INVESTIGATING GEOCHEMICAL FACTORS ASSOCIATED WITH CARBON STORAGE IN SOILS OF OKLAHOMA

By

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Abstract: In the realm of both soil science and environmental science, controls on soil carbon sequestration are of interest to both scientists and citizens. Increasing soil carbon sequestration garners significant attention for its ability to mitigate climate change and ensure a sustainable future. However, there remains substantial gaps in the literature and current knowledge about the controls on soil organic matter (SOM) dynamics across time and climactic regimes. An understanding of the factors associated with SOM informs soil carbon models and the best practices for preserving and increasing carbon storage in the long-term. Further investigation into the geochemical controls of SOM dynamics in surface and subsurface soils could close these gaps. Current research points to discrepancy in the accumulation of SOM in surface and subsurface soils. This project delved into this discrepancy by examining the mechanisms underlying carbon storage across a range of soil types with the express intent of uncovering its controls. By using archived and collected soils from across a range of sites in Oklahoma, new analyses revealed where the SOM resides, how different metal phases interact with SOM formation, and theories for what drives the discrepancy observed in other studies. To accomplish this goal, the soils were fractionated into mineral-associated organic matter (MAOM) and particulate organic matter (POM) and tested for total organic carbon (TOC) concentration. In addition, whole soil samples were analyzed for iron, aluminum, magnesium, and calcium metal concentrations for extractable short-range order (SRO) minerals and organo-mineral complexes. These analyses showed a significant difference in TOC between fractions and different soil orders. Additionally, almost every metal phase had significant differences between soil orders and with pH. When fraction TOC data and metal phases are compared by acidic and basic soils, a significant correlation was found between TOC and iron and aluminum within SRO minerals in acidic soils as well as magnesium in organo-metal complexes in basic soils. As SRO iron and aluminum increase, TOC increases in acidic soils. Contrastingly, TOC decreases as magnesium in organo-metal complexes increase in basic soils. Clay, usually considered a predictor of TOC, had no correlation. Further studies could explore these relationships.

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CHAPTER I

LITERATURE REVIEW

Soil conservation and soil health have been at the forefront of the minds of land managers since the dust bowl of the 1930s. This holds especially true with current estimates placing soil as a key sink for atmospheric carbon dioxide to mitigate the increasing effects of climate change (IPCC, 2022). Under natural processes, the carbon cycling from the atmosphere to plants to soil and back to the atmosphere would be balanced and lead to stable carbon concentrations. However, humankind has upset the balance through land use change, urban sprawl, and agricultural intensification, resulting in high, unprecedented levels of greenhouse gases like CO_2 , CH_4 , and nitrous oxides in the atmosphere (IPCC, 2022). These gases contribute to global climate change, causing the Earth to warm, intensifying weather systems, and raising the sea level. With greenhouse gases expected to continue rising, it is critical to understand different ways we can mitigate or slow the release of these increasing gases. Carbon sequestration provides one way of doing this through the formation and retention of soil carbon (Paul et al., 2020; Sokol et al., 2022). When plants and animals die, their decomposing residues contribute to soil carbon. Since plant and animal residues can remain in soil for long periods of time due to climate, biological, and chemical factors, soil carbon mitigates climate change by sequestering and stabilizing carbon that would otherwise return to the atmosphere as CO₂ ("Soil-Based Carbon Sequestration | MIT Climate Portal," 2021). Understanding the various controls on this process is vital for climate change mitigation.

It follows that we want to both increase and retain the organic carbon stored in soil. Several factors influence how long soil organic carbon (SOC) remains in the soil, including soil pH, soil moisture content, soil temperature, mineralogy, clay content, and dominant metal phases (Lawrence et al., 2015; Viscarra Rossel et al., 2019; Wang et al., 2019; Wiesmeier et al., 2019).

Soil organisms use SOC to provide energy for their cellular and systemic functions. Soil moisture is required for these processes to occur to facilitate microbial and enzymatic activity. In semiarid to arid ecosystems, soil moisture is the limiting factor in microbial breakdown and functioning, whereas limiting nutrients such as nitrogen or phosphorus regulate functioning in other environments (Cui et al., 2020; Schimel, 2018). Soil moisture also modifies the geochemical environment through weathering rates and nutrient cycling (Schwertmann, 1988; Zamanian et al., 2016). Since these minerals and metal phases can bind with SOC, soil moisture plays a role in how much SOC can be stored and for how long. The ability of plants to grow and contribute biomass inputs into the soil that then become SOC is affected by soil moisture as well (Cui et al., 2020). Lack of moisture in the soil restricts plant inputs due to stress and other physiochemical factors that limit plant growth, reducing SOC formation. Additionally, a recent study of Oklahoma soils found that soil moisture had the strongest relationship with SOC when considering sand content, clay content, bulk density, mean annual precipitation, mean air temperature, and mean soil moisture (Kerr and Ochsner, 2020). These findings shows that soil moisture should be considered when examining SOC.

SOC doesn't reside in the soil equally; some remains stored by the soil for years to decades, while the rest only remains stored for minutes to days. As such, examining SOC based on its relative persistence or lability allows for better informed predictions and understanding of SOC storage (Fox et al., 2017; Moni et al., 2012; Poeplau et al., 2018). Sorting soil based on particle size and density allows for an operational differentiation of the persistent and labile portions of SOC. While there is much contention regarding how to characterize SOC (Lavallee et al., 2020; Poeplau et al.,

2018), many scientists agree one way to further characterize soil organic matter (SOM) is using particle size to divide it into mineral-associated organic matter (MAOM) and particulate organic matter (POM) fractions (Lavallee et al., 2020; Moni et al., 2012).

This new paradigm describes POM as relatively undecomposed, lightweight fragments of plant-and fungal-derived materials. POM has larger particle sizes (anything greater than 53µm) than MAOM and thus includes sand-sized, partially decomposed plant-material. MAOM consists of single molecules or microscopic fragments of organic materials that either leached directly from plant materials or have undergone chemical transformation by the soil biota prior to binding to mineral surfaces (Keiluweit et al., 2015; Kleber et al., 2021). In this case, mineral refers to silt- and clay-sized particles. MAOM is usually smaller, denser, and more water-soluble compared to POM (Lavallee et al., 2020).

The main difference between these two groups lies in the level of protection each fraction has from decomposition. MAOM is protected from decomposition by the mineral associations it forms. These associations include occlusions in fine aggregates, organo-mineral clusters, and sorption to mineral surfaces. However, POM is not protected by such associations and is thus more available for microbial decomposition (Lavallee et al., 2020). MAOM generally has a lower C/N ratio that provides more nutrients for microbes and requires less energy to utilize when destabilized, while POM has a higher C/N ratio for microbes but is physically more accessible to decomposition by soil organisms. Based on these characteristics, POM belongs to a more labile pool of soil C whereas MAOM has a much longer residence time and belongs to a much more stable pool of soil C (Lavallee et al., 2020).

The difference between POM and MAOM provides a much more detailed look at SOC storage and potential turnover than simply measuring total organic carbon (TOC) of the whole soil profile. The whole soil simply portrays the amount of carbon within the soil while fractionating

allows scientists to examine how much of it is more likely to be stored in the long-term and which will only remain in the soil short-term. Studies show the majority of SOC resides in MAOM, as expected due to protection provided by mineral-organic associations (Keiluweit et al., 2015; Kleber et al., 2021; Schweizer et al., 2021), which begs the question of how to increase the formation of MAOM to lead to more long-term SOC.

The emphasis on the mechanisms of carbon stabilization challenges the previously held paradigm regarding SOC, which posits that SOC inherits its recalcitrance from litter inputs and gains protection from decomposition based on how much energy it takes for microbes to break it down. Litter inputs with high C/N ratios, such as lignin, take longer to decompose and were considered the main precursor to stable, recalcitrant organic matter, commonly referred to as humus (Andreux, 1996). The lower the C/N ratio, the less resistant to decomposition the humus. However, recent studies show the "humification" process does not work as previously thought by the older paradigm (Kleber et al., 2021; Lavallee et al., 2020). Instead of litter inputs driving the persistence of organic matter, experiments show the minerals and associations with other colloids within soil contribute to the persistence of SOC (Kleber et al., 2021; Rasmussen et al., 2018). As such, there is increasing interest in the mineralogy and metal phases present in the soil and a shift away from humification as the main control on SOC storage.

