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Research paper

Long-term fertilization increases soil organic carbon and alters its chemical composition in three wheat-maize cropping sites across central and south China

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ABSTRACT

Soil organic carbon (SOC) is at the core of soil fertility. Although fertilization strategies can alter SOC stocks, their effects on SOC chemical composition is less known. Using the solid-state ^{13}C nuclear magnetic resonance (NMR) spectroscopy, we examined changes in the SOC chemical composition of three soils (0–20 cm depth) from an annual wheat-maize double-cropping system across central to south China. These soils had been subjected to 22 years (1990–2012) long-term fertilization. Compared with no-fertilization control, SOC stocks were significantly increased under chemical fertilization (NPK), NPK plus straw (NPKS), and NPK plus manure (NPKM). The O-alkyl C (labile C), not the alkyl C (persistent C), was consistently increased across the three fertilized treatments. Additionally, all fertilized treatments decreased the ratio of alkyl-C/O-alkyl-C (SOC decomposition index) or aliphatic-C/aromatic-C (SOC complexity index), indicating that the SOC decomposition was delayed, or SOC was converted into a more complicated structure. The soil C of NMR-determined functional groups (alkyl C, O-alkyl C, aromatic C, and carbonyl C) was positively correlated with the cumulative C input ($P < 0.05$). The conversion rate of functional groups was highest in O-alkyl C, indicating a largest contribution to the increase of SOC accumulation. Soil C:N ratio, pH, and clay were the main factors affecting the functional-group conversion rates, whereas annual precipitation, temperature, and accumulated temperature (> 10 °C) played smaller roles. In conclusion, these results can be applied to the improvement of agricultural soil C sequestration capacity through changing SOC chemical structure under long-term fertilizer managements.

1. Introduction

Soil organic carbon (SOC) is a key indicator of soil fertility and health (Baldock et al., 2004; Liu et al., 2006) and soil fertility can be improved through soil C sequestration. In doing so, knowledge of soil C quantity and forms are required, because various C-containing compounds of soil C differ in their stability against decomposition under distinct environments. However, understanding the highly heterogeneous nature of external C input and the complexity of C compounds in soil remains a major challenge.

Fertilizer application (both chemical and organic) to agricultural soils is widely used as a common management practice to maintain or increase soil fertility and SOC stock. In general, fertilization with organic fertilizers alone or plus chemical fertilizers tend to increase SOC concentrations (Blair et al., 2006; Bhattacharyya et al., 2010; Ding et al., 2012; Maillard et al., 2015), whereas chemical fertilization alone yielded inconsistent outcomes (Purakayastha et al., 2008; Lemke et al., 2010; He et al., 2015). Despite a clear documentation of SOC gains and losses through fertilization, only contradictory data are available for the effects of long-term fertilization strategies on SOC that could affect SOC chemical composition. Potentially, the elucidation of the chemical composition of SOC can be tackled by a number of new techniques, such as Pyrolysis-field Ionization Mass Spectroscopy (Py-FIMS) (Leinweber and Schulten, 1995), Off-line TMAH thermochemolysis-GC/

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MS spectrometry (Spaccini and Piccolo, 2009), Fourier Transform Infrared spectroscopy (FTIR) and solid-state ^{13}C NMR spectroscopy (Schmidt et al., 1997), etc. By using these advanced techniques, Sleutel et al. (2009) found that the biologically labile SOM components like carbohydrates, peptides were increased but the plant materials-originated materials like lipids, alkylaromatics and sterols were decreased in two croplands in Belgium after sodium hypochlorite and hydrofluoric acid treatments. Besides, Spaccini et al. (2009) found significantly qualitative variations in the molecular characteristics of SOM between no-compost-amended and compost-amended soils after 1-year cultivation in Italy. Meanwhile, both organic or chemical fertilization increased the alkyl C content in the soil aggregates (Wang et al., 2012a, 2012b) and 18-years organic fertilization led to a low O-alkyl C, but a high aromatic C and alkyl C in soil particulate organic matter (Zhou et al., 2010). In contrast, two separate studies from China and England revealed that neither 16 years of chemical fertilization nor 100 years of organic fertilization affected bulk SOC chemical composition in clay- and silt-sized fractions (Bierke et al., 2008). As a result, a clear and detailed molecular characterization of SOC under various fertilization managements is required for understanding the stabilization of specific exogenous C input in soil.

The amount of C input is one of the most influential factors controlling the chemical composition of organic materials in agricultural soil (Oades et al., 1988; Baldock et al., 1992). For instance, Yan et al. (2013) found that an annual 4500 kg ha^{-1} addition of fresh pig manure did not alter SOC composition in a paddy soil from China. In contrast, Zhou et al. (2010) reported that an addition of 8400 kg ha^{-1} y^{-1} fresh pig manure increased aromatic-C and alkyl-C content in a Chinese paddy soil, thereby also increasing soil C sequestration. However, these studies did not quantify the amount of C sequestrated in different functional groups, nor provide details about the conversion rate of C input to C functional groups. Such data are necessary because they can identify the key fractions of SOC that contributed most to C sequestration and could be determined with nuclear magnetic resonance (NMR).

