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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.

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Study Site Description

Forest, grassland and cropland were chosen as three representative land-use types. The forest was composed of mixed deciduous hardwood (HF) trees which were approximately 120 years old. The dominant tree species included white oak (Quercus alba), northern red oak (*Quercus rubra*), yellow poplar (*Liriodendron tulipifera*), white ash (*Fraxinus americana*), and hickory (*Carya tomentosa*) [87]. The permeant grassland was continuously grazed (CG) with 0.5–0.75 dry dairy cows or/and heifers per hectare for 20 years. The dominant vegetation species included red clover (*Trifolium pretense*), white clover (*Trifolium repens*), ironweed (*Vernonia baldwinii*), smartweed (*Polygonum pensylvanica*), horsenettle (*Solanum carolinense*), kentucky bluegrass (*Poa pratensis*), and timothy (*Phleum pretense*). The cropland was a continuous corn (*Zea mays*) field with manure application (CM). Composted dairy manure had been incorporated at a rate of 2700 to 3600 kg dry matter per hectare each year for at least 20 years. Additional 100 kg urea per hectare was applied to corn at a 0.2–0.5-meter stage of growth. Winter wheat was planted as a cover crop after the corn was harvested. Before conversion to cropland and pasture, vegetation would have been typical for their landscape positions.

Soil Physical and Chemical Analysis

Fresh soil subsamples were air dried at room temperature, ground and sieved through a 2 mm sieve. Soil pH and electtrical conductivity (EC) were determined using a 1:1 (m:V) dry soil to distilled water ratio using the Mettler Toledo SevenCompact pH and electrical conductivity meter (Columbus, OH). Bulk density (BD) at the field site at depths of 10 cm and 10–25 cm was determined by taking three core samples (5 cm) in diameter from each plot, so twelve core samples were taken for each land use type. Soil particle size distribution was determined using methods described by Kettler et al. [88] Mehlich 3 extractable phosphorus (P), potassium (K), calcium (Ca), and magnesium (Mg) were determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES) (Waltham, MA) [89]. The physical and chemical properties were determined using the air-dried soil samples and are presented in Table 1. Another batch of fresh soil subsamples were sieved through a 2 mm sieve and stored at 4 °C until analysis within three days.

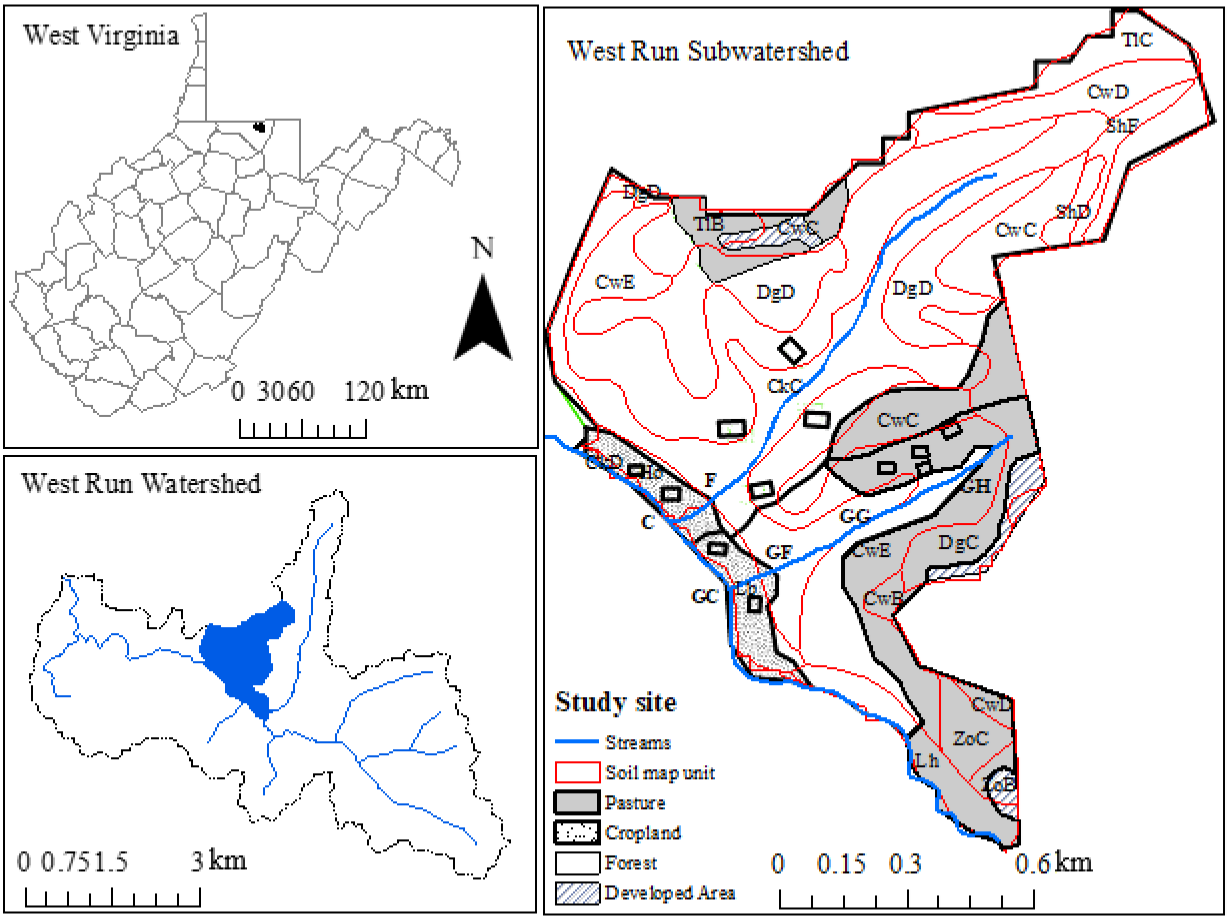

Figure S1. The location of study site. The rectangles represented 10 m × 10 m sampling plots (not to scale). The black dot in the West Virginia (WV) map at the bottom represented West Run watershed.

