

Article

Fe-Bound Organic Carbon and Sorption of Aromatic Dissolved Organic Carbon in Surface Soil: Comparing a Forest, a Cropland, and a Pasture Soil in the Central Appalachian Region, West Virginia, U.S.A

Lili Lei ^{1,2}, Ida Holásková ³, James A. Thompson ¹ and Louis M. McDonald ^{1,*}¹ Division of Plant and Soil Sciences, West Virginia University, Morgantown, WV 26505, USA² Department of Biology and Environmental Sciences, Sweet Briar College, Sweet Briar, VA 24595, USA³ Office of Statistics, Davis College of Agriculture, Natural Resources and Design, West Virginia Agriculture and Forestry Experiment Station, West Virginia University, Morgantown, WV 26506, USA

* Correspondence: lmmcdonald@mail.wvu.edu

Abstract: The essential roles of Fe oxides in stabilizing long-term soil organic carbon (SOC), especially aromatic dissolved organic carbon (DOC_{aro}), are well-established in forest soils and sediments. We chose to focus on these processes in agricultural soils in which the input and translocation of native DOC to deeper soils are impacted by management practices. We quantified SOC, Fe oxide bound SOC (Fe-bound OC), and the DOC_{aro} sorption in a forest, a cropland, and a pasture soil at 0–10 and 10–25 cm. Significantly larger amounts of Fe oxides in the cropland soil were observed compared to the forest and pasture soils at both depths ($p < 0.05$). Land management practices and depth both significantly influenced the Fe-bound OC percentage ($p < 0.05$). Larger maximum sorptions of DOC in the cropland (315.0 mg kg⁻¹) and pasture (395.0 mg kg⁻¹) soils than the forest soil (96.6 mg kg⁻¹) at 10–25 cm were found. DOC_{aro} sorption decreased in the three soils at 0–10 cm (slope of -0.002 to -0.014 L² mg⁻² m⁻¹) as well as the forest soil at 10–25 cm (-0.016 L² mg⁻² m⁻¹) with increasing equilibrium DOC concentration. Conversely, the cropland and pasture soils at 10–25 cm increased (0.012 to 0.014 L² mg⁻² m⁻¹). The different sorption behaviors of DOC_{aro} in these surface soils indicate that the forest, cropland, and pasture-managed soils may have more complex and various sorption behaviors in stabilizing DOC_{aro} and non-DOC_{aro}.

Keywords: soil organic carbon; agricultural soils; amorphous Fe; non-aromatic DOC; sorption

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1. Introduction

Soil organic carbon (SOC) bridges biogeochemical C cycling among soil, aquatic, and atmospheric environments [1]. Without appropriate soil management, SOC is linked to current environmental issues, such as global warming and surface water brownification [2,3]. Iron (Fe) oxides are critical in regulating SOC dynamics and significantly impact SOC biogeochemical cycling [4–8]. The SOC bound to Fe oxides (Fe-bound OC) is physically inaccessible to soil microorganisms, which inhibits the degradation and mineralization of SOC and thus has a long residence time [9,10]. In a changing climate, sequestering more SOC is a promising approach to mitigate these environmental issues [11], especially Fe-bound OC.

One dominant mechanism of stabilizing SOC is the sorption of DOC to soil mineral surfaces mediated by Fe oxides, which is supported by recent molecular level technologies [10,12–14]. SOC is a complex assemblage of various microbial-derived and plant-derived compounds, root exudates, and polyaromatic char with different reactivity caused by the various functional groups [1,11]. This SOC chemical heterogeneity, which is due to various sources and alteration factors, brings more uncertainty and diversity to a full understanding of the mechanisms of SOC stabilization, especially in agricultural soils

with varied management practices [15–17]. Carbon stocks in agricultural soils contribute a significant amount of C to global C stock and play an important role in mitigating global warming [18]. It has been reported that grass and cropland have a higher potential to preserve OC compared to forest soil [19]. However, the roles of Fe oxides in SOC stabilization in agricultural soils are not as well documented as in the forest soils and in sediment [7,20].

Agricultural management practices are commonly adapted as strategies to improve crop production and sequester more SOC [11,17,21]. Manure application in croplands and continuous grazing in pastures are common management practices in agricultural ecosystems, which increase the aromaticity of DOC in soil [21–26]. Agricultural management practices also alter the concentrations of Fe oxides in soil solution, which, in turn, influences the preservation of DOC by Fe oxides [27]. Poorly crystalline iron oxides in agricultural soils increased significantly due to manure application [28–30]. Since soil Fe occurs in various forms differing in reducibility, it is important to have a better understanding of Fe oxides with different reducibility in soil in stabilizing SOC, for example, exchangeable Fe and microbially reducible Fe [31,32]. However, multiple forms of Fe oxides with different reducibility in stabilizing SOC are still understudied in agricultural soils.

Plant-derived aromatic and lignin-like high molecular weight compounds are preferentially retained by reactive amorphous Fe oxides by forming irreversible inner-sphere bonds, which resist DOC desorption and thus contribute to long-term SOC preservation [12,14,33,34]. Long term agriculture inputs reshape the quantity and quality of SOC present in the soil including aromatic structures, structural complexity, and DOC molecular weight [26,35,36]. Interactions between DOC and Fe oxides are highly impacted by the changes in quantity and quality of DOC accessible to soil Fe minerals. Proper management practices are strategies to increase the aromaticity of DOC in soil and sequester more SOC, which improves crop production [11,17,21–23,25]. However, current studies mostly focus on Fe-bound OC in sediment, permafrost, and forest soils [7,33,37,38].

One of the major issues is soil degradation and carbon stock depletion, which is due to increasing anthropogenic disturbances in the central Appalachian region. The dominant land types in this region are the forest, pasture, and cropland, which account for 62, 18, and 8% of land use, respectively. SOC sequestration was studied in severely disturbed soils [39,40], and dissolved organic C was investigated in peatland soils and streams [41,42], which was the focus of most previous studies. However, there are few studies on the capacities of forest, cropland, and pasture soils for long-term SOC sequestration, especially by incorporating the role of Fe oxides. Thus, to develop the best management practices for restoration and sustainable agriculture, an improved understanding of Fe-bound OC and interactions between Fe oxides and DOC, especially aromatic DOC, is crucial for a better understanding of the mechanisms of long-term SOC sequestration in agricultural soils. Additionally, filling this research gap is essential for developing and evaluating the best management practices in terms of soil nutrient dynamics. It may provide useful information to accurately predict the global SOC changes in the warming environment.

