

# Manure acts as a better fertilizer for increasing crop yields than synthetic fertilizer does by improving soil fertility

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## ABSTRACT

Fertilization is an important management strategy for crop yields by mediating soil fertility. However, rare studies quantitatively assessed the interactions among fertilization, crop yields, and soil fertility. Here, data from a 25-year fertilization experiment in the humid subtropical region of Southern China were used to evaluate and quantify the effect of fertilization on crop yields via soil fertility. Seven treatments were chosen: CK (non-fertilizer); N (synthetic nitrogen); NP (synthetic N and phosphorus); NPK (synthetic N, P and potassium); NPKM<sub>1</sub> (synthetic NPK with manure); 1.5NPKM<sub>1</sub> (1.5 times of NPKM<sub>1</sub>); and M<sub>2</sub> (manure alone). Overall, the crop yields of wheat and maize under manure (1.36–1.58 and 3.85–5.82 Mg ha<sup>-1</sup>) were higher than those under CK (0.34 and 0.25 Mg ha<sup>-1</sup>) and synthetic fertilized treatments (0.27–0.97 and 0.48–2.65 Mg ha<sup>-1</sup>), as the averaged of 1991–2015. Higher SOC stocks were found under the NPKM<sub>1</sub>, 1.5NPKM<sub>1</sub>, and M<sub>2</sub> treatments with a pronounced increase in SOC over the first 10 years and stable over the last 15 years. By the boosted regression trees, manure, synthetic fertilizer and soil properties (SOC storage, soil pH, and soil nutrients) accounted for 39%, 21%, and 40% of the variation of the relative yield, respectively. Path analysis identified a network of inter-relations of manure, synthetic fertilizer, and soil properties in the relative yields. Compared to synthetic fertilized treatments, manure application strongly and positively affected the relative yield by increasing SOC storage, soil nutrients, and soil pH (path coefficients: 0.90, 0.88, and 0.76). These factors explained 72% of the crop yields' variance. These results suggest that manure application is a viable strategy for regulating crop yields due to its improvement in soil fertility.

## 1. Introduction

Promoting global crop productivity to feed the ever-increasing population and high living standards has become a great challenge (Fischer et al., 2014). The most debating question of recent times is “How to increase the crop yields?” (Foley et al., 2011). Technological progress in field management has contributed to large increases in crop yields (Deryng et al., 2011). Among all the management strategies, fertilization has been suggested as a promising strategy to increase crop yields. Based on 153 field experiments in China, Chen et al. (2014) observed an increase in crop yields of approximately 8.5–14.2 Mg ha<sup>-1</sup> following fertilization with manure without any increase in nitrogen (N) fertilizer. Using data from 20 field experiments in Europe, Hijbeek

et al. (2016) reported that crop yields increased by 2.0 Mg ha<sup>-1</sup> due to synthetic fertilization and had negligible change (an increase of 1.4%) in response to manure. It is obvious that the effect of different fertilizer types on crop yields is inconsistent via different mechanisms. Therefore, to achieve high crop productivity, it is important to understand the impact of different fertilizer inputs on crop yields.

Exogenous fertilization influences the crop yields by improving soil fertility, such as soil carbon, nutrients, and pH. Soil carbon content is the essential index for different yields (Tian et al., 2016). Soil organic carbon (SOC) sequestration can be enhanced by fertilization such as incorporation of crop residues or the direct application of manure, which implies by high carbon inputs (Cai et al., 2016). Synthetic fertilization can also change SOC by the return of crop residues. For

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instance, Zhang et al. (2012) showed that carbon inputs were 2.5–5.0 Mg ha<sup>-1</sup> year<sup>-1</sup> by synthetic fertilization in southern China. The greater amount of carbon inputs by green manure improved the SOC stock by 14–24% and reduced synthetic fertilization of 25–51% compared with fallow (Yao et al., 2017). In their meta-analysis, McDaniel et al. (2014) reported that the rate of SOC sequestration under cover crop is significantly higher than SOC sequestration rate under no cover crop. The application of farmyard manure, rice straw, and fertilizer nitrogen could maintain SOC almost at the same level as for the uncultivated soil for rice-wheat cropping systems in the Indo-Gangetic plains (Benbi et al., 2012). However, the mechanisms by which different fertilizer inputs affect crop yields by improving SOC remain unclear.

Soil nutrients are the major yield-limiting factors. Therefore, to achieve an efficient and profitable crop production relies on the large inputs of synthetic fertilizers. However, less than half of the total nutrients provided by synthetic fertilizers is effectively utilized and left-over having a range of negative ecological effects (Galloway et al., 2008). The application of manure could provide not only carbon but also different nutrients for crop uptakes. The residual effect of manure application was visible after many years, leading to higher nutrient availability for crop growth (Cai et al., 2018; Demelash et al., 2014). Soil acidification has received considerable attention in intensive agricultural systems due to its negative impacts on agricultural production and soil fertility (Cai et al., 2014; Guo et al., 2010). The excessive application of synthetic fertilizer is the main reason for soil acidification (Zhu et al., 2018). Although China has attained great achievements in crop yields, the major croplands have still been suffering from significant acidification since the 1980s (Guo et al., 2010). In general, the effect of manure on soil pH is concerned with the ash alkalinity of manure (Rukshana et al., 2013). The alkalinity of manure is one of the reasons for the increased pH following the manure application to soil, although the nitrogen nitrification can generate protons for decreased pH (Xu et al., 2006). Therefore, it is of interest to explore the mechanism how different fertilizers affect crop yields by soil nutrients and soil pH.

