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Altered humin compositions under organic and inorganic fertilization on an intensively cultivated sandy loam soil

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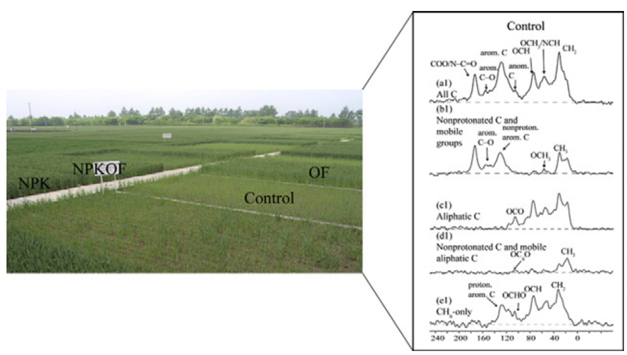
HIGHLIGHTS

- Organic fertilizer application decreased the alkyl/O-alkyl ratio of humin.
- Alkyl and aromatic C were major components of humin.
- A considerable proportion of aromatic C in humin was nonprotonated.
- Microbial biomass C significantly correlated with COO/N—C═O and OCH.

GRAPHICAL ABSTRACT



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ABSTRACT

Humin is the most recalcitrant fraction of soil organic matter (SOM). However, little is known about quantitative structural information on humin and the roles of soil mircoorganisms involved in the humin formation. We applied advanced solid-state ^{13}C nuclear magnetic resonance (NMR) spectroscopy to provide deep insights into humin structural changes in response to long-term balanced fertilization on a Calcaric Fluvisol in the North China plain. The relationships between humin structure and microbiological properties such as microbial biomass, microbial quotient (q_{mic}) and metabolic quotient (qCO$_2$) were also studied. The humins had a considerable (35–44%) proportion of aromatic C being nonprotonated and the vast majority of O-alkyl and anomeric C being protonated. Alkyl (24–27% of all C), aromatic C (17–28%) and O-alkyl (13–20%) predominated in humins. Long-term fertilization promoted the aliphatic nature of humins, causing increases in O-alkyl, anomeric and NCH functional groups and decreases in aromatic C and aromatic C—O groups. All these changes were more prominent for treatments of organic fertilizer (OF) and combined mineral NPK fertilizer with OF (NPKOF) relative to the Control and NPK treatments. Fertilization also decreased the alkyl/O-alkyl ratio, aromaticity and hydrophobic characteristics of humins, suggesting a more decomposed and humified state of humin in the Control soil. Moreover, the soil microbiological properties had strong correlations with functional groups of humins. Particularly, microbial biomass C was a relatively sensitive indicator, having positive correlations with oxygen-containing functional groups, i.e., COO/N—C═O and protonated O-alkyl C, and negative correlations with nonprotonated aromatic C. The q_{mic} and qCO$_2$ were also significantly positively correlated with NCH and aromatic C—O, respectively. Our results deepen our understanding of how long-term fertilization impacts the structure of humin, and highlight a linkage between microbiological properties and recalcitrant fraction of SOM besides labile fraction.
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1. Introduction

Soil organic matter (SOM) represents one of the largest carbon pools on the global scale (Zech et al., 1997). Humin, traditionally defined as the fraction insoluble in aqueous solvents at any pH, is the most recalcitrant and the largest fraction of SOM (Rice, 2001; Tadini et al., 2015). Humin plays an important role in the global carbon budget (Song et al., 2011). However, there have been relatively few studies on humin (Preston and Newman, 1995) compared with humic acid because of its inhomogeneity, structural complexity (Zhang et al., 2009), low solubility and difficulties in isolation and purification (Tan, 2014; Hayes et al., 2017).

Previous studies showed that the major components of humin are derived from plants and microorganisms and their residues (Preston and Newman, 1995; Song et al., 2011), such as cuticles (Olshansky et al., 2015) and microbial peptides (Mylotte et al., 2016). Although it is still unclear which sources contribute more to humin, the microbial biomass was presumed to provide important contributions by Mylotte et al. (2016). Recent studies showed that black carbon (BC) or char residues (hereinafter referred to as BC) also contributed to SOM (Mao et al., 2012a) including humin (Hayes et al., 2017; Schellekens et al., 2017). When the original organic materials are incorporated into humin through decomposition/humification, humin may present complex and distinct structural characteristics (Preston and Newman, 1995; Zhang et al., 2009). After the first study on the distribution of carbon functional groups in humin by ^{13}C solid-state nuclear magnetic resonance (NMR) (Hatcher et al., 1980), further studies also identified the prominent aliphatic nature of humin (Lichtfouse et al., 1998; Rice, 2001; Chang et al., 2014; Nakahara et al., 2016). This aliphatic nature was probably due to selective preservation of aliphatic components (Hatcher et al., 1980; Rice, 2001). Nebbioso et al. (2015) indicated that humin had similar molecular compositions to humic acid after chromatographic and chemical separation, and the two humic fractions mainly differed in tridimensional arrangement.