SOC dynamics are influenced by various important factors, such as climate and soil properties [43–45]. Current studies have been done in larger watersheds [45–49]. However, these studies are potentially confounded by differences within watershed other than land management practices, for example, different parent materials, topography, and climate. To minimize the effects of parent materials, topography, and climate within a watershed on SOC dynamics, pseudo-replicated studies to minimize these variations may be informative. Therefore, a single fine-scale watershed with a similar climatic condition was chosen, and a cropland, a pasture, and a forest soil within this small catchment were specially selected in our study, which was also derived from the same source parent material [50].

Sorption experiments in the majority of studies used DOC extracted from forest O horizon soils, which were different from the sorbent soils [7,12,33,51,52]. This prevents the interpretation of these studies for naturally occurring sorption processes; the DOC sources to sub-surface soils are from the in situ surface soils. Thus, we were interested in comparing the sorption behaviors of the DOC extracted from the cropland, pasture, and

forest managed topsoil at 0–10 cm to soils at 10–25 cm to reduce the uncertainty of using ex situ DOC sources to indicate soil DOC sorption behaviors.

The objectives of this study were to quantify and compare (1) three forms of Fe oxides (the exchangeable, amorphous Fe, and crystallized Fe oxides), three forms of SOC (total SOC (TOC), Fe-bound OC, and DOC released during amorphous Fe extraction), and (2) the sorption of DOC and changes of aromaticity of DOC after sorption using batch experiments from the pasture, cropland, and hardwood forest managed soils.

2. Materials and Methods

2.1. Study Site Description

This study was carried out using three representative land management types including forest, pasture, and cropland at the West Virginia University's Animal Science Farm in Morgantown, West Virginia (39°40' N, 79°56' W). The mean annual precipitation was 106.2 cm; the mean annual averages daily maximum was 17.1 °C; the mean annual averages minimum temperature was 6.3 °C, respectively, between 1981 to 2010 [50]. The deciduous hardwood forest (HF) stand was approximately 120 years old. The permanent pasture was continuously grazed (CG) with 0.5–0.75 dry dairy cows and/or heifers per hectare for 20 years. The cropland was a continuous corn (*Zea mays*) field with manure application (CM) for at least 20 years. Kellner et al. described this site with detailed information [50]; Other characteristics, management, and botanical composition of each land type are presented in Table 1 and illustrated in Table S1.

Table 1. The characteristics of the sampling plots in hardwood forest (HF), cropland with manure (CM) and continuous pasture (CP).

Land Type	Elevation (m)	Slope (%)	Topographic Position	Parent Materials
Forest	303.5–338.7	25–35	Backslope	loamy residuum weathered from limestone, sandstone, and shale
Pasture	324.4–341.8	25–35	Backslope	loamy residuum weathered from limestone, sandstone, and shale
Cropland	289.0–292.4	3–5	Flood plain	loamy alluvium derived from limestone, sandstone, and shale

Four 10 m × 10 m plots were selected within each land type after a thoroughly soil survey and computer mapping, which is illustrated in Figure S1. The forest and pasture soils were mapped as Celleoka-Westmoreland silt loams (Fine-loamy, mixed, active, mesic Ultic Haplusdalfs) [53]. In the cropland, the soil was mapped as Holly silt loam (Fine-loamy, mixed, active, nonacid, mesic Typic Fluvaquents) and Lobdell silt loam (Fine-loamy, mixed, active, mesic Fluvaquentic Eutrudepts) [53].

2.2. Soil Sampling

Soil samples were collected in June 2018. For each land type, four 10 m × 10 m soil plots were randomly selected in the field with similar micro-environmental conditions, like vegetation distribution. When sampling the forest soil samples, the thin and lightly decomposed layer was removed. To avoid the effects of supplemental feeding and watering post for cows in the pasture field, these areas were excluded. In addition, the pasture plots that at least 5 m away from the edge of the field were chosen. The plots that were at least 10 m away from the riparian grass buffer were chosen for collecting crop land soil samples.

The S patten was used to collect six soil sample cores to a depth of 25 cm at each plot using a soil sampling problem, which was 3 cm in diameter. All the collected cores were sectioned into 0–10 cm and 10–25 cm layers. Three pseudo-replication soil samples for both depth increment in each land type were obtained by combining and composing pairs of cores from each plot. The study and sampling site is presented in Figure S1.

For the adsorption experiment, three 0.5 m × 0.5 m subplots were chosen from each plot and the soil of the top 5 cm from the three subplots was collected. The collected soil samples from three subplots of all four plots within each land type were composited to make one representative and homogeneous sample for each land type. Then, the collected soil samples were used to extract DOC as a DOC source of mimicking DOC percolating from surface to deeper mineral soils in the field condition.

2.3. Soil Physical and Chemical Analysis

Upon returning to the lab, each bulk sample was divided into two subsamples. One subsample was air dried at room temperature until reach a constant weight; the subsample was ground and sieved through a 2-mm sieve, which was used for determination of soil pH, EC, and particle size distribution, total C, total N, exchangeable Ca, Mg, P, and K. The description of these determinations is summarized in S1 and are presented in Table S1. The other subsample was sieved through a 2-mm sieve and stored at 4 °C until analysis within three days.

To degas the inorganic C in soil for OC fraction determination, the air-dried soil samples were firstly treated with 1 M HCl with a 1:2 (m:V) solid:solution ratio; the mixtures were then dried for 24 h at 70 °C in an oven. TOC in the oven-dried soil samples was determined by dry combustion (Elementar Vario MAX Cube, Hanau, Germany). The Fe-bound OC was determined using citrate-bicarbonate-dithionite (CBD) method [37,38]. The reactive Fe concentrations in the filtrate after CBD extraction were determined using ICP-OES, which represented the crystalline Fe (III) oxides in soil [32]. Exchangeable Fe (Fe_{ex}) in fresh soil subsamples was determined to using 0.5 M HCl and the microbially reducible amorphous Fe (Fe_{amor}) was calculated as the Fe extracted from fresh soil using 0.25 M hydroxylamine hydrochloride and 0.25 M HCl minus the Fe extracted with 0.5 M HCl [31,32]. Exchangeable Fe represented the directly exchangeable Fe portion with the soil adsorption complex while the microbially reducible amorphous Fe represented the portion of amorphous Fe (III) oxyhydroxide which could be reduced by microorganisms [32]. The released Fe was determined according to methods described by Lovley and Phillips [31]. The released DOC in the filtrate was determined using Shimadzu-TOC V (Tokyo, Japan) and, as a measure of aromaticity, the specific ultraviolet absorbance at 254 nm ($SUVA_{254}$) of the released DOC was determined using method described by Weishaar et al. [53].

