

**The Dynamic Nature of Mineral Organic Matter Associations in Adsorption
Experiments**

by

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Abstract

Mineral-organic matter associations (MOAs) are predominant in soil environments and encompass a range of minerals and organic matter. MOAs sequester metal contaminants such as Cu and Ni more effectively than minerals and organic matter alone. A better understanding of the occurrences and associated forms of these metal ions in soils and pore waters is needed to understand contaminant retention in complex systems. This study characterizes changes in the structure and chemical composition of MOAs in the presence of metal ions of high (Cu) and low (Ni) affinity towards organic matter. It shows that MOAs are highly dynamic in terms of size, composition, and structure during their interactions with Cu- and Ni-bearing solutions. MOAs are synthesized using montmorillonite and ferrihydrite as the mineral components and polymerized fulvic acid (FA) as the organic component. Adsorption isotherms and Total Organic Carbon (TOC) analysis indicate that desorbed FA complexes both metal ions at lower metal ion concentrations and that the polymerization of Cu- and Ni-FA complexes occurs at higher metal concentrations. Structural characterization of MOAs using electron microscopy, spectroscopy, and X-ray diffraction indicates that Cu induces greater structural and compositional changes than Ni, owing to its higher affinity for polar organic functional groups. Here, the formation of Cu-carboxylate complexes in ferrihydrite-FA-OA increases with the concentration of Cu, and the interaction of Cu with montmorillonite-FA-OA follows a 2-step intercalation with the formation of higher polymerized Cu-FA complexes at higher Cu concentrations. Additionally, the formation and polymerization of Cu-FA complexes increased the number of polar functional groups, thereby increasing the number of binding sites. Future adsorption studies involving MOAs and metal ions with a high affinity for organic functional groups need to consider that neither the surface area, composition, nor the number of binding sites in MOAs remains constant as the metal ion concentration in solution

increases and should account for substantial structural and compositional changes in MOAs as metal-ion concentration increases. Also, it is recommended to conduct future experimental adsorption studies of other metal ions on MOAs and to examine how adsorption changes over time, pH, and temperature.

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Contributions Of Authors

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List of Abbreviations

MRT, mean residence time

MOA, Mineral organic matter associations

CDR, carbon dioxide removal

OM, organic matter

EOM, Exogeneous OM

POM, Particulate OM,

MAOM, Mineral-associated OM

OC, Organic carbon

SOM, Soil organic matter

ROS, reactive oxygen species

PZC, point of zero charge

IEP, Isoelectric point

IR, Infra-red

SEM, Scanning Electron Microscopy

TEM, Transmission Electron Microscopy

AFM, Atomic Force Microscopy

EELS, Electron Energy Loss Spectroscopy

HA, Humic Acid

FA, Fulvic acid

CEC, Cation Exchange Capacity

BET, Brunauer-Emmett-Teller

ICPMS, Inductively coupled plasma mass spectroscopy

TOC, Total Organic Carbon

NPOC, Non Purgeable Organic Carbon

FTIR, Fourier-transformed infrared spectroscopy

PXRD, Powder X-ray diffraction

BF, bright field

DF, dark field (DF)

SAED, Select area electron diffraction (SAED)

HRTEM, high-resolution TEM (HRTEM)

EDS, Energy dispersive X-ray spectroscopy

CD, MUSIC, Charge Distribution (CD)-Multisite Complexation (MUSIC) model

NEXAFS, near-edge X-ray absorption fine structure

Fh-FA-OA, Ferrihydrite -Fulvic acid- Association

Fh-OA, Ferrihydrite-Organic Matter-Association (organic matter refers to Fulvic acid in this study)

Mt-FA-OA, Montmorillonite-Fulvic acid-association

Mt-OA, Montmorillonite-Organic Matter Association (organic matter refers to Fulvic acid in this study)

Cu-FA, Copper-Fulvic acid

Ni-FA, Nickel-Fulvic acid

Chapter 1: Introduction

1.1 The global carbon cycle

Three reservoirs, namely the atmosphere, oceans, and terrestrial systems, are responsible for circulating carbon, causing changes in its chemical form. The lithosphere is considered the largest reservoir, and the atmosphere the smallest (Foley & Fischer, 2017). The terrestrial system, which includes soils, sediments, and rocks, stores two to three times as much carbon as the atmosphere (Le Quéré et al., 2016). They store significant amounts of carbon as carbon dioxide (CO₂), inorganic carbon, and organic matter (OM), with inorganic carbon being more abundant than organic carbon. The OM includes all living, dead, and decomposing plants, microbes, and animals in the soil. The main proportion of terrestrial OM occurs in soils, coastal systems, marine sediments, vegetation, and permafrost in the biosphere (Kleber et al., 2021).

Soil, which serves as the largest terrestrial reservoir of carbon to a depth of 3 meters (approximately 4,000 Pg), can function as either a source or a sink of atmospheric CO₂. It contains approximately 45% solid material, known as the soil's mineral fraction; 50% pore space, which contains equal amounts of air and water; and 5% OM (Kalev & Toor, 2018).

Carbon (C) sequestration in soils involves capture and storage of atmospheric CO₂, thereby increasing its mean residence time (MRT) and minimizing the likelihood of re-emission (Lal, 2004). Soil drives climate mitigation to a greater extent through Carbon release or sequestration, which is controlled by the formation and stability of SOM (soil OM) (Davidson & Janssens, 2006). Through photosynthesis, plants draw in carbon dioxide, transform it into energy-rich carbohydrates, and when they decompose, return this carbon to the earth as SOM or to water as dissolved OM. The latter matter and those of rhizodeposition (i.e. the release of organic and

inorganic compounds from plant roots into the surrounding soil), are considered the main source of SOM and the largest and most dynamic terrestrial C reservoir (Bölscher et al., 2025).

The soil microbial carbon pump concept is an important model for understanding how microbes affect soil organic C production and sequestration (Liang, Schimel, et al., 2017). Microorganisms play an important role in the sequestration of C in soil (Crowther et al., 2019; Woodcroft et al., 2018). Some microbes function similarly to plants, serving as primary producers of OM. These autotroph microbes accumulate CO₂ through various cycles, such as the Calvin pathway (Zheng et al., 2022). Heterotroph microbes decompose OM as they break down organic residues to obtain nutrients (Gougoulas et al., 2014). This soil microbial carbon pump concept describes the formation of new organic compounds through microbial anabolism and their role in stabilizing soil structures. This involves two distinct pathways: *ex vivo*, termed extracellular modification, and *in vivo* organic substrate turnover. The first pathway involves the breakdown of plant-produced OM into smaller oxidized compounds that are not readily consumed by microbes. The 2nd pathway involves the assimilation of organic substrates for microbial metabolism, leading to growth and cell uptake (Qiao et al., 2025).

Parallel to the soil microbial carbon pump, the soil mineral carbon pump concept describes (a) the role of soil minerals in the accumulation of organic C and in increasing carbon persistence in soil (Xiao et al., 2023) and (b) various interactions between SOM and minerals, such as aggregation, occlusion, adsorption, polymerization, and redox reactions (Xiao et al., 2023). Labile OM is stabilized against microbial degradation through interactions with soil minerals, such as iron oxides and phyllosilicates (Xiao et al., 2025). Reactive minerals bind to exoenzyme proteins (extracellular enzymes) secreted by microbes, influencing OM stability and chemistry. These enzymes have a strong affinity for a range of minerals; upon binding to minerals, they influence

the transformation and stabilization of OM in soil. Minerals can adsorb or coprecipitate with OM. Reactive minerals create microenvironments and microhabitats, thus forming pore networks and soil aggregates. These pore networks (especially in the 30–90 μm size range) play a significant role in protecting OM (Kravchenko & Guber, 2017; S. Wu et al., 2023). The mineral carbon pump concept enables the design of carbon dioxide removal (CDR) methods using minerals. Most CDR methods improve natural biogeochemical cycles that remove CO_2 from the atmosphere (Griscom et al., 2017). The application of crushed silicates to soil, the addition of minerals to soil, and the premediated addition of minerals to raw biomass are improved CDR methods, all of which aim to increase the stability of soil organic carbon (Buss et al., 2024).