Certain parameters such as soil pH, moisture content, and dominant metal phases are important controls of SOC storage and require consideration before measuring SOC. Most researchers rely on clay content as the predominant way of predicting soil carbon since the two are thought to correlate well (Schweizer et al., 2021). Since clays are much smaller in size than other soil particles and naturally have charge, they provide exponentially more surface area per bulk volume for SOC to bond to the soil surface and act as a reactive exchange site for other nutrients (Barton and Karathanasis, 2002; Goldberg, 2008; Schweizer et al., 2021). Most SOC compounds and nutrients have charge and thus are attracted to clays as well. Charged functional groups in organic matter associate with the surface of the clays to form chemical bonds that retain the nutrients and SOC, preventing their loss by decomposition from microbes.

Furthermore, different clay types or mineralogy significantly affect the reactivity of the soil. Clays are composed of layers made up by sheets. Sheets are interlocking layers of different elements such as SiO₄ or AlO₄ (Andreux, 1996; Barton and Karathanasis, 2002; Schwertmann, 1988). The composition and arrangement of these sheets is a product of long-term weathering processes. Sheets are arranged in variable ways to form layers that differ in surface charge properties. Layers that combine in certain ratios determine the type of clay formed as well as its behavior in soil. For example, 1:1 clays have a tetrahedral layer bonded to an octahedral layer and include specific minerals such as kaolinite. Clays with one octahedral layer sandwiched between two tetrahedral layers are considered 2:1 clays and include minerals like vermiculite and illite (Barton and Karathanasis, 2002). Clays with a 2:1 composition are typically able to expand due to their structure and can thus increase the surface area available to bond with nutrients and SOC within the soil. As such, clay content and dominant mineralogy were used by scientists for years as an estimator of SOC concentration, but clay content may not provide the best predictions of SOC.

For example, calcium carbonates and iron- and aluminum-oxyhydroxides play a large role in the storage and retention of SOC and other nutrients (Korzekwa, 2022; Rasmussen et al., 2018; Wagai et al., 2013). The abundance of these naturally occurring metal phases depends on the soil pH, soil moisture content, and parent material of the soil. These metal oxides can form in soil through a variety of ways. Wind and dry conditions usually lead to deposits of carbonates over time that accumulate and can move throughout the soil profile depending on the moisture content. Plants can also bring up carbonates through water and capillary action so they will accumulate along root channels and other connecting tunnels in the soil (Zamanian et al., 2016). Iron- and aluminumoxyhydroxides usually accumulate within soil as a product of long-term weathering processes that act upon residual iron- and aluminum-containing rocks and minerals (Schwertmann, 1988). Although clay can predict SOC concentration to an extent, exchangeable calcium is often a better predictor for soil carbon in water-limited, alkaline soils, whereas iron- and aluminumoxyhydroxides emerged as better predictors with increasing moisture availability and acidity (Rasmussen et al., 2018). Due to the reactivity and dominance of these metal oxides within soil, they can have disproportionate influence over SOC accumulation. The bonding process works similarly to clays in that most metals have a charged surface for SOC to bond (Barton and Karathanasis, 2002). The strength of the bond depends on many factors such as soil pH and soil moisture. When soils are dry and have a high pH, calcium carbonates tend to accumulate in the soil and dominate the metal phases otherwise present (Zamanian et al., 2016). As a result, SOC can be directly correlated with the exchangeable calcium. On the contrary, when the soil contains more moisture and has a lower pH, iron- and aluminum-oxyhydroxides dominate and the majority of SOC will bond with these metals instead (Goldberg, 2008; Schwertmann, 1988).

Metal phases can also affect the decomposition and mineralization of SOM. In particular, iron and aluminum hydroxides in soils provide significant support for SOM stabilization. By binding to metal hydroxides, SOM has protection from microbial decomposition and can thus remain in soil for longer periods of time (Wagai et al., 2013). To determine the exact nature of organo-mineral and organo-metal complexes in the soil samples, selective dissolutions or sequential extractions separate three different metal phases present: freely available metals, acid soluble and exchangeable metals, and metals associated with short-range order (SRO) minerals (i.e., poorly crystalline and amorphous minerals). Most SOC resides within the last two phases extracted, but a more complete picture of the mineral and metal proportions will better inform the conclusions drawn from this data (Fox et al., 2017; Heckman et al., 2018; Rao et al., 2008; Voelz et al., 2019).

One study using Oklahoma soils found that while SOC storage did not change over time on the whole soil profile basis, SOC concentrations increased near the surface and decreased at depth (Kerr, 2019). Another study in Oregon reports similar trends as above but with no losses in the subsoil (Sartori et al., 2007). Furthermore, a study in South Carolina found a similar trend for another long-term study with increases of SOC in the surface due to POM, but losses in subsoils from MAOM (Mobley et al., 2015). Since metal oxides can effectively bond with SOM to form MAOM and are typically leached down through the soil profile, investigating their concentrations in surface and subsoils would provide valuable insight into the behavior of SOC as well.

CHAPTER II

GEOCHEMICAL FACTORS ASSOCIATED WITH CARBON STORAGE

Introduction and Background

Our climate is rapidly changing, causing significant alteration to the environment with disastrous consequences for humankind (IPCC, 2022). Humanity can mitigate and decrease these effects through various methods, one of which is carbon sequestration. By increasing the amount of carbon stored and retained in the soil, soil organic carbon (SOC) sequestration can decrease the amount of CO₂ entering the atmosphere ("Soil-Based Carbon Sequestration | MIT Climate Portal," 2021). However, there is a gap in the literature concerning the factors that influence SOC dynamics in surface and subsurface soils and how SOC storage is affected over time. To accurately predict SOC storage over time, we need to better understand the distribution of SOC across functionally distinct pools and investigate the role of organo-mineral complexes in surface and subsoils.

Examining SOC in terms of its stabilization mechanisms allowed for more nuanced insight compared to whole soil analyses. I examined the geochemical controls on soil organic matter (SOM) storage and concentration in soils collected from Oklahoma Mesonet sites, a state-wide environmental monitoring network (McPherson et al., 2007). These soils span a wide gradient of precipitation (17-56" or 43-142 cm annually), temperature (56-63°F or 13-17°C annually), and soil types, providing a unique opportunity to test the geochemical factors associated with SOM.

Although these soils have remained relatively undisturbed for a period of ~26 years due to Mesonet site requirements, research indicates a marked increase in SOC over time at the 5 cm depth with a decrease of SOC over time below that depth (Kerr, 2019). Further research into this finding unveiled more studies with similar results. One of the first studies to report this result looked at various studies across the US Midwest and found no increase in SOC below 30 cm (Baker et al., 2006). Another study in Oregon found no significant increases in soil C despite marked increases of surface C (Sartori et al., 2007). A study in South Carolina observed the same decrease of SOC in subsoils, but an increase in surface layers. Interestingly, this study also noted the loss was largely from mineral-associated SOM while the surface accumulations were from labile SOM (Mobley et al., 2015).

The above studies sparked an interest in uncovering the reason for loss of SOC at depth despite an increase at the surface. Investigating the geochemical controls associated with SOC storage at depth fills in some of the gaps related to SOC dynamics and behaviors. The first objective of this project was to examine archived soils from 120 Mesonet sites to determine the distribution of SOC across particulate organic matter (POM) and mineral-associated organic matter (MAOM) fractions from 3-50 cm depths to gain more nuanced insight into SOC distribution with depth. The second objective was to explore the relationships between metal oxides and potential SOC storage.

It is expected the geochemical properties related to mineral composition will influence the SOC distribution across SOM fractions and concentrations within the whole soil. Specifically, it is hypothesized that higher concentrations of metal oxides will be associated with more SOC and MAOM within the soil profile. Furthermore, it is hypothesized that the dominant effect on SOM stability will be the amount and type of metal phases present and that this effect will depend on the pH.

