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Does P-deficiency fertilization alter chemical compositions of fulvic acids? Insights from long-term field studies on two contrasting soils: A Fluvisol and an Anthrosol

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ABSTRACT

Structural changes in fulvic acid (FA) in response to fertilization strategies, especially P-deficiency fertilization, have critical implications for soil carbon dynamics. This study examined how long-term fertilization influenced chemical compositions of soil FA and its humification degree. Advanced solid-state ^{13}C nuclear magnetic resonance techniques were used to evaluate structural changes of FAs from two soils (a Fluvisol and an Anthrosol) under four fertilizer treatments: organic fertilizer combined with or without NPK fertilizer (OF and NPKOF), deficient in phosphorus only (NK) and Control. The greater aromaticity, hydrophobicity and alkyl/O-alkyl (A/O-A) ratios of FAs were observed in the Anthrosol than in the Fluvisol. The Anthrosol FAs contained more alkyl and aromatic C but fewer O-alkyls (mostly being protonated) than did the Fluvisol FAs. Both FAs comprised some nonprotonated aromatics, which decreased with applications of organic and NK fertilizers. This trend was less obvious for the Anthrosol than for the Fluvisol. Organic fertilizer treatments (OF and NPKOF) in the Fluvisol increased the A/O-A ratio and aromaticity compared with P-deficient soils (NK and Control), indicating organic fertilization promoted the humification degree of its FA. The NK treatment in the Fluvisol increased H/C ratio of FA. Compared with the Fluvisol FAs, the Anthrosol FAs displayed similar chemical natures, implying their formation followed similar processes with a similar humification degree. The findings suggest that long-term fertilization differently influenced the FAs from the Fluvisol and Anthrosol. Clearly, the Anthrosol FAs shared more common features among the treatments compared with the Fluvisol FAs, whereas P-deficiency rendered the Fluvisol FAs simpler.

1. Introduction

Humic substances (HSs) are ubiquitous in soils, sediments, and natural waters (Piccolo, 2001). They are supposed to be formed through biochemical and chemical reactions as the plant and microbial residues undergo decay and transformation (IHSS, 2017). Traditionally, HS can be operationally categorized into fulvic acid (FA), humic acid (HA) and humin on the basis of the solubility (Stevenson, 1994). As the most mobile fraction among the three types of HS, FA displays great solubility and strong acidity probably due to small molecular sizes and large amounts of carboxyl groups (Tan, 2014).

The formation of FA, as a precursor for formation of HA or a degradation product of HA, is closely related to humification processes (Tan, 2014). The degree of humification can also to some extent be reflected by the amounts of FAs (Dai et al., 2006; Jindo et al., 2011). Thus, accurate characterization of FAs should be conducive to elucidating the turnover and evolutionary routes of soil organic matter (SOM). Previous studies showed that long-term fertilization as well as composting affected the amounts and compositions of FAs (Jindo et al., 2011; Jouraiphy et al., 2005; Spaccini et al., 2000; Wu et al., 2014). Generally, the addition of organic and chemical fertilizers increase the contents of soil FAs (Jindo et al., 2011; Spaccini et al., 2000; Zhang et al., 2017). However, Jouraiphy et al. (2005) found that the FA contents decreased after 135 days of composting of sewage sludge and green wastes, possibly due to the biodegradation of FA or polymerization of FA into HA. Fulvic acids have lower contents of C and N and

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higher O contents than do corresponding HAs (reviewed by Rice and Maccarthy (1991)). The elemental compositions of FAs from soil sources differed from those from freshwater by their greater H/C ratios (Rice and Maccarthy, 1991). Elemental compositions among soil FAs under different crop systems were also different, but these differences were less pronounced than their similarities (Ding et al., 2005). Iimura et al. (2012) concluded that FAs may exhibit only small differences among various soil types based on their ^{13}C nuclear magnetic resonance (NMR) spectra ($n = 36$). By using multidimensional fluorescence spectroscopy with parallel factor analysis, Ohno et al. (2009) claimed that the chemical compositions of FAs were not significantly affected by N treatments in a long-term cropping system. Long-term applications of chemical and organic fertilizers also had little effects on the compositions of fluorescent substances of FAs isolated from a Ferralic Cambisol (Wu et al., 2014). Nevertheless, Spaccini et al. (2000) reported that the NMR spectra of FAs extracted from soils were significantly changed after incubation with maize which contained more carbohydrates compared with those without maize addition. Jindo et al. (2011) found that the addition of composted materials to a soil increased the A/O-A ratios of FAs and also slightly increased their hydrophobicity. Zhang et al. (2017) argued that fertilization showed relatively smaller effects on the structures of FAs compared with the effects of particle-size fraction. Nevertheless, soil FAs have been attracting less interest compared with HAs (Tan, 2014) possibly due to difficulties in the separation of FAs from HAs (Stevenson, 1994). Moreover, the structures and functions of FAs are not well understood (Bai et al., 2015) owing to the complexity and heterogeneity of HSs (Piccolo, 2001) especially the limitations in quantitative studies and identification of specific functional groups (Barros Soares et al., 2013).