Both microbial and mineral carbon pumps play critical roles in C sequestration (Figure 1), as they are interconnected (Z. Li et al., 2025). As part of the microbial carbon pump, microbial necromass and biomass excrete extracellular polymeric substances, which can strengthen the interaction between minerals and OM (M. Xiao et al., 2023). These interactions exert an entombing or gluing effect on SOM stabilization in soil by forming mineral-OM associations (MOAs) (Qiao et al., 2025; Xiao et al., 2023).

Mineral-OM associations form through a range of physicochemical reactions. They control the transformation, stability, and persistence of OM in soil (Kleber et al., 2015a). Formation of MOAs is a key process in soil carbon stabilization and follows two pathways: direct adsorption or the in vivo turnover pathway (Liu et al., 2026). The direct adsorption pathway is a physicochemical process in which organic molecules bind directly to mineral surfaces. This is governed by mineral type, surface charge, and the polarity of the organic compound (Ahmad & Martsinovich, 2022; Strawn, 2021). The in vivo turnover pathway involves microbial processing of OM prior to its association with minerals, during which plant residues are converted into microbial

precipitates(Manzoni & Cotrufo, 2024). The relative contribution of these two pathways depends on the soil environment, soil type, type of organic matter, and ecosystem. For example, in vivo turnover is prominent in microbially active soils, whereas adsorption dominates in clay-rich soils. Furthermore, plant-derived compounds, such as lignin, carboxylic acids, and phenolic acids, form predominantly MOAs via the adsorption pathway, whereas microbial necromasses and microbial metabolism, such as polysaccharides and amino acids, form MOAs via the in vivo pathway. Lastly, higher microbial activity in tropical soils leads to the prevalence of MOAs via the in vivo pathway. Both pathways are common in temperate soils, whereas the adsorption pathway is prevalent in arid soils with limited microbial turnover rates(Liu et al., 2026) (see also section 1.4).

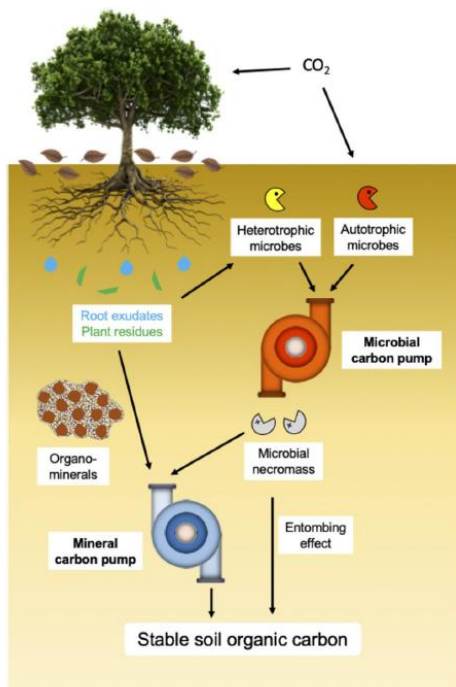


Figure 1.1 Schematic sketch showing how microbial and mineral organic pumps work together in stabilizing soil organic carbon (Qiao et al.,2025)

What is soil organic matter?

Organic matter includes dead plant, animal compounds, living animal or plant roots, which are present at different stages of decomposition, along with microorganisms combined with microbial excretions. The traditional definition of SOM is that it is composed of stable, large macromolecules known as humic substances. These humic substances are the end products of decomposition, composed of complex structures that retain plant nutrients and moisture. These end products are more resistant to further decomposition (Brady & Weil, 1996; Schnitzer & Monreal, 2011; Tan, 2014).

A modern definition of SOM is that it is a continuum of decomposing organic compounds, altered by interactions with soil minerals and microbes (Lehmann & Kleber, 2015). Here, SOM is described as a dynamic mixture of organic compounds that is continuously being transformed into various compounds, depending on the decomposition rate, environmental conditions, the availability of soil minerals, and microbial activity. So, instead of stable macromolecular humic substances with unique chemical compositions, humic substances in SOM are considered a continuum of organic material. These are closely associated with microbial and mineral pumps and are considered to be composed of smaller organic fragments that are degraded and accumulated together, forming a supramolecular association. These organic clusters bind with mineral surfaces, forming MOAs that exhibit a conceptual multilayer model. This model explains OM as a self-organized, discrete, multi-layer structure associated with mineral surfaces (Frederix et al., 2018; Kleber et al., 2007; Ransom et al., 1997; Sollins et al., 2006).

1.2 The organic phase in soil

In soil, OM comprises a minor fraction, accounting for 0.1-10% of soil mass(Chenu, 2006).

Organic matter plays a critical role in soil, providing several contributions to soil quality and health, such as binding of soil particles together to form soil aggregates, helping in soil moisture retention, acting as a nutrient reservoir, regulating acid base balance, supporting soil fauna, enhancing soils cation exchange capacity, enhancing soil structure, buffering soil pH, contributing to carbon sequestration and supporting microbial activity and diversity(Samota et al., 2024).

A series of higher-molecular-weight substances formed by secondary synthesis, termed humic substances, are considered the dominant components of SOM (Hayes et al., 2007). These substances can be further classified into 3 groups based on solubility: humic acid, fulvic acid, and humins (Hayes & Swift, 1978). Apart from humic substances, other organic components can be classified into several groups based on biochemistry, such as polypeptides, polysaccharides, and lignins, which can be found in their natural or transformed states(Hayes & Swift, 2020). Also, biota and biomolecules, including living organisms such as roots, fungi, and bacteria, as well as other microbial biomass, are integral components of SOM(Baldock et al., 2004; Chenu, 2006).

Traditionally, it has been assumed that humic substances form through the synthesis of macromolecular organic polymers. These macromolecules are treated as stable entities that are highly resistant to decomposition. They are of larger molecular size and contain strong covalent groups such as carboxyl, hydroxyl, carbonyl, quinone, amide and amino groups and thiol groups. (Lehmann & Kleber, 2015; Stevenson, 1994a)

At present, this synthesis concept is debated and has been replaced by a process that involves the oxidation and depolymerization of organic compounds. In this oxidative depolymerization concept, organic compounds decrease in molecular size through microbial decomposition, leading

to an increase in oxygen-containing functional groups, thereby increasing solubility and inducing greater ionic character (Kleber et al., 2015; Sutton & Sposito, 2005; Wershaw, 1993) (see section 1.4).

SOM can be categorized as exogenous OM (EOM), particulate (POM), mineral-associated OM (MAOM), based on the input and transformation in soil. EOM corresponds to fresh plant residues entering the soil. POM represents the intermediate stage ($>53 \mu\text{m}$), which includes partially decomposed organic particles, and MAOM are the fine ($<53 \mu\text{m}$) stabilized portion of OM. The difference between MAOM and MOAs is that MAOM refers directly to the OM portion attached to mineral, whereas MOAs refers to the whole mineral-organic matter association. Stabilization of EOM in POM and MAOMs controls carbon sequestration in soil (Brunmayr et al., 2024).