Methods and Materials

Sample and Site Description: Samples used for analysis consist of previously collected and dried soil samples archived at Oklahoma State University. These soils were collected from 2009-2010 using 5 depth intervals (cm): 3-10, 20-30, 30-40, 55-65, and 70-80. Such variable depths allowed for differentiation between the surface and subsoil SOM data. However, only the top three depth intervals were selected based on soil sample availability. Following testing procedures for soil physical properties, the samples were oven-dried at 105°C for 24 hours then stored for archival purposes in closed containers in folded envelopes. Sites were selected so that multiple soil orders were represented and consisted of the following: four Inceptisols, nine Mollisols, seven Alfisols, and two Ultisols. The number of sites varied depending on how much soil remained of the originally collected samples. Figure 1 shows the locations of the selected sites and their corresponding soil order for reference.



Figure 1. A map of Oklahoma showing the location of selected Mesonet sites. The site pins are color coded based on the soil order of that particular site.

Station ID	Name	N Latitude (°)	E Longitude (°)	Climate	Mean Annual	Mean Air	pН	Soil
				Division	Precipitation (cm)	Temperature (°C)		Order
ARNE	Arnett	36.07204	-99.90308	Panhandle	58.69	14.62	8.113	Inceptisol
BROK	Broken Bow	34.0433	-94.6244	Southeast	126.97	16.46	6.198	Ultisol
BUFF	Buffalo	36.83129	-99.64101	Panhandle	58.24	14.82	7.749	Mollisol
BUTL	Butler	35.5915	-99.27059	West Central	73.19	15.52	8.078	Inceptisol
CAMA	Camargo	36.02866	-99.34652	West Central	63.27	14.71	7.811	Inceptisol
CARL	Lake Carl Blackwell	36.1473	-97.28585	Central	90.40	15.65	5.902	Mollisol
CENT	Centrahoma	34.60896	-96.33309	South Central	102.10	16.35	6.957	Mollisol
CHEY	Cheyenne	35.54615	-99.7279	West Central	76.74	15.15	7.170	Alfisol
COPA	Copan	36.90987	-95.88553	Northeast	98.28	14.85	6.296	Mollisol
FAIR	Fairview	36.26353	-98.49766	North Central	74.22	15.56	7.447	Mollisol
FORA	Foraker	36.84053	-96.42777	Northeast	97.57	14.37	5.787	Mollisol
FTCB	Fort Cobb	35.14887	-98.46607	Southwest	73.23	15.90	6.679	Alfisol
GRA2	Grandfield	34.239444	-98.743583	Southwest	73.74	17.26	8.521	Mollisol
HASK	Haskell	35.74798	-95.64047	East Central	108.12	15.76	6.434	Alfisol
HINT	Hinton	35.48439	-98.48151	Southwest	80.68	15.37	6.499	Inceptisol
IDAB	Idabel	33.83013	-94.8803	Southeast	116.46	17.22	6.976	Alfisol
JAYX	Jay	36.4821	-94.78287	Northeast	112.67	14.80	4.971	Ultisol
SKIA	Skiatook	36.4153	-96.03706	Northeast	104.30	15.44	5.762	Alfisol
STIG	Stigler	35.26527	-95.18116	East Central	108.14	16.02	6.013	Alfisol
STIL	Stillwater	36.12093	-97.09527	Central	90.63	15.69	5.809	Mollisol
WATO	Watonga	35.84185	-98.52615	West Central	78.82	15.31	6.818	Mollisol
WILB	Wilburton	34.90092	-95.34805	Southeast	110.89	16.45	5.702	Alfisol

Table 1. Mesonet site location description. Mean annual precipitation and air temperature calculated based on averages from 1994-2010. pH measured from soils collected in 2009 and 2010. Information on station IDs, names, coordinates, and climate gathered from Mesonet.org. Soil orders determined using Web Soil Survey (NRCS).

Oklahoma Mesonet sites are required to maintain a specified level of vegetation, though the type of vegetation is not as strictly enforced. The area immediately surrounding the site should be as flat as possible and have a uniform low-cover vegetation with no bare soil visible except over the bare soil measurement area. These sites should also be in rural areas and as far away as possible from irrigated areas, lakes, and forests (McPherson et al., 2007). The goal for the site locations is to be representative of as large an area as possible. While not all sites meet these criteria for particularly forested, urban, or hilly regions of Oklahoma, most site vegetation is dominated by grasses such as bluestem species and Bermudagrass (The Great Plains Flora Association, 1986).

Fractionation and Acid Fumigation Process: Archived Mesonet soil samples were analyzed by determining the composition of POM and MAOM as well as the phases of metals present in the soil samples. By first determining the soil orders represented in the archived Mesonet samples and separating them further by climate regime to ensure a diverse sample set, samples were collected from as many different sites as possible from each of the soil orders represented.

Many methods exist for fractionating soil into POM and MAOM. I used the method derived from Cambardella and Elliott (1993) along with Gale and Cambardella (2000) and is described in brief detail in the following paragraph. First, the soil is sieved using a 2-mm mesh sieve then oven dried to remove water weight. 10 ± 0.1 g of dry soil is then weighed into a 50 mL centrifuge tube and shaken overnight with 30 mL of 0.5% sodium hexametaphosphate. Using an automatic wet sieve shaker with a 53-µm sieve, the soil suspension is then sieved. The suspended soils that pass through the sieve are collected in 500 mL centrifuge bottles and centrifuged to assist in the retrieval of the MAOM soil pellet. Once centrifuged, the soil pellet is transferred to a clean, pre-weighed and labelled aluminum drying pan using a squirt bottle of DI water. The POM soils retained on the 53-µm sieve were similarly transferred to separate drying pans. Both sets of pans were placed in an oven set at 105°C no longer than 24 hours to evaporate the water. After reaching a constant weight, the pans were weighed to calculate the amount of soil collected and the dried soils were ground and then stored until further analysis. Each fraction was tested for TC and TN content by dry combustion analysis (LECO) following methods derived from Schulte and Hopkins (2015). Approximately 200 ± 1 mg of ground soil is added to a small tin foil square and the actual weight is recorded for calculations. The squares are then sealed and placed in 96-well plates for analysis.

The above process was followed for all samples, but some samples contained a significant amount of inorganic carbon in the form of carbonates. Acid fumigation was necessary for samples above 7.2 pH to neutralize the carbonates and determine only organic carbon content of the samples. A modified method was followed based on procedures described by Dhillon et al. (2015) and Harris et al. (2001). All samples were fractionated and prepared the same way, except an additional procedure was followed for high pH samples. Instead of using tin foil squares, additional sample was weighed into silver weigh capsules to 200 ± 1 mg and left open in a desiccator. Approximately 0.8 mL of DI water was added to each capsule to saturate the soil to allow for increased efficiency of carbonate removal. A 150 mL beaker with 100 mL of 12M HCl was placed in the desiccator with the samples once they were all weighed out. The HCl fumes were then allowed to permeate the samples for no longer than 24 hours to remove the carbonates. After the fumigation, the beaker was removed and the desiccator ventilated for 15 minutes to remove excess HCl vapors from the samples. The well plates then went into a forced air convection oven at 50°C for 4 hours to evaporate most of the remaining HCl residues. After the 4-hour drying period, the samples were transferred to small aluminum weigh boats labelled with the corresponding sample number and placed into a gravity convection oven at 105°C for 16 hours to completely dry the samples and prevent sample loss from forced air convection. Once dried, the samples were carefully wrapped in a tin foil square to prevent any soil loss and analyzed for TC and TN content as previously described. The resulting content represents the organic carbon content and could then be used to calculate the amount of inorganic carbon by subtracting the TC of the fumigated sample from the TC of the unfumigated sample.

