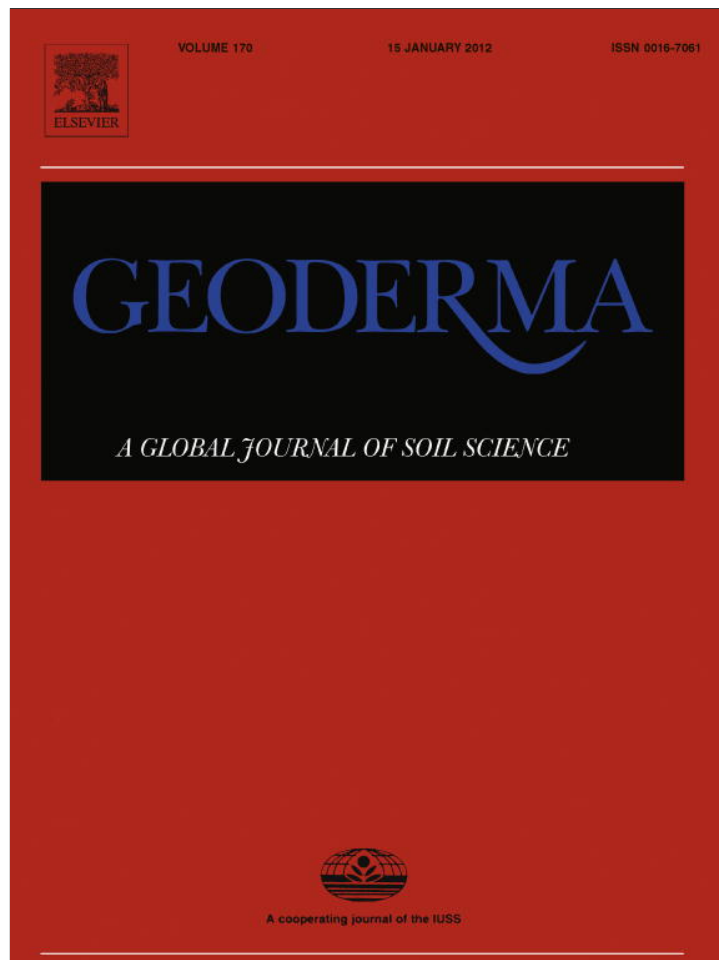


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## Temporal changes in soil organic carbon contents and $\delta^{13}\text{C}$ values under long-term maize–wheat rotation systems with various soil and climate conditions

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### ABSTRACT

Understanding soil organic carbon (SOC) decomposition and its replenishment by contrasting plant residues is critical to rationally manage soil carbon pools. Long-term (15 years) field experiments in maize–wheat (*Zea mays L.*–*Triticum aestivum L.*) rotation systems at diverse sites with contrasting climates and soil properties were conducted to evaluate the temporal dynamics of the C inputs, SOC concentrations and  $\delta^{13}\text{C}$  values. In the non-fertilized Control treatments mean annual C inputs (mainly roots) at the various sites ranged from 0.39 to 1.24 Mg C ha<sup>-1</sup>, and SOC contents remained largely unchanged during the 15 years study. However, results for the fertilized treatments indicated that SOC concentration increased by 1 g kg<sup>-1</sup> for every 24.3 (5.4–45.2) Mg C ha<sup>-1</sup> from roots alone in the NPK treatment and for every 29.4 (11.1–52.6) Mg C ha<sup>-1</sup> from crop roots plus straws in the NPKSt treatment. Furthermore, there was a positive correlation among changes in SOC, C<sub>4</sub>-derived C and C<sub>3</sub>-derived C and the  $\delta^{13}\text{C}$  values in all treatments across the four sites. Our results suggest that the  $\delta^{13}\text{C}$  value was a useful tool to quantify temporal changes of SOC from C<sub>4</sub> and C<sub>3</sub> plants, even when actual changes in soil C stock were small in these wheat–maize rotation cropping systems.

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### 1. Introduction

Conservation of soil organic carbon (SOC) is of primary importance to sustain soil fertility and productivity, to decrease agricultural CO<sub>2</sub> emissions to the atmosphere and increase global carbon sequestration (Dawson and Smith, 2007; McLaughlan, 2006). Agricultural soils could be a source or a sink for atmospheric CO<sub>2</sub> depending on the farm management practices (Lal, 2002). In the western United States, Canada (Kemper and Koch, 1966), and England and Wales (Greenland et al., 1975), soils showed significant decline in structural stability when SOC is less than 20 g kg<sup>-1</sup>. Additionally, nutrient supply from mineralization may not be sufficient to sustain satisfactory yields when SOC is <20 g kg<sup>-1</sup> (Greenland et al., 1975).

The SOC content was influenced by land use, tillage and crop rotation, especially by fertilization and crop residue management (Drury et al., 1998; Havlin et al., 1990; Murillo, 2001; Robinson et al., 1996). Kristiansen et al. (2005) reported that, in four Danish arable soils (0–20 cm), the average of SOC storage increased from 90 to 470 kg ha<sup>-1</sup> yr<sup>-1</sup> in soils that received inorganic fertilizers alone

and from 110 to 940 kg ha<sup>-1</sup> yr<sup>-1</sup> in soils that received an additional chopped maize biomass over 14 years. Furthermore, the rate of SOC change was directly related to C input from crop residues and amendments (Rasmussen and Parton, 1994), the SOC increased with greater quantities of residue returned (Robinson et al., 1996). Thus, crop residue inputs are crucial for the long-term maintenance of the SOC pool. However, little is known of the impact of crop residues on SOC storage in different soils in long-term maize–wheat rotation systems.