The area of subtropical arable land in China is approximately 446,890 km<sup>2</sup> and 4% of the world's subtropical arable land surface, which could support 23% of China's population. Soil acidification and available nutrients restrict crop growth. Therefore, we tried to answer: Which is the driving factor of manure, synthetic fertilizer, and soil property controls over crop yields? How do fertilizer applications affect overall crop yields in Southern China?

## 2. Materials and methods

### 2.1. Study site

The experiment was conducted at the experimental station of the Chinese Academy of Agricultural Sciences (26°45'N, 111°52'E), Southern China. The area receives an average temperature of 18.1 °C, and the active effective accumulated temperature of 4947 °C. The area receives an average annual precipitation of 1431 mm. The soil type is Eutric Cambisol and ferrosols soil based on Chinese soil classification system. The initial topsoil (0–20 cm) properties were as follows: soil organic matter of 13.6 g kg<sup>-1</sup>; total N (TN) of 1.07 g kg<sup>-1</sup>; total P (TP) of 0.45 g kg<sup>-1</sup>; total K (TK) of 13.7 g kg<sup>-1</sup>; soil bulk density (BD) of 1.19 kg m<sup>-3</sup>; soil pH of 5.70; soil available N, P and K of 79, 14, and 104 mg kg<sup>-1</sup>.

### 2.2. Experimental design

This experiment was randomly designed, and seven treatments were selected for this research (Table 1): (1) CK (no fertilizer); (2) N (synthetic nitrogen); (3) NP (synthetic N and phosphorus); (4) NPK (synthetic N, P and potassium); (5) NPKM<sub>1</sub> (synthetic NPK and manure); (6)

1.5NPKM<sub>1</sub> (1.5 times NPKM<sub>1</sub>); and (7) manure (M<sub>2</sub>). Each plot was replicated twice (20 × 9.8 m) and isolated by 1 m cement baffle plates. The synthetic fertilizers were applied as urea, calcium superphosphate, and potassium chloride. Manure was pure pig manure (solid manure) and composed of approximately 75% water with an average content (during the experiment) of 413, 20.1, 12.9, and 12.5 g kg<sup>-1</sup> for carbon, nitrogen, phosphorus, and potassium (dry weight). The average content (during the experiment) of nitrogen and phosphorus was 6.1 and 0.81 g kg<sup>-1</sup> for wheat residues and 9.5 and 1.3 g kg<sup>-1</sup> for maize residues. Crop yields and straw were removed and crop residues remained. Therefore, the amount of nitrogen input was the same under all fertilizer treatments except the 1.5NPKM<sub>1</sub> treatment. All of the fertilizers were applied before the sowing, 30% and 70% of fertilization were assigned to wheat and maize, respectively. Specific fertilization amounts are shown in Table 1.

### 2.3. Crop management

The experimental field was cultivated under a wheat-maize rotation system. Three years were taken to dispose of the experimental field to ensure the same soil physical and chemical property. Annual winter wheat variety Xiangmai was sown in early November with the rate of about 160 seeds per m<sup>2</sup> (63 kg ha<sup>-1</sup>) and harvested in early May of next year. Summer maize of variety Yedan 13 was sown in early April at a planting density of 60,000 seeds ha<sup>-1</sup> and was harvested in late July. No-irrigation was applied for winter wheat and summer maize due to large amounts of annual precipitation. Omethoate and carbofuran pesticides were applied to control the wheat aphid population during the postulation period and maize borers. Glyphosate herbicide was applied to control grassy weeds after maize harvest. The crop was harvested manually, the stubble was approximately 6 cm in height, and the roots were left in the soil. The collected straw and grains were air-dried and weighed separately for each species.

### 2.4. Soil sampling and analysis

Soil samples were collected from the cultivated horizon (0–20 cm) in September. Each treatment was randomly sampled for five to ten cores, which was 0.05 m in diameter. Then, the soil samples were thoroughly mixed and then stored for later analysis. To measure soil nutrients, the air-dried soil samples were crushed to pass through a 0.25-mm sieve. The SOC content was measured using the oxidation method by vitriol acid potassium dichromate oxidation (Page et al., 1982). Total soil nitrogen, phosphorus, and potassium were measured with the methods of Black (1965); Murphy and Riley (1962), and Knudsen et al. (1982), respectively. Available N was measured in accordance with the methods of Lu (2000), and available P (Olsen-P) and available K were determined in accordance with the Olsen-P method (Olsen, 1954) and the methods of Page et al. (1982), respectively. Soil BD was measured with cutting ring (inner diameter, 50.46 mm; sampling depth, 50 mm; volume, 100cm<sup>3</sup>) method and three repetitions (Lu, 2000).

### 2.5. Calculations

The SOC content was converted to SOC density by the equation (Lal and Bruce, 1999):

$$SOC_{density} = SOC_{content} \times d \times BD \times 10 \quad (1)$$

where SOC<sub>density</sub> is soil organic carbon density (Mg ha<sup>-1</sup>); SOC<sub>content</sub> is soil organic carbon content (g kg<sup>-1</sup>); d and BD are the depth of the soil layer (0.20 m) and soil dry BD (kg m<sup>-3</sup>).