Carbon values were represented in a few ways. The whole soil organic carbon content, referred to as SOC%, was used from prior analyses to track whole-soil trends. Measured TC values were used to compare the organic carbon content of the fractions themselves, which were referred to as either MAOM-C% or POM-C%. Measured values of TC or TN (MAOM-C% or POM-C%) were converted from the percent C found in the combusted sample to the mass of fraction-C found for the whole soil sample. I refer to this calculated value as the concentration of MAOM-C or POM-C. It represents the quantity of carbon each fraction contributes to the soil as a whole. The following equation was used for this conversion, where g fraction C/100g fraction represents the percent C resulting from combustion analysis, 100g fraction/g fraction represents the conversion from a percent, g fraction/g soil represents the recovered fraction mass or mass distribution of recovered fractions, and 1,000mg fraction/g fraction represents the conversion from g fraction to mg fraction:

$$\frac{g \ fraction \ C}{100g \ fraction} \times \frac{100g \ fraction}{g \ fraction} \times \frac{g \ fraction}{g \ soil} \times \frac{1,000mg \ fraction}{g \ fraction} = \frac{mg \ fraction \ C}{g \ soil}$$

Metal Extractions: Naturally occurring metal phases within the samples were measured by selective dissolution with two different metal extractant solutions. Sodium pyrophosphate (referred to as NaPP hereafter) was used to extract the organo-metal complexes, while ammonium oxalate (referred to as AOX hereafter) extracted short-range order (SRO) minerals (i.e., poorly crystalline and amorphous minerals). Based on prior procedures used by Heckman et al. (2018) as well as Shang and Zelazny (2015), these metal extractions selectively dissolved metal phases present within the soil samples to determine the proportion of metals. An inductively coupled plasma optical emission spectrometer (ICP-OES) analysis was used to determine the composition of the samples.

Briefly, the procedure for extracting organo-metal complexes with NaPP was followed according to a modified method based on Shang and Zelazny (2015). We began by preparing the

soil as per usual with oven drying and sieving then weighing triplicates of 300 ± 1 mg into a labelled 50 mL centrifuge tube. The exact weight was recorded then 30 mL of 0.1M NaPP adjusted to 10 pH was added to the vials. Immediately after adding the NaPP, the vials were covered in aluminum foil to block out sunlight as this can interfere with the photo-redox reaction and overestimate the amount of Fe bound to OM. The covered vial is then shaken on low for 16 hours and centrifuged after this period. The resulting supernatant is diluted by placing 20mL into a polypropylene syringe and filtering with a 0.22-µm filter tip into a clean new container then raising it to 50 mL with DI water. Lastly, the 2.5X dilution was analyzed by the ICP-OES (Spectro) for the concentration of Fe, Al, Si, Ca, Mg, and Mn, while the remaining portion was later analyzed by a liquid TOC analyzer (Elementar) for TC/TN.

The procedure for AOX was similarly followed except triplicates were weighed to 200 ± 1 mg of dried soil and 40 mL of 0.2M AOX adjusted to 3 pH was used. Moreover, the samples were only shaken for 2 hours and were not analyzed for TC/TN using the TOC due to AOX containing both C and N which would contaminate the measured values. Concentrations of Ca and Mg were not usable for this extraction due to the formation of insoluble precipitates in the presence of oxalate (Wagai et al., 2011).

Both metal extraction concentrations were calculated the same way. Since the ICP-OES returned values in mg metal/L solution, the concentrations were converted to mg metal/g soil for easier comparisons with the last step multiplying by the dilution factor (usually 2.5X). The following equation was used for this conversion:

$$\frac{mg \text{ metal}}{L \text{ solution}} \times \frac{\text{solution used in } L}{\text{soil used in } g} \times \frac{f \text{ inal volume in } mL}{\text{initial volume in } mL} = \frac{mg \text{ metal}}{g \text{ soil}}$$

Statistical Analysis: RStudio (4.2.1) and other analytical software such as Excel or JMP were used for statistical analyses. ANOVA and Tukey HSD tests for unbalanced replications were used to test

for statistically different results at α =0.05. Due to the uneven distribution of the data, Spearman's rank correlation coefficient analysis was used to test for significant correlations between variables instead of Pearson correlation analysis. RStudio was used to create the figures and ArcGIS Pro 2.8.2 was used to create the map.

Results

Fractionations: The fraction data revealed MAOM contains more SOM and more mass overall than POM. Additionally, Mollisols and Alfisols contained more SOM, specifically MAOM, than Inceptisols and Ultisols. The mass distribution and MAOM-C concentration (mg fraction C/g soil) were both significantly different between fractions and were still significantly different even when splitting by soil order, except for Inceptisols, or depth. However, significant differences were only detected in Mollisols and Ultisols when splitting both by fractions and soil orders for SOC% and MAOM-C%. Within the fractions themselves, Tukey HSD tests found no significant differences in POM-C% or concentrations by depth or between soil orders when splitting by both soil order and depth or just by soil order (α =0.05). Table 2 summarizes the F-values based on the results from the three-way ANOVA test. Figure 2 visualizes the means and standard errors of these samples.



Figure 2. Representation of the means and standard error of concentration of organic carbon classified as MAOM and POM by depth and soil order.

	TOC Concentration
Treatment	F-value
Fraction	87.609***
Soil Order	4.414**
Depth	5.387**
Fraction X Order	3.314*
Fraction X Depth	0.600
Order X Depth	0.402
Fraction X Order X Depth	1.179
* indicates a p-value ≤ 0.05	
** indicates a p-value ≤ 0.01	
*** indicates a p-value ≤ 0.001	

Table 2. Summary of F-values from a three-way ANOVA test for significance between TOC concentration by fraction, depth, and soil order.

Metal Extractions: Analyses revealed the extractions measured distinctly different components of metal phases. Although only Fe and Al can be compared between extractions, they have different concentrations at depth as Al increases with depth and Fe decreases. NaPP extracted metals have some overlap but show diverse trends between metal phases, with Mg showing the lowest

concentrations in the upper depths and increasing while Fe shows the opposite trend (Figure 3). Ca has the highest concentrations overall but remains fairly steady throughout the profile (Figure 3). Al follows a similar trend to Ca except it mirrors the trends Ca displays (Figure 3). In the whole soil, Tukey HSD observed significant differences between the top and bottom depths for AOX-extracted Fe and Al, but no significant differences by depth were found for any metal phase extracted by NaPP (α =0.05).

While Figure 3 shows the distribution of the extracted metal phases by extraction type, Table 3 shows the results of two-way ANOVA tests on individual metal phases with soil order and pH as factors. Due to observed differences in metal dominance at different pH levels, the metals were split according to acidic and basic soils with anything above 7 counting as basic and anything below 7 counting as acidic. Overall, most metal phases had markedly different trends when accounting for soil orders and pH, with only Mg not having different behaviors when both soil order and pH are considered (Table 3). Mollisols and Alfisols contain higher concentrations of both phases of Fe and NaPP extracted Al in acidic soils, while all soil orders but Ultisols contained higher concentrations of Ca and Mg in basic soils (Table 3). All metal phases were higher in basic Inceptisols than acidic Inceptisols (Table 3). Moreover, two-way ANOVA tests found significant effects of soil order and pH on Fe, Al, Mg, and Ca for all relevant phases (Table 3). Fe, Al, and Ca all had significant interactions between these two factors as well (Table 3).



Figure 3. The distributions of different metal phase concentrations by the type of extraction performed. Ca and Mg extracted by AOX were not displayed due to inaccurate measurements based on the chemistry. AOX stands for ammonium oxalate extraction, NaPP stands for Napyrophosphate extraction.

Table 3. Summary of the means, standard errors, and F-values for a two-way ANOVA of metal concentrations with soil order and pH as factors. Rows 3-9 display the means and standard errors (se) of the listed variables in the form of "mean (se)." Rows 11-13 represent the F-values for the listed variables with the number of asterisks representing their significance. Note: All metal concentrations for acidic Alfisols had 23 total site depths except for Mg which had 22, as denoted by $\frac{1}{2}$.

