



Adsorptive fractionation of corn, wheat, and soybean crop residue derived water-extractable organic matter on iron (oxy)hydroxide

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ABSTRACT

Plant biomass is the primary source material for the formation of soil organic matter, which comprises the largest terrestrial pool of the global C cycle. Adsorption of water-extractable organic matter (WEOM) to soil mineral surfaces is a critical step in the process of organic matter accumulation. In this study, we examined the molecular fractionation of WEOM derived from field-grown corn, wheat, and soybean crop residues upon adsorption to iron (oxy)hydroxide (FeOOH) mineral using ultrahigh resolution mass spectrometry. The results show that aromatic, N-containing aliphatic as well as lignin-like molecules with higher O/C atomic ratios have preferential affinity for FeOOH surfaces. Lignin-like molecules with low and high numbers of O atoms were adsorbed, while those with intermediate O numbers were not adsorbed. This pattern is likely due to two different mechanisms of adsorption that is dependent on molecular size: smaller molecules with low O numbers bond through an inner-sphere ligand exchange mechanism, and the larger molecules with high O numbers bond through the formation of multiple H-bonds between the WEOM and FeOOH surface functional groups. Adsorption of WEOM to soil mineral surfaces has wide ecosystem implications, since adsorbed organic matter molecules are now believed to be more protected from microbial decomposition reactions. This study shows that WEOM chemical composition is an important factor controlling its adsorption to mineral surfaces. Understanding these soil and crop chemical interactions at the molecular level will be increasingly important for developing production systems that maintain high SOM levels and soil health in the decades ahead.

1. Introduction

Soil organic matter (SOM) constitutes the largest terrestrial pool of the global C cycle with its estimated 1461 Pg of C storage to a soil depth of 1 m and provides critical ecosystem services that include nutrient cycling, C stabilization, and erosion control (Scharlemann et al., 2014; Olson et al., 2016). The annual input of plant biomass is the principal source material for SOM formation (Kaiser and Guggenberger, 2000; Kögel-Knaber, 2002, 2017). In the U.S., corn and wheat production predominate on a combined 52.5 million ha of farmland, resulting in the annual production of 250 Tg of corn residue and 90 Tg of wheat residue (Karlen and Huggins, 2014). These estimates can be used to calculate an average corn and wheat residue production rate of 6500 kg ha⁻¹. Combining this average production rate with the mean water-soluble C content of 142 g kg⁻¹ residue and lignin content of 53 g kg⁻¹ residue (Redin et al., 2014) leads to the estimated potential annual input of water-soluble C of 920 kg ha⁻¹ and 344 kg ha⁻¹ for annual lignin input on these agricultural fields. It is likely that this level of water-soluble C inputs will influence the biogeochemical C cycle in

soils. Water-extractable organic matter (WEOM) is the water-soluble fraction of the soil C pool, which leads it to be the dominant fraction present in soil solution and most directly involved in adsorption to mineral surfaces and complexation with ions in soil solution (Zsolnay, 2003). WEOM from crop residues are subject to adsorption by mineral surfaces, which is a critical step in the soil C stabilization process (Kaiser and Guggenberger, 2000). Adsorption of WEOM onto mineral surfaces increases its resistance to microbial biodegradation (Saidy et al., 2015). The adsorptive stability may be a function of mineral surface availability, WEOM chemical composition, and inorganic ions in soil solution competing for surface adsorption sites (Schneider et al., 2010). Incubation studies have shown that the mineralization rates of adsorbed WEOM to CO₂ is significantly lower than that of WEOM in solution, indicating that adsorption is a major mechanism of WEOM stabilization (Mikutta et al., 2007; Schneider et al., 2010; Eusterhues et al., 2014).