The amounts of C input include plant residues plus returned manure. The annual C input (C<sub>input</sub>, t ha<sup>-1</sup>) was calculated from belowground biomass C (C<sub>roots</sub>, Mg ha<sup>-1</sup>) and stubble (C<sub>stubble</sub>, Mg ha<sup>-1</sup>), which was incorporated into the topsoil (as Eqs. (3) and (4)), as well as

**Table 1**

Annual rate (kg ha<sup>-1</sup>) of synthetic nitrogen (Sy-N), phosphorus (Sy-P), and potassium (Sy-K) fertilizer addition and organic nitrogen (Or-N), phosphorus (Or-P), and potassium (Or-K) fertilizer applied in the various fertilization treatments. Notes: CK, no fertilizer; N, synthetic nitrogen; NP, synthetic N, and phosphorus; NPK, synthetic N, P, and potassium; NPKM<sub>1</sub>, synthetic NPK, and manure; 1.5NPKM<sub>1</sub>, 1.5 times NPKM<sub>1</sub>; and M<sub>2</sub> manure. Synthetic N fertilizer is urea; P added as calcium superphosphate; K added as KCl.

Fertilizations	Wheat						Maize					
	Sy-N	Sy-P	Sy-K	Or-N	Or-P	Or-K	Sy-N	Sy-P	Sy-K	Or-N	Or-P	Or-K
CK	0	0	0	0	0	0	0	0	0	0	0	0
N	90	0	0	0	0	0	210	0	0	0	0	0
NP	90	16	0	0	0	0	210	37	0	0	0	0
NPK	90	16	30	0	0	0	210	37	70	0	0	0
NPKM <sub>1</sub>	27	16	30	63	40	39	63	37	70	147	94	91
1.5NPKM <sub>1</sub>	40	24	45	94	61	59	95	55	105	220	141	137
M <sub>2</sub>	0	0	0	90	58	56	0	0	0	210	135	131

the amount of manure ( $C_{\text{manure}}$ , Mg ha<sup>-1</sup>). The method of carbon inputs was the following:

$$C_{\text{input}} = C_{\text{belowground}} + C_{\text{stubbles}} + C_{\text{manure}} \quad (2)$$

$$C_{\text{belowground}} = R_{\text{bg}} \times C_{\text{biomass}} \quad (3)$$

$$C_{\text{stubbles}} = R_{\text{stubbles}} \times C_{\text{biomass}} \quad (4)$$

where  $R_{\text{bg}}$  is the ratio of annual underground carbon from crops to above-ground biomass carbon, which is estimated as 30% from Kundu et al. (2007).  $R_{\text{stubbles}}$  is the ratio of stubble incorporated into the soil to aboveground biomass.

The relative yields (YR) were used to allow the datasets from the individual treatments to be more comparable. The relative yield was calculated as follows:

$$YR = Y_{\text{treatment}} - Y_{\text{control}} \quad (5)$$

where  $Y_{\text{treatment}}$  is the actual yield under the fertilization treatments (Mg ha<sup>-1</sup>) in a given year and  $Y_{\text{control}}$  is the yield of the no-fertilization treatment (Mg ha<sup>-1</sup>) in the same year.

## 2.6. Statistical analyses

To assess the different fertilization treatment effects on the relative crop yields; three periods were analyzed (1991–2000, 2001–2005 and 2006–2015) by one-way ANOVA as implemented with the SPSS 19.0 software package. We also explored the trends of SOC under the different fertilization treatments. Different equations were selected and performed by SigmaPlot 10.0. Boosted regression tree (BRT) was constructed using the recommended parameter values (Elith et al., 2008). The procedure of boosted regression tree was applied using the gbm package in R version 3.3.3. Structural equation model (SEM) was used to quantify the relationships among relative yields, soil fertility, and different fertilizations as conducted with the Amos package. All of the graphs were prepared with SigmaPlot 10.0 software.

## 3. Results

### 3.1. Crop yields

Crop yields in each treatment exhibited similar changes among years, which increased over time in NPKM<sub>1</sub>, 1.5NPKM<sub>1</sub>, and M<sub>2</sub> and decreased in CK, N, NP, and NPK despite some fluctuations in some years (Fig. 1). There was no crop yield in the N treatment after 12-year fertilization. The crop yields varied from 0.34 (CK) to 1.58 Mg ha<sup>-1</sup> (NPKM<sub>1</sub>) and from 0.25 (CK) to 5.82 Mg ha<sup>-1</sup> (1.5NPKM<sub>1</sub>), respectively, as averaged over 1991–2015 (Table 2). Significantly higher yields were observed in the NPKM<sub>1</sub>, 1.5NPKM<sub>1</sub>, and M<sub>2</sub> treatments during the period 2001–2005. Compared with the period of 1991–2000, CK caused 10% to 41% decrease of wheat yield while maize yield showed 45% to 56% during the period of 2001–2005. The

largest decrease (26–100%) of crop yields was found in N, NP, and NPK treatments. However, 2–65% increases in crop yields were found in NPKM<sub>1</sub> and M<sub>2</sub> treatments during 2006–2015, whereas 1.5NPKM<sub>1</sub> decreased wheat and maize yields by 12–23% during 2006–2015.