		AOX			NAPP				
Soil Order	pH level	Ν	Fe	Al	Fe	Al	Mg	Ca	Ν
Inceptisol	Acidic	6	0.131 (0.011)	0.242 (0.016)	0.080 (0.013)	0.194 (0.034)	0.174 (0.019)	0.963 (0.105)	6
	Basic	18	0.223 (0.016)	0.915 (0.072)	0.110 (0.020)	0.434 (0.073)	0.334 (0.049)	3.555 (0.319)	18
Mollisol	Acidic	26	1.059 (0.127)	1.023 (0.114)	0.994 (0.124)	1.508 (0.160)	0.380 (0.025)	1.505 (0.121)	26
	Basic	17	0.380 (0.035)	0.782 (0.080)	0.120 (0.023)	0.253 (0.048)	0.709 (0.092)	3.000 (0.350)	18
Alfisol	Acidic	23	1.031 (0.163)	0.546 (0.084)	0.832 (0.129)	1.166 (0.188)	0.485 (0.145)	0.930 (0.111)	23ŧ
	Basic	10	0.940 (0.244)	1.093 (0.188)	0.475 (0.091)	0.959 (0.193)	0.979 (0.284)	2.161 (0.102)	10
Ultisol	Acidic	9	0.879 (0.277)	0.735 (0.047)	0.598 (0.105)	0.784 (0.132)	0.102 (0.008)	0.740 (0.121)	12
Treatment						F-value			
Soil Order			9.197***	1.931	10.415***	7.043***	5.679**	21.928***	
pН			6.880*	4.787*	31.126***	21.175***	13.347***	71.625***	
Order x pH			3.553*	10.469***	7.286**	10.966***	0.787	3.307*	

[‡] Mg had a value of 22 for N instead of 23

* indicates a p-value ≤ 0.05

** indicates a p-value ≤ 0.01

*** indicates a p-value ≤ 0.001

Correlations: All relationships were assessed with correlation analyses for metals and other variables such as MAOM-C% and SOC. Since the variables were not normally distributed, a Spearman's rank correlation test was used to evaluate these relationships. As pH increases in whole soils, the concentration of Ca and Mg increases while the concentration of Fe and Al decreases (Figure 8). Many metal phases in whole soils increase the amount of SOC as their concentration increases. SOC% increases as the concentration of both phases of Fe and Al increases, while MAOM-C concentration increases only as both phases of Fe and NaPP extracted Al increase for whole soils (Figure 8). In acidic soils, MAOM-C concentration increases as both phases of Fe and Al increase (Figure 9). However, MAOM-C% increase as both phases of Al, AOX extracted Fe, and Mg increase while SOC% only increases as both phases of Fe, NaPP extracted Al, Ca, and Mg increase (Figure 9). Basic soils showed few trends but were quite different than whole and acidic soils. MAOM-C% decreases both as clay content and NaPP extracted Mg increases (Figure 10). Additionally, NaPP extracted Mg increases as clay content increases (Figure 10). Of all correlations, however, increasing clay content did not increase carbon content in any form (Figures 8, 9, & 10). Figures 8, 9, and 10 summarize the extent of the relevant correlations, but several were of particular interest and significance. In acidic soils, Fe in SRO minerals was positively correlated to MAOM-C% (Figure 4) and concentration (Figure 5), while Al in SRO minerals (Figure 6) was only positively correlated to MAOM-C%. Basic soils showed a negative correlation between Mg in organo-metal complexes and MAOM-C% (Figure 7), indicating that MAOM-C% decreases as Mg concentrations increase.



MAOM Organic Carbon (MAOM-C) vs. AOX Iron (Fe) for Acidic Soils

Figure 4. Correlation between organic carbon percent within MAOM and AOX extracted iron in acidic soils. AOX stands for ammonium oxalate. Values of statistical significance calculated using a Spearman correlation test.



Concentration of MAOM Organic Carbon (MAOM-C) vs. AOX Iron (Fe) for Acidic Soils

Figure 5. Correlation between organic carbon concentration within MAOM and AOX extracted iron in acidic soils. AOX stands for ammonium oxalate. Values of statistical significance calculated using a Spearman correlation test.



MAOM Organic Carbon (MAOM-C) vs. AOX Aluminum (Al) for Acidic Soils

Figure 6. Correlation between organic carbon percent within MAOM and AOX extracted Al in acidic soils. AOX stands for ammonium oxalate. Values of statistical significance calculated using a Spearman correlation test.



MAOM Organic Carbon (MAOM-C) vs. NaPP Magnesium (Mg) for Basic Soils

Figure 7. Correlation between organic carbon percent within MAOM and NaPP extracted Mg in basic soils. NaPP stands for sodium pyrophosphate. Values of statistical significance calculated using a Spearman correlation test.



Figure 8. Spearman correlation matrix for whole soil measured variables. The size of the sphere indicates the strength of the correlation while the red or blue color indicates either a negative or positive correlation, respectively. Significance was measured at the α=0.05 level. pH: pH of the whole soil; TOC: whole soil total organic carbon or SOC (%); Clay: clay content (%); M_TOC: TOC within the MAOM fraction (%); M_Conc: concentration of TOC within the MAOM fraction (g fraction C/g soil); P_TOC: TOC within the POM fraction (%); P_Conc: concentration of TOC within the POM fraction (g fraction C/g soil); Ca_NaPP: organo-metal complexed calcium extracted using NaPP (mg Ca/g soil); Mg_NaPP: organo-metal complexed magnesium extracted using NaPP (mg Mg/g soil); Fe_NaPP: organo-metal complexed iron extracted using NaPP (mg Al/g soil); Fe_AOX: SRO iron extracted using AOX (mg Fe/g soil); Al_AOX: SRO aluminum extracted using AOX (mg Al/g soil)



Figure 9. Spearman correlation matrix for measured variables in acidic soils. The size of the sphere indicates the strength of the correlation while the red or blue color indicates either a negative or positive correlation, respectively. Significance was measured at the α=0.05 level. pH: pH of the whole soil below 7; TOC: whole soil total organic carbon or SOC (%); Clay: clay content (%); M_TOC: TOC within the MAOM fraction (%); M_Conc: concentration of TOC within the MAOM fraction (g fraction C/g soil); P_TOC: TOC within the POM fraction (%); P_Conc: concentration of TOC within the POM fraction (g fraction C/g soil); Kg_NaPP: organo-metal complexed calcium extracted using NaPP (mg Ca/g soil); Mg_NaPP: organo-metal complexed magnesium extracted using NaPP (mg Mg/g soil); Fe_NaPP: organo-metal complexed iron extracted using NaPP (mg Al/g soil); Fe_AOX: SRO iron extracted using AOX (mg Fe/g soil); Al_AOX: SRO aluminum extracted using AOX (mg Al/g soil)



Figure 10. Spearman correlation matrix for measured values in basic soils. The size of the sphere indicates the strength of the correlation while the red or blue color indicates either a negative or positive correlation, respectively. Significance was measured at the α=0.05 level. pH: pH of the whole soil above 7; TOC: whole soil total organic carbon or SOC (%); Clay: clay content (%); M_TOC: TOC within the MAOM fraction (%); M_Conc: concentration of TOC within the MAOM fraction (g fraction C/g soil); P_TOC: TOC within the POM fraction (%); P_Conc: concentration of TOC within the POM fraction (g fraction C/g soil); Ca_NaPP: organo-metal complexed calcium extracted using NaPP (mg Ca/g soil); Mg_NaPP: organo-metal complexed magnesium extracted using NaPP (mg Mg/g soil); Fe_NaPP: organo-metal complexed iron extracted using NaPP (mg Al/g soil); Fe_AOX: SRO iron extracted using AOX (mg Fe/g soil); Al_AOX: SRO aluminum extracted using AOX (mg Al/g soil)

Discussion

The sites selected provided an opportunity to test hypothesized mechanisms of carbon stabilization and generate more detailed insight into the patterns of carbon dynamics. Moreover, these sites show the geochemical properties vary widely with depth, pH, and across soil orders. The results from the metal extractions further supported that the two extractions targeted different metal phases. Significant differences between acidic and basic soils also supported the dominance of Fe and Al at acidic levels while Ca and Mg dominated at basic levels (Lawrence et al., 2015; Rasmussen et al., 2018), demonstrating the need to examine these metal phases depending on the pH. Significant differences in metal concentrations by soil order also supports the literature (Goldberg, 2008; "Soil Management," 2022; Wagai et al., 2011). Each soil order contains different proportions of minerals and degrees of weathering, which influences the dominance of metal phases. Inceptisols didn't have significant differences at depth for SOC, which makes sense due to their relatively young and undeveloped state. As the degree of weathering increases, an interesting trend occurs with Mollisols containing a significantly higher concentration of MAOM. It would also seem Alfisols and Ultisols typically lose some or most of the MAOM from the middle depth via leaching so that it accumulates in the lower depth. While not reported, extracted iron phases tended to follow this trend for the older soils, with the surface layers containing less iron and lower depths accumulating more iron. Aluminum phases followed this trend similar to Mollisols with the surface depths containing higher concentration of aluminum than the lower depth. From what we know about the solubility of iron and leaching in weathered soils, we can hypothesize the SOC leaches with the iron in more weathered soils and perhaps binds to aluminum in younger, organic-rich soils.

