Compositional tracking of dissolved organic matter in semiarid wheat-based cropping systems using fluorescence EEMs-PARAFAC and absorbance spectroscopy

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Compositional tracking of dissolved organic matter in semiarid wheat-based cropping systems using fluorescence EEMs-PARAFAC and absorbance spectroscopy

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Highlights

- Annual cropping sequestered more SOC than fallow-based systems over a 10 year period.
- The accretion of SOC within annual cropping occurred at a rate of 0.61 Mg ha^{-1} yr^{-1}.
- Soil DOM bulk optical properties did not respond to changes in decadal SOC stocks.
- PARAFAC analysis identified four different fluorescent components of the EEMs.
- Sub-soil DOM was comprised by low molecular size constituents.

Abstract

We conducted this study to quantify long-term cropping related changes in soil organic carbon (SOC) stocks and characterize the optical properties of dissolved organic matter (DOM) after a decadal on-farm experiment in Montana, USA. Soil samples (0-50 cm) were collected from minimum till (MT) and no-till (NT) fields under fallow-winter wheat (Triticum aestivum L.; FW) and pea-winter wheat (Pisum sativum L.; P-W) rotations. Stocks of $SOC_{(0\text{-}50\ cm)}$ averaged 65.6 Mg C ha^{-1} and 60.6 Mg C ha^{-1} for P-W and F-W, respectively. The net SOC accretion rate for P-W equate to 0.61 Mg ha^{-1} yr^{-1} relative to F-W. We used absorbance spectroscopy and excitation-emission matrices to characterize DOM composition of samples collected from MT F-W and NT P-W. The two cropping systems exhibited similar estimates of aromaticity (absorbance at 254 nm; 0.33-0.39 a.u.) and humification index (1.83-1.86). Parallel factor (PARAFAC) analysis revealed humic-like (C1, C2), monolignol/amino acid-like (C3), and amino acid-/tannin-like (C4) components with equivalent fluorescent intensities among MT F-W and NT P-W. Fluorescence efficiencies increased with depth, suggesting a shift from larger, plant-like material to smaller, microbial-derived precursors. Overall, we found DOM composition to be minimally affected by cropping system in this semiarid climate of the northern Great Plains.

Key words: northern Great Plains; soil C sequestration; excitation emission matrices; humification.

1. Introduction

Organic matter (OM) is a key parameter for agronomic productivity and ecosystem functioning. Total OM includes a mixture of plant and animal matter in a decomposition continuum (Ohno et al., 2009; Masoom et al., 2016). The majority of OM (40-60%) is comprised of humic substances, recalcitrant compounds with decadal and centennial turnover times (Guimarães et al., 2013; Vázquez et al., 2013, 2016). The complex structure and spatial variability of humic substances limit our ability to identify OM recovery trends over short-time periods (Plaza-Bonilla et al., 2014; Necpálová et al., 2014). In contrast, dissolved OM (DOM), or the water-extractable portion of OM, may respond more rapidly to changes in OM supply because it provides a C source for soil microbes (Haynes, 2005; Armas-Herrera et al., 2013; Abril et al., 2013a). Previous studies have reported that DOM is sensitive to land use and agricultural management (Kalbitz et al., 2000; Chantigny, 2003). For example, the return of organic residues to soils under annual cropping is known to increase the size of DOM over fallow-based systems in semiarid climates (Campbell et al., 1999). Therefore, the DOM fraction is sometimes considered a standardized metric of soil quality (Wander, 2004; Haynes, 2005).

The northern Great Plains (NGP) of North America is a semiarid steppe landscape with a significant role in preserving OM and reducing environmental pollution through land use and land cover change (DeLuca and Zabinski, 2011; Watts et al., 2011; Munson et al., 2012). A century of cultivation and the presence of till fallow-wheat (F-W) rotations decreased surface OM and labile-C fractions by ~50-60% (Norton et al., 2012; Hurisso et al., 2013). More intensive cropping frequency and no-till have prompted OM recovery through increased biomass-C inputs and minimal disturbance of soils (Collins et al., 2012; Engel et al., 2017). The expected range in OM or soil organic C (SOC) gains with crop intensification, and tillage reduction varies within semiarid NGP sub-regions. In North Dakota, annual cropping resulted in soil C sequestration rates of 0.23 Mg C ha^{-1} yr^{-1} under no-till compared with 0.025 Mg C ha^{-1} under minimum-tillage (0-30 cm) (Halvorson et al., 2002). In eastern Montana, annual spring wheat under no-till resulted in 8.4 Mg C ha^{-1} greater SOC (0-20 cm) than tilled F-W after 21 years (Sainju et al., 2007, 2009). In a region of Montana proximal to the Rocky Mountains, annual wheat under no-till resulted in 4.2 Mg C ha^{-1} greater SOC (0-30 cm) than tilled F-W after 10 years (Engel et al., 2017).

Sub-soil OM contains a large reservoir of recalcitrant-C and has a critical role within the global C cycle (Jobbagy and Jackson, 2000; Rumpel and Kogel-Knabner, 2011). The stability of sub-soil OM is largely determined by the physical protection of C within soil aggregates, and also by the spatial separation of OM, microorganisms, and extracellular enzymes occurring in deeper soil layers (Rumpel and Kogel-Knabner, 2011). Several reports have shown that the pool size of DOM decreases significantly with soil depth (Kalbitz et al., 2000). The OM is sorbed to the soil matrix via cation bridging and ligand-exchange reactions, resulting in a chromatographic fractionation of DOM along the soil column (Hassouna et al., 2010; Sanderman et al., 2008). Recent studies have concluded that sub-soil DOM is enriched by simple, microbial-like precursors and deprived of energy-rich, plant-derived materials compared to surface soil DOM (Hassouna et al., 2010; Sanderman et al., 2008; Romero et al., 2017, 2018).

Ultraviolet-Visible (UV/Vis) absorbance spectroscopy is used to probe DOM physicochemical features (Weishaar et al., 2003). Previous reports have shown that UV/Vis absorbance at 254 nm (Abs_{254}) and the specific UV absorbance ($SUVA_{254}$; C normalized Abs_{254}) are proxies of average DOM aromaticity, with >2.0 L mg C^{-1} m^{-1} values indicating a higher polycondensation degree of DOM (Zhang and He, 2015). Three-dimensional excitation-emission matrix fluorescence spectroscopy (EEMs) is a fast, non-destructive analytical approach that provides relevant information regarding the source and nature of aquatic (Coble, 1996; Cao et al., 2016) and terrestrial (Zhang and He, 2015) DOM. Combined with multivariate parallel factor (PARAFAC) analysis, EEMs-PARAFAC are now routinely employed to determine and model meaningful fluorescent components in the environment (Coble et al., 2014).

The chemical profile of DOM across soil depths may be altered by long-term cultivation, as biomass-C inputs and microbial activity are typically greater under annual cropping than within conventional fallow systems (Sainju et al., 2007; Collins et al., 2012). Yet, compositional changes of DOM in sub-surface soil layers of wheat-based cropping systems are not well elucidated and are, in consequence, poorly understood. Thus, a comprehensive characterization of DOM depth-related changes induced by different cropping systems is required, having the potential to yield new insights on the cycling and turnover of soil OM in semiarid environments.

The objective of this on-farm study was to identify quantitative and qualitative changes of soil OM after 10 years for a F-W and annual cropping system in a semiarid climate of the NGP. Specifically, we aimed to (i) quantify decadal cumulative SOC stocks accrual rates (i.e. its quantity) as a function of tillage type and cropping intensity; and (ii) characterize bulk optical properties of DOM (i.e. its quality) on selected treatments as a function of tillage type and cropping intensity combination (i.e. cropping system) within a 0-50 cm soil depth profile. We hypothesized that annual cropping would increase SOC stocks relative to F-W, and lead to a greater composition of labile and recalcitrant-C compounds in DOM (Engel et al., 2017; Romero et al., 2017).