### 3.2. Dynamic changes of SOC and responses to fertilization treatment

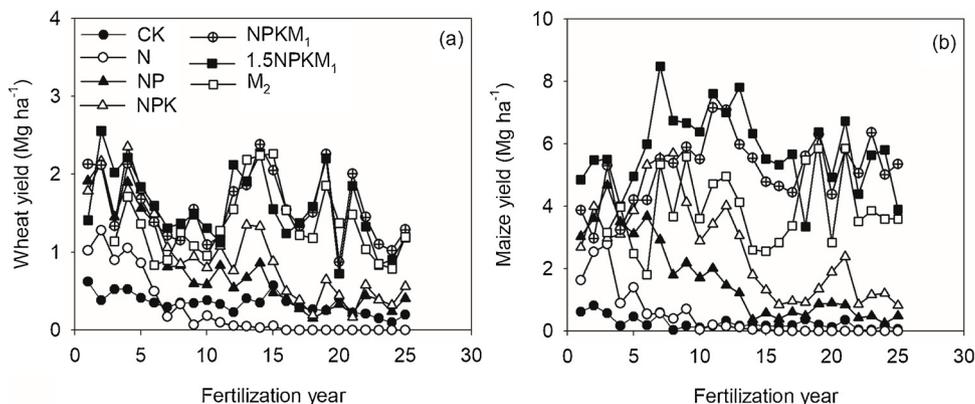
The average annual carbon inputs in the CK treatment were 0.17 (wheat) and 0.13 Mg ha<sup>-1</sup> (maize), respectively, each year from crop residue (Fig. 2). The applications of NP and NPK significantly increased carbon biomass, with 0.36–0.61 Mg ha<sup>-1</sup> year<sup>-1</sup>. Carbon inputs under NPKM<sub>1</sub> and 1.5NPKM<sub>1</sub> treatments were 1.72–1.87 times for the wheat and 1.98–2.31 times for the maize under the NPK treatment. SOC was unchanged under the CK treatment and slightly decreased under the N treatment (Fig. 3). Higher SOC values were observed under the NPKM<sub>1</sub>, 1.5NPKM<sub>1</sub>, and M<sub>2</sub> treatments, depicting a pronounced increase over the first 10 years and then a high stable level over the last 15 years. The relationship between annual SOC sequestered and duration was described with  $y = 0.80e^{-0.08x}$  and  $y = 3.16e^{-0.05x}$  under the synthetic fertilizer and manure treatments (Appendix 4a and b). A significant and positive relationship was found between carbon inputs and annual SOC sequestered (Fig. 4). The estimated decomposition rate of SOC was 0.17 Mg ha<sup>-1</sup> each year (when carbon inputs were zero), and the minimum rate of carbon inputs necessary to maintain SOC content was 0.36 Mg ha<sup>-1</sup> each year (when soil carbon sequestration rate was zero).

### 3.3. Soil nutrients changes

Soil nutrients, pH, and BD were displayed in Table 3. Soil TN, available N, and K showed no significant differences among CK, N, and NP during 1991–2000, 2001–2005 and 2006–2015 periods. Compared with CK, NPK treatment significantly increased soil TN and available K during both 2001–2005 and 2005–2015 periods but did not significantly affect soil TN, available N, and available K during 1991–2000 periods. Soil TP and available P did not significantly differ between the CK and N treatments but were significantly increased in NP and NPK treatments relative to CK treatment in all three fertilization periods. Soil TK did not differ among the fertilizer treatments. Compared with CK, the synthetic fertilizers (N, NP, and NPK) significantly decreased soil pH. Compared with their initial values, soil TN, available K, pH, and BD decreased on average by 9, 9, 19, and 1%; available N, TP, available P and TK increased on average by 20, 50, 81, and 1%, respectively, under the synthetic fertilizer treatments. Soil TN, AN, TP, AP, TK, AK, pH, and BD increased by 24, 54, 208, 815, 3, 180, 8, and 13%, respectively, under manure treatments.

### 3.4. Mechanisms of relative yield

The result of BRT suggested that manure was the most influential trigger on relative yields among the studied 11 variables (39%, Fig. 5a).



**Fig. 1.** Annual wheat (a) and maize (b) grain yields under various fertilization treatments of a long-term experiment in a wheat-maize system. Notes: CK, no fertilizer; N, synthetic nitrogen; NP, synthetic N, and phosphorus; NPK, synthetic N, P, and potassium; NPKM<sub>1</sub>, synthetic NPK, and manure; 1.5NPKM<sub>1</sub>, 1.5 times NPKM<sub>1</sub>; and M<sub>2</sub> manure.

**Table 2**

Wheat and maize grain yields for the periods 1991–2015, 1991–2000, 2001–2005 and 2006–2015 under various fertilization treatments in a long-term experiment in a wheat-maize system. Notes: CK, no fertilizer; N, synthetic nitrogen; NP, synthetic N, and phosphorus; NPK, synthetic N, P, and potassium; NPKM<sub>1</sub>, synthetic NPK, and manure; 1.5NPKM<sub>1</sub>, 1.5 times NPKM<sub>1</sub>; and M<sub>2</sub> manure. Different letters in the same column indicate significant differences ( $P < 0.05$ ) among treatments.