The modes of organic carbon occurrence can also be described by the terms *unprotected organic carbon* (OC), *physically protected*, and *chemically and biochemically protected* (Stewart et al., 2008). Here, *unprotected* OC refers to the portion of OC that is found in EOM, as it consists of fresh plant residues not closely associated with soil minerals. The *physically protected* OC corresponds to POM, which is the portion of OC associated with the macro and micro-aggregates. Chemically protected OC is the MAOM in which non-hydrolyzable or hydrolyzable OC such as aromatic, humified components, long-chain aliphatics, proteins, polysaccharides, and nucleic acids are sorbed and complexed. Here, the transformations EOM (lowest stability) $\rightarrow$ POM (moderate stability) $\rightarrow$ MAOM (highest stability) represent an increasing sequence of OM stability in soil (Angst et al., 2024; Manzoni & Cotrufo, 2024; Y. Peng et al., 2025; T. Zhu et al., 2021).

1.3 Mineral phase in soil

On average, 45% of the soil consists of minerals that interact with the soil solution and OM, exhibiting a range of chemical properties. These minerals mainly consist of two types: primary minerals, which are directly derived from geochemical and geological processes in the Earth's crust, and secondary minerals, which are formed under ambient conditions on the Earth's surface. Since the primary minerals are no longer thermodynamically stable, they weather under various biogeochemical conditions, which result in the release of some of their chemical components into the soil solution (Karathanasis.,2006). The abundance and solubility of secondary Si-, Al-, and Fe-bearing minerals varies with the local geology and climatic and soil conditions (Warren & Spiers, 2021).

Table 1. Major soil minerals in soil with their respective mineral group, formulas, and properties.

Mineral	Group	General Composition	Properties
kaolinite	phyllosilicate (secondary clay)	$\text{Si}_2\text{Al}_2\text{O}_5(\text{OH})_4$	Low CEC, low specific surface area
montmorillonite	Phyllosilicate-Smectite (secondary clay)	$((\text{Na},\text{Ca})_{0.33}(\text{Al},\text{Mg})_2[\text{Si}_4\text{O}_{10}](\text{OH})_2.n\text{H}_2\text{O})$	High CEC, High swelling capacity
illite	Phyllosilicate-mica (primary) (secondary clay mineral)	$(\text{K},\text{H}_3\text{O})(\text{Al},\text{Mg},\text{Fe})_2(\text{Si},\text{Al})_4\text{O}_{10}[(\text{OH})_2,(\text{H}_2\text{O})]$	Moderate CEC, 2:1 layers are held together by K^+ in interlayer
quartz	Framework Silicates (primary)	SiO_2	Extremely resistant to weathering
feldspars	Framework Silicates (primary)	$(\text{Ca},\text{Na},\text{K})(\text{Al}_x\text{Si}_{(3-x)})\text{O}_8$	Weather faster than quartz upon weathering release major precursors K,Ca,Na
muscovite biotite	Phyllosilicate-mica (primary)	Muscovite- $\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2$ Biotite- $\text{K}(\text{Mg},\text{Fe})_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$	Release K,Fe,Mg during weathering
hematite	Fe-(hydr) oxide	Fe_2O_3	Highly crystalline, positive surface charge at typical soil pH

goethite	Fe-(hydr) oxide	FeO(OH)	Well crystalline, most abundant and common
ferrihydrite	Fe-(hydr) oxide	$\text{Fe}^{3+}_{10}\text{O}_{14}(\text{OH})_2$ $\text{Fe}^{3+}_5\text{O}_7(\text{OH})$ $\text{Fe}^{3+}_2\text{O}_3 \cdot 0.5(\text{H}_2\text{O})$	Higher surface area and higher reactivity, poorly crystalline
gibbsite	Al-hydroxide	$\text{Al}(\text{OH})_3$	Most abundant Al hydroxide, Contain positive surface charge at typical soil pH
calcite	Carbonate	CaCO_3	Solubility increase at low Ph High exchangeable Ca
brucite	Mg-hydroxide	$\text{Mg}(\text{OH})_2$	positive surface charge at typical soil pH
birnessite	Mn-oxide	$\text{MnO}_2 \cdot n\text{H}_2\text{O}$	Poorly crystalline layered Mn oxide

Adapted from Warren and Spiers (2021)

Key mineral phases such as goethite, gibbsite, ferrihydrite, birnessite, and kaolinite (Table 1) play a key role in soils, forming OM interactions due to their distinct properties, such as surface charge, bond strength, and degree of structural ordering. The latter controls particle size, as the growth of larger crystals is favored by a higher degree of ordering, whereas disordering of structural components inhibits crystal growth and results in minerals with so-called nanocrystallinity. The latter minerals have a greater surface area for interactions with OM and the soil solution. The topography of the mineral surface also controls its reactivity, with surface defects such as steps, pits, and kinks increasing the surface area and the number of underbonded atoms (Bölscher et al., 2025; Mikutta et al., 2011; Schneider et al., 2010). The mineral's surface can be permanently charged, uncharged, or variably charged (Cao et al., 2024; Kleber et al., 2015), thereby controlling the size of the diffuse layer (double or triple layer) and the bonding between surface atoms and solution species. Minerals can dissolve depending on the charge density and redox sensitivity of the ions that form the mineral's crystal structure, the covalency or ionic character of the bonds, and the acid-base character of the elements; all of which control the thermodynamic chemical stability of the mineral (Bölscher et al., 2025; Essington, 2015; Swindle et al., 2014).

1.4 Physiochemical interactions in mineral organic matter associations (MOAs)

Humic substances play an important role in soils, stabilizing soil aggregates and improving soil fertility. Various reaction mechanisms (Figure 2) control the interaction between mineral surfaces and humic substances, including sorption, coprecipitation, redox reactions, polymerization, and catalysis (Z. Xu & Tsang, 2024). A wide range of minerals, including phyllosilicates, Fe-(hydr)oxides, Al-(hydr)oxides, Mn-(hydr)oxides, and carbonates, act as adsorbents for humic and fulvic acids in soil (Islam et al., 2020).

The interaction of SOM with minerals via sorption is mainly controlled by the minerals' surface properties, such as surface charge, specific surface area, and surface topography (Kleber et al., 2015; Tong et al., 2024). Isomorphic substitution, which is the replacement of an atom in a crystal structure with a similar-sized atom without causing any changes to the mineral structure, results in permanent charge in minerals, as for example, phyllosilicates often have permanent negative surface charges. With this surface charge, smectites are more likely to attract positively charged cations such as Ca, Fe, and Mg ions, which results in the reversal of their surface charge, allowing the adsorption of negatively charged organic substances via cation bridging (Mineral-cation-organic matter association). With variably charged minerals, the soil pH mainly controls their surface charge through protonation or deprotonation of hydroxyl groups. Under acidic conditions, surface O-atoms can be highly protonated and bind to negatively charged OM moieties via ligand-exchange mechanisms and electrostatic interactions (Ni & Pignatello, 2018; Schwarzenbach et al., 2017). Under alkaline conditions, surface hydroxyl groups on minerals deprotonate, resulting in decreased adsorption of SOM on mineral surfaces (W. Li et al., 2018). In these instances, the availability of cations such as Fe and Ca might promote the formation of bridging complexes between OM and minerals (X. Peng et al., 2005; Shaker et al., 2012).

On uncharged, neutral mineral surfaces, hydrophobic interactions, H-bonding, and van der Waals forces will be the primary mechanisms controlling sorption (Sparks & Antanasovic, 2015; Willemsen et al., 2019). First, the sorption of OM on mineral surfaces forms a monolayer and is followed by the polymerization of OM towards a multilayer structure (Huang et al., 2020; Kleber et al., 2007). This multilayer structure is promoted by the presence of cations such as Ca in the soil solution, and hydrophobic interactions between organic molecules (Gao et al., 2020; Piccolo & Mbagwu, 1999; Wuddivira & Camps-Roach, 2007).