The natural <sup>13</sup>C abundance ( $\delta^{13}\text{C}$ ) technique to determine the sources of SOC is based on the difference in isotopic <sup>13</sup>C signatures of C<sub>4</sub> plants and C<sub>3</sub> plants during photosynthesis (Bender, 1971; Smith and Epstein, 1971). The  $\delta^{13}\text{C}$  values from plants with C<sub>3</sub> photosynthesis such as wheat typically range from –40 to –23‰ with a mean of –27‰, while  $\delta^{13}\text{C}$  with C<sub>4</sub> photosynthesis such as maize range from –19 to –9‰ with a mean of –14‰ (Boutton et al., 1998; Collins et al., 1999; Diels et al., 2001). When vegetation becomes compositionally stable for a long time, the  $\delta^{13}\text{C}$  values of SOC in the plough layer (0–20 cm) approach the values of the plant community (Nadelhoffer and Fry, 1988) because only slight isotope fractionation may occur during early stages of organic matter decomposition in soils (Boutton, 1996). Thus the analysis of  $\delta^{13}\text{C}$  values of SOC could be a valuable tool for studying the turnover of SOC in soils where C<sub>3</sub> plants have been replaced by C<sub>4</sub> plants (Balesdent and Mariotti, 1996). Wang et al. (2006) reported that the  $\delta^{13}\text{C}$  values had increased

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linearly at an annual rate of 0.07% during 13 years under continuous maize cultivation.

Maize and wheat are major staple crops in China and the production area and grain yield accounted for 47.3% and 49.1% of the total crop production area and yield in China in 2010, respectively (CAY, 2011). Organic manures have traditionally been used as the major source of nutrients for maize and wheat production in China for thousands of years. However, in recent years, there has been a large increase in the use of inorganic fertilizers alone or combined with crop residues (above-ground biomass) with a concomitant decrease in the use of farmyard manure for maize and wheat production (CAY, 2011). There is a concern that current fertilization practices could lead to a decrease in SOC. Long-term effects of tillage with application of inorganic fertilizers alone or in combination with crop residues on the turnover of soil organic carbon, especially the dynamics of SOC for different crops, soil types and climate conditions, have not been investigated under maize–wheat cropping systems. Therefore, the objectives of the present study were to investigate the changes of contents and  $\delta^{13}\text{C}$  values of SOC under long-term maize–wheat rotation systems and to estimate the contribution of wheat and maize crops to SOC using the  $\delta^{13}\text{C}$  technique.

## 2. Materials and methods

### 2.1. Site description and experimental design

This study is based on a sub-set of data from a long-term, multi-site cropping systems study. Field experiments were initiated in 1990 and the most recent sampling was in 2005. For this study we selected four sites with winter wheat–summer maize rotations (these crops were grown sequentially and both were harvested within a single year). The sites had contrasting soils and climate conditions, and included: Changping (northern China), Zhengzhou (central China), Yangling (south-western China) and Qiyang (southern China). Selected soil characteristics from these four sites at the beginning of experiments in 1990 are presented in Table 1. Other soil properties and climate conditions were reported previously by Tang et al. (2008) and Ma et al. (2009).

At each of the four sites under the wheat–maize rotations selected for this study, three nutrient management treatments had been imposed according to a randomised complete block design. The fertility treatments included: (1) Control (without fertilization), (2) NPK (nitrogen, phosphorus and potassium inorganic fertilizers), (3) NPKSt (NPK plus straw = above-ground plant tissues excluding the grain). Details on the fertility treatments were reported previously (Tang et al., 2008). Briefly, the annual application rates of inorganic fertilizers were 165–362 kg N ha<sup>-1</sup>, 25–41 kg P ha<sup>-1</sup>, and 68–146 kg K ha<sup>-1</sup>. Urea, single superphosphate, and KCl were used as fertilizers.

All above-ground phytomass, including grain and straw (minus the 4 cm of stubble immediately above the soil surface), was removed for Control and NPK treatments. For the NPKSt treatment, the mean annual amounts of above-ground crop residues (excluding 4 cm

stubble) applied were 2.2, 3.7, 5.9 and 6.0 Mg ha<sup>-1</sup> at the Qiyang, Yangling, Zhengzhou and Changping sites, respectively. Under the NPKSt treatment at all sites except Qiyang, all maize stover was incorporated into soils after harvest, but none of the wheat residues were incorporated. Under NPKSt at Qiyang, half of maize and half of the wheat residues were incorporated after each harvest.

During growing seasons, weeds were removed manually upon emergence. To avoid moisture stress, the crops were irrigated when necessary. From 1988 to 1989, before the current experiments were established, maize and winter wheat had been grown at the four sites without fertilizers in an attempt to decrease yield variability among field plots. In the course of the experiments (1990 through 2005), maize hybrids and winter wheat cultivars were changed according to availability. The cultivation histories before 1988 had not been fully documented. The  $\delta^{13}\text{C}$  values for SOC in 1990 (Table 1), however, suggested that C<sub>4</sub> plants had been relatively more prevalent at Changping, and C<sub>3</sub> plants at the other sites.

### 2.2. Soil sampling and analysis

Soil samples of the plough layer (0–20 cm) were collected at all sites in fall after maize harvest and prior to the next round of fertilizer applications from 1990 to 2005. An auger with 5 cm diameter was used to collect soil at five places in each plot, and then the five sub-samples were mixed to obtain a composite soil sample for each plot. The fresh soil samples were air-dried and sieved to pass 2.0 mm before they were stored for subsequent analyses.