2.4. Adsorption Experiments

A DOC stock solution from each land type was obtained by percolating the composited soil samples with 12.5 mM $CaCl_2$ solution using a 1:1 (m:V) fresh soil to solution ratio [54,55]. The mixture was shaken at 200 cycles per minute for 6 days at room temperature. The percolates were centrifuged and filtered through 0.45- μ m filters. The filtrate was used as DOC stock solution and stored at -20 °C until used in adsorption experiments. The extracted DOC stock solution was 119, 120, and 150 mg L⁻¹ for forest, cropland, and pasture soils. The stock solution was diluted to five DOC concentrations (forest and cropland: 12, 24, 48, 60, 72 mg L⁻¹; pasture: 15, 30, 60, 75, and 90 mg L⁻¹) using 12.5 mM $CaCl_2$ solution, which was adjusted using the same ratio for each DOC concentration level of each soil. Since the pH and ionic strength have significant influences on DOC sorption behaviors [56,57], the pH and EC were adjusted to be about 7 using 1 M HCl and 1 M NaOH and 2.5 μ S cm⁻¹ using 0.0125 M $CaCl_2$ before starting the sorption experiment to minimize the effects of pH and ionic strength. The initial $SUVA_{254}$ of DOC extracted solution of each land type were 0.8 L m⁻¹ mg⁻¹ (forest), 1.4 L m⁻¹ mg⁻¹ (cropland), and 1.2 L m⁻¹ mg⁻¹ (pasture), which was lower than some studies [33,58] and similar to other studies [59–61]. The same $SUVA_{254}$ as the initial $SUVA_{254}$ of extracted DOC was used for each land type soil sorption experiment.

For generating adsorption data, 3.0 g of air-dried soil was mixed with 30.0 mL of one of the five DOC solutions in 50 mL centrifuge tubes with two replications each. The control for each isotherm was done by using 12.5 mM $CaCl_2$ with 0 mg L⁻¹ DOC.

The mixtures were shaken for 24 h at 30 rpm on a rotary shaker. Then, the mixtures were centrifuged for 30 min at 3000 rpm (1600× g). The supernatant was filtered through 0.45- μm filters. The filtrate was stored at 4 °C and analyzed within two days. The pH, EC, DOC concentration, and SUVA₂₅₄ of DOC in the filtrate were determined after the sorption experiment as described above. The change of aromaticity of DOC during sorption processes (ΔSUVA_{254}) were calculated as SUVA₂₅₄ of the DOC after 24 h sorption minus the SUVA₂₅₄ at the beginning of sorption experiment. A negative ΔSUVA_{254} meant the SUVA₂₅₄ of DOC in solution decreased after adsorption, which indicated the net loss of aromatic DOC in solution, while a positive ΔSUVA_{254} meant the SUVA₂₅₄ of DOC in solution increased after sorption, which indicated the net gain of aromatic DOC in solution.

2.5. Isotherm

The modified Langmuir isotherm (Equation (1)), which added a desorption term b , in mg kg^{-1} , to correct for the desorption of native adsorbed solute on the soil surface, was used [62].

$$\text{ADS} = \frac{k \times Q_{\max} \times q_e}{1 + k \times q_e} - b \quad (1)$$

where ADS is amount of adsorbed DOC in mg kg^{-1} , k is binding affinity in L mg^{-1} , Q_{\max} is the maximum adsorption capacity in mg kg^{-1} , and q_e is the equilibrium concentration in mg L^{-1} .

2.6. Statistical Analysis

Analysis of variance (repeated measure: rmANOVA) and Tukey adjustment were conducted to assess main effects of land management practice, depth, and their interaction on TOC, Fe-bound OC, reactive Fe, microbially reducible Fe, released DOC and SUVA₂₅₄ of released DOC during microbially reducible Fe extraction, exchangeable Fe, and released DOC and SUVA₂₅₄ of released DOC during exchangeable Fe extraction at $\alpha = 0.05$ using SAS PROC MIXED procedure (Version 11. SAS Institute Inc., Cary, NC, USA). Across all three land management practices and two depths, a linear regression was conducted between released DOC and Fe during extracting exchangeable Fe and microbially reducible Fe, assuming independence. Similarly, a non-linear regression was performed between the SUVA₂₅₄ of released DOC and released Fe. The isotherms were fit using a G-Newton iterative method with least square functions to estimate the fit using JMP [62]. The performance of the fit was evaluated using the minimum root mean square error (RMSE) when estimating how well the model fit the data [62]. The linear regression was performed between the changes in SUVA₂₅₄ of the DOC solution and equilibrium DOC concentrations for the adsorption experiment.

3. Results

3.1. The TOC, Fe-Bound OC, and Reactive Fe in Forest, Cropland, and Pasture Managed Soils

Significant influences of land management practices, depth, and the interactions between management and depth were observed on TOC, Fe-bound OC proportion, and amount of Fe-bound OC ($p < 0.01$) except for main effects of land management practices on TOC and main depth effects on the amount of Fe-bound OC ($p > 0.05$). No significant differences in TOC were observed among the forest, cropland, and pasture managed soils at 0–10 cm. The cropland managed soil at 10–25 cm had significantly higher TOC (17.79 g kg^{-1}) compared to the forest soil (12.13 g kg^{-1}) and pasture soil (9.61 g kg^{-1}) (Figure 1A). The forest, cropland, and pasture managed soils at 0–10 cm showed significant higher amounts of Fe-bound OC than the three soils at 10–25 cm while no significant differences in amount of Fe-bound OC observed in each depth (Figure 1C). The pasture (34.1%) and forest soils (32.0%) at 10–25 cm had significant higher percentage of Fe-bound OC than other soils at both 0–10 cm and 10–25 cm (Figure 1B).

Only land management practices had significant influence on reactive Fe concentration ($p < 0.01$). The crop land soil had a significantly higher reactive Fe concentration at both

0–10 cm (23.86 g kg^{-1}) and 10–25 cm (23.72 g kg^{-1}) than forest and pasture soils at both depths (Figure 1D). The forest and pasture soils at both depth increments had similar reactive Fe contents ($\text{HF}_{0-10\text{cm}}$: 16.93 g kg^{-1} ; $\text{HF}_{10-25\text{cm}}$: 16.75 g kg^{-1} ; $\text{CG}_{0-10\text{cm}}$: 12.98 g kg^{-1} ; $\text{CG}_{10-25\text{cm}}$: 14.71 g kg^{-1}) (Figure 1D).