Co-precipitation is another reaction mechanism that leads to the formation of MOAs. It is controlled by the pH and redox conditions along the mineral-bulk soil interface. In addition to physical entrapment of SOM with minerals, coprecipitation also significantly alters the reactivity of both minerals and OM. Coprecipitation results in the formation of dense agglomerates, thereby decreasing surface area (Zhang et al., 2023).

A common example is the coprecipitation of Fe(hydr)oxides with humic substances, mostly in fluctuating redox environments such as wetlands and paddy fields (Kato et al., 2004; Riedel et al., 2013). The OM in these coprecipitates suppresses short-range-ordered Fe-(hydr)oxides, such as ferrihydrite, thereby promoting their transformation into more crystalline Fe-(hydr)oxides with long-range order (Noor & Thompson, 2022). Sorption and coprecipitation depend on the concentration of SOM in soil, where a lower concentration of SOM facilitates sorption onto minerals, and higher concentration enhances coprecipitation with minerals (Jamoteau et al., 2025).

Redox reactions between SOM and redox-active minerals can involve the direct electron transfer between minerals and OM, the formation of reactive oxygen species (ROS) (B. Li et al., 2024) as a result of redox transformations, and electron transfer induced by microorganisms. In a direct electron-transfer reaction, functional groups such as phenolic hydroxyl groups act as electron

donors, reducing cations on the mineral surface. Here, electron-donating groups in SOM undergo oxidative transformation, and the resulting changes in molecular size occur as aromatic rings or fractured C chains (Kleber et al., 2021; Tong et al., 2024). ROS, such as peroxides and superoxides, are derived from minerals and play an important role in redox reactions, increasing the oxygen-containing groups in OM and decreasing the size of organic molecules. Microorganisms are involved in mineral redox transformations, using SOM as the electron source. Some redox-active minerals containing Fe and Mn can promote the oxidative polymerization of SOM by acting as strong oxidants. SOM donates electrons to these minerals, forming organic radicals and reactive intermediates that subsequently cross-link to yield larger OM macromolecules via radical coupling. Non-redox-active minerals do not show a particular impact on the above oxidative polymerization of organic compounds relative to Fe/Mn minerals. The latter polymerization is commonly catalyzed by minerals containing redox-active metals (Bu et al., 2017; LaCroix et al., 2021; Moore et al., 2023; Z. Xu & Tsang, 2022; Zhuang et al., 2022).

According to Kleber et al. (2021), five types of chemical processes occur between minerals and OM, affecting OM stability: (1) Electrolytic breakdown of OM due to oxidation of OM caused by minerals. This includes highly redox-sensitive minerals such as MnO_2 , which result in much smaller oxidized OM fragments. (2) The formation of large OM molecules, which is promoted by radical-mediated polymerization and nucleophilic addition. (3) Hydrolytic breakdown on hydrophilic surface produces smaller, more soluble OM compounds. (4) ROS adsorbed to mineral surfaces lead to heterogeneous oxidation of OM along the OM-mineral interface. (5) Electron-transfer reactions between OM and mineral alter the structure and coordination environment in the surface of the latter.

OC in SOM can be grouped as Fe-bound OC and silicate-bound OC based on the abundance of Fe-(hydr)oxides and silicates in soil. Silicate-bound OC is observed as a major and more stable MAOM reservoir in coastal wetlands. Silicate-bound OC account for ~58% of total OC in the coastal wetland, much greater than the Fe-bound OC (~13%)(Ma et al., 2025).

In MOAs, OM acts as an active self-protector, inhibiting mineral transformation while preserving surface area, thus, promoting the stability of MAOM. Different environmental conditions affect the stability and degradation of MOAs. In flooding areas of paddy fields under anoxic conditions, crystalline Fe-(hydr)oxides can undergo reductive dissolution, forming non-crystalline Fe-(hydr)oxides. These oxic and anoxic cycles lead to the formation of amorphous Fe-(hydr)oxides, which have a greater surface area, binding capacity, and reactivity towards organic functional groups, thereby increasing the stability of MOAs (Kaiser & Guggenberger, 2000; Kleber et al., 2007; Wagai & Mayer, 2007).

To better understand the interactions between minerals and organic matter in natural soil, MOAs were synthesized using synthetic or natural minerals and organic matter components (Table 2) and characterized using various analytical techniques (Wei & Xiang, 2013; Zhang et al., 2023; Zhao et al., 2023).

Table 2 Model organic compounds used in previous experimental studies to synthesize MOAs

organic compound	Used mineral	properties	reference
humic acid	Fe(NO) ₃ 0.9H ₂ O bentonite kaolinite Ca-montmorillonite hematite magnetite	Presence of reactive functional groups, which promotes binding mechanisms	(Demangeat et al., 2020; Fariña et al., 2018)
Fulvic acid	bentonite kaolinite montmorillonite goethite ferrihydrite	Presence of high % of carboxyl groups, low molecular weight, high solubility	(Dubbin et al., 2014; Zhang et al., 2023)
teichoic acids, nucleic acids, phospholipids	goethite and Al hydroxides	Presence of Phosphoryl groups	(Mikutta et al., 2009; Omoike & Chorover, 2006)
Acetic acid	poorly crystalline Al(OH) ₃ goethite	low-molecular weight organic acid	(Masion et al., 1994)
polygalacturonic acid (PGA)	ferrihydrite-PGA complexes	a typical SOC that controls transformation of ferrihydrite	(J. Wu et al., 2026)
hexadecyltrimethylammonium (HDTMA)	montmorillonite	long-chain alkylammonium cations	(Bonczek et al., 2002a)
Oxalic acid	lepidocrocite boehmite alumina α-Al ₂ O ₃ goethite	low-molecular weight organic acids ability to form bidentate inner-sphere complexes	(Hug & Bahnemann, 2006; Persson & Axe, 2005)
Bacterial cells	ferrihydrite	Rich in proteins and lipopolysaccharides which contain functional groups	(Rancourt et al., 2005)

Fatty acids palmityl palmitate stearic acid	montmorillonite	Consist of double and single alkyl chains	(Dubbin et al., 2014)
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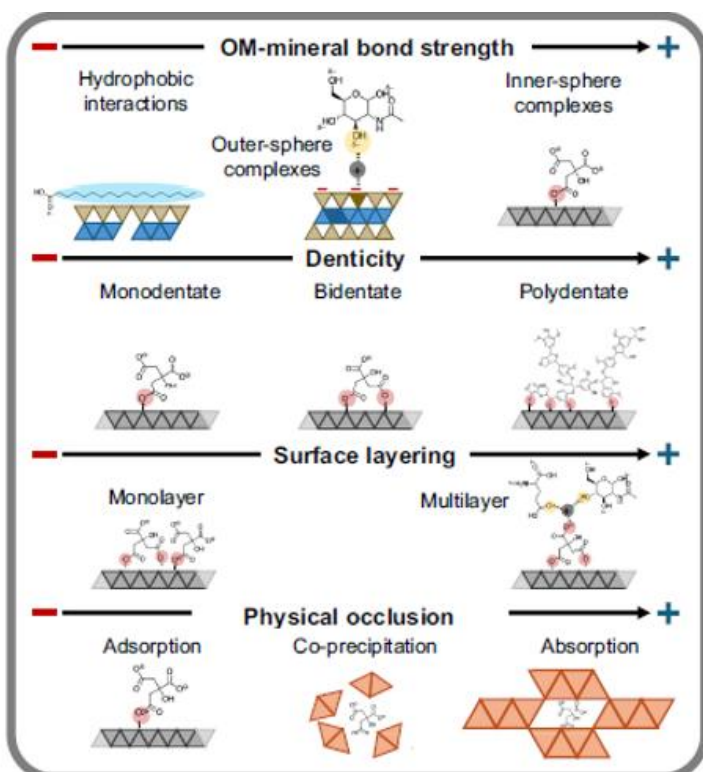