Soil sub-samples were further fine ground to pass 0.15 mm sieve and analyzed for total N and total C by dry combustion/Dumas conversion using an automated CN analyzer (NA-1500, CE Instruments, Milan Italy). SOC and its  $\delta^{13}\text{C}$  value were determined using a method similar to that described by Nieuwenhuize et al. (1994). Briefly, finely-ground sub-samples were weighed into Ag capsules and acidified with 6 M HCl to eliminate inorganic C. After acidification the samples were dried for 24 h at 60 °C to drive-off water and HCl, and then the capsules were crimped closed for analysis of SOC by combustion-gas chromatography using a CN analyzer (Baccanti et al., 1993). The CN analyzer was interfaced, via continuous flow, to an isotope ratio mass spectrometer (Optima, VG Isogas, Manchester UK) to determine the  $\delta^{13}\text{C}$  value for the SOC (Ellert and Rock, 2008).

### 2.3. Calculations

The yields of both grain and above-ground residues were measured at all four sites throughout the experiment, and yields of below-ground residues (mainly roots) were assumed to be proportional to above-ground production. In wheat and maize the relative distribution of dry matter in grain, above-ground and below-ground residues was roughly 43, 37 and 20% (Buyanovsky and Wagner, 1997; Follett et al., 1997). Hence the root dry matter was calculated as 54% of that of the above-ground crop residues. The concentrations of C in the dry matter were assumed to be 44% in the above-ground

**Table 1**  
Soil characteristics before treatments in 1990 and climate conditions in different sites. <sup>a</sup>Annual precipitation and temperature are the means over 15-years (1990–2005). <sup>b</sup>P<sub>C4</sub> was the proportion of soil organic carbon derived from C<sub>4</sub> plants to total soil organic carbon.

Item	Changping	Zhengzhou	Yangling	Qiyang
Soil classification in China	Fluvo-aquic soil	Fluvo-aquic soil	Loessial soil	Red earth
Soil classification in FAO	Haplic Luvisol	Calcaric Cambisol	Calcaric Regosol	Eutric Cambisol
Annual precipitation (mm) <sup>a</sup>	529.7	645.6	525.0	1407.5
Mean annual temperature (°C)	13.0	14.8	13.8	18.1
Soil pH (H <sub>2</sub> O, 1:2.5)	8.2	8.3	8.6	5.7
Soil organic carbon (g kg <sup>-1</sup> )	8.25	7.33	7.07	8.22
Soil clay (<0.002 mm, %)	14.7	12.8	16.8	61.4
$\delta^{13}\text{C}$ (‰)	-19.5	-22.3	-21.7	-23.8
P <sub>C4</sub> (%)	60.7	40.9	44.8	30.2

crop residues (Izaurrealde et al., 2001) and 38% in roots (Parr and Papendick, 1978).

Subtle differences in the natural abundances of  $^{13}\text{C}$  (the relatively rare heavy but stable isotope of C) are expressed using the delta notation, as follows:

$$\delta^{13}\text{C}(\text{‰}) = \left[ \frac{(R_{\text{samp}} - R_{\text{stand}})}{R_{\text{stand}}} \right] \times 1000 \quad (1)$$

where  $R_{\text{samp}}$  is the  $^{13}\text{C}/^{12}\text{C}$  ratio of the sample and  $R_{\text{stand}}$  is the  $^{13}\text{C}/^{12}\text{C}$  ratio of the international VPDB standard (0.0112372) (Coplen, 1995).

The proportion of SOC derived from  $\text{C}_4$  plant ( $P_{\text{C}_4}$ ) was estimated by the following Eq. (2):

$$P_{\text{C}_4}(\%) = (0.0714X + 2) \times 100 \quad (2)$$

where  $P_{\text{C}_4}$  is the proportion (%) of SOC derived from  $\text{C}_4$  plant and  $X$  is the  $\delta^{13}\text{C}$  value (‰) of SOC (Ellert and Rock, 2008). This assumes that the natural abundance of SOC inputs from  $\text{C}_3$  and  $\text{C}_4$  plants is  $-28$  and  $-14$ ‰, respectively. The proportion of SOC derived from  $\text{C}_3$  plant ( $P_{\text{C}_3}$ ) was  $1 - P_{\text{C}_4}$ . The SOC derived from  $\text{C}_4$  plant ( $\text{C}_4\text{-C}$ ) was estimated by the total SOC multiplied by  $P_{\text{C}_4}$  (%).

#### 2.4. Statistical analysis

Differences among experimental treatments were determined by analysis of variance (ANOVA) using SAS 9.1 (SAS Institute, 2004). When treatment effects were significant at  $P < 0.05$ , the Duncan's multiple range test was used to separate the treatment means. Simple correlation analysis by SAS was used to determine the relationship between the contents of SOC,  $\delta^{13}\text{C}$  values and cultivation time, cumulative C inputs and annual change in the SOC, the differences of SOC derived from  $\text{C}_4$  plant and  $\text{C}_3$  plant and the  $\delta^{13}\text{C}$  values.