Crop residues add large quantities of lignin annually to soils, and its fate in soils has been enigmatic. Classically, lignin has been viewed as a highly recalcitrant component of plant biomass due to its high

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aromaticity. It has been thought that lignins are involved in SOM formation through stepwise microbially-driven conversion to phenolic aldehydes and then to quinones, which undergo polymerization reactions and conversion to high molecular weight SOM molecules (Sparks, 2003). However, recent studies have shown that plant biomass lignin can undergo rapid decomposition in the presence of available C energy sources, suggesting that lignin does not have inherent chemical recalcitrance (Dignac et al., 2005; Heim and Schmidt, 2007; Klotzbücher et al., 2011). These findings, in part, have informed current thinking about SOM as a continuum of smaller biomolecules stabilized by its interaction with mineral surfaces (Schmidt et al., 2011; Lehmann and Kleber, 2015).

Recent studies have also shown that SOM, in general, can be formed from lignin subjected to oxidation by reactive oxygen species catalyzed by iron oxides (DiDonato et al., 2016). Waggoner et al. (2015) showed that this process can occur abiotically. Lignin biodegradation is believed to be a coordinated process where: (1) lignin is initially depolymerized releasing mainly aromatic water-soluble products; (2) followed by transformation of these aromatic water-soluble molecules through microbial processes, and (3) incorporation into biomass, release of further transformed compounds, or complete mineralization to CO₂ (Klotzbücher et al., 2016). Lignin-derived compounds that have been partially oxidized leading to increased carboxyl group content have been shown to have greater sorption to soil minerals, as well as becoming more stabilized by protection from microbial attack (Grünwald et al., 2006). Enzymatic depolymerization of a wheat straw lignin material was shown to produce mainly low molecular weight aromatic monomers and oligomers (Gasser et al., 2017). Aromatic molecules have been shown to be preferentially adsorbed to soil minerals, suggesting that the chemical composition of WEOM is likely to control its interaction with minerals (Kramer et al., 2012; Chassé et al., 2015).

Ultrahigh resolution Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS) has emerged as a powerful state-of-the-art method for the molecular characterization of natural organic matter (Sleighter and Hatcher, 2007). Studies utilizing FT-ICR-MS have supported the idea that SOM is comprised of non-covalently bonded, supramolecular colloidal aggregates of heterogeneous molecules (Sutton and Sposito, 2005; Kleber and Johnson, 2010; Lehmann and Kleber, 2015). The van Krevelen diagram, which can ascribe biochemical classes to each assigned elemental formula based on their H/C and O/C ratios, is a common approach to comparing FT-ICR-MS data (Hockaday et al., 2009; Sleighter et al., 2015). Studies using FT-ICR-MS have generally shown that aromatic and aliphatic molecules with high O/C ratios have the highest adsorption affinities for Al₂O₃ and FeOOH minerals (Galindo and Del Nero, 2014, 2015; Lv et al., 2016; Fleury et al., 2017). A study using WEOM from a composted biosolid indicated preferential sorption of the lignin-like, carbohydrate-like, and polyphenol type molecules to a low total C soil dominated by montmorillonite (Avneri-Katz et al., 2017).

A study using atomic force microscopy (AFM) and FT-ICR-MS reported that higher molecular mass carboxyl-rich aromatic and N-containing aliphatic WEOM molecules were correlated with high binding force between WEOM and FeOOH functionalized AFM tips (Chassé et al., 2015). Another AFM study showed a strong correlation between aromatic molecules > 600 Da and the reduced binding force of orthophosphate to FeOOH, suggesting that higher molecular mass aromatic WEOM components compete with orthophosphate for adsorption to FeOOH (Chassé and Ohno, 2016). Our first objective is to determine the chemical fractionation of WEOM extracted from field-grown corn, wheat, and soybean crop residues that occurs when adsorbed onto FeOOH. This study aims to directly provide supporting data demonstrating the adsorptive preference for aromatic and high molecular mass molecules that has been predicted by statistical analysis of an adsorption study using AFM and FT-ICR-MS techniques (Chassé et al., 2015; Chassé and Ohno, 2016). Our second objective is to evaluate