Figure 2. Schematic sketch showing Chemical and physical properties of OM-mineral interactions based upon bond strength between OM and mineral, surface layering of OM, denticity and physical occlusion (Bölscher et al., 2025)

1.4.1 Point of zero charge concept

The point of zero charge (PZC) and the Isoelectric point (IEP) are two specific metrics used to quantify surface charge and provide important insights into processes such as adsorption and particle aggregation. IEP is the pH at which the electrokinetic potential of the surface is equal to zero and exhibits a zero net electrophoretic mobility. PZC is defined as the pH at which the net

surface charge density equals zero for solid materials in solutions (Alvarez-Silva, Mirnezami, et al., 2010; Kollannur & Arnepalli, 2019). The latter can be measured using potentiometric titrations or the measurement of a material's surface charge in the presence of an inert electrolyte (Kosmulski, 2023; Mullet et al., 1999). The PZC concept does not explain the complete absence of surface charge; rather, it defines the zero net charge density as the point at which the total negative charge equals the total positive charge. If the contact pH of a solution in contact with a mineral is larger than the point of zero charge, the net proton surface charge of that mineral is negative. In contrast, if the pH is smaller than the point of zero charge, the surface charge is positive. Hence, the pH of the solution can be used to increase or decrease electrostatic attractions between mineral surfaces and dissolved species. Table 3 indicates PZC of some common minerals in soil.

This principle is used in this thesis to synthesize MOAs by creating positively charged mineral surfaces that attract negatively charged fulvic acid molecules. Organic matter contains acidic functional groups such as carboxylic and phenolic groups (Islam et al., 2020), which deprotonate, forming carboxylate and phenolate anions depending on the environmental pH of soil solutions and natural waters, thereby imparting a negative charge to the OM. Average pK values corresponding to ionization of carboxylic groups in fulvic acid fall in the range of pH 3.0-4.5 (Schnitzer & Kodama, 1972).

Table 3. Point of Zero Charge (PZC) of common minerals in soil

Mineral	PZC	Reference
ferrihydrite	7.6-8	(Mendez & Hiemstra, 2020)
hematite	8- 9.2	(Qin et al., 2015; Ramos-Tejada et al., 2003)

goethite	9.2	(Saito et al., 2004)
magnetite	6-6.5	(Fan et al., 2015; Tang et al., 2016)
kaolinite	4.5-5.0	(Hur & Schlautman, 2003; Schroth & Sposito, 1996)
α -Al ₂ O ₃	5.5	(K. Yang et al., 2009)
γ -AlOOH	8.7	(Tombácz et al., 2000)
pyrolusite(β -MnO ₂)	2.5	(Bernard, 1997)
montmorillonite	3.5-5	(Ijagbemi et al., 2009)
clinochlore	4.7	(Alvarez-Silva, Uribe-Salas, et al., 2010)

1.4.2 Role of Calcium in the stabilization of organic matter

Exchangeable Ca is often associated with SOM and clay minerals. The element plays a significant role in controlling physicochemical interactions between minerals and OM, thereby reducing SOM in soil through processes such as complexation, co-precipitation, and sorption(Barreto et al., 2021; Rowley et al., 2018).

SOM stabilization through ion complexation (e.g., with Ca, Al, and Fe), and soil pH are important processes for the sequestration of carbon(Kalbitz & Kaiser, 2008; Scheel et al., 2008). Under acidic conditions (pH 4-6), coagulation of humic acid occurs upon the introduction of aqueous cationic species, with Ca²⁺ having a greater effect (due to its higher affinity for the carboxyl groups of humic acid) than Al³⁺ or Fe³⁺ (Christl & Kretzschmar, 2007a)

Na and Ca are common cations in soils that drive SOM aggregation and stabilization and hinder degradation. Among these cations, Ca²⁺ is observed to cluster a higher number of COO⁻ groups due to its stronger electrostatic interactions than Na⁺(Galicia-Andrés et al., 2021). Also, Ca-

induced cation bridging among humic acid molecules stabilizes organic matter aggregates, thereby forming stronger humic acid complexes. The presence of Ca^{2+} leads to the formation of compact molecular aggregates by coordinating with various humic acid, fulvic acid, and water molecules. Calcium reduces the repulsion between negatively charged organic ligands, promoting flocculation and forming stable aggregates. For example, Ca ions promote the aggregation of HA- Ca^{2+} complexes, their adsorption on the surface of kaolinite, and the subsequent formation kaolinite-HA MOAs. Furthermore, the stability of HA-clay decreases in the absence of Ca^{2+} due to reduced HA compaction and rigidity. This results in the formation of small, individual HA molecules, strong evidence that Ca^{2+} acts as a stabilizing agent in MOAs by enhancing the stability of OM coatings on mineral surfaces(Barreto et al., 2021; Galicia-Andrés et al., 2021; Kloster et al., 2013).

1.5 Soil contamination by metals

Heavy metal contamination in soil and water is a significant environmental issue, as these metals pose a significant threat to plant and human health due to their toxicity and persistence in the environment(Adnan et al., 2022; M. Wu et al., 2021). The bioavailability of heavy metals in soils varies with their chemical forms and speciation, which mainly influence their mobility in the environment and the risk of entering food chains in the biosphere (Essalmi et al., 2024; S. Liu et al., 2021). Mining, smelting, agricultural activities, and various other industries cause heavy metals such as Pb, Cd, Zn, Cu, Ni, Mn, Co and Hg to enter and accumulate in soils (C. Li et al., 2019; Shahid et al., 2017).

Various factors, including pH, soil organic matter, mineral content, soil porosity, soil surface area, and microbial activity, influence the chemical forms of metals in polluted soils. Chemical properties of these metals, such as redox activity and Lewis acidity, and physical properties, like

ionic radius, control the behavior of these heavy metals in soils (Violante et al., 2010; Wan et al., 2024). Heavy metals exhibit distinct chemical behaviors in soil, with Cd, Cu, and Zn showing higher solubility and Phyto availability in the rhizosphere than other metals. A study conducted near a Pb smelter showed that migration of heavy metals from the surface to the deeper parts of the Pedon decreased in the sequence $Cd > Zn > Pb > As$ (C. Li et al., 2024). Heavy metals introduced into soil as ions, such as Cu^{2+} and Pb^{2+} , can sorb onto mineral surfaces or exchange with other cations, such as Al^{3+} and H^+ (Setia et al., 2023). Hence, the sequestration of heavy metals is promoted by minerals of larger surface areas such as clays and migration is promoted by a higher sand content. Primarily, the deposition of heavy metal pollutants is controlled by the spatial distance from the emission source. For example, Zhu et al., 2018 observed a reduction in Hg concentration with increasing distance from Hg factories.