### 3. Results

#### 3.1. Carbon input

The cumulative C inputs during 15 years for maize and wheat at all experimental sites were shown in Table 2. Regardless of the crop and the treatment used, the lowest cumulative C input was observed at Qiyang, while the highest input was at Zhengzhou. In general, the cumulative C inputs were in the increasing order: Control < NPK < NPKSt, regardless of the crop and the experimental sites. The mean total C input for both crops across the four sites for NPKSt treatment were more than 5 and 2 times values from Control and NPK treatments. Furthermore, inputs for the NPK treatment were roughly 2.5 times

**Table 2**

The cumulative C inputs during cultivation period. <sup>a</sup>For Control and NPK treatments, the accumulative C inputs derived from crop root C alone. For NPKSt treatment, the accumulative C inputs were derived from the sum of crop root and straw C. Total C inputs from maize straw were 40.2, 39.6, 25.0 and 12.6  $\text{Mg ha}^{-1}$  for Changping, Zhengzhou, Yangling and Qiyang, respectively and from wheat straw in the NPKSt treatment was 10.5  $\text{Mg ha}^{-1}$  for Qiyang.

Treatment <sup>a</sup>	Item	Site				
		Changping	Zhengzhou	Yangling	Qiyang	Mean
		$\text{Mg C ha}^{-1}$				
Control	Maize	10.9	11.0	6.70	2.99	7.88
	Wheat	3.34	7.61	5.34	2.93	4.82
	Total	14.2	18.6	12.0	5.92	12.7
NPK	Maize	17.5	17.2	12.9	10.1	14.4
	Wheat	15.7	24.2	21.1	8.67	17.4
	Total	33.2	41.3	34.0	18.8	31.8
NPKSt	Maize	58.6	59.6	37.0	24.7	45.0
	Wheat	16.0	25.4	23.1	20.6	21.3
	Total	74.6	85.0	60.1	45.3	66.3

those of the Control, so the relative increase from inorganic fertilizer exceeded that for retaining above-ground crop residues.

Comparing the two crops, the mean cumulative C inputs across all sites from maize were 1.63 and 2.11 time values from wheat in the Control and NPKSt treatments, respectively, but differences between the two crops were small for NPK treatments.

#### 3.2. SOC

The mean SOC contents averaged across all 15 years differed among the three treatments (Table 3). The greatest mean SOC contents were found under the NPKSt and the smallest contents usually occurred under the Control treatment. The SOC contents, after 15 years, averaged across all sites decreased in the following treatment order: NPKSt ( $9.11 \text{ g kg}^{-1}$ ) > NPK ( $8.41 \text{ g kg}^{-1}$ ) > Control ( $7.66 \text{ g kg}^{-1}$ ).

There were no significant changes in SOC contents for Control treatments over the 15 years of maize-wheat rotation (Fig. 1). In contrast, net primary production, grain yields, crop root C inputs increased when the soils were amended with inorganic fertilizer. Under these treatments (i.e. NPK) SOC contents increased at an average rate of  $0.160 \text{ g kg}^{-1} \text{ yr}^{-1}$  across all sites ( $0.068, 0.074, 0.241$  and  $0.256 \text{ g kg}^{-1} \text{ yr}^{-1}$  for Zhengzhou, Changping, Yangling and Qiyang, respectively) (Fig. 1). Furthermore, when the soils received additional crop residues (NPKSt), the SOC contents increased at an average rate of  $0.201 \text{ g kg}^{-1} \text{ yr}^{-1}$  ( $0.071, 0.156, 0.273$  and  $0.304 \text{ g kg}^{-1} \text{ yr}^{-1}$  for Zhengzhou, Changping, Yangling and Qiyang, respectively). Thus, the average increasing rate of SOC in the soils with NPKSt treatments was 25.6% higher than that in the soils with NPK treatments across all sites.

The mean annual C inputs of  $0.39\text{--}1.24 \text{ Mg ha}^{-1}$  from crop roots under the Control treatments had no impact on the SOC contents for this treatment at all sites (Fig. 2). The reciprocals of the slopes of regression lines (Fig. 2) indicated the cumulative amounts of plant C input were required to increase SOC concentrations by  $1 \text{ g C kg}^{-1}$  soil. These values for the NPK treatments receiving only root residues ranged from 5.4 to 45.2 (mean 24.3)  $\text{Mg C ha}^{-1}$  and for the NPKSt treatments also receiving above-ground crop residues ranged from 11.1 to 52.6 (mean 29.4)  $\text{Mg C ha}^{-1}$ . The smaller values for the NPK treatment suggest that SOC decomposition rates were lower for this treatment than those under the NPKSt treatments at all the four sites. Furthermore, the decomposition rates of SOC at Qiyang were lowest among the four sites.

#### 3.3. $\delta^{13}\text{C}$ values of SOC

The  $\delta^{13}\text{C}$  values for SOC averaged over 15 years were unaffected by the treatments at all sites (Table 3). The range between the largest ( $-19.7\%$ ) and smallest ( $-22.1\%$ ) values was only 2.4‰. However, the  $\delta^{13}\text{C}$  values increased significantly for all treatments over time at Qiyang (Fig. 3). There was a similar trend in Control and NPKSt treatments at Zhengzhou and Yangling. In contrast, there was a decreasing trend for the NPK treatment at Yangling and in the next 11 years at Zhengzhou. For Changping, the  $\delta^{13}\text{C}$  values decreased

**Table 3**

The values of SOC and  $\delta^{13}\text{C}$  on average over years at different sites. <sup>a</sup>For each parameter, means in a column followed by different lower case letters differ at  $P < 0.05$ .