Deficiency of P availability is common in arable soils, especially in the typical soils from the Huang-Huai-Hai Plain of northern China, namely Calcaric Fluvisol (Jing et al., 2017) and from the hilly subtropical China, namely Hydragric Anthrosol (Su et al., 2015). Studies on these two soils have demonstrated that deficiency of available P is a critical constraint to soil fertility and crop yields (Su et al., 2015; Xin et al., 2017) probably due to the limit of microbial activities (Zheng et al., 2009). Such limitation influences soil C dynamics via decomposition and incorporation of organic materials into SOM (Schmidt et al., 2011). The amount and chemical structures of FAs, as part of SOM, may also be changed when the soil is deficient in P availability, and exert a considerable influence on humification processes (Steinberg, 2003; Stevenson, 1994; Tan, 2014). However little is known about FA chemical composition under P-deficiency and long-term application of organic fertilizers. As an ecological resource, organic fertilizer application is an effective strategy to overcome these negative effects and has been encouraged as a sustainable alternative to fertilization strategies all over the world (Jindo et al., 2011; Shang et al., 2014; Shindo et al., 2006). Addition of organic fertilizers such as organic manure and crop straw can promote P accumulation and availability in surface soils (Shang et al., 2014; Xin et al., 2017), thus is beneficial to improving microbial activities, soil fertility and plant growth (Su et al., 2015; Zheng et al., 2009). Our previous studies also indicated that P-deficiency (NK) treatment resulted in low content of soil organic carbon (SOC) and large degree of decomposition of organic matter in the Fluvisol, but had small changes in SOC chemical compositions for the Anthrosol (Xu et al., 2017b).

Based on these studies, we hypothesize that P-deficiency could alter chemical compositions of the FAs from the Fluvisol used for dryland production but not those from the Anthrosol used for paddy production. The aim of this work was therefore to provide detail information on the chemical compositions of FAs isolated from two typical soils (the Fluvisol and Anthrosol) in China to evaluate their humification degree and effects of organic and NK fertilizers. The ^{13}C multiple cross-polarization/magic angle spinning (multiCP/MAS) solid-state NMR spectroscopy (Johnson and Schmidt-Rohr, 2014) and spectral-editing techniques were applied to obtain quantitative structural information of the FAs.

2. Materials and methods

2.1. Experimental sites and soil sampling

The two experimental sites and field management have been described in detail before (Xu et al., 2017b). One is located at Fengqiu (Henan Province, China; 35°00′N, 114°24′E), where the Fengqiu Agro-ecological Experimental Station has been established since 1989. The soil at this site is a Calcaric Fluvisol with a sandy loam texture, developed from alluvial sediments of the Yellow River. The soil contained 4.42 g organic C kg^{-1}, 0.45 g total N kg^{-1}, 0.50 g total P kg^{-1} and 18.6 g total K kg^{-1} and had a pH of 8.65 prior to the start of the experiment. The other site is at the Taoyuan Agro-ecosystem Research Station (Hunan Province, China; 28°55′N, 111°33′E) (1990–present). Soil is a Hydragric Anthrosol formed in a paddy soil with a clayey loam texture. In 1990, the soil had 14.1 g organic C kg^{-1}, 1.78 g total N kg^{-1}, 0.55 g total P kg^{-1}, 12.6 g total K kg^{-1} and a pH of 5.38.

We focused on the four different fertilizer treatments (four and three replicates each at Fengqiu and Taoyuan, respectively), i.e. (i) organic fertilizer (OF), (ii) combined N, P and K mineral fertilizers with organic fertilizer (NPKOF), (iii) deficient in phosphorus only (NK) and (iv) an unamended control (Control). Fertilization rates and cropping systems are summarized in Table 1. The chemical N, P and K fertilizers used were urea, calcium superphosphate and potassium sulfate, respectively, for the Fluvisol. The OF used at Fengqiu was composed of wheat straw, soya bean cake and cotton seed cake in a ratio of 100:40:45. Additional mineral fertilizers were also added to ensure the total P and K in the OF treatment was the same as in the NPKOF treatment. The total P fertilizer in the OF treatment was 32.7 kg ha^{-1} for maize and 26.2 kg ha^{-1} for wheat growing season. At Taoyuan, the chemical N and K fertilizers were added as urea and potassium chloride, respectively. The OF was rice straw produced from the plot, and contained average content of 1.9 g kg^{-1} P in the rice straw. The size of each plot was 48 m^2 at Fengqiu and 33 m^2 at Taoyuan. All the plots were arranged in a randomized complete block design.

Five soil subsamples (0–20 cm depth) were collected from each plot and mixed to form one sample before the winter wheat growing season in August 2013 at Fengqiu and before the early rice growing season in March 2011 at Taoyuan. The samples were then kept on ice in coolers, immediately transported back to the laboratory, and stored at 4 °C before further analysis.

Table 1
Average annual nutrients (N, P and K) input from different fertilizer treatments in the Fluvisol and Anthrosol.

	Mineral fertilizer			Organic fertilizer (Mg ha^{-1})	Cropping system
	N (kg ha^{-1})	P (kg ha^{-1})	K (kg ha^{-1})		
Fluvisol					Winter wheat (*Triticum aestivum* L.)–summer maize (*Zea mays* L.)
OF[a]	NA	10.4/3.9[b]	70.7/70.7	2.758/2.758	
NPKOF	75/75	21.5/15	97.6/97.6	1.379/1.379	
NK	150/150	NA	124.5/124.5	NA	
Control	NA	NA	NA	NA	
Anthrosol					Early rice–late rice (*Oryza sativa* L)
OF	NA	NA	NA	8.5/8.5	
NPKOF	54/72	20/0	30/50	8.5/8.5	
NK	54/72	NA	30/50	NA	
Control	NA	NA	NA	NA	

NA, not available.
[a] OF, organic fertilizer; NPKOF, combined NPK fertilizer with organic fertilizer; NK, N and K mineral fertilizer; Control, without fertilizer.
[b] The first value is the fertilizer rate for maize at Fengqiu or early rice at Taoyuan, and the second value is the rate for wheat at Fengqiu or late rice at Taoyuan.