Contamination of soil by Cu and Ni significantly impacts the environment by increasing their bioavailability (Begum et al., 2022). Although both Cu and Ni are essential micronutrients for plant and human health, elevated concentrations can be toxic, inhibiting plant growth and nutrient uptake and causing diseases in humans (Alloway BJ, 2013; Yruela, 2009). In Canada, typical Cu concentrations in soils average $20 \text{ mg} \cdot \text{kg}^{-1}$ (ranging from 2 to $100 \text{ mg} \cdot \text{kg}^{-1}$), while background levels for Ni are about $26.8 \text{ mg} \cdot \text{kg}^{-1}$ (Paria & Yuet, 2006). Smelting and mining of metal ores are among the most significant sources of soil and water contamination, releasing Cu- and Ni-bearing particulate matter into the environment (Nriagu et al., 1998). Soils act as direct repositories for both metals, especially fine particulates ($<0.5 \text{ mm}$) that can disperse over long distances (Ettler et al., 2005). This is exemplified by the severe Ni and Cu contamination in the Sudbury mining and smelting region of Ontario and by decades of Ni deposition from industrial activities in Port Colborne, Ontario (Dutton et al., 2019; Hutchinson & Whitby, 1974).

1.5.1 Sequestration of metal contaminants by MOAs

According to (Shuman (1991), when metal contaminants are introduced into soil through anthropogenic activities, they are incorporated into one of the following pools: dissolved fraction in soil solution, adsorbed onto inorganic components, occupying exchange sites on minerals, precipitating, or associated with soil organic matter.

Heavy metals could form ternary complexes with mineral and OM associations, with two types of ternary complexes observed: (A) the metals act as a bridge between organic matter and the mineral, and (B) the metals bond to organic matter that is adsorbed to the mineral. Furthermore, heavy metals form binary complexes with either OM or mineral. The sequestration of metals by MOAs is commonly controlled by the organic matter-to-mineral mass ratio, the heavy metal concentration, and the pH of the soil solution(Q. Li et al., 2022; Yu et al., 2023).

Clay minerals, including smectite clays, absorb heavy metals via two different mechanisms: 1) inner-sphere complexation at clay edges via Al-O or Si-O groups, 2) interlayer cation exchange mechanism due to the negative charge on the clay mineral surface(Abollino et al., 2003). Phyllosilicate-bearing MOAs show increased sorption of heavy metals such as Pb, Cd, and Cu due to a higher number of functional groups on their surfaces, resulting from humic substances adsorbed on them(Zhang et al., 2017). Yet in some cases, the presence of OM adsorbed onto clay minerals reduces the amount of adsorbed heavy metals, possibly due to the complexation of metals by organic ligands in solution and the saturation of mineral surface-active sites by organic functional groups (Yan et al., 2022).

Adsorption of heavy metals onto (hydr)oxides increases in the presence of humic and fulvic acids, resulting in higher adsorption capacity. Here, the presence of humic substances reverses the surface

charge of the (hydr)oxides under acidic to near-neutral pH conditions (from positive to negative), thereby enhancing the affinity towards metals (Demangeat et al., 2020; Fariña et al., 2018)

1.5.2 Metals that have a higher affinity towards OM or Minerals

In soil, metal ions like Fe^{3+} , Al^{3+} , Cu^{2+} , Zn^{2+} , and Pb^{2+} form stronger complexes with organic ligands, than the more mobile metal ions Mg^{2+} , Mn^{2+} , Cr^{6+} , and Ni^{2+} , with the stability of the latter metal-organic ligand complexes being more dependent on pH, ionic strength, and cation exchange (Christl et al., 2001; Duan et al., 2024; Parvin et al., 2022). Some showed that Pb and Cu exist primarily in complexes, whereas Cd, Zn, and Ni can occur as free ions in soil solutions. Higher pH enhances the dissolution of soil organic matter, thereby increasing dissolved Cu concentration through Cu-organic complexation (McBride, 1989). In soils, the amounts of Cu adsorbed to OM and complexed by dissolved organic carbon are almost equal (Temminghoff, 1998). The complexation of Pb, Cd, and Zn by organic ligands in soil solution correlates with OM content, with the latter favoring their retention and suppressing their bioavailability (Weng et al., 2002; zhang et al., 2017). Although Ni has a lower affinity for organic matter than e.g. Cu, the abundance of Ni-OM complexes depicts a positive correlation with the OM content. In this regard, the trend to be sorbed by mineral surfaces and organic matter in organic- and clay-mineral-rich soils decreases in the sequence $\text{Pb} > \text{Cu} > \text{Cd} > \text{Zn} > \text{Ni}$ (Christl et al., 2001; Jalali & Moradi, 2013). As with OM, metals exhibit different affinities for common soil minerals, such as Fe-(hydr)oxides and phyllosilicates. Most of the metals' binding affinity towards most of the substrates and donor ligands follows the Irving–Williams series: $\text{Mn}^{2+} < \text{Fe}^{2+} < \text{Co}^{2+} < \text{Ni}^{2+} < \text{Cu}^{2+} < \text{Zn}^{2+}$. The total adsorption capacity of montmorillonite towards metals increases in the sequence $\text{Pb}^{2+} = \text{Cd}^{2+} < \text{Cu}^{2+} < \text{Zn}^{2+} < \text{Mn}^{2+} < \text{Ni}^{2+} < \text{Cr}^{3+}$ (Abollino et al., 2003). On the contrary, diffusion of these metals

into the interlayer of montmorillonite occurs with greater difficulty with increasing atomic weight (Abollino et al., 2008), a trend also observed for alkaline-earth metal ions (Wild & Keay, 1964).

In this study, Cu and Ni ions were used as cationic species because they are toxic to plants and human health at elevated concentrations. Furthermore, we have a good understanding of how Cu and Ni interact with OM and minerals with Cu and Ni depicting higher and lower affinities for OM, respectively.

1.5.3 Low-T geochemistry of Copper

Cu occurs in three phases in the environment: 1) in the aqueous phases as soluble complexes and free ions, 2) in the solid phase with soil, sediments, and as colloids, 3) in the biological phase, where it is incorporated or adsorbed into biota—adsorption, complexation, and precipitation control the availability, forms, and levels of Cu in the environment. Copper adsorbs onto a range of mineral species, with the order of affinity as follows: clay minerals < Fe-oxides < Mn-oxides (Oorts et al., 2006) Various clay minerals, such as kaolinite, montmorillonite, and illite, have different Cu adsorption capacities that correlate with their respective cation exchange capacities (Riemer & Toth, 1970). Cu adsorbs onto mineral surfaces via chemisorption and physisorption, with adsorption strengths ranging from weak van der Waals forces to stronger covalent bonding (Ramamoorthy & Rust, 1978). Majority of the total Cu was associated with organic matter in soil and that Cu^{2+} outcompetes most other divalent cations for adsorption sites on organic matter (Machado et al., 2023).

Abiotic precipitation of Cu depends on the pH of the soil solution or natural waters with CuO and CuCO_3 the dominant phases under near neutral pH conditions and $\text{Cu}(\text{OH})_2$ at high pH. In natural waters, the most prominent inorganic Cu complexes are CuOH^+ , $\text{Cu}(\text{OH})_2^\circ$, $\text{Cu}_2(\text{OH})_2^{2+}$,

(CuCO_3° , $\text{Cu}(\text{CO}_3)_2^{2-}$), with the latter being dominant at high CO_2 (Stiff, 1971; Sylva, 1976). Cu^{2+} forms very strong complexes with organic compounds containing electron-donating groups. Most importantly, Cu-fulvate and Cu-humate complexes in natural waters and in natural soil solutions are the major drivers of Cu binding in the environment (Flemming & Trevors, 1989). CuS forms at high H_2S under anaerobic environments (Evanko & Dzombak, 1997).