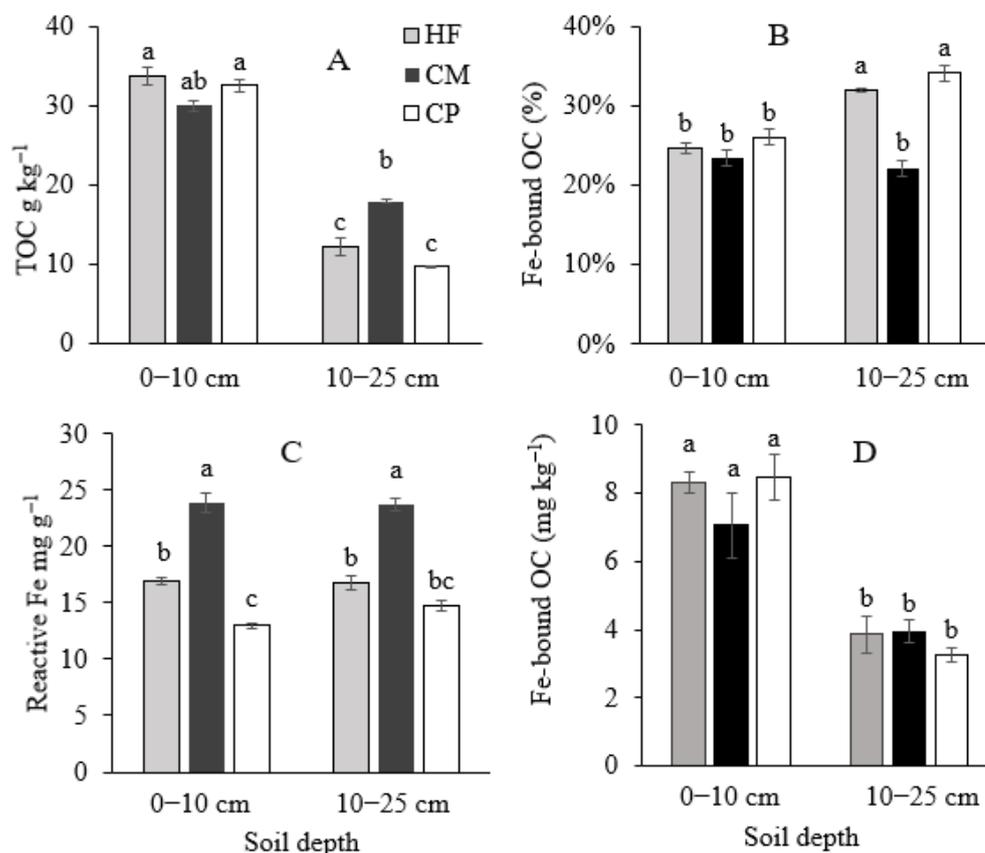


Figure 1. Total organic carbon (TOC) (A), organic carbon preserved by Fe (OC_{Fe}) (B), reactive Fe (C), and Fe-bound OC (D) in forest (HF), cropland (CM), and pasture (CP) soils at 0–10 cm and 10–25 cm depth. Different lower-case letters indicated significant differences at $\alpha = 0.05$. The error bar represented the standard deviation ($n = 3$).

3.2. Amorphous and Exchangeable Fe and Extracted DOC

For the microbially reducible amorphous Fe, the cropland soil (1.53 g kg^{-1}) had a significantly higher amount than the forest (1.38 g kg^{-1}) and the pasture soils (1.23 g kg^{-1}) at 0–10 cm, which were all significantly higher than that in the soils at 10–25 cm (Table 2). The forest and pasture soils at 0–10 cm had significantly higher released DOC (0.63 g kg^{-1} and 0.57 g kg^{-1} , respectively) than other soils while the pasture and cropland soils at 10–25 cm had the lowest released DOC (0.30 g kg^{-1}) (Table 2). The pasture and cropland soils at 0–10 cm had the highest SUVA_{254} of released DOC (48.46 and $45.38 \text{ L m}^{-1} \text{ mg}^{-1}$ per g soil, respectively) than all other soils (Table 2). There were no differences in released DOC and the SUVA_{254} of released DOC observed among all soils at 10–25 cm (Table 2).

For the exchangeable Fe, the cropland soil (0.24 g kg^{-1}) had a significant amount than pasture soil (0.18 g kg^{-1}) at 0–10 cm, which was significantly higher than the cropland and pasture soils at 10–25 cm and forest soil at both depths (Table 2). Similar to the trends of the released DOC of microbially reducible amorphous Fe extraction, the forest and pasture soils at 0–10 cm had significantly higher released DOC (0.37 g kg^{-1} and 0.42 g kg^{-1} , respectively) than other soils while the pasture and cropland soils at 10–25 cm had the lowest released DOC (0.16 g kg^{-1}) (Table 2). The pasture and cropland soils at 0–10 cm had the highest SUVA_{254} of released DOC (28.93 and $27.99 \text{ L m}^{-1} \text{ mg}^{-1}$ per g soil, respectively) than all

other soils (Table 2). The cropland soil at 10–25 cm ($22.68 \text{ L m}^{-1} \text{ mg}^{-1}$ per g soil) had a significantly higher SUVA_{254} of released DOC than the forest and pasture soil at 10–25 cm (13.50 and $15.67 \text{ L m}^{-1} \text{ mg}^{-1}$ per g soil, respectively) (Table 2).

Table 2. Amount of released Fe, DOC (dissolved organic carbon), and SUVA_{254} (absorbance of DOC at 254 nm) of DOC released from soils after 0.5 N HCl at 0–10 cm and 10–25 cm, 0.25 N HCl and 0.25 N $\text{NH}_2\text{OH}\cdot\text{HCl}$ extraction (**bold and italicized**) at 0–10 cm and 10–25 cm in hardwood forest (HF), cropland with manure (CM) and continuous pasture (CP).

