments. Biol. Fertil. Soil.: Coop. J. Int. Soc. Soil.Sci. 50 (5), 715–725. https://doi.org/10.1007/s00374-013-0891-6.
- Shi, R., Liu, Z., Li, Y., Jiang, T., Xu, M., Li, J., Xu, R., 2019. Mechanisms for increasing soil resistance to acidification by long-term manure application. Soil Tillage Res. 185, 77–84. https://doi.org/10.1016/j.still.2018.09.004.
- Silvertown, J., Poulton, P., Johnston, E., Edwards, G., Heard, M., Biss, P., 2006. The park grass experiment 1856-2006: its contribution to ecology (https://doi-org.ezproxy. library.wur.nl/). J. Ecol. 94 (4), 801–814. https://doi.org/10.1111/j.1365-2745.2006.01145.x.
- Stanford, G., Smith, S.J., 1972. Nitrogen mineralization potentials of soils. Soil Sci. Soc. Am. J. 36 (3), 465–472. https://doi.org/10.2136/ sssai1972.03615995003600030029x.
- Tao, H., Donough, C., Gerendas, J., Hoffmann, M.P., Cahyo, A., Sugianto, H., Wandri, R., Rahim, G.A., Fisher, M., Rötter, R.P., Dittert, K., Pardon, L., Oberthuir, T., 2018. Fertilizer management effects on oil palm yield and nutrient use efficiency on sandy soils with limited water supply in central kalimantan. Nutr. Cycl. Agroecosystems: (Former. Fertil. Res.) 112 (3), 317–333. https://doi.org/10.1007/s10705-018-9948-

Team, R. C. (2013). R: A language and environment for statistical computing.

- Tilman, D., Balzer, C., Hill, J., Befort, B.L., 2011. Global food demand and the sustainable intensification of agriculture. Proc. Natl. Acad. Sci. U. S. A. 108, 20260–20264. https://doi.org/10.1073/pnas.1116437108.
- Vandermeer, J., 1989. The Ecology of Intercropping. Cambridge University Press, Cambridge. https://doi.org/10.1017/CB09780511623523.
- Wang, Q., Li, F., Zhao, L., Zhang, E., Shi, S., Zhao, W., Song, W., Vance, M.M., 2010. Effects of irrigation and nitrogen application rates on nitrate nitrogen distribution and fertilizer nitrogen loss, wheat yield and nitrogen uptake on a recently reclaimed sandy farmland (https://doi.org.ezproxy.library.wur.nl/). Plant Soil 337 (1–2), 325–339. https://doi.org/10.1007/s11104-010-0530-z.
- Yadav, R.L., Dwivedi, B.S., Prasad, K., Tomar, O.K., Shurpali, N.J., Pandey, P.S., 2000. Yield trends, and changes in soil organic-c and available npk in a long-term ricewheat system under integrated use of manures and fertilisers. Field Crops Res. 68 (3), 219–246. https://doi.org/10.1016/S0378-4290(00)00126-X.
- Yan, H., Duan, Y., Xu, M., Wu, L., 2011. Nitrogen use efficiency of wheat as affected by long-term fertilization in the typical soil of China. Sci. Agric. Sin. 44, 13.
- Yang, J., Gao, W., Ren, S., 2015b. Long-term effects of combined application of chemical nitrogen with organic materials on crop yields, soil organic carbon and total nitrogen in fluvo-aquic soil. Soil Tillage Res. 151, 67–74. https://doi.org/10.1016/j. still.2015.03.008.
- Ye, Q., Zhang, H., Wei, H., Zhang, Y., Wang, B., Xia, K., Huo, Z., Dai, Q., Xu, K., 2007. Effects of nitrogen fertilizer on nitrogen use efficiency and yield of rice under different soil conditions (https://doi-org.ezproxy.library.wur.nl/). Front. Agric. China 1 (1), 30–36. https://doi.org/10.1007/s11703-007-0005-z.
- Yu, F., Shi, W., 2015. Analysis of nitrogen use efficiency of main grain crops in mainland China in recent 10 years. Acta Pedol. Sin. 52 (06), 1311–1324.
- Zeng, M., Vries, de, W., Bonten, L.T.C., Zhu, Q., Hao, T., Liu, X., Xu, M., Shi, X., Zhang, F., Shen, J., 2017. Model-based analysis of the long-term effects of fertilization management on cropland soil acidification (https://doi-org.ezproxy.library.wur.nl/ ). Environ. Sci. Technol. 51 (7), 3843–3851. https://doi.org/10.1021/acs. est.6b05491.
- Zhang, F., Wang, J., Zhang, W., Cui, Z., Ma, W., Chen, Q., Jiang, R., 2008. Nutrient use efficiencies of major cereal crops in China and measures for improvement. Acta Pedol. Sin. 45 (5), 915–924.

#### X. Zhu et al.

- Zhang, J., Cai, Z., Muiller, C., 2018. Terrestrial n cycling associated with climate and plant-specific n preferences: a review. Eur. J. Soil Sci. 69 (3), 488–501. https://doi. org/10.1111/ejss.12533.
- Zhang, X., Davidson, E.A., Mauzerall, D.L., Searchinger, T.D., Dumas, P., Shen, Y., 2015. Managing nitrogen for sustainable development. Nature 528 (7580), 51–59. https:// doi.org/10.1038/nature15743.
- Zhang, X., Xu, M., Liu, J., Sun, N., Wang, B., Wu, L., 2016. Greenhouse gas emissions and stocks of soil carbon and nitrogen from a 20-year fertilised wheat-maize intercropping system: a model approach. J. Environ. Manag. 167, 105–114. https:// doi.org/10.1016/j.jenvman.2015.11.014.
- Zhou H. (2015). Soil acidification effect and improvement regulation of intensive farmland in Jiaodong. China Agricultural University. (In Chinese).
- Zhu, Q., Liu, X., Hao, T., Zeng, M., Shen, J., Zhang, F., Vries, de, W., 2020. Cropland acidification increases risk of yield losses and food insecurity in China. Environ. Pollut. 256. https://doi.org/10.1016/j.envpol.2019.113145.
- Pollut. 256. https://doi.org/10.1016/j.envpol.2019.113145.
   Ziadi, N., Bélanger, Gilles, Cambouris, A.N., Tremblay, N., Nolin, M.C., Claessens, A., 2008. Relationship between phosphorus and nitrogen concentrations in spring wheat, 470–470 Agron. J. 100 (2). https://doi.org/10.2134/agronj2007.0119er.
- Zou, J., Huang, Y., Qin, Y., Liu, S., Shen, Q., Pan, G., Lu, Y., Liu, Q., 2009. Changes in fertilizer-induced direct N2O emissions from paddy fields during rice-growing season in China between 1950s and 1990s (https://doi.org.ezproxy.library.wur.nl/). Glob. Change Biol. 15 (1), 229–242. https://doi.org/10.1111/j.1365-2486.2008.01775.x.