1.5.4. Low- T geochemistry of Nickel

Nickel is a siderophile element and is commonly associated with Fe- and Mn-(hydr)oxides (Machado et al., 2023). Hence, its mobility is strongly coupled to the stability of the latter minerals, which dissolve under reducing conditions due to the reduction of Fe^{3+} and Mn^{4+} . Less common sinks of Ni^{2+} in soils are clay minerals such as smectite and kaolinite (Machado et al., 2023) and OM (Cameron & Vance, 2014). Under anoxic conditions, Ni can be immobilized by sulfide or sulfate ions. Ni solubility is high under acidic conditions, such as acidic soils and mine wastewater. There is a dynamic cycling of Ni in wetland environments. Under anoxic conditions, it precipitates as sulfides, whereas under oxic conditions, the sulfides oxidize, releasing Ni into solution (Neubeck & Kirschning, 2026).

1.6 Analytical characterization of mineral-organic matter associations and their interface

Reactions and processes between minerals and organic matter occur along mineral-OM interfaces. The organo-mineral interface is a complex system, where excess free energy is associated with mineral and OM. The mineral-OM interface is a dynamic system that changes with the chemical and mineralogical compositions of OM, mineral, and aqueous phases (Kleber et al., 2021). Once an OM molecule is adsorbed onto a mineral surface, it, in turn, undergoes changes in its structure,

hydration, and electron delocalization, which depend on the type of bonding in the soil pore-water solution (Kleber et al., 2021). Mostly, low-molecular-weight organic ligands with amphiphilic properties bind to the mineral-OM interface in soil pore water. These organic ligands can bind to mineral surfaces via ligand exchange, hydrophobic interactions, hydrogen bonding, van der Waals forces, and cation-bridging and exchange mechanisms (Ni & Pignatello, 2018; Schwarzenbach et al., 2017; Willemsen et al., 2019).

A range of advanced analytical techniques, including spectroscopic methods such as IR, Raman, and Fluorescence, and microscopy techniques such as SEM, TEM, and AFM, are most commonly used to characterize spectroscopic and mineralogical features along mineral-organic matter interfaces (Tong et al., 2024). Electron energy-loss spectroscopy, associated with TEM, is another technique for characterizing the speciation of elements at organic-mineral and organo-organic interfaces (Possinger et al., 2020).

1.6.1 BET surface area analysis

BET stands for Brunauer-Emmett-Teller and is a technique that measures the surface area of a material such as MOA (Dollimore et al., 1976). Here, an analyzer measures the physical adsorption of N₂ on the surface of a material, including porosity. The sample is degassed and heated under vacuum in the presence of an inert gas to remove contaminants and moisture, respectively. The clean sample is cooled using liquid N, and the adsorbate gas (N₂) is introduced into the sample chamber at increasing pressure while the temperature is constant. The change in pressure with the amount of gas adsorbed on the material is monitored, and the surface area is determined using the BET equation :

$$\frac{1}{v\left[\left(\frac{p}{p_0}\right) - 1\right]} = \frac{c - 1}{v_m c} \left(\frac{p}{p_0}\right) + \frac{1}{v_m c}$$

V = adsorbed volume of gas

V_m = adsorbed monolayer volume

p = equilibrium gas pressure

p₀ = saturation pressure

c = BET constant

The intercept and slope of this equation can be used to calculate the specific surface area by following the equation.

$$S = \frac{v_m N A}{22,400 \times m}$$

N = Avogadro's number

A = cross-sectional surface area of a single adsorbed gas molecule

M = mass of nanomaterials used in the measurement

22,400 = Standard Temperature and pressure (STP) volume of one mole of gas

BET analysis requires that the material's surface is homogeneous, a local equilibrium exists between the uppermost layer and gas/vapor molecules and that limited molecular interactions, between adsorbed molecules and gas phase molecules exist. (Brame & Griggs, 2016).

1.6.2 TOC analyzer

The amount of organic carbon is measured using two distinct methods: the Total Organic Carbon (TOC) method and Non Purgeable Organic Carbon (NPOC) method. In the TOC method, both organic and inorganic carbon (TC) in the sample are measured; inorganic carbon is removed as

CO₂ upon acidification, and the remaining carbon is quantified upon subtracting inorganic carbon from total carbon.

The NPOC method used in this study involves the following four major steps:

1. The sample undergoes acidification (conversion of IC to CO₂);
2. The CO₂ is purged using an inert gas such as N₂;
3. The remaining non-volatile organic carbon remains in solution and is then injected into a high-temperature combustion tube;
4. The resulting CO₂ is carried into a non-dispersive infrared (NDIR) detector, where the amount of CO₂ is quantified using the absorption intensity of the CO₂ peak (at 4.26μm wavelength) and a calibration curve based on the Beer-Lambert law.

1.6.3 UV- vis spectrophotometer

Absorption of visible or ultraviolet light by sample molecules is measured using UV-Vis spectroscopy. Absorbance A is measured by the logarithm of the intensity of incident radiation (I₀) divided by the intensity of transmitted radiation(I)

$$A = \epsilon L c = \log_{10} \left(\frac{I_0}{I} \right) = \log_{10} \left(\frac{1}{T} \right) = -\log_{10}(T)$$

Beer-Lambert law is applied to find the concentration of the sample, where

A = amount of light absorbed/transmitted by the sample

ε = molar absorptivity constant

c = concentration of the sample

L = distance that light travels through the sample (path length)

The basic components of a UV-visible spectrophotometer are a light source that produces electromagnetic radiation in the UV-visible region, a dispersing device (possibly a monochromator) that selects a specific wavelength, a sample cuvette, and a detector that measures transmitted light, thereby allowing the instrument to calculate absorbance(Khalid et al., 2024).

1.6.4 Fourier-transformed infrared spectroscopy (FTIR)

FTIR is a widely used analytical technique for characterizing organic samples because it selectively absorbs infrared light at specific wavelengths. FTIR generates an absorption or transmission spectrum of the sample, which corresponds to the characteristic functional groups it contains. The emitting source emits a broad spectrum of IR light toward the sample through an interferometer, which splits the light. Then this light passes through the sample; depending on the sample's properties, specific IR frequencies can be absorbed or reflected, corresponding to molecular functional groups and chemical bonds. When the frequency of incident IR light matches the vibrational frequency of a specific bond in the sample, the light is absorbed. The detector records the transmitted light, which is then converted to a readable format using Fourier transform equations (Al-Amin et al., 2025; Nagaraju & Amreen Sulthana, 2025)

1.6.5 Powder X-ray diffraction (PXRD)

Powder X-ray diffraction (PXRD) is a fingerprinting and crystal structure analysis technique for solid-state materials. In non-crystalline (amorphous) material, only the short-range order can be detected with XRD in the form of a broad peak (Bates et al., 2006). Nanocrystalline phases such as ferrihydrite can have various degrees of crystallinity, which results either in the occurrence of

two (2-line ferrihydrite) or six diffraction peaks (6-line ferrihydrite)(Carta et al., 2009; Funnell et al., 2020). Powder X-ray diffraction patterns of crystalline phases show a lower and higher number of diffraction peaks for high- and low-symmetry structures, respectively.

A PXRD consists of three main components: X-ray tube, a sample holder, and an X-ray detector. In the X-ray tube, Cu is used as the anode material. A shutter is located in the X-ray tube as a safety device to prevent X-rays from exiting. An X-ray detector reads the X-ray signal from the sample by counting the number of X-rays diffracted at a given angle, two-theta. All the above components are part of goniometer circle, whereas the sample is along the focusing circle.

According to Bragg's law,

$$n(\lambda) = 2d \sin \theta$$

When the X-ray is incident onto a crystal surface, its angle of incidence,

θ , will reflect with the same angle of scattering, θ (70).

n - positive integer

λ - wavelength of X-ray

d - distance between the lattice planes

$\sin \theta$ - incident angle

A diffraction peak is, however, only observed when there is positive interference between the diffracted X-rays. Whether positive interference for a given lattice plane is observed depends on the d -spacing (d) and symmetry relations between lattice planes.