Item	Treatment	Site				Mean
		Changping	Zhengzhou	Yangling	Qiyang	
SOC ( $\text{g kg}^{-1}$ )	Control	8.41b <sup>a</sup>	6.26c	7.34c	8.64b	7.66
	NPK	8.45b	6.96b	8.21b	10.0a	8.41
	NPKSt	9.15a	8.03a	9.17a	10.1a	9.11
$\delta^{13}\text{C}$ (‰)	Control	-19.7a	-21.5a	-21.0a	-21.3a	-20.9
	NPK	-20.2a	-21.7a	-22.1a	-21.5a	-21.4
	NPKSt	-20.1a	-21.5a	-20.9a	-20.8a	-20.8

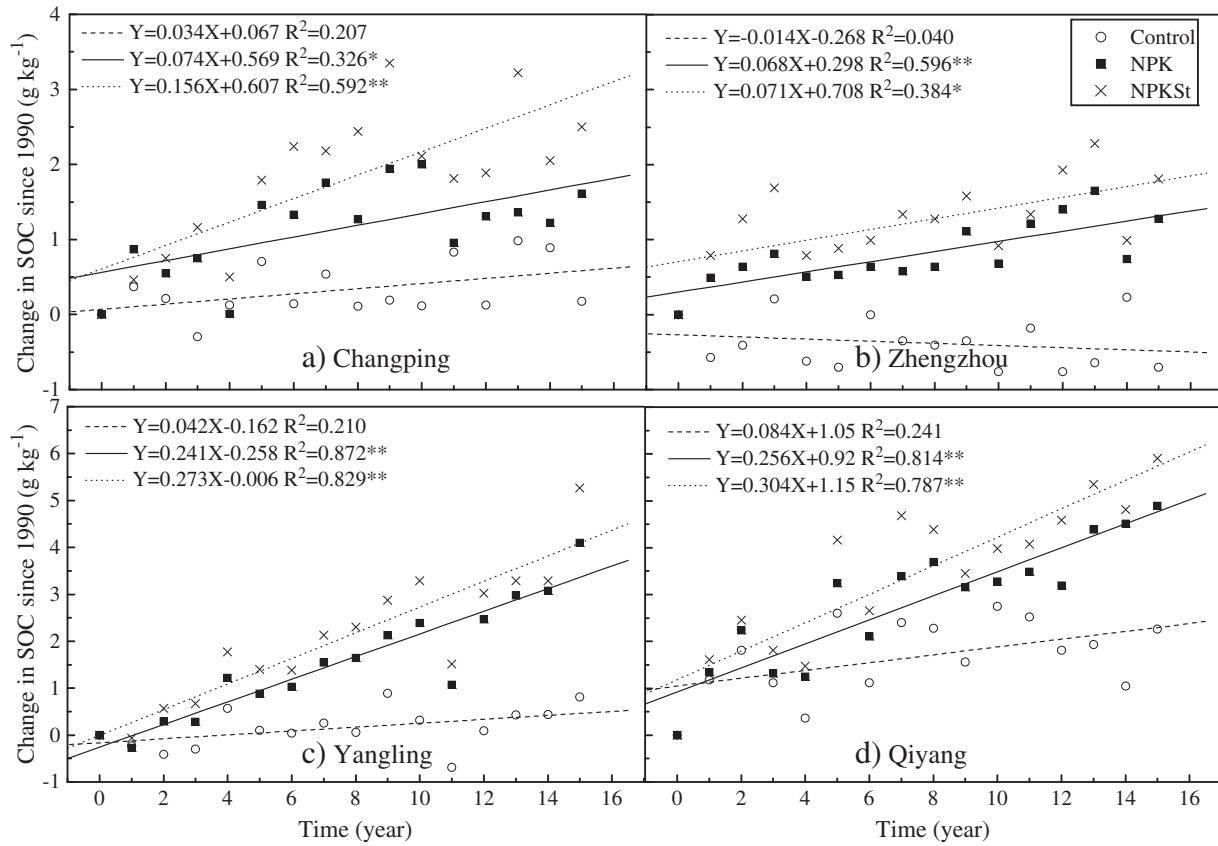


Fig. 1. Relationship between the changes in soil organic carbon (SOC) and cultivation time (year) at different experimental sites. (Change in SOC since 1990 = SOC<sub>i</sub> - SOC<sub>0</sub>, where i = 1, 2, ... 15 years of treatment; C<sub>0</sub> is the SOC before treatment).