2. Materials and Methods

2.1 Study site and experimental design

Soil for this study was collected from a long-term cropping system experiment established in north-central Montana (47° 29' N, 111° 00' W). Mean annual precipitation and ETo was 411 mm and 278 mm, respectively. The field site was on a private farm under no-till (NT) since the mid-1990's and under a F-W management system before the initiation of this study in 2002. Selected soil properties (0-10 cm layer) were: pH (H_2O, 1:1): 6.9, EC 1:5 (dS m^1): 0.15, CEC 1:2 ($cmol_c$ kg^{-1}): 19.0, total N (TN): 1.9 g kg^{-1}, organic C: 17.7 g kg^{-1}, inorganic C (IC): 0.5 g kg^{-1}, and sand, silt and clay content: 200 g kg^{-1}, 240 g kg^{-1} and 560 g kg^{-1}. The soil series, Lawther silty clay, was classified as a Typic Haplustert (Vertisol-type); soils are very deep and slowly-permeable, formed in calcareous clay lake sediments (Soil Survey Staff, 2013). The study consisted of two tillage systems, NT and minimum till (MT), factored with two cropping systems, F-W and annual cropping. Tillage under the MT system consisted of one or two shallow (0-10 cm) chisel plow events per rotation cycle. The annual cropping consisted of a two-year system with pea (Pisum sativum L.) grown in rotation with winter or spring wheat (PW). Nitrogen fertilization was applied during the wheat phases at 90 to 110 kg N ha^{-1}. Approximately, 10 kg N ha^{-1} was applied with the seed in a starter mix of N and P, and the remainder as a top-dressed urea application during the spring. A nominal amount of N (10-15 kg N ha^{-1}) was applied to peas as part of a seed-placed starter mix. The four cropping systems (NT F-W, MT F-W, NT P-W, and MT P-W) were compared in field-scale strips (8 ha each) positioned adjacent to each other but without fixed replications. Within each strip or treatment, four geo-referenced locations for soil and biomass sampling were identified with a hand-held GPS and permanently buried metal rods. The sampling locations were considered as replications or pseudo-replications because the four strips were under similar edaphic conditions. Use of pseudo-replication was considered a viable approach for our on-farm study (Hurlbert, 1984).

2.2 Soil sampling and SOC analysis, Net Primary Productivity

Soil sampling (n=48) occurred in September 2002 and 2012 using a truck-mounted hydraulic probe. Five soil cores (5 cm dia.) were collected to a depth of 50 cm in a star pattern centered around four geo-referenced locations in each treatment. The distance between the sampling point and center of the star was approximately 5 m. The soil cores around each georeferenced location were composited after separating into three depth increments (0–10, 10–20, and 20–50 cm). The composite samples were placed in plastic-lined bags, dried (50 °C), and then manually crushed to pass through a 2-mm sieve. Samples were ground and analyzed for total C (TC) and TN concentrations by dry combustion using a CN analyzer (TruSpec CN, LECO, Saint Joseph, MI); inorganic C concentration was determined by the modified pressure-calcimeter sensu Sherrod et al. (2002). The total SOC fraction was calculated by subtracting IC from TC concentrations. The SOC content for each depth layer was converted to a mass per unit area basis multiplying the concentration, bulk density, and the sampling depth increment. Bulk density was determined by a gravimetric approach, or by measuring the dry mass (corrected to 105° C) of each composite core segment of known volume. The principle of equivalent soil mass (Ellert and Bettany, 1995) was applied to the final comparisons of SOC among the four cropping systems. With this protocol, the equivalent soil mass was set to that of the cropping system with the least mass or NT F-W. Thus, the effective depth for calculating SOC mass was less for the MT F-W, NT P-W, and MT P-W cropping systems than the stated depth so that an identical mass was applied to all treatment comparisons.

Crop biomass for each treatment was estimated by hand-harvesting three areas totaling 2 m^2 around the center of each georeferenced sampling location. Samples were composited, and oven dried at 50°C for four days to estimate biomass production. Cumulative biomass or net primary productivity (NPP) was estimated by summing the biomass over the 10 year life-cycle of this study.

2.3 Dissolved organic matter analysis

The DOM from 2012 was obtained from soil samples (MT F-W and NT P-W) by adding 100 mL of ultrapure MilliQ® water to a 250-mL Erlenmeyer flask containing 50 g of soil. The flasks were shaken (15 min, 100 rpm) and then allowed to settle for 15 min at room temperature. The supernatant was subsequently passed through a pre-combusted Fisherbrand Glass Fiber Circle (1.6 µm) and then vacuum filtered through a 0.7 µm Millipore glass fiber filter. Waterextractable DOM concentrations, expressed as dissolved organic carbon ([DOC]; mg C L^{-1}) were quantified using a total C Shimadzu combustion analyzer (TOC-VCSH, Shimadzu Corp., Kyoto, Japan). Aqueous extracts (n=24) were characterized for optical properties of Abs_{254},

$SUVA_{254}$ (Weishaar et al., 2003), and fluorescence spectroscopy by EEMs, humification index (HIX) (Zsolnay et al. 1999), and fluorescence index (FI) (Cory and McKnight, 2005), following the protocol and fluorescent instrument settings outlined in Romero et al. (2017).

2.4 EEMs-PARAFAC modelling

Parallel factor (PARAFAC) analysis was applied to the EEMs data using drEEM (Decomposition Routines for Excitation Emission Matrices; v. 0.1.0) and the N-way toolbox in MATLAB R2016b (The MathWorks, Inc., Natick, MA) (Murphy et al., 2013; Stedmon and Bro, 2008). A non-negativity constraint was applied to both excitation and emission loadings, considering that negative fluorescent intensities and concentrations are chemically impossible (Ohno and Bro, 2006). The PARAFAC model was validated by split-half analysis with all the components of the split model test finding a match with a Tucker correlation coefficient > 0.95

(Murphy et al., 2013). The fluorescence efficiency (FE, R.U. cm^{-1}), or quantum yield, was calculated by dividing the PARAFAC component fluorescence maxima by the Abs_{254} per sample with higher FE indicating lower DOM size and molecular weight (Wu et al., 2003).

2.5 Statistical analysis

Soil organic C stocks were analyzed using the MIXED procedure of SAS 9.4 (SAS Institute, Cary, NC) with the Kenward–Roger degree of freedom option. This option uses an adjusted estimator of the covariance matrix to reduce small sample bias (Kenward and Roger, 1997). The model considered cropping intensity, tillage type, and cropping intensity x tillage type as fixed effects. Replication (or pseudo-replication) and rep x tillage type were treated as random effects.

The effects of tillage type and cropping intensity combination (i.e. cropping system) and soil depth on DOM size and spectroscopic features were analyzed with a two-way ANOVA on selected soil treatments (i.e. MT F-W, NT P-W) using the GLM procedure of SAS 9.4 (SAS Institute, Cary, NC). When significant effects were observed, treatment means were compared using Fisher's least significant difference (LSD) procedure at $\alpha=0.05$. Pearson correlation coefficients (r-value) were used to examine relationships between DOM properties.

3. Results and discussion

3.1 Cumulative NPP among cropping systems

Cropping system intensity significantly affected ($P<0.05$) cumulative biomass over ten years (2002-2012) with the annual cropping system (P-W) producing more biomass than the FW system. Specifically, NPP averaged 61.6 and 65.8 Mg ha^{-1}, for the two F-W and P-W systems, respectively (data not shown).

3.2 SOC stocks decadal change

Soil organic C stocks, or equivalent mass (SOC_{em}, 0-50 cm), in 2012 were significantly affected ($P < 0.05$) by cropping intensity, averaging about 65.6 Mg C ha^{-1} for the P-W systems, and 60.6 Mg C ha^{-1} for the two F-W systems (Fig. 1). The SOC_{em}(0-50 cm) in 2002 averaged 59.4 Mg C ha^{-1} (± 2.0 Mg ha^{-1}) for the four treatments. Therefore, SOC accretion with annual cropping occurred at rate of 0.61 Mg ha^{-1} yr^{-1} (or 6.1 Mg C ha^{-1} cumulative) over the 10 year lifecycle of this study. Our results are generally consistent with a review of cropland and C dynamics in the semiarid U.S. (Collins et al., 2012) that identify fallow as negatively affecting the reservoir of OM because of lower annual biomass-C inputs (Engel et al., 2017) and increased microbial activity and surface soil temperature (Collins et al., 2012). The SOC_{em} accretion rate from annual cropping, relative to F-W (i.e., 0.61 Mg C ha^{-1} yr^{-1}), was considerably higher than other estimates from this region (Engel et al., 2017; Sainju et al., 2009). The very high clay content of the soil (56-63%) likely contributed to this response. Soils with high clay content will typically provide higher SOC sequestration rates in the longer term because of the ability of clay minerals to form stable organo-mineral complexes, and because clay soils are often more oxygen deprived (Sparks, 2003; Galantini et al., 2004). Most regional soil C models (e.g., Century) show greater SOC gains in the presence of high clay (Parton et al., 1987).