The C-input-to-SOC conversion rate is the slope of a linear regression between the sequestered SOC and cumulative C input in soil (Kundu et al., 2007). This conversion rate in bulk soil is mainly regulated by climate and soil properties (Zhang et al., 2012). Specially, fertilization treatments in a warm-temperate regions or areas with higher precipitation tended to have lower C conversion rate, compared with mild-temperate or drier regions (Zhang et al., 2010). Furthermore, fertilization to soils with higher clay content increased C conversion rate over soil with lower clay content (Gami et al., 2009). However, those studies only examined correlations between C conversion rate and a single factor (climate or soil properties), rather than using multivariate analyses to evaluate the relative contribution of each factor to the conversion rate. Moreover, information regarding key factors affecting the C conversion rate in different NMR-determined C functional groups is limited, particularly in the varied arable lands developed from diverse climate conditions and subjected to long-term fertilization.

In this study, the solid-state ^{13}C NMR spectroscopy was used to investigate the chemical composition of total SOC in the topsoil (0–20 cm) of three wheat-maize cropping sites across central to south China (temperate to subtropical climates). We aimed to investigate: (1) the effects of long-term (22 years) fertilization on SOC chemical composition and (2) the relative contribution of climate and soil properties to the conversion rate of soil C functional groups. The generated results should identify the key functional fractions that sequestrate soil C and the primary factors that affect C conversion rates under long-term fertilizer management.

Table 1
General description of geography and soil properties (0–20 cm depth) in 1990 at three sites subjected to 22 years (1990–2012) fertilization in China.

	Yangling	Zhengzhou	Qiyang
Location	34°17′, 108°00′	34°47′, 113°40′	26°45′, 111°52′
Climate	Warm-temperate, semi-humid	Warm-temperate, semi-humid	Subtropical, humid monsoon
Precipitation (mm)	575	632	1250
Mean temperature (°C)	13.0	14.3	18.0
Cropping system	maize/wheat annually	maize/wheat annually	maize/wheat annually
FAO soil classification	Calcaric Regosol	Calcaric Cambisol	Ferralic Cambisol
Soil texture	Silt loam	Silt loam	Clay
Clay content (%)	16.8	13.4	35.2
Bulk density (g cm^{-3})	1.35	1.41	1.19
Initial SOC (g kg^{-1})	6.32	6.70	7.89
Total N(g kg^{-1})	0.83	0.67	1.07
pH (soil: water = 1:2.5)	8.6	8.3	5.7
Alkyl (%)	25.8	19.3	26.5
O-alkyl (%)	50.0	42.3	47.2
Aromatic (%)	13.2	24.9	17.3
Carbonyl (%)	11.0	13.5	9.1
alkyl/O-alkyl	0.52	0.46	0.51
(alkyl + O-alkyl)/ aromatic	5.74	2.47	4.26

2. Materials and methods

2.1. Site description

The three selected long-term fertilization sites were established in September 1990. The areas range from central to southern China, and are located in Yangling (YL), Shaanxi, northwest China; Zhengzhou (ZZ), Henan, central China; and Qiyang (QY), Hunan, south China. Table 1 describes their basic climate, soil chemical properties, cropping systems, and initial soil chemical composition in 1990. To reduce soil fertility variability, crops were cultivated without fertilization for two years before site establishment.

2.2. Cropping systems and plant harvest

The three sites were subjected to an annual wheat-maize double-cropping system, with seasonal variation depending climate conditions. At YL and ZZ, wheat was grown between mid-October and early June, while maize was grown between mid-June and late September. At QY, wheat was grown from early November to early May, whereas maize was planted between wheat strips during early April and July. No irrigation was given to crops at QY, but at YL and ZZ, wheat was irrigated two or three times and maize once (about 75 mm each time), depending on precipitation. Herbicides and pesticides were applied during growth when needed. All above-ground biomass was manually harvested, separated into grains and straws, then oven-dried to constant weight.

2.3. Experimental design and fertilization rates

The field experiments were in a randomized block design, with three replicate plots at ZZ (plot size 45 m^2), two replicates at QY (plot size 196 m^2), and no replicate at YL (plot size 196 m^2). Four fertilization treatments were examined in this study: (1) unfertilized control; (2) chemical nitrogen, phosphorus, and potassium (NPK); (3) NPK plus manure (NPKM, hereafter “manure”); (4) NPK plus straw (NPKS, hereafter “straw return”).

The annual fertilization rates are summarized in supplementary Table 1. At each site, an equivalent amount of N was applied to all