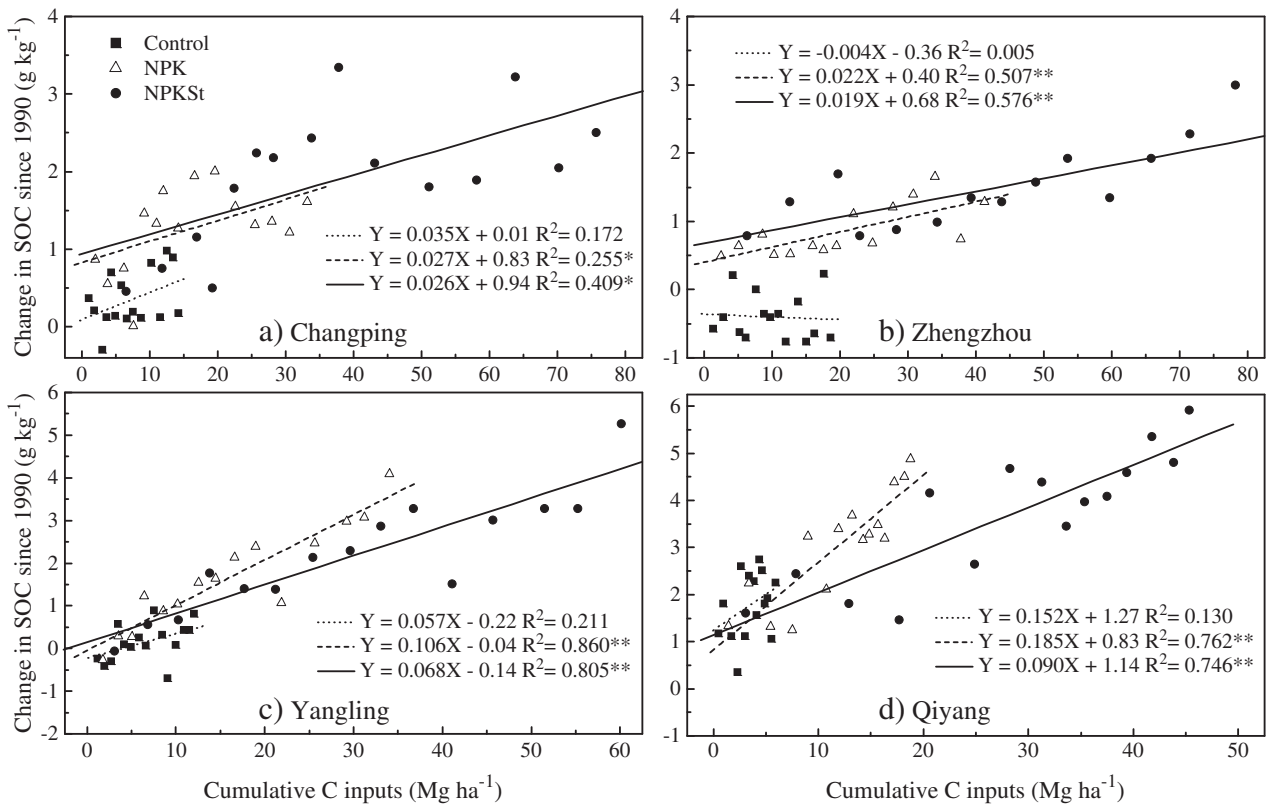
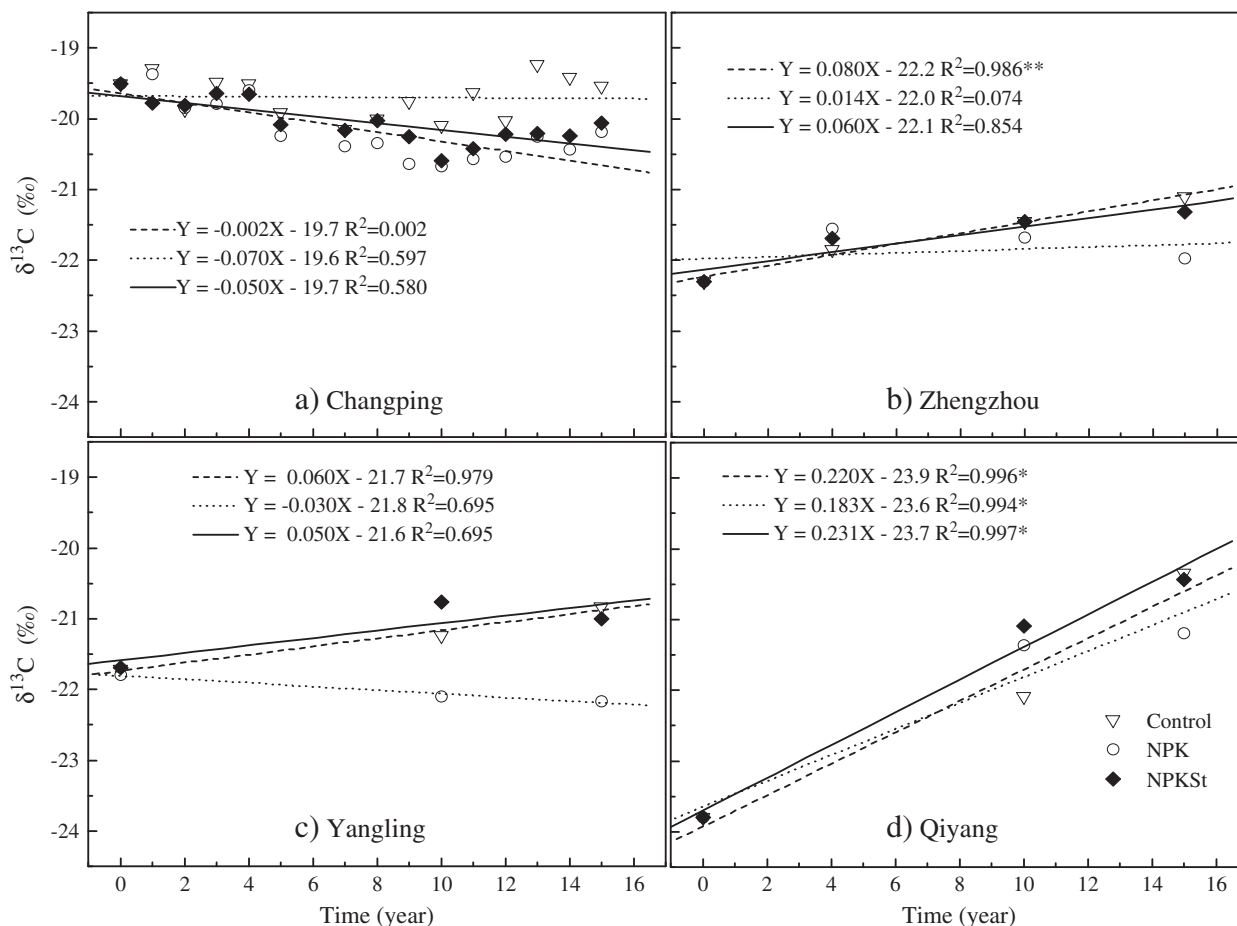