Our study did not find a beneficial effect on SOC stocks from NT relative to MT. This response was expected as tillage intensity under MT was nominal, being performed only one to two times per rotation cycle, during this study. Also, tillage intensity has been found to be less important to SOC sequestration than cropping intensity in semiarid climates (Halvorson et al., 2002; Janzen et al., 1998; Lin and Chen, 2014; Galantini et al., 2014).

3.3 Dissolved organic carbon concentration

Dissolved organic C concentrations decreased with soil depth ($P<0.0001$; Table 1). The 0-10 cm layer contained more DOC than the 10-20 and 20-50 cm layers, averaging 31.87, 15.24, and 10.53 mg C L^{-1}, respectively. However, no significant differences were noted in DOC concentration among cropping systems ($P=0.0862$; Table 1). Furthermore, DOC concentration was strongly correlated to SOC ($r=0.79$, $P<0.0001$) and TN levels ($r=0.74$, $P<0.0001$). We anticipated this response given previous reports for cultivated soils (Jinbo et al., 2006; Romero et al., 2017) and that DOM is a proxy of SOC (Bolan et al., 2011).

3.4 Bulk optical characterization of DOM

Estimates of DOM Abs_{254} decreased significantly with soil depth from 0.67 to 0.19 ($P<0.0001$; Table 1) and consistent with Hassouna et al. (2012) and Toosi et al. (2012). We attribute this response to adsorptive interaction of aromatic DOM with reactive mineral surfaces, e.g., Ca^{2+}-bridging in neutral/alkaline soils (Oades, 1988). Cropping system did not affect DOM Abs_{254} properties. The distribution of $SUVA_{254}$ was not affected by cropping system or soil depth (Table 1). Similarly, fluorescence indexes HIX and FI were not influenced by cropping system ($P>0.05$; Table 1). The FI increased with soil depth from 1.35 to 1.40 ($P=0.0093$; Table 1); whereas HIX estimates peaked within the 10-20 cm layer (2.12) ($P=0.0023$; Table 1). Our results did not support our second hypothesis that cropping system would affect DOM composition. Apparently, higher biomass-C inputs with NT P-W did not induce the accumulation of ligninlike materials in solution. These results contrast with a previous report from southwestern Montana (Romero et al., 2017), where DOM optical features were found to be affected by biomass-C deposition. For example, annual cropping with no-till increased DOM aromaticity, while diminishing DOM humification or maturity degree, relative to conventional F-W systems (Romero et al., 2017). Soil OM dynamics are known to differ among soil orders and textural classes (Galantini et al., 2004) with Mollisols being more sensitive than Vertisols to changes in cropping intensity (Novelli et al., 2011). An increased aggregate stability within Vertisols, mostly due to a high clay content (i.e. smectite), may mask management induced effects on DOM throughout physical protection. In this regard, Akagi and Zsolnay (2008) concluded that there is a strong buffering of freshly introduced OM within fine-textured soils; most vegetal inputs must be initially sequestered into the soil matrix from which it is then subsequently released. Likewise, the very high swelling and shrinking capacity of Vertisols is thought to favor soil OM homogenization throughout the profile (Stephan et al., 1983). This implies our DOM was rapidly sorbed in the soil matrix, undergoing no major alteration over the 10 year life-cycle of this study.

3.5. Fluorescent DOM chemical characterization by EEMs-PARAFAC analysis

Average EEMs, representative of cropping system by soil depth fluorescent profiles, are shown in Fig. S1. All samples contained DOM species fluorescing at low (< 240–280/300–330 nm) and high (< 240–275/390–540 nm) excitation/emission (Ex/Em) wavelengths, including overlapping regions commonly associated with fluorophore peaks B (tyrosine-like), T (tryptophan- like), A (humic-like), and C (humic-like) (Coble, 1996; Coble et al., 1998). Fluorescence intensities decreased upon increasing soil depth, but were similar among MT F-W and NT P-W cropping systems. Since DOM is a complex mixture of biomolecules that can fluoresce in overlapping Ex/Em wavelength regions, the application of PARAFAC analysis was used to discriminate the overlapping fluorescence in the EEMs into individual DOM fluorescing components characterized by their Ex/Em maxima (Ohno and Bro, 2006). PARAFAC analysis of the EEMs data determined four components (Table 2). The four components (C1, C2, C3, and C4) explained 99.8% of the fluorescent variability. PARAFAC C1 contained one Ex region maximum at <240-250 nn and one Em region maximum at 390-440 nm, describing mid-size terrestrial humic-like material characteristic of soil, sediment, and freshwater environments (Ishii and Boyer, 2012; Zhao et al., 2012). Fluorescent C2 was characterized by one Ex region maximum at <240-275 nn and one Em region maximum at 450-540 nm, describing large-size humic-like material from cultivated soils (Zhao et al., 2012; Sharma et al., 2017). PARAFAC C3 contained an Ex peak at <240 nm and an Em peak at 300-330 nm, characteristic of overlapping low Ex/Em amino acid-like and monolignol-like fluorescent chemical species (Sierra et al., 2005; Coble et al., 2014; Mielnik and Kowalczuk, 2018). PARAFAC C3 also contained fluorescence indicative of more complex lignin-like precursors, e.g., Ex: 240 nm spanning Em: 308–556 nm, similar to the results previously found in cultivated soils from southwestern Montana (Romero et al., 2017). PARAFAC C4 had one Ex maxima at 280 nm and one Em maxima at 300-330 nm. This component overlaps amino acid- and tannin-like DOM fluorescent markers (Murphy et al., 2008; Pan et al., 2017; Gao et al., 2018), or microbially produced substances thought to be indicators of less degraded soil peptide materials (Zhang et al., 2017).

3.6. Variations of PARAFAC component fluorescence

The distribution of PARAFAC component fluorescent maxima (Fmax; R.U.) among soil depths and cropping systems are presented in Fig. 2 a, b, c, and d. The Fmax average values of the PARAFAC components followed an order of C3 (0.65 ± 0.05) > C1 (0.37 ± 0.03) > C2 (0.23 ± 0.01) > C4 (0.19 ± 0.02). The Fmax values exhibited a decrease with depth layer from 0-10 cm to 10-20 cm for all PARAFAC components. This pattern was more evident for C1 and C3 (~0.3 R.U.) than for C2 and C4 (~0.1 R.U.). Beyond 20 cm, Fmax remained relatively constant for C1, C2, and C4 with MT F-W and NT P-W exhibiting a similar behavior. In contrast, Fmax was considerably augmented for C3 at 50 cm, having the largest Fmax value overall; particularly under MT F-W (~0.4 R.U.) relative to NT P-W (~0.1 R.U.) soil (Fig. 2). Across all depths, mean Fmax of C1 to C4 were similar among MT F-W and NT P-W (Table 3). The similarity in the relative Fmax of each component suggested that soils have similar amounts of individual fluorescent DOM constituents, irrespective of the type of cropping system (Grebliunas et al., 2016). It was initially predicted that soils under NT P-W would have a higher proportion of fluorescent DOM constituents, due to the increased biomass-C input relative to MT F-W (Romero et al., 2017). Minimal differences in fluorescence spectra between cropping systems may arise from the fact that P-W did not contribute significantly to the aromatic pool of DOM, due to the high quality (low C:N ratio) of pea residues (Raiesi, 2006). On the other hand, NT annual cropping with winter-wheat (W-W) may have provided a stronger effect than P-W due to the low quality (high C:N ratio) and higher recalcitrance of wheat residues (Abril et al., 2013b; Duval et al., 2016). It has also been noted that the effects of cover crops on the occurrence of PARAFAC components within DOM mixtures may be ephemeral and only evident after harvest or crop termination (Grebliunas et al., 2016). The FE sharply increased with soil depth regardless of its intrinsic chemical character (Table 4). Specifically, FE (0-50 cm) increased by a factor of 1.8, 2.5, 4.0, and 2.1 for C1, C2, C3, and C4, respectively. Across all depths, mean FE of C1 to C4 were similar among MT F-W and NT P-W. Correlations among different fluorescent variables, DOC concentration, and absorbance properties were unique to C quality or type. Strong positive correlations were found between C1, C2, C4, Abs_{254}, and DOC concentration (Table 5). Both humic-like and amino acid/tannin-like material contributed to the bulk pool of fluorescent DOM capable of absorbing light at 254 nm (Sharma et al., 2017). Furthermore, associations between DOM concentration and PARAFAC components may steam from: i) similar patterns of changes of DOM variables within soil extracts, ii) their pooled presence within OM mixtures, and iii) a resemblance in their water extractability (Borisover et al., 2012). PARAFAC C3 was negatively related with HIX (r=-0.74; P<0.0001). This implied PARAFAC C3 was more indicative of complex lignin precursors than tyrosine-like constituents.