Since iron forms in soil as Fe^{2+} and Fe^{3+} , we must consider both forms for a full picture of iron behavior within soil. Reduced iron (Fe^{2+}) forms in anaerobic conditions, typically as a result of saturated soils. Iron in this state is highly soluble and can be leached by water as it drains, removing it from the soil profile or moving it deeper down the profile(Schwertmann, 1988).

However, oxidized iron (Fe³⁺) forms a precipitate and coats soil surfaces, giving them a distinctive red color (Schwertmann, 1988). Oxidized iron has a much higher potential to store SOC than reduced iron because it will stay bound with SOC rather than releasing it into the soil solution. As such, iron may store more SOC in lower depths of because it's already been leached and accumulated at those depths. Aluminum does not display a similar trend to this because it does not become soluble in anaerobic conditions (Goldberg, 2008). Thus, aluminum can accumulate in surface depths where it can then store SOC.

The results from the fractionation data supports previous literature regarding the distribution of SOC across POM and MAOM (Cambardella and Elliott, 1993; Fox et al., 2017; Lavallee et al., 2020), with the majority of carbon residing within MAOM (Sokol et al., 2022). We would expect to have significantly different proportions of POM and MAOM as well as the concentration of carbon within those fractions across the whole soil. Since MAOM tends to be more resistant to decomposition, it follows that the relative abundance of it would increase as the degree of weathering increases because there will be more availability of reactive surfaces as well as a longer period of time for consistent inputs of plant and animal residues to accumulate (Lavallee et al., 2020; Poeplau et al., 2018). Interestingly, the same trend is not observed for SOC% unless the data is split along fraction type and soil order. This could indicate limited binding capacity across the mineral surfaces or greater potential to increase carbon concentration. Additionally, inconsistent land management of the Mesonet sites and the possible influence of different vegetation types could affect the formation of SOC through biomass inputs or differences in soil physical properties (Jilling et al., 2021; McPherson et al., 2007; Shabtai et al., 2022).

The correlations portray a set of interesting relationships. As hypothesized, Fe and Al in acidic soils are significantly correlated with MAOM-C% and concentration in iron's case. This indicates as Fe and Al concentrations increase, they are partially responsible for an increase in MAOM which supports the literature (Song et al., 2022; Wagai et al., 2011).

Correlations within basic soils point to a distinctly different mechanism. The only significant relationship between MAOM-C and extracted metals lies with Mg within organo-metal complexes. In contrast to the relationships in acidic soils, as Mg concentrations increase, they are partially responsible for a decrease within MAOM-C. This does not support this project's hypothesis nor the findings from literature (Behera and Shukla, 2015). This could indicate another mechanism at play that warrants further investigation such as vegetation influences or a lack of organic matter inputs. Furthermore, the negative relationship between clay and Mg points to a potential interaction between clay, Mg, and MAOM-C. Basic soils used for this study could have high clay contents that restrict plant growth, causing lower amounts of OM inputs into the soil which would decrease the formation of MAOM-C.

When Figures 8, 9, and 10 are viewed together, the relationship between clay content (%), typically thought to be a predictor of SOC storage, and TOC of any variety is noticeably lacking. The only relationship is a significantly negative one in basic soils between clay content and MAOM-C. As such, the results of this project partially supports the claim posed by Rasmussen et al. (2018) that clay is not the most reliable predictor of SOC at all pH levels due to a lack of significant correlations. In addition to the lack of a relationship for clay content, looking at the three tables together demonstrates how splitting the soil by pH visibly strengthens most of the relationships in meaningful ways. It illustrates further how pH is a master variable in soil that needs consideration for any SOC analyses and models.

The results of this project provide further insight into the controls associated with SOC storage. While this project demonstrated the importance of metal phases for storing SOC, shifts in precipitation, temperature, and other climatic factors could alter the dominance of these metals and the capacity of soil to store carbon. Since climactic factors control the type of vegetation that can grow in an area along with pH, weathering, and microbial activity, metals could shift in dominance as well. With the potential for shifts in weathering of soils and likely increased degradation, the

metal phases and other minerals responsible for retaining soil carbon could decrease or be altered in some soil systems. Moreover, increases in soil temperature and moisture could lead to increased microbial respiration and further decrease the stores of MAOM within soil. In contrast, some areas could have decreases in soil temperature and moisture which could decrease microbial respiration. This might lead to potential increases in MAOM stores with less active microbial decomposition or less organic matter inputs from less resources for vegetative and microbial growth.

Regarding the trends observed in prior studies of surface SOC gain and SOC loss at depth, this study has provided preliminary insight into SOM pools and geochemical factors that could cause the trend. Most soils showed a decrease in MAOM with POM mirroring at lower concentrations. However, POM could be increasing or remaining stable over time while MAOM decreases. This would explain why surface soils see an increase in SOC due to POM remaining while MAOM cannot or is not being replenished at lower depths where it is more dominant. This study cannot comment on trends over time, but it points to iron and aluminum as part of potential reason for the observed discrepancies as well. Since SOC increases as these metal phases increase in acidic soils, any decrease or removal of these phases could decrease the amount of SOC in lower depths.

Future research could involve characterizing the SOM fraction with depth at other time points to build a better-informed story of the potential changes in SOM distribution. Perhaps MAOM is more vulnerable to loss over time than POM, which is usually more vulnerable in the short-term. Since MAOM relies on organic matter inputs and available mineral surfaces to form, a decrease in either of these factors could negatively impact MAOM stores. Mesonet sites are uniquely suited to this type of long-term study due to the accessibility of climate and soil data, stable locations, and previous studies for more robust analyses. In addition, further characterization of the SOM fraction with more sites and soil orders would contribute to a more complete story of the SOC at these sites.

CHAPTER III

CONCLUSION

The first objective of this study was to examine the distribution of soil organic carbon (SOC) using the relatively new paradigm of SOM formation as a framework. This model of SOC, which emphasizes the mechanisms of carbon stabilization on mineral particles, allowed the project to view SOC differently than previous studies. We determined that the selected Mesonet sites follow the expected trends regarding SOC fractions, with soils containing more mineral-associated organic matter (MAOM) than particulate organic matter (POM). Moreover, this project's second objective viewed the geochemical factors for SOC storage to determine their effect. SOC storage in acidic soils was dominated and increased by increasing concentrations of Al and Fe as expected. However, SOC storage in basic soils unexpectedly decreased with increasing concentrations of Mg and clay contents. Clay content also had no significant relationships with SOC storage at all or acidic pH levels, which supports the claim that clays shouldn't be solely used as a predictor of SOC storage.

This project contributes to the body of research into SOC storage and the factors that control it. While soils at Oklahoma Mesonet sites have been previously analyzed for SOC concentration and other variables, this is the first time fractionation and geochemical analyses have been done on these soils at this scale. The results show that clay content does not adequately reflect the soil's potential to store SOC. Future development of soil carbon models should consider the role of metal phases and the specific role of pH. Further studies could explore the SOC distribution at all Mesonet sites with a wider variation of soil orders and soil moisture regimes to determine a more complete picture.

REFERENCES

- Andreux, F., 1996. Humus in World Soils. Humic Substances in Terrestrial Ecosystems 45–100. https://doi.org/10.1016/B978-044481516-3/50003-7
- Baker, J. M., Ochsner, T. E., Venterea, R. T., & Griffis, T. J. (2006). Tillage and soil carbon sequestration-What do we really know? *Agriculture, Ecosystems and Environment*, 118, 1–5. https://doi.org/10.1016/j.agee.2006.05.014
- Barton, C.D., Karathanasis, A.D., 2002. CLAY MINERALS.
- Behera, S.K., Shukla, A.K., 2015. Spatial Distribution of Surface Soil Acidity, Electrical Conductivity, Soil Organic Carbon Content and Exchangeable Potassium, Calcium and Magnesium in Some Cropped Acid Soils of India. Land Degradation & Development 26, 71–79. https://doi.org/10.1002/LDR.2306
- Cambardella, C.A., Elliott, E.T., 1993. Methods for physical separation and characterization of soil organic matter fractions. Soil Structure/Soil Biota Interrelationships 449–457. https://doi.org/10.1016/B978-0-444-81490-6.50036-4
- Cui, Y., Wang, X., Zhang, X., Ju, W., Duan, C., Guo, X., Wang, Y., & Fang, L. (2020). Soil moisture mediates microbial carbon and phosphorus metabolism during vegetation succession in a semiarid region. *Soil Biology and Biochemistry*, 147, 107814. https://doi.org/10.1016/j.soilbio.2020.107814
- Dhillon, G.S., Amichev, B.Y., de Freitas, R., van Rees, K., 2015. Accurate and Precise Measurement of Organic Carbon Content in Carbonate-Rich Soils. http://dx.doi.org/10.1080/00103624.2015.1089271 46, 2707–2720. https://doi.org/10.1080/00103624.2015.1089271
- Fox, P.M., Nico, P.S., Tfaily, M.M., Heckman, K., Davis, J.A., 2017. Characterization of natural organic matter in low-carbon sediments: Extraction and analytical approaches. Organic Geochemistry 114, 12–22. https://doi.org/10.1016/j.orggeochem.2017.08.009
- Gale, W.J., Cambardella, C.A., 2000. Carbon Dynamics of Surface Residue– and Root-derived Organic Matter under Simulated No-till. Soil Science Society of America Journal 64, 190–195. https://doi.org/10.2136/SSSAJ2000.641190X