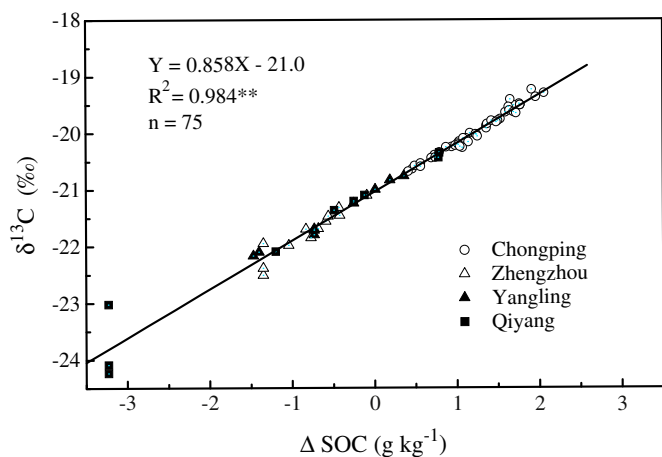
Fig. 2. Relationship between annual change in the contents of SOC and cumulative C inputs year by year in the three treatments across all sites (Change in SOC since 1990 = SOC<sub>i</sub> - SOC<sub>0</sub>, where i = 1, 2, ... 15 years of treatment; C<sub>0</sub> is the SOC before treatment).



**Fig. 3.** Changes of the  $\delta^{13}\text{C}$  values in soil organic matter over the cultivation time of 15 years in response to the fertilization and in combination with crop residue returns at different experimental sites. Soil samples in 1990, 1994, 2000, and 2005 at Zhengzhou, from 1990 to 2005 at Changping every year except for 1996, in 1990, 2000 and 2005 at Yangling and Qiyang were analyzed in 2008 for the  $\delta^{13}\text{C}$  values of organic matter in soils.

over the first 10 years, the decline was significant in NPK and NPKSt treatments, and then gradually increased in the next five years in all the three treatments.

There was a positive correlation between the differences of SOC  $\text{C}_4$ -derived and  $\text{C}_3$ -derived and the  $\delta^{13}\text{C}$  values in all treatments across the four sites (Fig. 4). The correlation coefficient ( $R < 0.05$ ) was significant ( $R^2 = 0.984^{**}$ ).



**Fig. 4.** Relationship between the differences of SOC derived from  $\text{C}_4$  and  $\text{C}_3$  plants and the  $\delta^{13}\text{C}$  values at different experimental sites ( $\Delta\text{SOC} = \text{C}_4\text{-C} - \text{C}_3\text{-C}$ , where  $\text{C}_4\text{-C}$  is the SOC derived from  $\text{C}_4$  plant and  $\text{C}_3\text{-C}$  is the SOC derived from  $\text{C}_3$  plant).

## 4. Discussion

### 4.1. SOC

In the present study, cultivation under maize-wheat rotations for 15 years had little effect on SOC concentrations without fertilization (Control). Apparently, the annual root C inputs of  $0.39\text{--}1.24 \text{ Mg ha}^{-1}$  were balanced by  $\text{CO}_2$  outputs from SOC decomposition in the Control treatment with relatively low grain yields of  $0.9 \text{ Mg ha}^{-1}$  for wheat and  $1.9 \text{ Mg ha}^{-1}$  for maize (Tang et al., 2008). The SOC did not decline appreciably during the initial years of this study suggests that previous plant C inputs had been similarly low. However, applying inorganic NPK fertilizers generally led to a higher SOC content than Control as fertilizers increased both above-ground (Tang et al., 2008) and below-ground (e.g. roots) crop growth resulting in annual C inputs from crop roots in NPK treatments higher than in the Control (Table 2). Furthermore, SOC content in NPK treatments increased over time, which suggested that annual C inputs of  $1.25\text{--}2.76 \text{ Mg ha}^{-1}$  would promote SOC accumulation in soils. Applying inorganic fertilizers in combination with crop residues led to the highest SOC contents, similar to those reported from a field experiment of continuous maize cropping in Denmark (Kristiansen et al., 2005). This is due to the increased C inputs from organic residues both above-ground and below-ground (Table 2). Moreover, the crop residues are the substrates for microbial activities and these will lead to an increase in soil microbial biomass (Hao et al., 2008; Ocio et al., 1991). Thus, incorporation of above-ground crop residue biomass into soils generally increases the contents of organic matter in soils.

Rasmussen and Parton (1994) reported that the rate of SOC change was directly related to C input from crop residues and amendments. Our study also showed that there was a positive correlation between annual change in SOC and cumulative C inputs in the soils applying inorganic fertilizers with or without crop residues input (Fig. 2). This agreed with the results of Robinson et al. (1996), who found that the SOC increased with greater quantities of residue returned. SOC at Zhengzhou was least responsive to increased plant C inputs, whereas SOC at Qiyang was most responsive to increased SOC inputs. Soils at Qiyang have a higher clay content (61.4% <0.002 mm) than those at Zhangzhou (12.8%), Changping (14.7%) and Yangling (16.8%) (Ma et al., 2009). We suspect that the finer-textured soils at Qiyang probably were more effective at physically protecting incoming plant residue C against decomposition, so greater proportions became stabilized as SOC, though to a lesser extent than the sites studied by Robinson et al. (1996). Campbell et al. (1996) reported that greater increase in SOC for fine-textured than coarse-textured soils based on long-term studies conducted on Brown Chernozemic soils of Saskatchewan.

