



Dominant effects of organic carbon chemistry on decomposition dynamics of crop residues in a Mollisol



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ABSTRACT

Understanding the change in chemical composition of crop residues during their decomposition is crucial to elucidate the mechanisms underlying the effects of residue retention on soil carbon (C) sequestration and nutrient cycling. Here a field experiment was carried out to investigate the decomposition process of maize, soybean, and wheat residues in a cultivated Mollisol in northeast China over a year. Using a litterbag method, we monitored the dynamics of residue mass loss, concentration of C and nitrogen (N), and C/N ratio, and evaluated the decomposition rates of residues and C functional groups. Chemical compositions of the crop residues were determined by solid-state ¹³C nuclear magnetic resonance spectroscopy, and the cellulose crystallinity, lignin concentration, and syringyl to guaiacyl (S/G) ratio of lignin were estimated. After one year of incubation in field conditions, mass loss was 57% for soybean residues, significantly greater than 52% for maize and 45% for wheat. The decomposition rate of residues significantly decreased from 0.223 to 0.379 month⁻¹ during the first month to 0.054–0.076 month⁻¹ over the whole period. The proportion of decomposed C ranged at 57–63% among different residues, and had a positive relationship with the mass loss of O-alkyl C, di-O-alkyl C, and carbonyl C. The decomposition rates of these three C functional groups were greater in soybean than those in maize and wheat residues, which was also the case for lignin S/G ratio, possibly accounting for the higher decomposition extent of soybean residues. As decomposition progressed, the C chemistry of maize, soybean, and wheat residues exhibited an increasing divergence, which was mainly related to relative decreases in O-alkyl C and di-O-alkyl C contents, and relative increases in phenolic C and aromatic C contents in the residues. Net N release was observed for all residues after one-year decomposition, and was significantly related to the mass loss of alkyl C, O-alkyl C, and aromatic C. Overall, our study provides insight into chemical changes of crop residues over the degradation processes in the field, and highlights the significant effects of organic C chemistry on residue decomposition.

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1. Introduction

The global soil organic carbon (SOC) storage is estimated at 1502 Pg in the upper meter of soil, more than 10% of which is stored

in croplands (Jobbágy and Jackson, 2000). Enhancing SOC sequestration in agricultural systems has been regarded as a cost-effective and environmentally friendly strategy for ensuring food security and offsetting anthropogenic carbon dioxide emission (Lal, 2004). Among the numerous recommended management practices for sequestering C in cropping systems, residue retention has attracted great attention (Freibauer et al., 2004). It is estimated that every year 3.8 billion tons of crop residues are produced globally (Thangarajan et al., 2013), and a total potential of 0.6–1.2 Pg C can be sequestered by returning crop residues to soils (Lal, 2009).

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Based on a meta-analysis of a global dataset from 176 studies, Liu et al. (2014) reported that crop residue incorporation significantly increased SOC concentration by 12.8% on average, in soils with initial SOC concentration of $12.5 \pm 9.8 \text{ g kg}^{-1}$ ($n = 343$). Likewise, Zhao et al. (2015) conducted a meta-analysis and found that SOC concentration could be increased by 0.81 g kg^{-1} at 0–30 cm depth with crop retention in China. However, as shown in the above two studies, there were large differences in the magnitude and even the direction of the responses of SOC contents to residue retention. For example, Poeplay et al. (2015) reported that the effects on improving SOC content were negligible with above-ground residue amendment of barley, wheat, and oat in six Swedish long-term experiments. Reicosky et al. (2002) also found no increase in SOC stocks after long-term returning of maize residues. Decreases in SOC content after residue application have also been observed in previous studies in China (e.g. Wang et al., 2011).

The responses of SOC dynamics to crop residue input can be regulated by many factors, such as moisture, temperature, and soil properties, of which the type of crop residues is an important determinant (Bradford et al., 2016). Many studies have proposed that different organic materials with various chemical compositions may show different behaviors during decomposition in the same soils (Jensen et al., 2005; Powers et al., 2009; Bonanomi et al., 2011). It is likely that crop residues with large amounts of easily degradable C can increase microbial activity, leading to enhanced SOC decomposition and thus counteracting the positive effects of crop residues on SOC content (Guenet et al., 2010). Therefore, it is critical to gain insight into the chemical compositions of different types of crop residues to clarify their distinct impacts on soil C cycling.