- Goldberg, S., 2008. Interaction of aluminum and iron oxides and clay minerals and their effect on soil physical properties: A review. http://dx.doi.org/10.1080/00103629009368144 20, 1181–1207. https://doi.org/10.1080/00103629009368144
- The Great Plains Flora Association. 1986. Flora of the Great Plains. University Press of Kansas Publishers. Lawrence, KS 66045.
- Harris, D., Horwáth, W.R., Kessel, C. van, 2001. Acid fumigation of soils to remove carbonates prior to total organic carbon or CARBON-13 isotopic analysis. Soil Science Society of America Journal 65, 1853–1856. https://doi.org/10.2136/SSSAJ2001.1853
- Heckman, K., Lawrence, C.R., Harden, J.W., 2018. A sequential selective dissolution method to quantify storage and stability of organic carbon associated with Al and Fe hydroxide phases. Geoderma 312, 24–35. https://doi.org/10.1016/j.geoderma.2017.09.043
- IPCC, 2022: Climate Change 2022: Impacts, Adaptation, and Vulnerability. Contribution of Working Group II to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change [H.-O. Pörtner, D.C. Roberts, M. Tignor, E.S. Poloczanska, K. Mintenbeck, A. Alegría, M. Craig, S. Langsdorf, S. Löschke, V. Möller, A. Okem, B. Rama (eds.)]. Cambridge University Press. In Press.
- Jilling, A., Keiluweit, M., Gutknecht, J. L. M., & Grandy, A. S. (2021). Priming mechanisms providing plants and microbes access to mineral-associated organic matter. *Soil Biology and Biochemistry*, 158, 108265. https://doi.org/10.1016/j.soilbio.2021.108265
- Keiluweit, M., Bougoure, J.J., Nico, P.S., Pett-Ridge, J., Weber, P.K., Kleber, M., 2015. Mineral protection of soil carbon counteracted by root exudates. Nature Climate Change 5, 588–595. https://doi.org/10.1038/nclimate2580
- Kerr, D.D., 2019. Evaluating Environmental Influences on Grassland Soil Organic Carbon Temporal and Spatial Distribution (Master of Science). Oklahoma State University, Stillwater.
- Kerr, D.D., Ochsner, T.E., 2020. Soil organic carbon more strongly related to soil moisture than soil temperature in temperate grasslands. Soil Science Society of America Journal 84, 587–596. https://doi.org/10.1002/SAJ2.20018
- Kleber, M., Bourg, I.C., Coward, E.K., Hansel, C.M., Myneni, S.C.B., Nunan, N., 2021. Dynamic interactions at the mineral–organic matter interface. Nature Reviews Earth & Environment 1–20. https://doi.org/10.1038/s43017-021-00162-y
- Korzekwa, K., 2022. Extractable Metals and Soil Organic Carbon: Understanding the Relationship. CSA News 67, 10–14. https://doi.org/10.1002/CSAN.20748
- Lavallee, J.M., Soong, J.L., Cotrufo, M.F., 2020. Conceptualizing soil organic matter into particulate and mineral-associated forms to address global change in the 21st century. Global Change Biology 26, 261–273. https://doi.org/10.1111/gcb.14859

- Lawrence, C.R., Harden, J.W., Xu, X., Schulz, M.S., Trumbore, S.E., 2015. Long-term controls on soil organic carbon with depth and time: A case study from the Cowlitz River Chronosequence, WA USA. Geoderma 247–248, 73–87. https://doi.org/10.1016/j.geoderma.2015.02.005
- McPherson, R.A., Fiebrich, C.A., Crawford, K.C., Elliott, R.L., Kilby, J.R., Grimsley, D.L., Martinez, J.E., Basara, J.B., Illston, B.G., Morris, D.A., Kloesel, K.A., Stadler, S.J., Melvin, A.D., Sutherland, A.J., Shrivastava, H., Carlson, J.D., Wolfinbarger, J.M., Bostic, J.P., Demko, D.B., 2007. Statewide monitoring of the mesoscale environment: A technical update on the Oklahoma Mesonet. J. Atmos. Ocean. Technol. 24, 301–321. https://doi.org/10.1175/JTECH1976.1
- Mobley, M.L., Lajtha, K., Kramer, M.G., Bacon, A.R., Heine, P.R., Richter, D.D., 2015. Surficial gains and subsoil losses of soil carbon and nitrogen during secondary forest development. Global Change Biology 21, 986–996. https://doi.org/10.1111/gcb.12715
- Moni, C., Derrien, D., Hatton, P.-J., Zeller, B., Kleber, M., 2012. Density fractions versus size separates: does physical fractionation isolate functional soil compartments? Biogeosciences 9, 5181–5197. https://doi.org/10.5194/bg-9-5181-2012
- Paul, S.S., Coops, N.C., Johnson, M.S., Krzic, M., Chandna, A., Smukler, S.M., 2020. Mapping soil organic carbon and clay using remote sensing to predict soil workability for enhanced climate change adaptation. Geoderma 363, 114177. https://doi.org/10.1016/j.geoderma.2020.114177
- Poeplau, C., Don, A., Six, J., Kaiser, M., Benbi, D., Chenu, C., Cotrufo, M.F., Derrien, D., Gioacchini, P., Grand, S., Gregorich, E., Griepentrog, M., Gunina, A., Haddix, M., Kuzyakov, Y., Kühnel, A., Macdonald, L.M., Soong, J., Trigalet, S., Vermeire, M.L., Rovira, P., van Wesemael, B., Wiesmeier, M., Yeasmin, S., Yevdokimov, I., Nieder, R., 2018. Isolating organic carbon fractions with varying turnover rates in temperate agricultural soils A comprehensive method comparison. Soil Biology and Biochemistry 125, 10–26. https://doi.org/10.1016/j.soilbio.2018.06.025
- Rao, C.R.M., Sahuquillo, A., Lopez Sanchez, J.F., 2008. A review of the different methods applied in environmental geochemistry for single and sequential extraction of trace elements in soils and related materials. Water, Air, and Soil Pollution. https://doi.org/10.1007/s11270-007-9564-0
- Rasmussen, C., Heckman, K., Wieder, W.R., Keiluweit, M., Lawrence, C.R., Berhe, A.A., Blankinship, J.C., Crow, S.E., Druhan, J.L., Hicks Pries, C.E., Marin-Spiotta, E., Plante, A.F., Schädel, C., Schimel, J.P., Sierra, C.A., Thompson, A., Wagai, R., 2018. Beyond clay: towards an improved set of variables for predicting soil organic matter content. Biogeochemistry 137, 297– 306. https://doi.org/10.1007/s10533-018-0424-3
- Sartori, F., Lal, R., Ebinger, M.H., Eaton, J.A., 2007. Changes in soil carbon and nutrient pools along a chronosequence of poplar plantations in the Columbia Plateau, Oregon, USA. Agriculture, Ecosystems & Environment 122, 325–339. https://doi.org/10.1016/J.AGEE.2007.01.026
- Schimel, J.P., 2018. Life in Dry Soils: Effects of Drought on Soil Microbial Communities and Processes. Annual Review of Ecology, Evolution, and Systematics 49, 409–432. https://doi.org/10.1146/annurev-ecolsys-110617-062614