Land Type	Depth(cm)	Fe (g kg^{-1})	Released DOC (g kg^{-1})	SUVA_{254} of Released DOC ($\text{L m}^{-1} \text{ mg}^{-1}$ per g Soil)
HF	<i>0–10</i>	<i>1.38 ± 0.04 b</i>	<i>0.63 ± 0.04 a</i>	<i>36.89 ± 1.5 bc</i>
	<i>10–25</i>	<i>0.52 ± 0.01 e</i>	<i>0.44 ± 0.02 b</i>	<i>33.16 ± 1.1 c</i>
CM	<i>0–10</i>	<i>1.53 ± 0.02 a</i>	<i>0.42 ± 0.02 b</i>	<i>45.38 ± 3.2 ab</i>
	<i>10–25</i>	<i>0.81 ± 0.002 d</i>	<i>0.30 ± 0.02 c</i>	<i>35.03 ± 2.3 c</i>
CP	<i>0–10</i>	<i>1.23 ± 0.02 c</i>	<i>0.57 ± 0.01 a</i>	<i>48.16 ± 1.4 a</i>
	<i>10–25</i>	<i>0.47 ± 0.01 e</i>	<i>0.30 ± 0.01 c</i>	<i>32.04 ± 1.4 c</i>
HF	0–10	0.12 ± 0.006 d	0.37 ± 0.02 ab	15.36 ± 0.18 d
	10–25	0.07 ± 0.004 e	0.25 ± 0.01 cd	13.50 ± 0.2 d
CM	0–10	0.24 ± 0.009 a	0.28 ± 0.01 bc	28.93 ± 1.0 a
	10–25	0.15 ± 0.002 c	0.16 ± 0.01 d	22.68 ± 0.7 b
CP	0–10	0.18 ± 0.004 b	0.42 ± 0.03 a	27.99 ± 2.6 a
	10–25	0.06 ± 0.009 e	0.22 ± 0.02 cd	15.67 ± 2.5 d

Note: Different lower-case letters after each number indicated significant differences at $\alpha = 0.05$.

3.3. The Sorption of DOC to Three Land Management Practices Soils and Changes in ΔSUVA_{254}

The three land management practice soils had increasing sorption of DOC with increasing equilibrium concentration and a higher amount of DOC sorption at 10–25 cm than 0–10 cm (Figure 2 HF-a, CM-a, and CP-a). Larger maximum sorption of DOC in the cropland (315.0 mg kg^{-1}) and pasture (395.0 mg kg^{-1}) soils than the forest soil (96.6 mg kg^{-1}) at 10–25 cm was found (Figure 2 HF-a, CM-a, and CP-a). The desorption occurred at low equilibrium concentrations ($<30 \text{ mg L}^{-1}$) of the cropland soil, pasture soil, and forest soil at 10–25 cm (Figure 2 HF-a, CM-a, and CP-a). The forest soil at 0–10 cm had desorption of the studied equilibrium concentration range ($0\text{--}72 \text{ mg L}^{-1}$) at 0–10 cm (Figure 2 HF-a).

Cropland and pasture soils at 0–10 cm had positive ΔSUVA_{254} and similar decreasing trends with increased equilibrium concentrations while the pasture and cropland soils at 10–25 cm had negative ΔSUVA_{254} and increasing trends (Figure 2 CM-b and CP-b; Table 3). The increasing trends with increased equilibrium DOC concentrations in cropland and pasture soil at 10–25 cm had similar increasing slopes (0.014 and $0.012 \text{ L}^2 \text{ mg}^{-2} \text{ m}^{-1}$, respectively) (Figure 2 CM-b; Figure 2 CP-b; Table 3). Conversely, forest soils had decreasing trends of ΔSUVA_{254} with increased equilibrium concentrations (0–10 cm: $-0.014 \text{ L}^2 \text{ mg}^{-2} \text{ m}^{-1}$; 10–25 cm: $-0.016 \text{ L}^2 \text{ mg}^{-2} \text{ m}^{-1}$) (Figure 2 HF-b; Table 3).