Cellulose, hemicellulose, and lignin are three major biopolymers in crop residues (Valášková et al., 2007). These chemical compositions are traditionally analyzed by extraction methods, which are useful but time-consuming (Kelleher et al., 2006). Over the past decades, non-destructive solid-state ^{13}C crosspolarization magic angle spinning (CPMAS) nuclear magnetic resonance (NMR) spectroscopy has been frequently used to characterize the molecular compositions of organic matter (Baumann et al., 2009; Bonanomi et al., 2013). O-alkyl C and di-O-alkyl C (60–110 ppm), assigned to the monomeric units of cellulose and hemicellulose (De Marco et al., 2012), are preferentially consumed by r-strategists as C and energy resources (Clemente et al., 2013). Moreover, the resonances at 84 and 89 ppm were indicated to relate with the C-4 in the amorphous and crystalline cellulose, respectively (Martinez et al., 1999; Wikberg and Maunu, 2004). Davis et al. (1994a, b) reported that white rot fungi showed preference for the breakdown of amorphous cellulose, attributing to the easier penetration into amorphous over crystalline structure. In the cell walls of higher plants, lignin is chemically linked to cellulose and hemicellulose, encrusting carbohydrates from microbial degradation and providing resistance to environmental stress (Thevenot et al., 2010). In this case, lignin removal or modification is a prerequisite for the decomposition of lignin-shielded polysaccharides (Klotzbücher et al., 2013). As a complex macromolecule, lignin consists of vanillyl, syringyl, and cinnamyl monomers, each showing different methoxylation of the aromatic ring and each having distinct availability to microbes (White et al., 2016). Hence, investigating C substrate interactions and controlling components should illuminate the decomposition process of different crop residues.

Apart from the benefits of enhancing soil C level, applied residues can also be an important source of nutrient supply to crop growth. Nitrogen (N) in crop residues was estimated at 46.3 Tg, equivalent to 56.3% of fertilizer N consumption across the world in 2001 (Lal, 2009). Thus, recycling N resources in crop residues to

agricultural soils could partially substitute for energy-intensive and resource-reliant inorganic fertilizers (Abera et al., 2012). Factors driving organic material decomposition are also suggested to have impacts on N release (Varela et al., 2014). The C/N ratio of residues is commonly acknowledged as a main factor affecting microbial mineralization of N in crop residues (Vigil and Kissel, 1991; Tian et al., 1992). Trinsoutrot et al. (2000a) indicated that net N mineralization could occur when the C/N ratio of the decomposing residues was less than 24. Nonetheless, Parton et al. (2007) observed net N release when litter mass loss arrived at 60% and the average C/N ratio was lower than 40 in a 10-year field decomposition experiment. These inconsistent findings about C/N threshold for net N mineralization could be attributed to the differences in experimental conditions and duration, and also to the residue C and N characteristics (Abiven et al., 2005; Jensen et al., 2005; Gillis and Price, 2016). Trinsoutrot et al. (2000b) reported that the quantity of N released from roots, stems, and pod walls of *Brassica napus* L. were closely related to the initial N content. However, other researchers suggested that N mineralization was primarily dependent on the quality of organic C compounds (Piñeiro et al., 2006; Corre et al., 2007). There were close interactions between C and N compounds, for example, recalcitrant lignin can shield N from mineralization due to chemical binding or physical isolation (Boerjan et al., 2003; Talbot et al., 2012), and polyphenol-bound protein thus may result in N immobilization (Gentile et al., 2008). Consistently, Eldridge et al. (2017) found that the mineralized N from organic wastes was negatively related to the content of aromatic and phenolic C. Therefore, C chemical compositions of the crop residues should be incorporated into N-management strategies on farmlands under residue retention.

The cultivated Mollisol in northeast China, with an area of 14.7 million hectare (Liu et al., 2012), is generally considered as inherently fertile, and plays a significant role in national grain production. However, an overall loss of 22.3% in SOC concentration has occurred in this region over the past three decades, mainly attributed to high erosion and low input of organic materials (Yan et al., 2011). In this case, returning crop residues to soil is recommended to mitigate SOC loss and recover soil fertility (Liu et al., 2014). In the study region, maize, soybean, and wheat are three staple crops (Qiao et al., 2014). Different types of residues may have different decomposition patterns and rates due to their various chemical compositions, which need to be understood to provide scientific supports for crop residue management in this region. In the present study, we evaluated the decomposition of these crop residues in a year-long litterbag experiment, and determined the chemical composition of organic C in the crop residues with the solid-state ^{13}C NMR technique. The main objectives of this study were to: (1) quantify the decay rate of maize, soybean, and wheat residues, (2) identify the critical C functional groups responsible for the decomposition differences both among residue types and at different decay stages, and (3) analyze N dynamics and its interactions with C decomposition during residue decay process.

2. Materials and methods

2.1. Study site

The study was carried out in a rainfed cropland in Hailun National Agro-ecological Experimental Station, Heilongjiang Province, China ($47^{\circ}26'\text{N}$, $126^{\circ}38'\text{E}$). The region has a temperate continental monsoon climate. The mean annual air temperature is 1.9°C and the mean annual precipitation is 560 mm from 1953 to 2013, based on the data of the National Meteorological Information Center (<http://cdc.nmic.cn/home.do>). Air and soil (10 cm depth) temperature and precipitation during the study period (from 21 May 2013

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