Humic-like fluorescence intensities (C1 and C2 Fmax) declined with depth from 0-10 to 10-20 cm, which may have been a result of organo-mineral interactions (i.e. ligang exchange, cation bridging) preferentially sorbing aromatic DOM, as previously described. Alternatively, microbial degradation of labile-C, occurring in surface soil, can also limit the downward movement of humic-like DOM (Marinari et al., 2010). The distribution of PARAFAC C3 Fmax initially followed the same pattern, but beyond 20 cm, increased with the soil sampling depth, suggesting more mobilization of lower molecular weight chemical species, such as amino acid- or monolignol-like DOM. Zhang et al. (2011) indicated less condensed ring-structured N containing compounds are more mobile than humic-like DOM components. Moreover, the Fmax variability for C3 was the largest, which may indicate fluctuating qualitative changes from more complex to more simple materials at depth. The FE sharply increased with soil depth regardless of its intrinsic chemical character, indicating DOM molecular weights decreased with increasing soil depth (Corvasce et al., 2006). The molecular weight depth pattern detected in this study is consistent with our previous findings that subsoil DOM is comprised by low-molecular weight compounds (Romero et al., 2017, 2018). This implied a shift from fresh plant-derived to highly decomposed OM (Sanderman et al., 2008; Hassouna et al., 2010) of potentially higher biodegradability (Fellman et al., 2008). In sub-soil layers, DOM is comprised by constituents either transferred by seepage and diffusion from surface soil or locally produced during microbial processing of the native OM pool (Hassouna et al., 2010). The latter was substantiated by the modest but significant increase of FI (from 1.35 to 1.40) with soil depth. We acknowledge, however, that our FI values were lower than the estimated average for arable soils (i.e. 1.50-1.90) (Hassouna et al., 2012; Sun et al., 2017). In terrestrial ecosystems, DOM exists as a polydispersed mixture of organic fragments at various stages of oxidation and decay (Masoom et al., 2016). In this regard, PARAFAC analysis identified chemical compositions that we attribute to different stages of DOM decomposition. Average FE (n=24) was higher for C3 (2.54 ± 0.33) followed by C1 (1.28 ± 0.12), C2 (0.88 ± 0.10), and C4 (0.63 ± 0.06); indicating molecular weights decreased in the order C4>C2>C1>C3.

4. Conclusions

Our study supported the first portion of our hypothesis that SOC stocks for annual cropping would be greater than for F-W systems. Over ten years, SOC_{em}(0-50 cm) with annual cropping accreted at a 0.61 Mg C ha^{-1} yr^{-1} rate relative to F-W. However, annual cropping did not alter DOM chemical composition; in rejection of our second hypothesis that P-W would result in greater accumulation of DOM labile- and recalcitrant-C constituents relative to F-W. We found through UV/Vis and fluorescence spectroscopy similar estimates of aromaticity and humification among MT F-W and NT P-W. Similarly, our EEMs-PARAFAC analysis revealed four fluorescence components indicative of different stages of DOM decomposition, but with equivalent fluorescent intensities among MT F-W and NT P-W. Our results imply that within Vertisols greater inputs of biomass-C are not necessarily accompanied by a larger and more compositionally diverse DOM fraction. In contrast, a greater fluorescence efficiency of DOM from sub-soil versus surface layers indicate that low-molecular weight compounds, potentially of microbially derived origin, are major constituents of deep-DOM. Overall, our results suggest that annual cropping in the NGP governs the quantity and not the quality of OM accreted by

Vertisols. A time-scale longer than 10 years might be required to affect a change in DOM quality for soils with high clay contents (i.e. >50%).

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References

Abril, A., Merlo, C., Noe, L., 2013a. Realistic soil C sink estimate in dry forests of western Argentina based on humic substance content. J. Arid Environ. 91, 113-118.

Abril A., Casado-Murillo N., Vazques C., Olivera P., 2013b. Labile and recalcitrant carbon in crop residue and soil under no-till practices in central region of Argentina. Open Agr J. 7, 32–39.

Akagi, J., Zsolnay, Á., 2008. Effects of long-term de-vegetation on the quantity and quality of water extractable organic matter (WEOM): biogeochemical implications. Chemosphere 72, 1462–1466.

Armas-Herrera, C.M., J.L. Mora, C.D. Arbelo, and A. Rodriguez-Rodriguez. 2013. Labile carbon pools and biological activity in volcanic soils of the Canary Islands. Spanish J. Soil Sci. 3, 7-27.

Bolan, N.S., Adriano, D.C., Kunhikrishnan, A., James, T., McDowell, R., Senesi, N., 2011. Dissolved organic matter: biogeochemistry, dynamics and environmental significance in soils. Adv. Agron. 110, 1–75.

Borisover, M., Lordian, A., Levy, G.J., 2012. Water-extractable soil organic matter characterization by chromophoric indicators: effects of soil type and irrigation water quality. Geoderma 179-180, 28–37.

Campbell, C.A., Lafond, G.P., Biederbeck, V.O., Wen, G., Schoenau, J., Hahn, D., 1999. Seasonal trends in soil biochemical attributes: Effects of crop management on a Black Chernozem. Can. J. Soil Sci. 79:85–97.

Cao, F., Medeiros, P.M., Miller, W.L., 2016. Optical characterization of dissolved organic matter in the Amazon River plume and the Adjacent Ocean: examining the relative role of mixing, photochemistry, and microbial alterations. Mar. Chem. 186, 178–188.

Chantigny, M.H., 2003. Dissolved and water-extractable organic matter in soils: a review on the influence of land use and management practices. Geoderma 113, 357–380.

Coble, P.G., 1996. Characterization of marine and terrestrial DOM in seawater using excitationemission matrix spectroscopy. Mar. Chem. 51, 325–346.

Coble, P.G., Del Castillo, C.E., Avril, B., 1998. Distribution and optical properties of CDOM in the Arabian Sea during the 1995 Southwest Monsoon. Deep-Sea Res. II 45, 2195–2223.

Coble, P.G., Lead, J., Baker, A., Reynolds, D.M., Spencer, R.G.M., 2014. Aquatic Organic Matter Fluorescence. Cambridge University Press, New York, NY, pp. 35–74.

Collins, H.P., Mikha, M.M., Brown, T.T., Smith, J.L., Huggins, D., Sainju, U.M., 2012. Agricultural management and soil carbon dynamics: Western U.S. Croplands, in: Liebig, M.K., Franzluebbers, A.J., Follet, R.F. (Eds.), Managing Agricultural Greenhouse Gases.

Elsevier, Amsterdam, The Netherlands, pp. 59-77.

Corvasce, M., Zsolnay, A., D'Orazio, V., Lopez, R., Miano, T.M., 2006. Characterization of water extractable organic matter in a deep soil profile. Chemosphere 62, 1583–1590.

Cory, R.M., McKnight, D.M., 2005. Fluorescence spectroscopy reveals ubiquitous presence of oxidized and reduced quinones in dissolved organic matter. Environ. Sci. Technol. 39, 8142–8149.

DeLuca, T.H., Zabinski, C.A., 2011. Prairie ecosystems and the carbon problem. Front. Ecol. Environ. 9, 407–413.

Duval, M.E., Galantini, J.A., Capurro, J.E., Martinez, J.M., 2016. Winter cover crops in soybean monoculture: effects on soil organic carbon and its fractions. Soil Tillage Res. 161, 95–105.

Ellert, B.H., Bettany, J.R., 1995. Calculation of organic matter and nutrients stored in soils under contrasting management regimes. Can. J. Soil Sci. 75, 529–538.

Engel, R.E., Miller, P.R., McConkey, B.G., Wallander, R., 2017. Soil organic carbon changes to increasing cropping intensity and no-till in a semiarid climate. Soil Sci. Soc. Am. J. 81, 404–413.