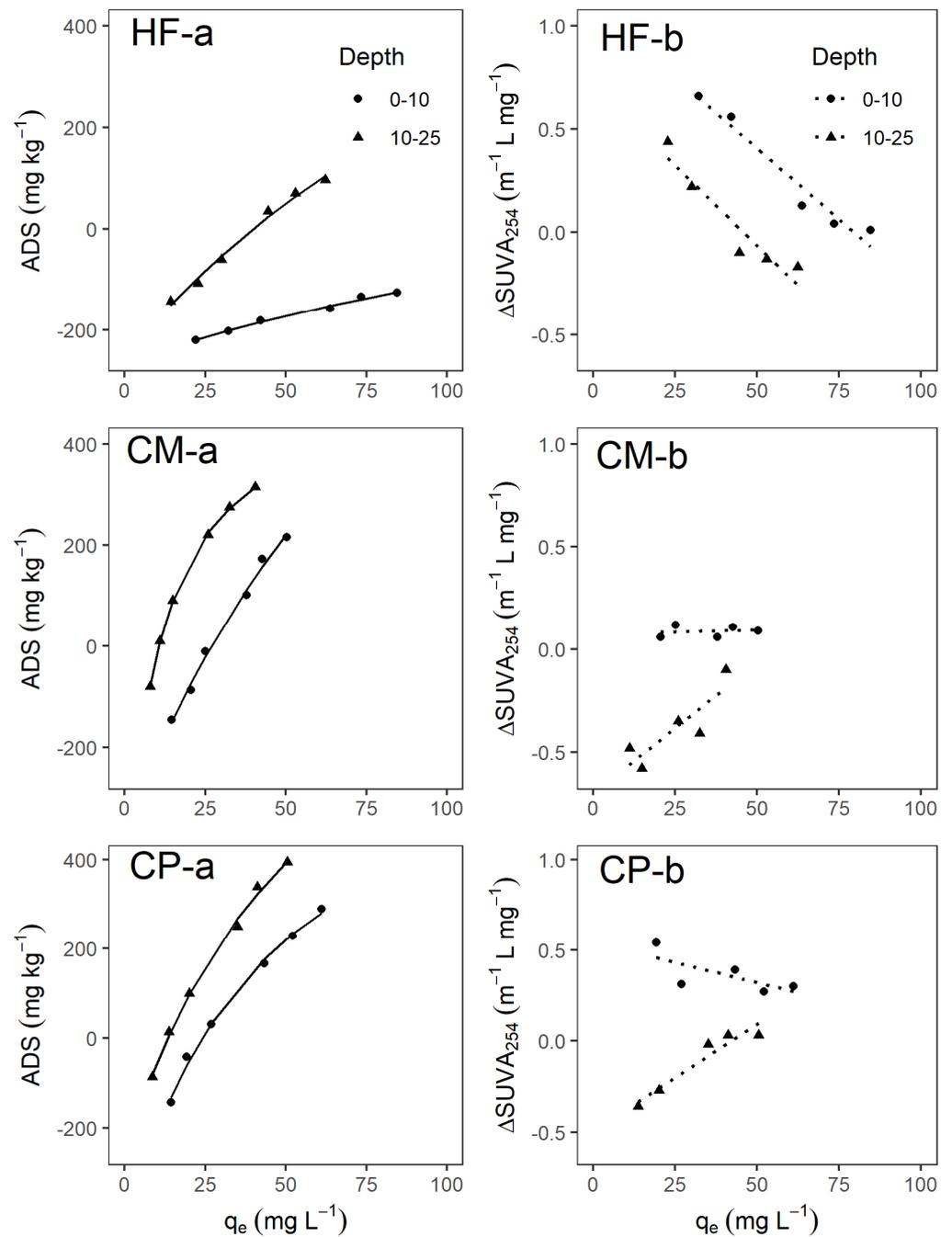


Figure 2. Dissolved organic carbon (DOC) sorption to the forest (HF-a), cropland (CM-a), and pasture (CP-a) soils and the change of SUVA_{254} (ΔSUVA_{254}) of the DOC solution after sorption to the hardwood forest (HF-b), cropland with manure (CM-b), and continuous pasture (CP-b) soils at 0–10 cm and 10–25 cm depth. The solid lines were the fitted modified Langmuir isotherm. The dashed lines were the fitted linear regression. ADS: adsorbed DOC; ΔSUVA_{254} : The specific ultraviolet absorbance at 254 nm of filtered DOC in solution at equilibrium minus that of DOC at original solutions.

Table 3. Linear regression between the change in SUVA₂₅₄ of a DOC solution and equilibrium DOC concentration for three land type soils at 0–10 cm and 10–25 cm depths.

Land type	Depth	Equation	Adjusted r ²	p
Forest	0–10 cm	$\Delta\text{SUVA}_{254} = -0.014 q_e + 1.10$	0.93	0.005
	10–25 cm	$\Delta\text{SUVA}_{254} = -0.016 q_e + 0.71$	0.86	0.014
Cropland	0–10 cm	$\Delta\text{SUVA}_{254} = -0.002 q_e + 0.18$	0.68	0.053
	10–25 cm	$\Delta\text{SUVA}_{254} = 0.014 q_e - 0.76$	0.78	0.031
Pasture	0–10 cm	$\Delta\text{SUVA}_{254} = -0.006 q_e + 0.61$	0.77	0.031
	10–25 cm	$\Delta\text{SUVA}_{254} = 0.012 q_e - 0.49$	0.89	0.01

ΔSUVA_{254} (m⁻¹ L mg⁻¹): The specific ultraviolet absorbance at 254 nm of filtered DOC in solution at equilibrium minus that of DOC at original solutions; q_e (mg L⁻¹): The equilibrium concentration of filtered DOC solution.

4. Discussion

4.1. Comparison of Three Forms of Fe Minerals and Associated Organic Carbon in Three Soils

Fe oxides correlate with SOC content, mineralization, and thus long-term storage [63]. There were no significant differences in TOC and amount of Fe-bound OC in three soils at 0–10 cm as well as amount of Fe-bound OC at 10–25 cm while significantly higher TOC in cropland soil at 10–25 cm (Figure 1A,C). This indicated that cropland soil at 10–25 cm had more TOC that did not bound with Fe minerals. Due to this, a significantly relative higher percentage of Fe-bound OC was found in the forest (32%) and pasture (34%) soils at 10–25 cm than other soils (Figure 1B), which was similar to the percentage of Fe-bound OC in forest soils reported by Zhao et al. [37]. The significantly lower Fe-bound OC in forest (25%) and pasture soils (26%) at 0–10 cm and cropland soil at both 0–10 cm (23%) and 10–25 cm (22%) were observed (Figure 1B), which had similar ranges as marine sediments and soils of permafrost ecosystem (approximate 20%) [20,38]. Our studies also indicated that the reactive Fe was more efficient in stabilizing SOC in the pasture and forest soil at 10–25 cm than the soils at 0–10 cm, which may reveal different mechanisms of Fe oxides in stabilizing SOC between top and subsurface layer of forest and pasture managed soils [64].

The three soils had similar reactive Fe range compared to the forest soil reported by Zhao et al. [37] (up to 19.3 g kg⁻¹) and a lower range than that reported by Waigi et al. [8] (up to 180 g kg⁻¹). The cropland soil at both depths had the highest reactive Fe content while no differences in the amount of Fe-bound OC in three soils at 0–10 cm or 10–25 cm were found (Figure 1). This indicated that there were more Fe minerals that was not bounded with SOC in cropland soils at both depths. Huang et al. [27,29] reported that manure application increased total SOC content and reactive Fe content, such as less crystalline ferrihydrite. This may indicate limited influence of manure applications on increasing recalcitrant SOC bounded with crystalline Fe oxides that have a longer residence time [65]. Zong et al. [66] reported that tillage reduced most soil Fe/Al oxides at 0–150 cm, which can lead to potential SOC loss. The significantly higher reactive Fe content and lower content of Fe-bound OC in cropland soil may lead to a higher SOC mineralization and loss due to tillage which inverts deep soil SOC lacking of Fe/Al oxides protection to the surface [66]. This indicated other non-Fe oxides associated SOC play an important role in stabilizing SOC and contributed to the observed differences in Fe-bound OC percentage in soils with three management practices, for example, Al oxides [33,66]. However, we did not have data to confirm this in our study.

Amorphous Fe oxides are strongly associated with SOC [5,52,67] and contribute to 64% of SOC storage [33]. Similar to the trend of reactive Fe, microbially reducible Fe and exchangeable Fe in cropland soil at 0–10 cm or 10–25 cm had significantly higher amount than both forest and pasture soil at either depth (Table 2), which may be due to long-term manure application. This is consistent with Zhang et al. [28] who reported long term non-crystalline Fe increases due to long-term manure applications. Unlike Fe-bound OC, the forest and pasture soils at 0–10 cm had the highest amounts of released DOC during microbially reducible amorphous (0.63 and 0.57 g kg⁻¹, respectively) and exchangeable Fe extraction (0.37 and 0.42 g kg⁻¹, respectively) (Figure 3A; Table 2), which were significantly higher than the cropland soil at 0–10 cm (Table 2). Although these variations were observed,

a significantly positive linear relationship was found between the released DOC and Fe concentration across all land management practices ($R^2 = 0.54$, $p < 0.01$) (Figure 3). This is consistent with Kramer et al. [33] which reported the released DOC during extraction was linearly related to the amount of short range ordered Fe minerals.