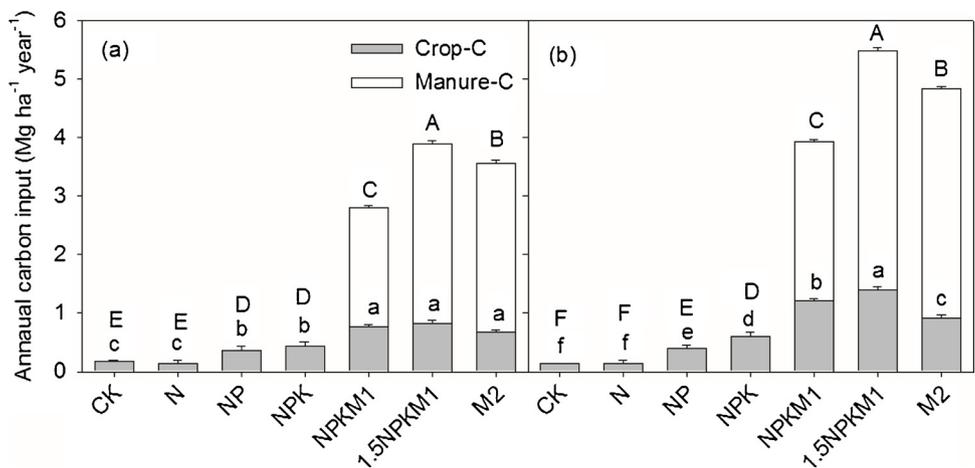
Crops	Treatments	Mg ha <sup>-1</sup>				Change (%)	
		1991-2015	1991-2000	2001-2005	2006-2015	2001-2005	2006-2015
Wheat	CK	0.34 d	0.42 c	0.38 d	0.25 d	-10	-41
	N	0.27 d	0.64 c	0.06 e	0.00 e	-91	-100
	NP	0.79 c	1.32 ab	0.68 cd	0.31 cd	-49	-76
	NPK	0.97 bc	1.46 ab	1.08 b	0.42 c	-26	-71
	NPKM <sub>1</sub>	1.58 a	1.58 a	1.85 a	1.44 a	17	-9
	1.5NPKM <sub>1</sub>	1.57 a	1.71 a	1.80 a	1.32 ab	5	-23
	M <sub>2</sub>	1.36 ab	1.16 b	1.90 a	1.25 b	65	8
Maize	CK	0.25 e	0.36 d	0.20 e	0.16 d	-45	-56
	N	0.48 e	1.15 d	0.11 e	0.00 d	-91	-100
	NP	1.66 d	3.02 c	1.12 c	0.57 d	-63	-81
	NPK	2.65 c	4.02 bc	2.72 b	1.24 c	-32	-69
	NPKM <sub>1</sub>	5.19 a	4.61 b	6.11 a	5.30 a	33	15
	1.5NPKM <sub>1</sub>	5.82 a	5.91 a	6.86 a	5.21 a	16	-12
	M <sub>2</sub>	3.89 b	3.70 bc	3.79 b	4.08 b	2	10

The synthetic N, P, and K accounted for 21% of the relative yields. The relative individual influence of soil properties was small. The BRT model driven by these variables explained 98% of the relative yields (Fig. 5b). In the SEM analysis, different pathways were constructed to examine the effect of the different variables on the variation of crop yields (Fig. 6). These variables were grouped to two latent variables (synthetic fertilizers and soil nutrients) and three factors (manure, soil

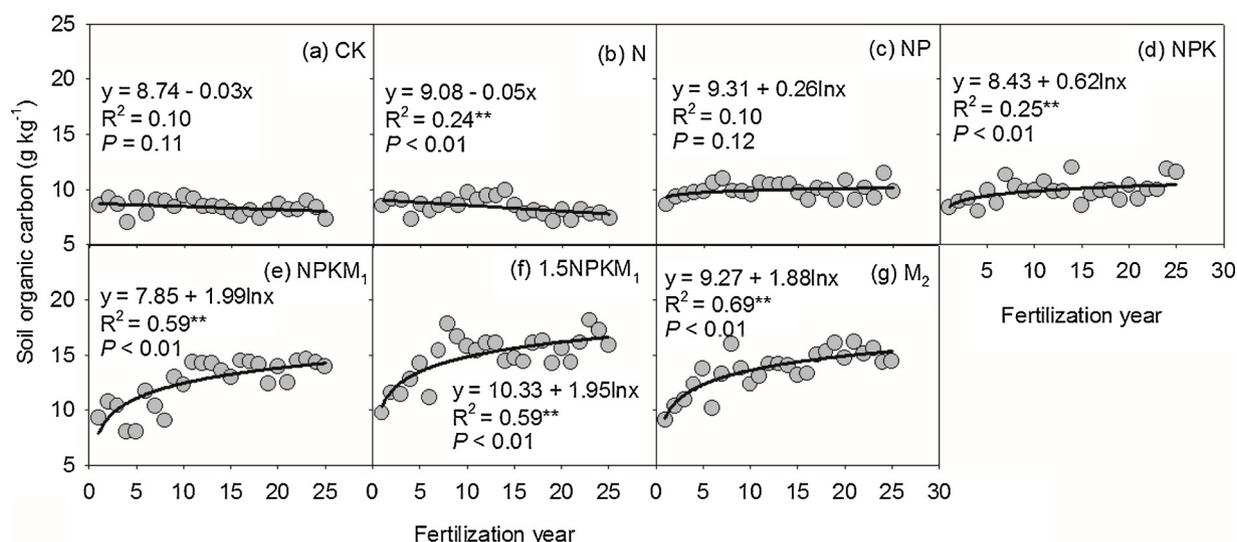
pH, and SOC storage) in the path analysis. The loading scores suggested that synthetic phosphorus application and soil available phosphorus were more powerful indicators of synthetic fertilizer and soil nutrients, respectively, than were synthetic N application and soil available N. Synthetic fertilizer was significantly and positively associated with relative soil nutrients (0.27), while its associations with relative soil pH (-0.36) and SOC storage (-0.12) were significantly negatively correlated. Manure application strongly and positively affected the soil nutrients, soil pH, and SOC storage (path coefficients: 0.90, 0.76, and 0.88). The soil nutrients, soil pH and SOC storage directly influenced the relative yields (path coefficients: 0.23, 0.44, and 0.25). The path analysis explained 72% of the variance of relative yields ( $R^2 = 0.72$ ).