Fellman, J.B., D'Amore D.V., Hood, E., Boone, R.D., 2008. Fluorescence characteristics and biodegradability of dissolved organic matter in forest and wetland soils from coastal temperate watersheds in southeast Alaska. Biogeochemistry 88, 169-184.

Galantini, J.A., Senesi, N., Brunetti, G., Rosell, R., 2004. Influence of texture on organic matter distribution and quality and nitrogen and sulphur status in semiarid Pampean grassland soils of Argentina. Geoderma 123, 143–152.

Galantini, J.A., Duval, M., Iglesias, J.O., Krüger, H., 2014. Continuous wheat in semiarid regions: long-term effects on stock and quality of soil organic carbon. Soil Sci. 179, 284–292.

Gao, J., Lv, J., Wu, H., Dai, Y., Nasir, M., 2018. Impacts of wheat straw addition on dissolved organic matter characteristics in cadmium-contaminated soils: Insights from fluorescence spectroscopy and environmental implications. Chemosphere 193, 1027-1035.

Grebliunas, B.D., Armstrong, S.D., Perry, W.L., 2016. Changes in water-extractable organic carbon with cover crop planting under continuous corn silage production. Air, Soil, Water Res. 9, 45–49.

Guimarães, D.V., Silva Gonzaga, M.I., da Silva, T.O., da Silva, T.L., da Silva Dias, N., Silva Matias, M.A., 2013. Soil organic matter pools and carbon fractions in soil under different land uses. Soil Till. Res. 126, 177–182.

Halvorson, A.D., Wienhold B.J., Black A.L., 2002. Tillage, nitrogen, and cropping system effects on soil carbon sequestration. Soil Sci. Soc. Am. J. 66, 906–912.

Hassouna, M., Massiani, C., Dudal, Y., Pech, N., Theraulaz, F., 2010. Changes in water extractable organic matter (WEOM) in a calcareous soil under field conditions with time and soil depth. Geoderma 155, 75–85.

Hassouna, M., Théraulaz, F., Massiani, C., 2012. Production and elimination of water extractable organic matter in a calcareous soil as assessed by UV/Vis absorption and fluorescence spectroscopy of its fractions isolated on XAD-8/4 resins. Geoderma 189- 190, 404–414.

Haynes, R.J. 2005. Labile organic matter fractions as central components of the quality of agricultural soils: an overview. Adv. Agron. 85, 221-268.

Hurisso, T.T., Norton, J.B., Norton, U., 2013. Soil profile carbon and nitrogen in prairie, perennial grass–legume mixture and wheat–fallow production in the central High Plains, USA. Agric. Ecosyst. Environ. 181, 179–187.

Hurlbert, S.H., 1984. Pseudoreplication and the design of ecological field experiments. Ecology Monograph 54, 187-211.

Ishii, S.K.L., Boyer, T.H., 2012. Behaviour of reoccurring PARAFAC components in fluorescent dissolved organic matter in natural and engineered systems: a critical review. Environ. Sci.

Technol. 46, 2006–2017.

Janzen, H.H., Campbell C.A., Izaurralde R.C., Ellert B.H., Juma N., McGill W.B., Zentner R.P., 1998. Management effects on soil C storage on the Canadian prairies. Soil Tillage Res. 47, 181–195.

Jinbo, Z., Changchun, S., Wenyan, Y., 2006. Land use effects on the distribution of labile organic carbon fractions through soil profiles. Soil Sci. Soc. Am. J. 70, 660-667.

Jobbagy, E.G., Jackson, R.B., 2000. The vertical distribution of soil organic carbon and its relation to climate and vegetation. Ecol. Appl. 10, 423–436.

Kalbitz, K., Solinger, S., Park, J.H., Michalzik, B., Matzner, E., 2000. Controls on the dynamics of dissolved organic matter in soils: a review. Soil Sci. 165, 277–304.

Kenward, M.G., Roger, J.H., 1997. Small sample interface for fixed effects from restricted maximum likelihood. Biometrics 53, 983–997.

Lin R., Chen C., 2014. Tillage, crop rotations and nitrogen management strategies for wheat in Central Montana. Agron J. 106, 1-11.

Marinari, S., Dell'Abate, M.T., Brunetti, G., Dazzi, C., 2010. Differences of stabilized or- ganic carbon fractions and microbiological activity along Mediterranean Vertisols and Alfisols profiles. Geoderma 156, 379–388.

Masoom, H., Courtier-Murias, D., Farooq, H., Soong, R., Kelleher, B.P., Zhang, C., Maas, W.E., Fey, M., Kumar, R., Monette, M., Stronks, H.J., Simpson, M.J., Simpson, A.J., 2016. Soil organic matter in its native state. Unravelling the most complex bioma- terial on earth. Environ. Sci. Technol. 50, 1670–1680.

Mielnik, L., Kowalczuk, P., 2018. Optical characteristic of humic acids from lake sediments by excitation-emission matrix fluorescence with PARAFAC model. J. Soil Sediments 18, 2851-2862.

Murphy, K.R., Stedmon, C.A., Waite, T.D., Ruiz, G.M., 2008. Distinguishing between terrestrial and autochthonous organic matter sources in marine environments using fluorescence spectroscopy. Mar. Chem. 108, 40–58.

Murphy, K.R., Stedmon, C.A., Graeber, D., Bro, R., 2013. Fluorescence spectroscopy and multiway techniques. PARAFAC. Anal. Methods 5, 6557–6566.

Munson, S.M., Lauenroth, W.K., Burke, I.C., 2012. Soil carbon and nitrogen recovery on semiarid Conservation Reserve Program lands. J. Arid. Environ. 79, 25-31.

Necpálová, M., et al., 2014. What does it take to detect a change in soil carbon stock? A regional comparison of minimum detectable difference and experiment duration in the north central United States. J. Soil Water Conserv. 69, 517–531.

Norton, J.B., Mukhwana, E.J., Norton, U., 2012. Loss and recovery of soil organic carbon and nitrogen in a semiarid agroecosystem. Soil Sci. Soc. Am. J. 76, 505–514.

Novelli, L.E., Caviglia, O.P., Melchiori, R.J.M., 2011. Impact of soybean cropping frequency on soil carbon storage in Mollisols and Vertisols. Geoderma 167–168, 254–260.

Oades, J.M., 1988. The retention of organic matter in soils. Biogeochemistry 5, 35–70.

Ohno, T., Bro, R., 2006. Dissolved organic matter characterization using multiway spectral decomposition of fluorescence landscapes. Soil Sci. Soc. Am. J. 70, 2028–2037.

Ohno, T., He Z., Tazisong I.A., Senwo Z.N., 2009. Influence of tillage, cropping, and nitrogen source on the chemical characteristics of humic acid, fulvic acid, and water-soluble soil organic matter fractions of a long-term cropping system study. Soil Sci. 174, 652-660.

Pan, H., Yu, H., Song, Y., Liu, R., Du, E., 2017. Application of solid surface fluorescence EEM spectroscopy for tracking organic matter quality of native halophyte and furrow- irrigated soils. Ecol. Indic. 73, 88–95.

Parton, W., Schimel, D., Cole, C., Ojima, D., 1987. Analysis of factors controlling soil organic matter levels in Great Plains grasslands. Soil Sci. Soc. Am. J. 51.

Plaza-Bonilla, D., J. Alvaro-Fuentes, and C. Cantero-Martinez. 2014. Identifying soil organic carbon fractions sensitive to agricultural management practices. Soil Till. Res. 139, 19-22.

Raiesi, F., 2006. Carbon and N mineralization as affected by soil cultivation and crop residue in a calcareous wetland ecosystem in Central Iran. Agric. Ecosyst. Environ. 112, 13–20.

Romero, C.M., Engel, R.E., D'Andrilli, J., Chen, C., Zabinski, C., Miller, P.R., Wallander, R., 2017. Bulk optical characterization of dissolved organic matter from semiarid wheat-based cropping systems. Geoderma 306, 40–49.

Romero, C.M., Engel, R.E., D'Andrilli, J., Chen, C., Zabinski, C., Miller, P.R., Wallander, R., 2018. Patterns of change in permanganate oxidizable soil organic matter from semiarid drylands reflected by absorbance spectroscopy and Fourier transform ion cyclotron resonance mass spectrometry. Org. Geochem. 120, 19-30.

Rumpel, C., Kogel-Knabner, I., 2011. Deep soil organic matter-a key, but poorly understood component of terrestrial C cycle. Plant Soil 338, 143–158.