Chemical retention of aromatic DOC by amorphous Fe contributes to long-term SOC storage, especially for subsurface soil [33]. In our study, the aromaticity of released DOC had a significantly positive relationship with amorphous and exchangeable Fe content ($r^2 = 0.89$, $p < 0.001$) (Figure 3B). These results were consistent with Kramer et al. [33]. This indicated amorphous Fe had similar roles in preserving aromatic DOC across different land management practices. Although forest and pasture soils released higher amounts of DOC during microbially reducible amorphous and exchangeable Fe, a higher aromaticity of released DOC stabilized by microbially reducible amorphous Fe was found in pasture and cropland soils than forest soil only at 0–10 cm (Figure 3B; Table 2). These results indicated that microbially reducible amorphous and exchangeable Fe oxides were more efficient in stabilizing aromatic DOC in the cropland soils than the forest and pasture soil. This may be due to manure application in cropland soil and grazing effects in pasture soil, which increase the hydrophobic aromatic DOC components [68]. The interactions of amorphous Fe and SOC may be promoted by manure application, or other non-sorptive mechanisms could be a reason for the low amounts of SOC associated with amorphous Fe oxides in cropland soil [29,69]. These differences suggested interactions between aromatic DOC and amorphous Fe differed at different depths in these three soils.

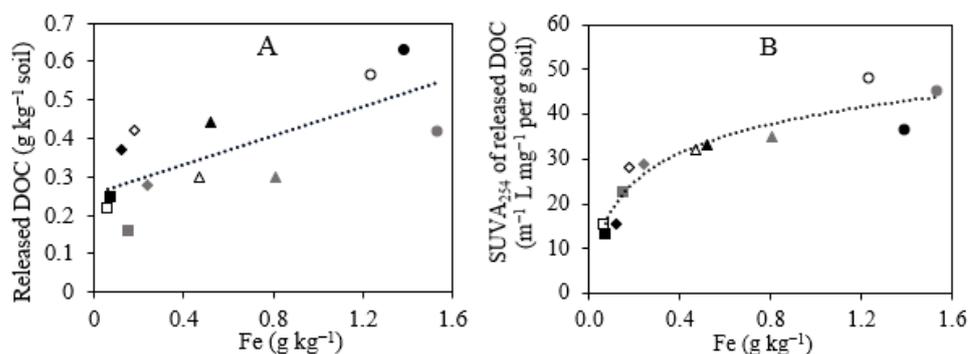


Figure 3. Regression relationship between the amount of released DOC (A) and SUVA₂₅₄ of DOC released (B) from soils after 0.5 N HCl at 0–10 cm (diamonds) and 10–25 cm (squares), 0.25 N HCl and 0.25 N NH₂OH-HCl extraction at 0–10 cm (circles) and 10–25 cm (triangles) in hardwood forest (black fill), cropland with manure (gray fill), and continuous pasture (no fill). Panel A: Released DOC (g kg^{-1} soil) = $0.19 \times \text{Fe (mg L}^{-1}) + 0.16$, $r^2 = 0.54$, $p < 0.01$; Panel B: SUVA₂₅₄ of released DOC ($\text{m}^{-1} \cdot \text{L mg}^{-1}$ per g soil) = $9.27 \times \ln(\text{Fe (mg L}^{-1})) + 39.84$, $r^2 = 0.89$, $p < 0.0001$.

4.2. Changes of DOC and Aromaticity of DOC during Sorption

The three land management practice soils had increasing sorption of DOC with increasing equilibrium concentration and a higher amount of DOC sorption at 10–25 cm than 0–10 cm (Figure 2 HF-a, CM-a, and CP-a). The desorption occurred at low equilibrium concentrations ($< 30 \text{ mg L}^{-1}$) of the cropland soil, pasture soil, and forest soil at 10–25 cm, while implied sorption and stabilization of DOC from soil solution only occurred at higher soil DOC concentrations. Overall, agricultural soils had a higher DOC sorption (Figure 2) and maximum capacity to sorb and stabilize DOC than the forest soil in this study (Table S3). The soil DOC is dynamically altered by a multitude of soil conditions, for example, the stabilization of DOC only occurs in conditions leading to high soil DOC production, like continuing flooding or wet-dry cycles [70]. This revealed that forest topsoil released DOC to solution, which could be leached and percolated to deep surface soil for sorption and stabilization (Figure 2 HF-a). Overall, agricultural soils had a higher maximum capacity to sorb and stabilize DOC than the forest in this study (Table S3), which was consistent with higher SUVA₂₅₄ of agricultural soils than forest soil (Table 3) [71]. This is consistent with

Wiesmeier et al. [19] who reported a higher SOC saturation in forest soil than crop and pasture soils and thus a higher potential of cropland and pasture to sequester more SOC. These differences could be also due to different soil mineralogy. For example, goethite was shown to preferentially retain aromatic OC while montmorillonite was shown to retain low molecular weight OC and no preference to aromatic OC [4]. In addition, the dissolved Fe and Al in the DOC solution added may influence the DOC sorption behavior in these different soils [72]. However, future study is still needed to confirm this.

The changes of aromaticity of DOC in the solution were significantly related to the equilibrium concentration (Figure 2 HF-b, CM-b, and CP-b; Table 3). Kramer, Sanderman, Chadwick, Chorover and Vitousek [33] reported a similar retention trend of aromatic DOC by short-ranged Fe minerals across all soil types. Rumpel et al. [73] found the main decomposed plant-derived OC (high aromaticity) in the topsoil layer and microbial-derived OC (low aromaticity) in the deep soil layer, which leads to different SOC stabilization processes. The observed different sorption trends at different land type soils at different depths may be due to different DOC sources [73].

Agricultural soils at 0–10 cm had positive ΔSUVA_{254} and thus showed desorption processes of aromatic DOC from soil mineral surface (Figure 2 CM-b and CP-b; Table 3). This is different from the majority of current studies that report preferential sorption of aromatic and phenolic moieties of DOC to soil or iron minerals when using exogenous DOC sources [12,14,33,74].

Sowers et al. [75] and Coward et al. [12] proposed a three-step sequential sorption processes of DOC (aromatic, lignin-like, and aliphatic compounds) on Fe oxyhydroxide and bacteriogenic Fe oxides within the first four hours of sorption. Surface exchange of DOC between mineral surface and solution still occurs beyond four hours, which may lead to mobilization of stabilized DOC [14,75]. The binding of aromatic and carboxyl moieties with soil minerals are typically irreversible by forming inner-sphere bonds, while outer-sphere bonding with carboxyl moieties are readily desorbed [14]. Our study indicated more reversible bonding with non-aromatic DOC might be the mechanisms occurring in agricultural topsoil, like multiple exchange processes [76]. Adhikari and Yang [77] found that stabilized aliphatic acid by hematite was more resistant than aromatic carbon during reduction release. This reveals that stabilization of non-aromatic DOC, like carboxyl-rich DOC, and reduction release of aromatic OC may be important pathways of SOC stabilization and destabilization in topsoil [10,12,75,78]. In addition, specific mineral composition as well as N enrichment to soils resulted in different retention mechanisms of SOC by minerals with different interactive zones [79]. This may explain different DOC sorption behavior in cropland and pasture soils compared to the forest soil in our study.