However, the detailed chemical compositions of humin and its functions are still not well understood. Questions still remain as to whether and how the humin compositions are influenced by management practices. In particular, few studies were conducted on the effect of long-term fertilization on the chemical compositions of humin (Zhang et al., 2009). Preston and Newman (1995) reported that long-term N fertilization slightly decreased the alkyl/O-alkyl ratio of humin in a forest soil. Ding et al. (2001) also found an increase in O-alkyl C and a decrease in the degree of decomposition of humin caused by fertilization on an agricultural soil. Unlike these studies, O-alkyl and aromatic C were depleted in the humin under the NP fertilizer treatment in a Typic Hapludoll of Northeast China (Zhang et al., 2009). However, there were no noticeable differences in the Fourier transform infrared spectra of humins from a field planted with rye grass under different N fertilization rates (Naidja et al., 2002).

Microorganisms play an important role in biogeochemical processes in soil (Veum et al., 2014). Microbial biomass can influence the composition of soil organic materials (Baldock et al., 1992) and formation of humic substances (Kögel-Knabner, 2002). As an eco-physiological indicator, the metabolic quotient (qCO_2), defined as the ratio of basal respiration to microbial biomass carbon (MBC), is sensitive to changes in microbial activities and community structure (Anderson and Domsch, 1990; Leita et al., 1999; Marinari et al., 2010). Thus, it has been widely used as an indicator of soil C utilization efficiency at ecosystem steady-state (Leita et al., 1999). Microbial quotient (q_{mic}), defined as the ratio of microbial biomass C to soil organic carbon, can also reflect the state of soil system equilibrium (Anderson and Domsch, 1989; Vittori Antisari et al., 2011). Marinari et al. (2010) found that microbial biomass decreased in the lower horizons of Alfisols compared to the upper horizons, and the humic acid became more aromatic with depth. The aromatic groups of organic matter in a Chromic Haploxerert in Italy showed significant positive correlations with qCO_2 and negative correlations with MBC and q_{mic} (Laudicina et al., 2015). However, little is known about the relationship between chemical characteristics of humin and microbiological properties, and their feedback mechanisms.

The aim of this study was to investigate the structural changes in humin after long-term balanced fertilization in a sandy loam soil on the North China plain, and to explore the potential relationships between structural characteristics of humin and microbiological properties i.e., MBC, qCO_2 and q_{mic}. Specially, the structural information on the humin was obtained by the combination of ^{13}C multiple cross-polarization/magic angle spinning (multiCP/MAS) NMR (Johnson and Schmidt-Rohr, 2014) and spectral-editing techniques (Mao et al., 2012b). We hypothesized that organic fertilizer application could alter humin structures such that the aliphatic nature should be more prominent. We also hypothesized that microbiological properties had significant correlations with humin chemical compositions.

2. Materials and methods

2.1. Description of the long-term field fertilization experiment

The long-term field fertilization experiment was conducted at the Fengqiu Agro-ecological Experimental Station (1989–present) in Henan Province of China (35°00′N, 114°24′E). The soil, with a sandy loam texture, is classified as a Calcaric Fluvisol (FAO) and was derived from alluvial sediments of the Yellow River. The crop rotation was winter wheat (*Triticum aestivum* L.) grown from October to May and summer maize (*Zea mays* L.) from June to September.

Four fertilizer treatments, i.e., organic fertilizer (OF), combined N, P, and K mineral fertilizers with organic fertilizer (NPKOF), balanced N, P, and K mineral fertilizers (NPK), and no fertilization (Control) were employed in this study. The treatments (four replicates each) were established in a randomized complete block design. Each replicate plot measured 48 m^2, and was separated from neighboring plots by cement banks. Detail on the fertilizer application rates is summarized in Table 1.

For the OF and NPKOF treatments, the organic fertilizer was a mixture of composted wheat straw, soybean cake and cotton seed cake in a ratio of 100:45:45. To achieve the same levels of total N, P, and K input as those of the NPK treatment, mineral fertilizers were added to supplement the organic fertilizer in the OF and NPKOF treatments.

2.2. Soil sampling

After 23 consecutive cropping cycles, each plot was sampled at five random locations to the depth of 0–20 cm to form a composite soil sample on August 31, 2013 before the 2013–2014 winter wheat growing season. The soil composites were immediately placed on ice in coolers, brought directly to the laboratory, and stored at 4 °C until further

Table 1
Annual application rates for the fertilizer treatments on the Fluvisol after 23 consecutive cropping cycles.

Treatment	Mineral fertilizer			Organic fertilizer (Mg ha^{-1})
	N (kg ha^{-1})	P (kg ha^{-1})	K (kg ha^{-1})	
OF	0/0[a]	10.4/3.9	70.7/70.7	2.758/2.758
NPKOF	75/75	21.5/15	97.6/97.6	1.379/1.379
NPK	150/150	32.7/26.2	124.5/124.5	0/0
Control	0/0	0/0	0/0	0/0

OF, organic fertilizer; NPKOF, combined NPK mineral fertilizer with organic fertilizer; NPK, balanced N, P and K mineral fertilizer; Control, without fertilization.
[a] The first value for each treatment is the fertilizer rate for maize, and the second value is the rate for wheat.

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