Sainju, U.M., Caesar-Tonthat T., Lenssen A.W., Evans R.G., Kohlberg R., 2007. Long-term tillage and cropping sequence effects on dryland residue and soil carbon fractions. Soil Sci. Soc. Am. J. 71, 1730–1739.

Sainju, U.M., Caesar-Tonthat T., Lenssen A.W., Evans R.G., Kohlberg R., 2009. Tillage and cropping sequence impact on nitrogen cycling in dryland farming in eastern Montana, USA. Soil Tillage Res. 103, 332– 341.

Sanderman, J., Baldock, J.A., Amundson, R., 2008. Dissolved organic carbon chemistry and dynamics in contrasting forest and grassland soils. Biogeochemistry 89, 181–198.

Sharma, P., Laor, Y., Raviv, M., Medina, S., Saadi, I., Krasnovsky, A., Vager, M., Levy, G.J., Bar-Tal, A., Borisover, M., 2017. Compositional characteristics of organic matter and its water-extractable components across a profile of organically managed soil. Geoderma 286, 73–82.

Sherrod, L.A., Dunn, G., Peterson, G.A., Kolberg, R.L., 2002. Inorganic carbon analysis by modified pressure-calcimeter method. Soil Sci. Soc. Am. J. 66, 299–305.

Sierra, M.M.D., Giovanela, M., Parlanti, E., Soriano-Sierra, E.J., 2005. Fluorescence fingerprint of fulvic and humic acids from varied origins as viewed by single-scan and excitation/emission matrix techniques. Chemosphere 58, 715–733.

Soil Survey Staff, 2013. Web Soil Survey. NRCS, USDA. <http://websoilsurvey.nrcs. usda.gov> (accessed 20/07/2017).

Sparks, D.L., 2003. Environmental Soil Chemistry. Academic Press, London, UK.

Stedmon, C.A., Bro, R., 2008. Characterizing dissolved organic matter fluorescence with parallel factor analysis: a tutorial. Limnol. Oceanogr. Methods 6, 572–579.

Stephan, S., Berrier, J., De Petre, A.A., Jeanson, C., Kooistra, M.J., Scharpenseel, H.W., Shiffmann, H., 1983. Chararcterization of in situ organic matter constituents in Vertisols from Argentina, using submicroscopic and cytochemical methods — first report. Geoderma 30, 21–34.

Sun, H.Y., Koal, P., Gerl, G., Schroll, R., Joergensen, R.G., Munch, J.C., 2017. Response of water extractable organic matter and its fluorescence fractions to organic farming and tree species in poplar and Robinia-based alley cropping agroforestry systems. Geoderma 290, 83–90.

Toosi, E.R., Castellano, M.J., Singer, J.W., Mitchell, D.C., 2012. Differences in soluble organic matter after 23 years of contrasting soil management. Soil Sci. Soc. Am. J. 76, 628–637.

Vázquez, C., Merlo, C., Noé, L., Romero, C., Abril, A., Carranza, C., 2013. Sustainability/resilience of soil organic matter components in an Argentinean arid region. Spanish J. Soil Sci. 3, 73–77.

Vázquez, C., Iriarte, A.G., Merlo, C., Abril, A., Kowaljow, E., Meriles, J.M., 2016. Land use impact on chemical and spectroscopical characteristics of soil organic matter in an arid ecosystem. Environ. Earth Sci. 75, 883.

Wander, M., 2004. Soil organic matter fractions and their relevance to soil Function. In: Magdoff, F., Weil, R.R. (Eds.), Soil Organic Matter in Sustainable Agriculture. CRC Press, Boca Raton, FL, pp. 67–102.

Watts, J.D., Lawrence, R.L., Miller, P., Montagne, C., 2011. An analysis of cropland carbon sequestration estimates for North Central Montana. Clim. Chang. 108, 301–331.

Weishaar, J.L., Aiken, G.R., Bergamaschi, B.A., Fram, M.S., Fujii, R., Mopper, K., 2003. Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon. Environ. Sci. Technol. 37, 4702–4708.

Wu, F.C., Tanoue, E., Liu, C.Q., 2003. Fluorescence and amino acid characteristics of molecular size fractions of DOM in the waters of Lake Biwa. Biogeochemistry 65, 245–257.

Zhang, M., He, Z., Zhao, A., Zhang, H., Endale, D.M., Schomberg, H.H., 2011. Waterextractable soil organic carbon and nitrogen affected by tillage and manure application. Soil Sci. 307-312.

Zhang, M., He, Z., 2015. Characteristics of dissolved organic carbon revealed by ultraviolet–visible absorbance and fluorescence spectroscopy: the current status and future exploration. In: He, Z., Wu, F. (Eds.), Labile Organic Matter—Chemical Compositions, Function, and Significance in Soil and the Environment. Soil Science Society of America, Inc., Madison, WI, pp. 1–22.

Zhang, A., Zhou, X., Li, M., Wu, H. 2017. Impacts of biochar addition on soil dissolved organic matter characteristics in a wheat-maize rotation system in Loess Plateau of China. Chemosphere. 186, 986-993.

Zhao, A., Zhang, M., He, Z., 2012. Characteristics of soil water-soluble organic C and N under different land uses in Alaska. Soil Sci. 177, 683–694.

Zsolnay, Á., Baigar, E., Jimenez, M., Steinweg, B., Saccomandi, F., 1999. Differentiating with fluorescence spectroscopy the sources of dissolved organic matter in soils subjected to drying. Chemosphere 38, 45–50.

Table 1. Two-way ANOVA of the effect of cropping system and soil depth on dissolved organic carbon (DOC) concentration, absorbance at 254 nm (Abs_{254}), specific UV absorbance at 254 nm ($SUVA_{254}$)[a], humification index (HIX)[b], and fluorescence index (FI)[c] of soil DOM.

	DOC (mg C L^{-1})	Abs_{254} (a.u.)	$SUVA_{254}$ (L mg^{-1} C m^{-1})	HIX	FI
Cropping system (CS)					
MT F-W[d]	16.65	0.33	1.83	1.86	1.37
NT P-W	20.86	0.39	1.83	1.83	1.37
Soil depth (cm)					
0-10	31.87b	0.67b	2.15	1.76a	1.35a
10-20	15.24a	0.26a	1.63	2.12b	1.37a
20-50	10.53a	0.19a	1.77	1.65a	1.40b

Factors	df	DOC		Abs_{254}		$SUVA_{254}$		HIX		FI	
		F	P	F	P	F	P	F	P	F	P
Cropping System (CS)	1	3.37	0.0862	2.02	0.1753	0.00	0.9882	0.08	0.7756	0.03	0.8643
Soil depth (D)	2	19.12	<0.0001	25.70	<0.0001	2.99	0.0808	9.33	0.0023	6.49	0.0093
CS x D	2	1.26	0.3116	1.03	0.3818	2.98	0.0814	0.22	0.8058	3.86	0.0443

[a] (Weishaar et al., 2003)

[b] (Zsolnay et al., 1999)

[c] (Cory and McKnight, 2005)

[d] MT F-W minimum till fallow - winter wheat; NT P-W no-till pulse crop - wheat.

Means followed by a common letter within a column are not significantly different (LSD Fisher $P < 0.05$)

Table 2. Maximum fluorescence regions, representative parallel factor (PARAFAC) contour plots, and fluorescence spectral loadings for the four components identified by EEM-PARAFAC analysis. Ex: excitation wavelength; Em: emission wavelength.