The pasture and cropland soils at 10–25 cm had negative ΔSUVA_{254} and showed sorption of aromatic DOC and decreasing sorption of aromatic DOC occurred with increasing DOC concentration (Figure 2 CM-b; Figure 2 CP-b; Table 3). This indicates more irreversible bonds with aromatic DOC were formed in agricultural soils at 10–25 cm, especially at lower equilibrium concentrations [76]. Unlike cropland soils with an aromatic sorption of the studied DOC concentration range (0–72 mg L⁻¹), the pasture soils reached a zero-net sorption of aromatic DOC. This may indicate that desorption processes of aromatic DOC occurs, which may reveal more complex processes between aromatic DOC and soil surfaces than reported interactions between Fe pure minerals and DOC [12,75].

Unlike the sorption pattern of the cropland and pasture soils at both 0–10 and 10–25 cm, forest soils had decreasing trends of ΔSUVA_{254} with increasing equilibrium concentrations (Figure 2 HF-b; Table 3). The 0–10 cm soil materials reached zero net sorption of aromatic DOC at high equilibrium DOC concentrations (Figure 2 HF-b). The 10–25 cm soils had net desorption of aromatic DOC at low equilibrium DOC concentration (<35 mg L⁻¹) and sorption of aromatic DOC at high equilibrium DOC concentration (35–72 mg L⁻¹) (Figure 2 HF-b). Confirmation of molecular level characteristics of sorbed or released DOC remains unclear, which are still in need for future research to uncover the reasons behind these trends in different land managed soils.

4.3. Implications for Land Use and Stabilization of DOC for Long-Term SOC Sequestration

Although most well documented studies had the role of amorphous Fe on aromatic DOC sorption and Fe oxides on SOC preservation in forest soils and marine sediments [6,19,37,64,69,78], we did not find direct and aligned evidences of significant influence of reactive Fe and amorphous Fe in increasing aromatic sorption in 0–10 cm or 10–25 cm soils of forest, pasture, and cropland. The three land managed soils had different sorption trends of aromatic DOC between the two agricultural soils (pasture and cropland) and the forest soil, as well as between agricultural soils from 0–10 cm and soils from 10–25 cm (Figure 2 HF-b, CM-b, CP-b). The stabilization of aromatic DOC was only enhanced in agricultural soils at 10–25 cm with low DOC concentration and in forest soils with high DOC concentration (Figure 2 HF-b, CM-b, CP-b). This indicated non-aromatic sorption might be a preference or desorption of aromatic OC from soil surfaces occurred in forest soil and agricultural soils at 0–10 cm at low soil DOC concentrations (Figure 2). Thus, a uncertainty exists regarding interactions of soil Fe minerals and DOC or aromatic DOC in different land managed soils at different depths and multiple factors may regulate DOC and aromatic DOC sorption processes, such as DOC composition [80], soil mineralogy [81], soil mineral surface chemistry [4], and structural features of soil aggregates [51]. Future studies are still necessary to uncover the influencing factor behind these phenomena.

Land types and management practices highly influence the quantity and quality of soil Fe minerals and DOC and also the conditions of transferring and transformation processes [36,82–85]. This causes more uncertainty in understanding Fe oxides and DOC interactions in agricultural soils with different land management practices, and points to a need for future studies using a wide range of agricultural soils. This study revealed important contributions of non-aromatic sorption to soil mineral surfaces in agricultural topsoil. This indicated the limitation of current generalized understanding of highly selected sorption of aromatic DOC to Fe oxides, which is still weakly supported by our studies using DOC from in situ soils and specifying the soils with different management practices at different depth.

Although Leinemann et al. [76], Lützow et al. [15], and Scott and Rothstein [74] proposed models that showed stepwise processes or several sorption mechanisms simultaneously occurring during sorption, our study indicated more specific context studies in different land soils and field studies deserve more efforts and should be the subject of future study [10,15,73,76]. Since cropland and pasture are two dominant land types in the world [86], it is essential to incorporate more studies in terms of the mechanisms of Fe oxides in stabilizing SOC, especially for both non-aromatic and aromatic DOC, to provide theories for appropriate management practices in agriculture and robust global C cycling models for C dynamics prediction.

5. Conclusions

Our study confirmed the different patterns of total reactive Fe, amorphous Fe, and exchangeable Fe in stabilization of SOC in both agricultural and forest soils. Although no significant differences in amount of Fe-bound OC among three soils at 0–10 cm or 10–25 cm, cropland soil at both depths showed significant higher reactive Fe, microbially reducible Fe, and exchangeable Fe than the forest and pasture soils at each depth. Forest and pasture soils showed higher DOC stabilized by microbially reducible Fe, and exchangeable Fe than the cropland soil at 0–10 cm.

Furthermore, a higher sorption of DOC in the cropland and pasture soils than the forest soil was observed. The sorption behaviors of aromatic DOC between the cropland and pasture soils were similar at both 0–10 cm and 10–25 cm, which were different from that of the forest soil. Unlike other studies, our study indicated the significant role of non-aromatic DOC in stabilizing DOC in the cropland and pasture soils at 0–10 cm. Additionally, this study indicated the native DOC concentrations significantly altered the sorption of aromatic and non-aromatic DOC. Overall, our study indicated agricultural soils may have a higher potential to stabilize SOC. However, the changes in the quality and quantity of

DOC due to various management practices may reshape SOC dynamics. The potential for these central Appalachian region soils to sequester carbon may be influenced by the quality and quantity of DOC and interactions between DOC and Fe minerals.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/environments9090113/s1>, Figure S1: The location of study site.; Table S1: The soil properties of in hardwood forest, cropland with manure application, and continuous pasture soils at 0–10 cm and 10–25 cm depth; Table S2. The estimated linear regression using the standard square least approach between total organic carbon, Fe-bound OC and reactive Fe and the combined silt and clay content in in hardwood forest, cropland with manure application, and continuous pasture soils at 0–10 cm and 10–25 cm depth; Table S3. The adsorption characteristics of three land type soils at 0–10 cm and 10–25 cm depths. References [87–95] are cited in the supplementary materials.

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