**4. Discussion**

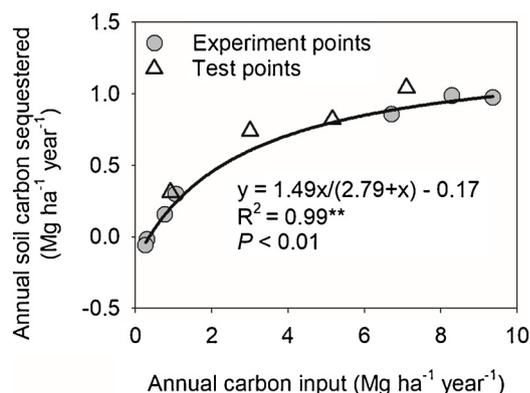
Crop yields increased over time in the NPKM<sub>1</sub>, 1.5NPKM<sub>1</sub>, and M<sub>2</sub> and decreased over time in CK, N, NP, and NPK, although there were some fluctuations in some years (Fig. 1 and Table 2). These results could be attributed to the residual effect of manure application (Shen et al., 2007). The residual effect could maintain crop yields for several years after manure application ceases (Demelash et al., 2014). A positive residual effect on crop yields is observed with improvements in plant dry matter production. Another reason is the indiscriminate use of synthetic fertilizer, which has caused soil acidification, particularly in the south of China (Cai et al., 2014; Guo et al., 2010). The extent and intensity of soil acidification are the main factors that contribute to the dramatic yield reduction (Zhu et al., 2018). Accordingly, there was no yield in the N treatment after 12 years with the lower soil pH (Fig. 1 and Table 3). N fertilization acidifies the soil by the oxidation of dry-deposited compounds, loss of basic cations through ion exchange, and plant uptake and nitrification of ammonium. The lower pH not only



**Fig. 2.** Average annual carbon input from crop and manure under various fertilization treatments in wheat (a) and maize (b) system. Notes: Different lower-case letters (annual carbon input from crops) and upper-case letters (total annual carbon input) indicate significant differences at the  $P < 0.05$  level for each treatment. CK, no fertilizer; N, synthetic nitrogen; NP, synthetic N, and phosphorus; NPK, synthetic N, P, and potassium; NPKM<sub>1</sub>, synthetic NPK and manure; 1.5NPKM<sub>1</sub>, 1.5 times NPKM<sub>1</sub>; and M<sub>2</sub> manure.



**Fig. 3.** Trends in soil organic carbon under various fertilization treatments in a long-term experiment in a wheat and maize system. Notes: CK, no fertilizer; N, synthetic nitrogen; NP, synthetic N, and phosphorus; NPK, synthetic N, P, and potassium; NPKM<sub>1</sub>, synthetic NPK, and manure; 1.5NPKM<sub>1</sub>, 1.5 times NPKM<sub>1</sub>; and M<sub>2</sub> manure.



**Fig. 4.** Correlation between soil organic carbon storage and annual carbon input in a long-term experiment in a wheat-maize system. Notes: Experiment points come from our study site and test points come from Cai et al. (2018) reported site.

increases the availability of potentially toxic heavy metals but also contribute to the severe reduction of the microbial community that promotes the root functions (Stevens et al., 2009). A combination of manure and synthetic fertilizers could improve nutrient availability for plant uptake with a positive effect on crop yields (Diacono and Montemurro, 2010). The results of our study showed that wheat yield was significantly higher under manure than NPK treatment (Table 2). The application of manure alone has a vibrant increasing effect on maize yield but a weaker increasing effect than NPK on wheat yield. One potential reason for this finding was that the manure was applied before the wheat was sown. Another potential reason is that the higher soil temperatures and precipitation in summer increase nutrient mineralization (Agehara and Warncke, 2005). Meanwhile, the effect of manure on crop yields is crucial by improving soil pH (Fig. 6c). Overall, the crop yields were significantly higher under manure than synthetic fertilizer treatments.

Apparently, manure treatments can increase SOC and soil nutrients over long-term cropping. Manure not only directly increases carbon inputs into the soil but also influences crop residues, which determine the benefits of agricultural SOC sequestration and nutrient release (Fig. 2 and Appendix 2) (Kuz'yakov and Blagodatskaya, 2015; Lal, 2008). The observed non-linear relationship between SOC sequestration and carbon inputs indicated that SOC was approaching an equilibrium

level. This result agrees with many previous studies (Cong et al., 2012; Stewart et al., 2007; Zhang et al., 2012), but differs from other researches (Kong et al., 2005; Majumder et al., 2007) that reported linear relationships. The contrasting findings may be partially due to differences in the ranges of carbon inputs and carbon stabilization. Our carbon inputs rate showed a much wider range than observed in previous studies, being 0.30–9.36 Mg ha<sup>-1</sup> y<sup>-1</sup>. Another long-term experiment is being performed to examine the relationship between SOC sequestration and carbon inputs (Fig. 4 and Appendix 5). In contrast, Majumder et al. (2007) reported a carbon input of only 1.96–4.10 Mg ha<sup>-1</sup> each year. We estimated that the minimum rate of carbon inputs required maintaining SOC content was 0.36 Mg ha<sup>-1</sup> each year. The value is slightly higher than N treatment (0.26 Mg ha<sup>-1</sup> each year), resulting in a significantly decreasing trend. The minimum carbon inputs under NPK treatment (1.06 Mg ha<sup>-1</sup> each year) were significantly higher than the minimum rate of carbon inputs (0.26 Mg ha<sup>-1</sup> each year), contributing to the increasing trend in SOC. These results demonstrated that balanced fertilization (NPK) could maintain or even improve SOC via the return of crop residues.