- Schweizer, S.A., Mueller, C.W., Höschen, C., Ivanov, P., Kögel-Knabner, I., 2021. The role of clay content and mineral surface area for soil organic carbon storage in an arable toposequence. Biogeochemistry 2021 1–20. https://doi.org/10.1007/S10533-021-00850-3
- Schwertmann, U., 1988. Occurrence and formation of iron oxides in various pedoenvironments. Iron in soils and clay minerals 267–308. https://doi.org/10.1007/978-94-009-4007-9_11/COVER/
- Schulte, E. E., & Hopkins, B. G. (2015). Estimation of Soil Organic Matter by Weight Loss-On-Ignition. Soil Organic Matter: Analysis and Interpretation, 21–31. https://doi.org/10.2136/SSSASPECPUB46.C3
- Shabtai, I. A., Das, S., Inagaki, T. M., Azimzadeh, B., Richards, B., Martínez, C. E., Kögel-Knabner, I., & Lehmann, J. (2022). Soil organic carbon accrual due to more efficient microbial utilization of plant inputs at greater long-term soil moisture. *Geochimica et Cosmochimica Acta*, 327, 170– 185. https://doi.org/10.1016/J.GCA.2022.04.028
- Shang, C., Zelazny, L.W., 2015. Selective Dissolution Techniques for Mineral Analysis of Soils and Sediments. Methods of Soil Analysis, Part 5: Mineralogical Methods 5, 33–80. https://doi.org/10.2136/SSSABOOKSER5.5.C3
- Soil Management [WWW Document], 2022. The University of Hawai'i. URL https://www.ctahr.hawaii.edu/mauisoil/a_factor_mineralogy.aspx (accessed 6.28.22).
- Soil-Based Carbon Sequestration | MIT Climate Portal [WWW Document], 2021. MIT Climate Portal. URL https://climate.mit.edu/explainers/soil-based-carbon-sequestration (accessed 6.28.22).
- Sokol, N.W., Whalen, E.D., Jilling, A., Kallenbach, C., Pett-Ridge, J., Georgiou, K., 2022. Global distribution, formation and fate of mineral-associated soil organic matter under a changing climate: A trait-based perspective. Functional Ecology 36, 1411–1429. https://doi.org/10.1111/1365-2435.14040
- Song, X., Wang, P., van Zwieten, L., Bolan, N., Wang, H., Li, X., Cheng, K., Yang, Y., Wang, M., Liu, T., Li, F., 2022. Towards a better understanding of the role of Fe cycling in soil for carbon stabilization and degradation. Carbon Research 2022 1:1 1, 1–16. https://doi.org/10.1007/S44246-022-00008-2
- Viscarra Rossel, R.A., Lee, J., Behrens, T., Luo, Z., Baldock, J., Richards, A., 2019. Continental-scale soil carbon composition and vulnerability modulated by regional environmental controls. Nature Geoscience 12, 547–552. https://doi.org/10.1038/s41561-019-0373-z
- Voelz, J.L., Johnson, N.W., Chun, C.L., Arnold, W.A., Penn, R.L., 2019. Quantitative Dissolution of Environmentally Accessible Iron Residing in Iron-Rich Minerals: A Review. ACS Earth and Space Chemistry. https://doi.org/10.1021/acsearthspacechem.9b00012
- Wagai, R., Mayer, L.M., Kitayama, K., Shirato, Y., 2013. Association of organic matter with iron and aluminum across a range of soils determined via selective dissolution techniques coupled with dissolved nitrogen analysis. Biogeochemistry 112, 95–109. https://doi.org/10.1007/s10533-011-9652-5

- Wagai, R., Mayer, L.M., Kitayama, K., Shirato, Y., 2011. Association of organic matter with iron and aluminum across a range of soils determined via selective dissolution techniques coupled with dissolved nitrogen analysis. Biogeochemistry 2011 112:1 112, 95–109. https://doi.org/10.1007/S10533-011-9652-5
- Wang, G., Huang, W., Mayes, M.A., Liu, X., Zhang, D., Zhang, Q., Han, T., Zhou, G., 2019. Soil moisture drives microbial controls on carbon decomposition in two subtropical forests. Soil Biology and Biochemistry 130, 185–194. https://doi.org/10.1016/j.soilbio.2018.12.017
- Wiesmeier, M., Urbanski, L., Hobley, E., Lang, B., von Lützow, M., Marin-Spiotta, E., van Wesemael, B., Rabot, E., Ließ, M., Garcia-Franco, N., Wollschläger, U., Vogel, H.J., Kögel-Knabner, I., 2019. Soil organic carbon storage as a key function of soils A review of drivers and indicators at various scales. Geoderma. https://doi.org/10.1016/j.geoderma.2018.07.026
- Zamanian, K., Pustovoytov, K., Kuzyakov, Y., 2016. Pedogenic carbonates: Forms and formation processes. Earth-Science Reviews 157, 1–17. https://doi.org/10.1016/J.EARSCIREV.2016.03.003

APPENDICES

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Table A1. Mesonet site location information with detailed soil classification information. Data collected from Mesonet.org and NRCS's Web Soil Survey.

Station ID	Name	Soil Order	Series Name	Soil Taxonomy
ARNE	Arnett	Inceptisol	Enterprise	Coarse-silty, mixed, superactive, thermic Typic Haplustepts
BROK	Broken Bow	Ultisol	Cahaba	Fine-loamy, siliceous, semiactive, thermic Typic Hapludults
BUFF	Buffalo	Mollisol	St. Paul	Fine-silty, mixed, superactive, thermic Pachic Argiustolls
BUTL	Butler	Inceptisol	Woodward	Coarse-silty, mixed, superactive, thermic Typic Haplustepts
CAMA	Camargo	Inceptisol	Enterprise	Coarse-silty, mixed, superactive, thermic Typic Haplustepts
CARL	Lake Carl Blackwell	Mollisol	Norge	Fine-silty, mixed, active, thermic Udic Paleustolls
CENT	Centrahoma	Mollisol	Bates	Fine-loamy, siliceous, active, thermic Typic Argiudolls
CHEY	Cheyenne	Alfisol	Grandfield-	Fine-loamy, mixed, superactive, thermic Typic Haplustalfs -
CODA	0	N C 11' 1	Nobscot	Loamy, mixed, superactive, thermic Arenic Paleustalts
COPA	Copan	Mollisol	Dennis	Fine, mixed, active, thermic Aquic Argiudolls
FAIR	Fairview	Mollisol	Port	Fine-silty, mixed, superactive, thermic Cumulic Haplustolls
FORA	Foraker	Mollisol	Coyle	Fine-loamy, siliceous, active, thermic Udic Argiustolls
FTCB	Fort Cobb	Alfisol	Binger	Fine-loamy, mixed, active, thermic Udic Rhodustalfs
GRA2	Grandfield	Mollisol	Tillman	Fine, mixed, superactive, thermic Vertic Paleustolls
HASK	Haskell	Alfisol	Taloka	Fine, mixed, active, thermic Mollic Albaqualfs
HINT	Hinton	Inceptisol	Ironmound- Dill	Loamy, mixed, active, thermic, shallow Udic Haplustepts - Coarse-loamy, mixed, active, thermic Typic Haplustepts
IDAB	Idabel	Alfisol	Wrightsville- Elysian	Fine, mixed, active, thermic Typic Glossaqualfs - Coarse- loamy, siliceous, active, thermic Haplic Glossudalfs
JAYX	Jay	Ultisol	Clarksville	Loamy-skeletal, siliceous, semiactive, mesic Typic Paleudults
SKIA	Skiatook	Alfisol	Bartlesville	Fine-loamy, siliceous, active, thermic Oxyaquic Hapludalfs
STIG	Stigler	Alfisol	Stigler	Fine, mixed, active, thermic Aquic Paleudalfs
STIL	Stillwater	Mollisol	Norge	Fine-silty, mixed, active, thermic Udic Paleustolls
WATO	Watonga	Mollisol	St. Paul	Fine-silty, mixed, superactive, thermic Pachic Argiustolls
WILB	Wilburton	Alfisol	Counts	Fine, mixed, active, thermic Albaquic Paleudalfs

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