whether the adsorptive fraction observed using humic substances is also evident for WEOM. This is important, because humic substances have been extensively used to study adsorptive fractionation (Hur and Schlautman, 2003; Galindo and Del Nero, 2014, 2015; Lv et al., 2016), however recent developments have questioned the existence of humic substances outside of the laboratory extractions used to isolate these substances (Kleber and Johnson, 2010; Lehmann and Kleber, 2015). Molecular-level information of the sorption of WEOM on FeOOH may contribute to increase our mechanistic understanding of how WEOM interacts with mineral surfaces, which provides critical ecosystem functions and services.

2. Materials and methods

2.1. WEOM extraction and sorption to FeOOH

Crop residues were obtained after harvest from field-grown corn (*Zea mays* L.), wheat (*Triticum aestivum* L.), and soybean (*Glycine max* L. Merr.). The WEOM was obtained in duplicate by extracting 2.0 g of crop residue with 80 mL of deionized-distilled water (DI-H₂O) and shaking for 24 h at 4 °C. The extractions were centrifuged (900 × g) for 20 min prior to vacuum filtering through 0.4 μm polycarbonate filters. The dissolved organic carbon (DOC) concentration was measured using a Shimadzu 5000 TOC analyzer. Catalysis-grade FeOOH was purchased from Sigma-Aldrich (#371254) and used after repeated rinsing with DI-H₂O. An adsorption isotherm for each WEOM was determined in duplicate in the range between ~20 and ~600 mg DOC L⁻¹. A suspension of 1.00 g FeOOH in 30 mL of DI-H₂O was set-up 24 h prior to the WEOM sorption study in glass Erlenmeyer flasks to pre-hydrate the FeOOH mineral. WEOM adsorption was then determined by replacing the DI-H₂O with 30 mL of WEOM solution, adjusting the pH to 6.0, and shaking the flasks for 48 h at 4 °C. Controls were established with DI-H₂O. The solutions were then filtered and analyzed for their DOC concentrations as described above. The quantity adsorbed was calculated by difference from the initial DOC solution concentration. The initial mass isotherm method was used to describe the sorption of WEOM to FeOOH by a linear regression of the quantity of DOC adsorbed as a function of DOC added (Nodvin et al., 1986). The slope term of the linear regression is a measure of the affinity of the WEOM sorbate to the FeOOH sorbent.

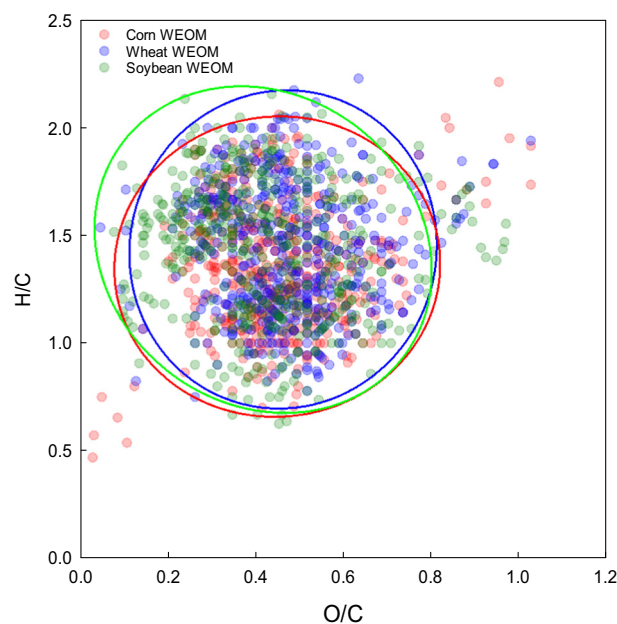


Fig. 1. van Krevelen diagram from the molecular formula assignments to the corn, wheat, and soybean water-extractable organic matter (WEOM). The ellipses represent the 95% confidence region of the respective WEOM.

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