Exogenous application of synthetic fertilizer accelerated soil acidification, whereas manure or interactive application of manure with synthetic fertilizer prevented this process (Table 3). Plants generally extrude net excess of H<sup>+</sup>; conversely, they extrude net excess of OH<sup>-</sup>/HCO<sub>3</sub><sup>3-</sup> or consume H<sup>+</sup> when anion uptake exceeds cation uptake (Tang et al., 2010). NH<sub>4</sub><sup>+</sup>-fed plants are characterized by a high cation/anion uptake ratio, while NO<sub>3</sub><sup>-</sup>-fed plants have a low cation/anion uptake ratio (Tang et al., 2010). Synthetic N application significantly reduced the exchangeable base cations in soils, which lead to declined soil pH. Additionally, synthetic N application has shifted soils into the Al<sup>3+</sup> buffering stage. Al is released into solution at a pH below 5 by the hydrolysis of both Al-hydroxides and silicates on clay mineral surfaces. A number of other heavy metals behave in a manner similar to Al. A decline in base saturation is symptomatic of soil acidification (Stevens et al., 2009). Accordingly, many studies reported that synthetic fertilizer application could significantly decrease soil pH (Cai et al., 2014; Zhu et al., 2018). In general, the ash alkalinity of manure is associated with soil acidification with protons to neutralize soil acidity (Rukshana et al., 2013). The alkalinity of organic materials following the decarboxylation of organic anions and the ammonification of organic N are the major causes of increases in soil pH, although nitrification of mineralized N can generate protons for the decrease of soil pH to some degree (Xu et al., 2006). Following long-term manure application, soil

**Table 3**

Contents of soil nutrients of dry soil for the period of 1991–2015, 1991–2000, 2001–2005 and 2006–2015 under various fertilizations of long-term experiments in wheat-maize systems. Notes: CK, no fertilizer; N, synthetic nitrogen; NP, synthetic N, and phosphorus; NPK, synthetic N, P, and potassium; NPKM<sub>1</sub>, synthetic NPK and manure; 1.5NPKM<sub>1</sub>, 1.5 times NPKM<sub>1</sub>; and M<sub>2</sub> manure. Different letters in the same column during year indicate that there are significant differences ( $P < 0.05$ ) among the different treatments.

Treatments	Treatments	TN	AN	TP	AP	TK	AK	pH	BD
Initial year		1.07	79	0.45	14	13.7	104	5.7	1.19
1991-2000	CK	0.80 e	96 c	0.46 d	5 d	14.63 a	82 c	5.75 b	1.15 ab
	N	0.94 de	120 bc	0.45 d	4 d	15.76 a	70 c	4.98 c	1.11 b
	NP	0.95 de	101 bc	0.69 c	20 c	14.61 a	89 c	5.05 c	1.12 b
	NPK	1.06 cd	112 bc	0.77 c	21 c	15.32 a	128 c	4.90 c	1.22 ab
	NPKM <sub>1</sub>	1.23 ab	114 bc	1.00 b	49 b	14.54 a	198 b	6.04 ab	1.32 a
	1.5NPKM <sub>1</sub>	1.31 a	130 bc	1.30 a	74 a	16.88 a	288 a	6.05 ab	1.23 ab
	M <sub>2</sub>	1.13 bc	142 ab	0.82 c	37 b	12.76 a	200 b	6.48 a	1.30 a
2001-2005	CK	0.81 c	64 c	0.44 e	5 e	13.64 a	56 d	5.63 a	1.17 d
	N	0.90 c	90 bc	0.41 e	4 e	11.66 a	47 d	4.30 b	1.15 d
	NP	0.87 c	81 c	0.70 d	37 d	12.92 a	51 d	4.53 b	1.17 d
	NPK	1.03 b	85 c	0.79 d	43 d	12.13 a	136 c	4.59 b	1.30 c
	NPKM <sub>1</sub>	1.36 a	119 ab	1.35 b	148 b	12.85 a	283 b	5.77 a	1.48 a
	1.5NPKM <sub>1</sub>	1.44 a	133 a	1.74 a	226 a	12.74 a	404 a	5.68 a	1.42 b
	M <sub>2</sub>	1.22 a	91 bc	1.05 c	100 c	12.11 a	190 c	6.58 a	1.40 b
2006-2015	CK	0.86 d	60 c	0.45 e	4 d	14.72 a	59 e	5.75 c	1.23 b
	N	0.86 d	86 c	0.45 e	4 d	13.54 a	50 e	4.04 e	1.16 c
	NP	0.96 cd	85 c	0.86 d	51 c	13.72 a	64 e	4.30 d	1.19 c
	NPK	1.05 c	86 c	0.98 d	48 c	14.79 a	201 d	4.35 d	1.18 c
	NPKM <sub>1</sub>	1.34 b	115 b	1.69 b	170 b	14.62 a	350 b	5.88 bc	1.36 a
	1.5NPKM <sub>1</sub>	1.55 a	138 a	2.32 a	245 a	14.43 a	484 a	5.94 b	1.33 a
	M <sub>2</sub>	1.49 a	119 b	1.50 c	147 b	14.22 a	253 c	6.66 a	1.39 a

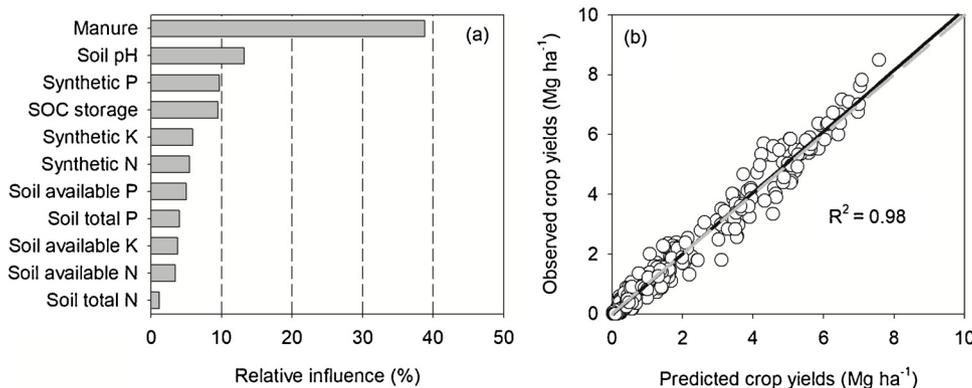
pH increased due to manure residues.