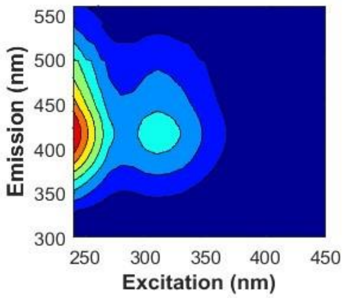
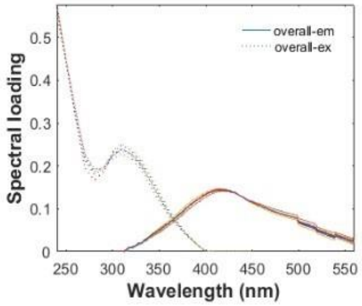
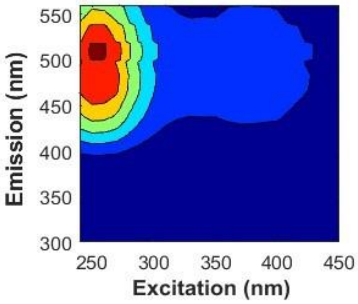
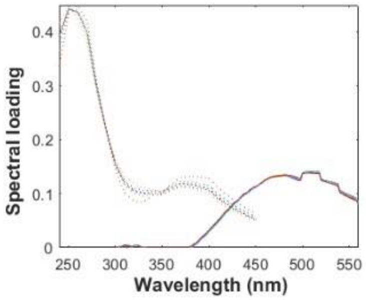
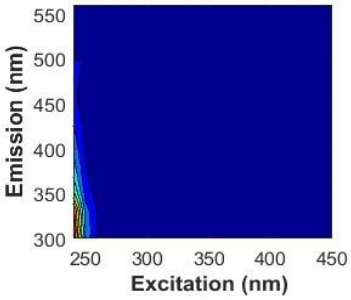
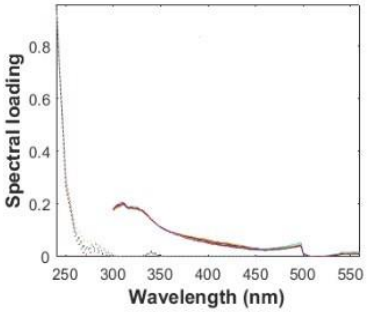
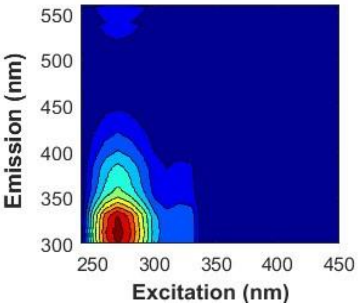
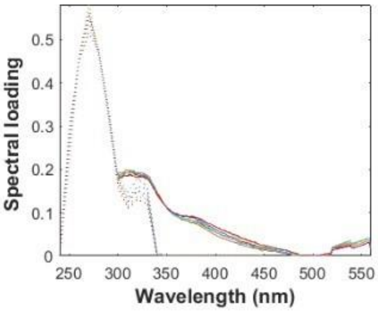
Component	Ex/Em λ (nm)	PARAFAC contours	Spectral Loadings
C1	Ex= <240-250 Em=390-440		
C2	Ex= <240-275 Em=450-540		
C3	Ex= <240 Em=300-330		
C4	Ex= 280 Em=300-330		

Table 3. Two-way ANOVA of the effect of cropping system (MT F-W, minimum till fallow winter wheat; NT P-W no till pulse crop-wheat) and soil depth (0-10, 10-20 and 20-50 cm) on fluorescence maxima (Fmax) in Raman units (R.U.) of PARAFAC components one through four (C1, C2, C3 and C4).

	C1	C2	C3	C4
	Fmax (R.U.)			
Cropping System (CS)				
MT F-W	0.36 ± 0.05	0.23 ± 0.02	0.68 ± 0.07	0.19± 0.02
NT P-W	0.37 ± 0.05	0.23 ± 0.02	0.64 ± 0.07	0.19 ± 0.03
Soil depth (D)				
0-10 cm	0.51 ± 0.05a	0.28 ± 0.03a	0.66 ± 0.06ab	0.26 ± 0.03a
10-20 cm	0.30 ± 0.02b	0.20 ± 0.01b	0.51 ± 0.07b	0.12 ± 0.01b
20-50 cm	0.28 ± 0.03b	0.20 ± 0.01b	0.82 ± 0.09a	0.17 ± 0.02b

ANOVA

Factor	df	C1		C2		C3		C4	
		F	P	F	P	F	P	F	P
CS	1	0.02	0.8812	0.05	0.8252	0.19	0.6662	0.00	0.9960
D	2	8.47	0.0044	4.44	0.0339	4.25	0.0379	8.79	0.0039
CS x D	2	0.21	0.8155	0.38	0.6908	1.04	0.3795	0.32	0.7307

Data are mean ± SE (n=8). Means followed by a common letter within a column are not significantly different (LSD Fisher P<0.05).

Table 4. Two-way ANOVA of the effect of cropping system (MT F-W, minimum till fallow winter wheat; NT P-W no till pulse crop-wheat) and soil depth (0-10, 10-20 and 20-50 cm) on fluorescence efficiency (FE) in Raman units (R.U. cm^{-1}) of PARAFAC components one through four (C1, C2, C3 and C4).

	C1	C2	C3	C4
	FE (R.U. cm^{-1})			
Cropping System (CS)				
MT F-W	1.30 ± 0.18	0.90 ± 0.14	2.66 ± 0.40	0.66 ± 0.08
NT P-W	1.23 ± 0.17	0.85 ± 0.15	2.49 ± 0.55	0.60 ± 0.09
Soil depth (D)				
0-10 cm	0.78 ± 0.06b	0.44 ± 0.04b	1.02 ± 0.09c	0.40 ± 0.03c
10-20 cm	1.56 ± 0.21a	1.08 ± 0.16a	2.55 ± 0.32b	0.64 ± 0.11b
20-50 cm	1.46 ± 0.18a	1.10 ± 0.17a	4.16 ± 0.43a	0.85 ± 0.06a

ANOVA

Factor	df	C1		C2		C3		C4	
		F	P	F	P	F	P	F	P
CS	1	0.23	0.6364	0.65	0.4352	0.16	0.6996	0.13	0.7231
D	2	9.27	0.0031	10.42	0.0020	29.43	<0.0001	12.21	0.0010
CS x D	2	3.60	0.0571	3.68	0.0540	1.96	0.1799	3.38	0.0656

Data are mean ± SE (n=8). Means followed by a common letter within a column are not significantly different (LSD Fisher P<0.05).

Table 5. Pearson correlation coefficients (r) between various DOM parameters for all soil depths and cropping systems.

	DOC[a]	Abs_{254}	$SUVA_{254}$	HIX	FI	C1[b]	C2	C3	C4
Abs_{254}	0.96^{***}	1.00							
$SUVA_{254}$	0.29	0.52^{**}	1.00						
HIX	-0.08	-0.14	-0.41^{*}	1.00					
FI	-0.10	-0.20	-0.28	-0.27	1.00				
C1	0.83^{***}	0.87^{***}	0.43^{*}	0.05	-0.20	1.00			
C2	0.69^{***}	0.79^{***}	0.54^{**}	-0.02	-0.22	0.96^{***}	1.00		
C3	0.19	0.30	0.63^{**}	-0.74^{***}	0.28	0.37	0.51^{*}	1.00	
C4	0.79^{***}	0.85^{***}	0.53^{*}	-0.34	-0.05	0.90^{***}	0.89^{***}	0.65^{***}	1.00

[a] Dissolved organic carbon (DOC) concentration (mg C L^{-1}), absorbance at 254 nm (Abs_{254}; a.u.), specific UV absorbance at 254 nm ($SUVA_{254}$; L mg^{-1} C m^{-1}), humification index (HIX), and fluorescence index (FI).

[b] C1, C2, C3 and C4 refers to PARAFAC fluorescent components.

*, **, *** significant at $P<0.05$; $P<0.01$ and $P<0.001$, respectively.

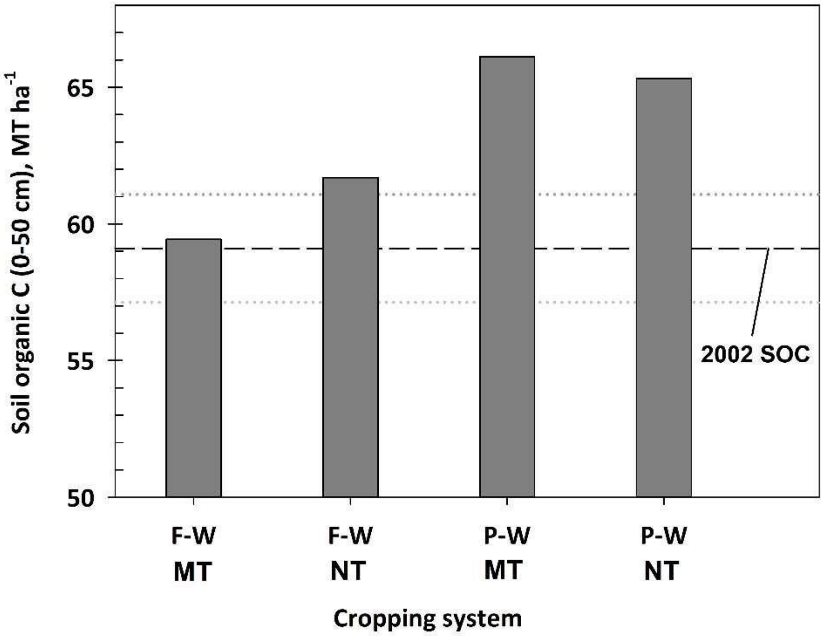


Figure 1. Soil organic carbon (SOC; 0-50 cm) mass in 2012 as affected by cropping and tillage intensity over 10 yr. F-W, fallow-wheat, P-W, pulse-wheat. Cropping intensity means (F-W vs. P-W) were significantly different at $P < 0.05$ level. Dash-line (black) indicates approximate baseline SOC levels in 2002 and 95% confidence intervals are shown with gray dotted lines.