Table S1. The soil properties of in hardwood forest (HF), cropland with manure application (CM), and continuous pasture (CP) soils at 0–10 cm and 10–25 cm depth.

	Forest (HF)		**Cropland (CM)**		**Pasture (CP)**	
	0–10 cm	**10–25 cm**	**0–10 cm**	**10–25 cm**	**0–10 cm**	**10–25 cm**
pH	5.3	4.8	7	6.3	5.5	5.8
EC (μs cm^{-1})	134.4	59.9	260.5	152.6	194.2	103.3
Total N (g kg^{-1})	3.4	1.1	2.7	1.5	4.1	1.0
Total C (g kg^{-1})	41.4	12.8	32.3	20.8	40.4	10.3
Exchange Ca (mg kg^{-1})	912.3	154.2	2856	1450.5	1246.0	587.5
Exchange Mg (mg kg^{-1})	121.7	40.1	250.9	159.0	141.6	84.2
Exchange K (mg kg^{-1})	114.6	55.8	201.5	53.7	241.9	121.5
Exchange P (mg kg^{-1})	22.4	8.3	42.5	8.1	49.3	9.8
Bulk density (Mg m^{-3})	1.08	1.3	1.38	1.53	1.46	1.67
Sand (%)	36.0%	26.9%	33.3%	35.1%	44.7%	35.6%
Silt (%)	53.6%	57.6%	51.4%	49.1%	45.7%	52.3%
Clay (%)	10.4%	15.5%	15.3%	15.8%	9.6%	12.1%

Effects of Soil Texture on TOC, Fe-bound OC in Proportion, and Reactive Fe

Although soil texture is an important factor influencing SOC dynamics, we didn't find significant relationships between the combined silt and clay content and TOC, reactive Fe, and Fe-bound OC in proportion in soil ($p > 0.05$) (Table S2). It has been reported that SOC is significantly linearly correlated with the combined silt and clay content in soils with similar climates, vegetation, and topography at 0–1 m depth [90,91]. Increasing clay content increases the stability and decreases the mineralization of sensitive SOC fractions, such as particulate SOC [92]. However, Hassink [93] only observed this relationship in soil with a high water table [93]. This relationship was also shown to be different between the forest and cropland soils [94]. Other studies reported weak or no relationship between SOC and soil texture [93,95]. Our results indicated that soil texture didn't have significant influences on the TOC content and Fe oxides in the soils with different land management practices in our study. This may be due to the soils in this study being derived from the same source parent material and having similar climate and topology conditions.

Table S2. The estimated linear regression using the standard square least approach between total organic carbon (TOC), Fe-bound OC and reactive Fe and the combined silt and clay content in hardwood forest (HF), cropland with manure application (CM), and continuous pasture (CP) soils at 0–10 cm and 10–25 cm depth.

Investigator factor	Model equation	r^2	p
TOC	TOC = 0.25 (silt + clay) + 0.15	0.31	0.25
Fe-bound OC	Fe-bound OC = 0.57 (silt + clay) + 0.71	0.09	0.56
Reactive Fe	Reactive Fe = 0.44 (silt + clay) + 0.93	0.15	0.44

Table S3. The adsorption characteristics of three land type soils at 0–10 cm and 10–25 cm depths.

Parameters	Forest		Cropland		Grassland	
	0–10 cm	10–25 cm	0–10 cm	10–25 cm	0–10 cm	10–25 cm
Q_{max} (mg kg^{-1})	518	1685	1159	3203	1631	2638
k (L mg^{-1})	0.0029	0.0024	0.0018	0.0073	0.0039	0.0025
b (mg kg^{-1})	219	148	148	81	139	84
RMSE	3.6	8.2	7.8	3.2	5.6	7.3

Modified Langmuir isotherm (Equation 1) was used to describe the DOC sorption. The maximum adsorption capacity (Q_{max}) and binding affinity (b) were obtained to compare the sorption characteristics of three land types. The crop land soil at 0–10 cm had the highest Q_{max} (3203 mg kg^{-1}) while forest soil at 0–10 cm had the lowest Q_{max} (518 mg kg^{-1}). The forest and pasture soils had higher Q_{max} (forest: 1685 mg kg^{-1}; pasture: 2638 mg kg^{-1}) at 10–25 cm than the soils at 0–10 cm (forest: 518 mg kg^{-1}; pasture: 1631 mg kg^{-1}). The cropland had the opposite trend. The two highest adsorption affinity, k, was found in crop land soil at 10–25 cm (0.0073 mg L^{-1}) and grassland soil at 0–10 cm (0.0039 mg L^{-1}) while the lowest k was in cropland soil at 0–10 cm (0.0018 mg L^{-1}).

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