As expected, manure significantly affected crop yields, compared to other variables including synthetic fertilizer and soil fertility (Fig. 5). Manure mainly plays an important role in regulating plant growth, potential nutrient input, and microbial decomposition activity. This role can largely mediate the soil nutrient and soil micro-environment, which have a strong impact on crop growth. In addition, manure could also result in increased microbial biomass and changes in community structure, which provide a better environment for the growth of the crop (Peacock et al., 2001). Manure application to cropland can affect soil properties, but the effects may not be apparent over a short time period. We identified a network of correlations among synthetic fertilizer, manure, and soil fertility in determining crop yields (Fig. 6c). The application of manure strongly and positively affected crop yields by increasing SOC storage, soil nutrients, and soil pH. Synthetic fertilizer affected crop yields by weakly increasing soil nutrients and decreasing SOC storage and soil pH. SOC, soil nutrients, and soil pH directly influenced crop yields, and soil pH played a more important role in increasing crop yields than did soil nutrients and SOC in this experimental field in the south of China. Increased soil acidification can reduce the availability of soil nutrients to plants in the soil and it thereby reduced crop yields (Wright, 1989). Soil pH-induced changes in soil enzyme activity and microbial composition might be important mechanisms for alleviating acid stress on crop yields by various ameliorants. In

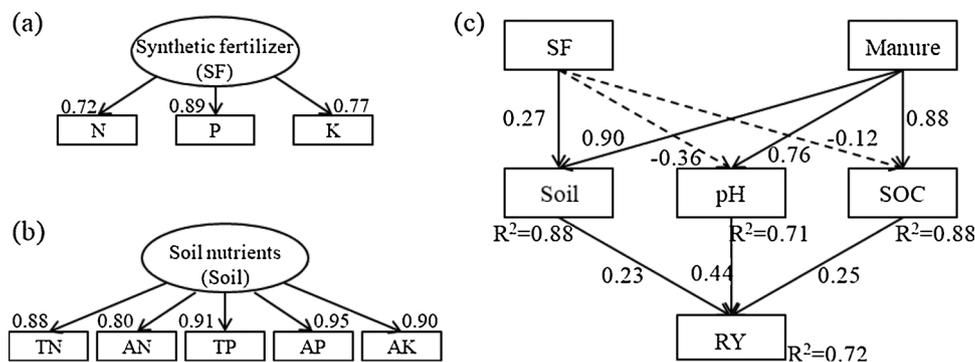
addition, the total effect of soil pH, the SOC and soil nutrients on crop yield were also identified. Cai et al. (2018) reported that manure influenced crop yields via affecting soil TN and available N and P (soil pH) based on an 8-year field experiment. Our results showed further evidence that the interplay of different fertilization, soil pH, SOC and soil nutrients and their interaction jointly influenced crop yields (Fig. 6). These results suggest that manure is a better fertilizer than synthetic fertilizer for regulating crop yields by improving soil fertility for Chinese subtropical arable soils.

**5. Conclusions**

Significant differences in soil fertility and crop yields among different fertilization treatments were found in this study. The manure or combined with synthetic fertilizer significantly increased crop yields, SOC, soil nutrients and soil pH compared with CK. The crop yields increased with increasing amount of added manure. Manure inputs accounted for 39% of the relative influence on relative yield, followed by synthetic fertilizer of 21% and soil fertility of 40%. Synthetic fertilizers indirectly affected crop yields by weakly increasing soil nutrients and decreasing SOC storage and soil pH. Manure indirectly affected crop yields by strongly and positively increasing soil nutrients, SOC storage and soil pH. Our results suggest that manure acts as a better fertilizer than synthetic fertilizer in increasing crop yields by improving soil



**Fig. 5.** The relative contributions (%) of predictor variables for the boosted regression tree model of relative yield (a). Observed and predicted relative crop yield by the boosted regression tree model using predictors shown in Fig. 5b. The dashed line shows the 1:1 line. Notes: SOC, soil organic carbon; Manure, amounts of manure input; Synthetic N, P, and K, amounts of synthetic N, P, and K input.



**Fig. 6.** Latent variables with their indicators considered in the path analysis (a and b). Path analysis results of the direct and indirect effects of synthetic fertilizer, manure, and soil nutrients on relative yield (c). Numbers next to the endogenous variables are the explained variance. Numbers next to the arrows are the standardized path coefficients. A solid-line path indicates that the effect is significantly positive, and a dashed-line path indicates that the effect is significantly negative. Notes: synthetic fertilizer (SF): synthetic nitrogen (N), synthetic phosphorus (P), and synthetic potassium (K). Soil nutrients (Soil): TN, soil total nitrogen; AN, soil available nitrogen; TP, soil total phosphorus; AP, soil available phosphorus; AK, soil available potassium; SOC, soil organic carbon storage; RY, relative yields.

fertility for Chinese subtropical arable soils.

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### Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.still.2018.12.022>.

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