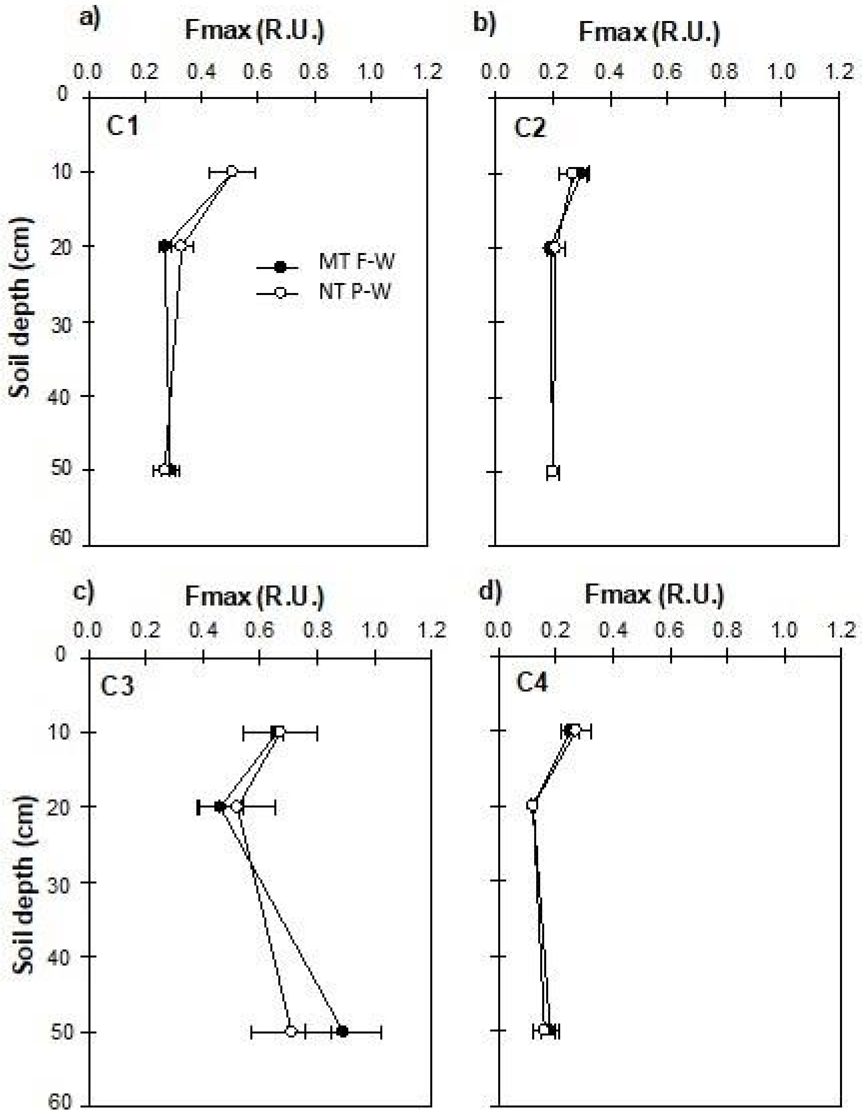


Figure 2. Fluorescence maxima (Fmax) in Raman units (R.U.) of PARAFAC components one through four (C1, C2, C3, and C4) of soil dissolved organic matter along the depth profile for minimum till (MT) fallow-wheat (F-W) and no-till (NT) pulse crop-wheat (P-W) cropping systems.

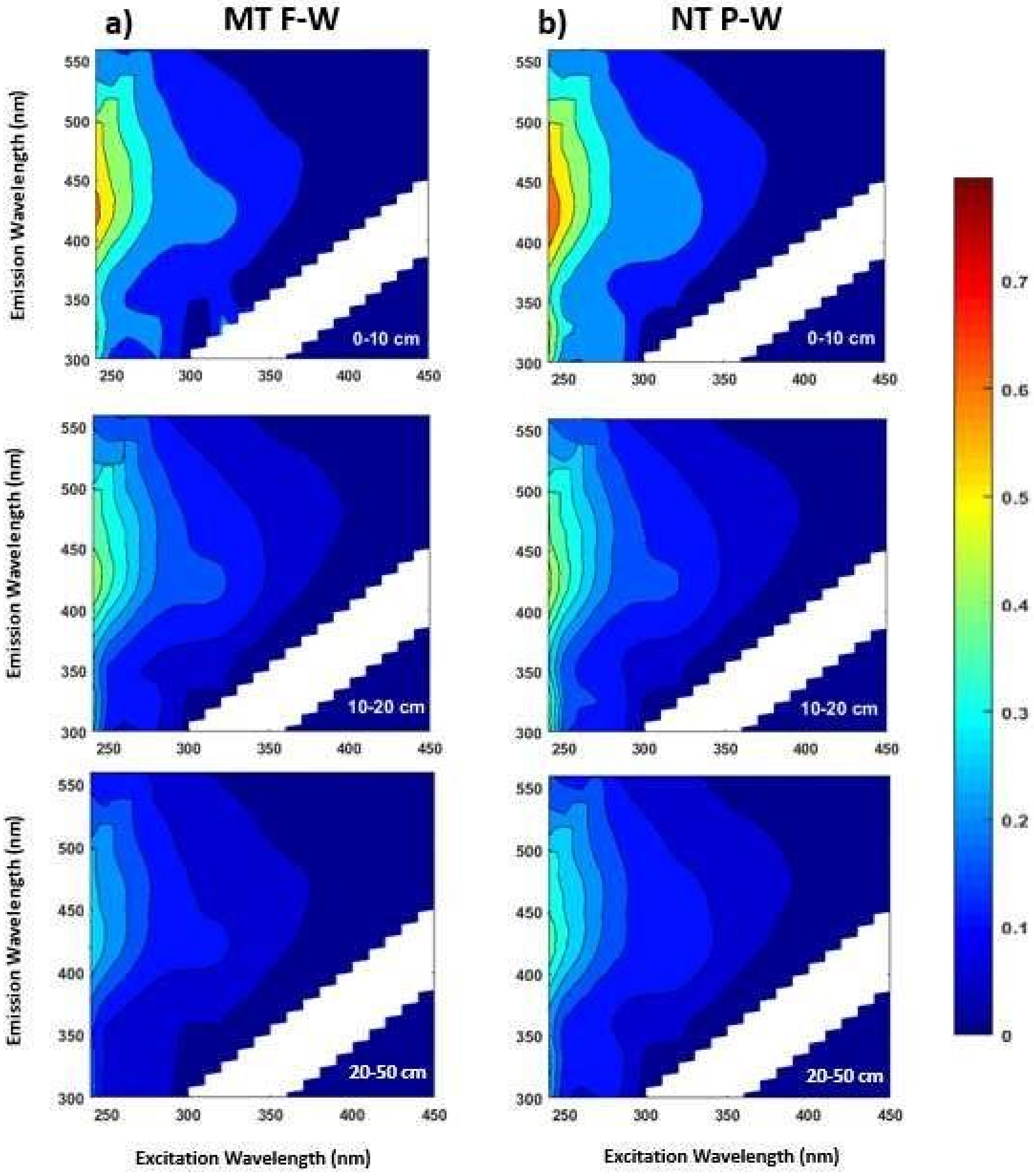


Figure S1. Average (n=4) excitation-emission matrices (EEMs) profiles of bulk soil dissolved organic matter by cropping system and soil depth (0-10, 10-20, 20-50 cm) for a) MT F-W, minimum till fallow- winter wheat, and b) NT P-W no-till pulse crop – wheat systems. Normalized fluorescence intensities are provided as the colorscale in Raman Units (R.U.).