The Control treatment is more representative of land use prior to Chinese land reform in 1980s, while since then land management has increasingly changed towards that represented by the NPK treatment. Still, most above-ground residues were removed from cropland and used as fuel sources for cooking and household heating. In contrast, the NPKSt treatment is more representative of current or increasingly adopted land use practices in China as farmers rely less on the above-ground crop residue as fuel source due to improved household income and living standard following the land and economic reform in China. Data from our study across four sites across in China has demonstrated the SOC could be increased substantially by returning crop residue to soil. Due to the low SOC content from years of land use practice as in the Control treatment, by returning above-ground crop residue to increasing SOC could be a viable option for C sequestration and combat global climate change.

#### 4.2. $\delta^{13}\text{C}$ values of SOC

At all four sites initial  $\delta^{13}\text{C}$  values of SOC were appreciably higher than typical values for  $\text{C}_3$  vegetation (28 to  $-26\%$ ). This indicates that the SOC at all four sites previously had been under the influence of plant C inputs that included a portion derived from the  $\text{C}_4$  photosynthetic pathway. This influence likely extended well before the two years of maize grown prior to initiation of this experiment. The initial values at the Zhengzhou and Yangling sites situated at the southern edge of the Loess Plateau are broadly consistent with  $\delta^{13}\text{C}$  values for SOC postulated to have been derived from palaeovegetation in this region (Lui et al., 2005). The initial  $\delta^{13}\text{C}$  value was the lowest and subsequent increase the greatest at the Qiyang site where previous contributions of inputs from  $\text{C}_4$  plants were smallest and subsequent retention of crop residues was the greatest.

The increase in  $\delta^{13}\text{C}$  values over the 15 years in Control soils was attributable to replacement of precious SOC (having smaller  $^{13}\text{C}$  abundance) with recent SOC derived from plant C inputs having greater  $^{13}\text{C}$  abundance attributable to maize. These  $\delta^{13}\text{C}$  values indicated a turnover of SOC, even without an increase in SOC concentration under the Control treatment. In addition to the influence of maize C inputs that are richer in  $^{13}\text{C}$ , subsequent decomposition tends to further enrich  $^{13}\text{C}$  in SOC, because microbial respiration has a slight preference for  $^{12}\text{C}$  which is released as  $\text{CO}_2$ , leaving the remaining SOC slightly enriched in  $^{13}\text{C}$  (Agren et al., 1996; Nadelhoffer and Fry, 1988).

The initial  $\delta^{13}\text{C}$  values for SOC were greatest at Changping where  $\text{C}_4$  plants had made relatively large contributions to plant C inputs before current experiments. Consequently,  $\delta^{13}\text{C}$  values of SOC at this site decreased for all three treatments during the first 10 years, because the proportion of C inputs derived from  $\text{C}_4$  plants decreased when this experiment was initiated. However, after ten years SOC turnover

appeared to have established a new equilibrium between  $^{13}\text{C}$  in plant C inputs and in the fraction of SOC decomposed each year. Thus, the  $\delta^{13}\text{C}$  values of SOC remained largely unchanged in the three treatments in the last five years. The new quasi-equilibrium  $^{13}\text{C}$  abundances reached after 10 years in SOC at Changping were greater for the NPKSt treatment because plant C inputs were greater as were the amount retained as SOC. At Zhengzhou and Yangling trends in  $\delta^{13}\text{C}$  values for SOC under the NPK treatment appeared to be distinct from the Control and NPKSt treatments. The static or declining trends under NPK at these two sites suggest that inputs of maize-derived C or its retention were comparatively smaller for inputs from  $\text{C}_3$  plants.

Our results indicated that crop residues returned under a long-term wheat–maize rotation influenced the proportions of SOC derived from  $\text{C}_3$  and  $\text{C}_4$  plant at all four experimental sites. SOC increased as plant C inputs increased in response to inorganic fertilizers and return of above-ground crop residues. Since the plant C inputs were isotopically distinct from initial SOC, changes in SOC concentration were closely related to the  $\delta^{13}\text{C}$  values (Fig. 4). In other words, the isotopic shifts showed the extent to which pre-1990 SOC was replaced by post-1990 plant C inputs, even when actual changes in soil C stock were small in these wheat–maize cropping systems.

## 5. Conclusions

In long-term wheat–maize rotations at four sites spanning some of the most important cropland in China the application of inorganic fertilizers and the return of above-ground crop residue influenced contents of SOC in soils. The SOC in the plough layer (0–20 cm) increased during the 15 years at average rates of  $0.160 \text{ g kg}^{-1} \text{ yr}^{-1}$  in the soils with application of NPK inorganic fertilizers alone and of  $0.201 \text{ g kg}^{-1} \text{ yr}^{-1}$  in the soils with application of inorganic fertilizers plus crop residues returned. There was a positive correlation between annual change in SOC and cumulative C inputs in the NPK and NPKSt treatments across all sites. Increasing crop residue input to low SOC soil has potential to increase soil C sequestration with implications for reducing  $\text{CO}_2$  emissions to the atmosphere. Moreover, there was a positive correlation between the differences of SOC  $\text{C}_4$ -derived and  $\text{C}_3$ -derived and the  $\delta^{13}\text{C}$  values. We conclude that the  $\delta^{13}\text{C}$  value was a useful tool to quantify temporal changes of SOC from  $\text{C}_4$  and  $\text{C}_3$  plants, even when actual changes in soil C stock were small in these wheat–maize rotation cropping systems.

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