Powder X-ray diffraction can also be used to determine the crystallinity of clay minerals and the swelling of their interlayer through intercalation of H_2O groups and organic molecules. For this purpose, the clay minerals are often deposited on sample holders in an orientated fashion, with

their basal plane parallel to the sample holder surface. This was, however, not conducted in this study, and all XRD patterns of montmorillonite samples were carried out in a non-oriented fashion.

1.6.6 Transmission electron microscopy

Transmission electron microscopy (TEM) is widely used in materials science, inorganic chemistry, and nanotechnology research. Advanced TEM can achieve a high spatial resolution of 0.05 nm and an energy resolution of 7 meV (Su, 2017). The basic working principle of the transmission electron microscope can be explained as follows: An electron gun generates a focused beam of high-energy electrons transmitted through the thin specimen. The transmitted electron beam is focused by three electromagnetic lenses, namely, a condenser lens, an objective lens, and a projector lens, to form an image on a screen. The condenser lens controls how strongly the beam is focused onto the specimen, while the objective lens focuses the transmitted electrons onto a projector lens, which magnifies the image to a screen or camera. Transmission Electron Microscopes (TEMs) typically consist of five major components: a high-voltage source, a vacuum system, a microscope column, detectors, and control computers with software. The high-voltage source, including the electron gun, controls the kinetic energy of the electron beam. In TEMs, either thermionic emitters or field emitters can be used as the high-voltage source. The microscope column consists of a series of electromagnetic lenses and apertures that focus the electron beam onto the sample while magnifying the TEM image on the viewing screen or detectors. A vacuum system is essential for maintaining the appropriate vacuum levels throughout the column.

Conventional TEM techniques, such as bright-field (BF) and dark-field (DF) imaging, selected area electron diffraction (SAED), high-resolution TEM (HRTEM), and energy dispersive X-ray spectroscopy (EDS), can provide information on particle size, morphology, crystal structure, and

local chemical composition (Liang et al., 2017). Here, Bruker ESPRIT software was used to process STEM-EDS chemical distribution maps, including the semiquantitative analysis of the EDS spectra. During the latter analysis, the Software normalizes the concentrations of the elements to 100% .

Bright field imaging is the most common TEM imaging mode, which uses directly transmitted electrons to form the image. Here, only the transmitted beam can pass the objective aperture to create images. Thicker areas and denser materials tend to scatter electrons more strongly, appearing as dark regions. Thinner, less dense regions scatter electrons less strongly, appearing as bright regions. Mass thickness and diffraction effects are the causes of the provided contrast. In dark-field imaging, only the diffracted electrons are used rather than the transmitted electrons. The diffracted electrons are allowed to pass the aperture to form either off-axis or tilted-beam images. Crystalline regions that satisfy Bragg's conditions appear bright, while other areas appear dark.

1.6.7 Electron energy-loss spectroscopy (EELS)

Electron energy-loss spectroscopy measures the energy loss of high-energy electrons as they pass through a material (Taioli et al., 2010). When an electron beam interacts with a sample, it can undergo either elastic scattering or inelastic scattering. In EELS, the loss of energy of inelastically scattered electrons is recorded. This energy loss can provide various information about the sample's bonding environment, composition, and electronic structure (Lazar et al., 2025). When high-energy electrons transmit through a sample, several energy-loss processes occur due to various physical and chemical processes; when the electrons do not induce any interaction, the energy loss is equal to zero (corresponds to a zero-loss peak). Electron oscillations give rise to plasmons, outer shell excitations (10-50 eV) cause a low loss region, and inner shell ionizations, which have higher

energy loss (>50 eV), correspond to the core loss region (Egerton, 2011) . These energy-loss events occur when the electron beam passes through the sample; as a result, those electrons undergo different processes before entering the spectrometer as a single beam. TEM-EELS instrumentation is primarily based on a magnetic prism, a spectrometer through which the electrons enter after interacting with the sample . In this magnetic prism, a uniform magnetic field causes the electrons to move in circular paths of radius R, as given by the equation below.

$$R = (m/e)Bv.$$

Here, R = bending radius

V=electron speed, where this electron speed is correlated with energy,

Here, higher-energy electrons bend less in the magnetic field and exit the magnetic prism at a larger radius. At the same time, low-energy electrons with a lower velocity bend more, leaving the magnetic prism in a smaller radius. Hence, the magnetic prism separates electrons by energy and simultaneously focuses electrons of the same energy to a single point , producing a spectrum that shows energy loss (on the x-axis) versus intensity (on the y-axis). In the latter spectrum also occurs the zero-loss peak, the low-loss region, plasmons, and the high-loss regions(Egerton, 2009).

1.7 M.Sc. Thesis Structure

This thesis comprises three chapters. The first chapter (current chapter) provides a detailed introduction to mineral-organic matter associations in soils and to the interactions between OM and mineral phases; an overview of the sequestration of heavy metals by MOAs; and a summary of the analytical instruments used in my thesis to characterize MOAs. This introductory chapter also includes research objectives, questions, a hypothesis, and a concise description of the research rationale. The second chapter is the main chapter of the thesis. It shows the dynamic nature of

MOAs in adsorption experiments involving Cu and Ni and has been accepted in the Journal Chemosphere (Elsevier). Chapter 3 provides an overall conclusion and recommendations for future research.

1.8 Research questions

This study addresses the following research questions:

1. How are the composition and structure of MOAs affected by the presence of different concentrations of Cu and Ni?
2. How are Cu and Ni sequestered by synthesized MOAs with *M* being either montmorillonite (Mt) or ferrihydrite (Fh) and *O* being fulvic acid (FA)?
3. How do their distribution and speciation change with different concentrations of Ni and Cu?
4. What is the role of polar surfaces on the surfaces of montmorillonite and ferrihydrite, and what is the role of the polar organic functional groups along the mineral-OM interfaces in the sequestration of Cu and Ni by MOAs?

1.9 Research Hypotheses

The studies were conducted based on the following research hypotheses:

1. The composition and structure of MOAs change in adsorption experiments with Cu and Ni ions, as these cations may cause desorption and polymerization of the bound OM component in MOAs.
2. Cu and Ni are more abundant at mineral-OM interfaces than in organic matter alone due to surface-induced polarization of the OM along the latter interfaces.

1.10 Research objectives

The objectives of this study are to

- Understand the mechanisms governing the interaction of mineral-organic matter associations with Cu and Ni.
- Synthesis and structural characterization of MOAs in the laboratory and the study of their sequestration of Cu and Ni.
- Characterize structural changes in MOAs in adsorption experiments with metals of high toxicity, high and low affinity for OM, and with well-known interactions with OM and the mineral component.
- Determine whether structural changes in MOAs are cation-dependent and whether they enhance the sequestration of toxic elements.

In this study, structural and compositional changes in the FA-Mt and FA-Fh associations with increasing concentrations of Cu^{2+} and Ni^{2+} are monitored using a unique combination of scanning-transmission (STEM) and transmission electron microscopy (TEM), ultraviolet-visible spectroscopy (UV-Vis), total organic carbon (TOC) analyzer, X-ray powder diffraction (XRD), Fourier transform infrared (FT-IR) spectroscopy, and electron energy loss spectroscopy (EELS).

1.11 Research Rationale

Previous studies (Bölscher et al., 2025; Keiluweit et al., 2015; Kleber et al., 2021), discuss the interaction of minerals and metals with OM and how these interactions and other environmental parameters in soils induce structural and compositional changes in OM. Most studies discuss this very generally, assuming that the existing minerals and cations in soil drive all reactions at the mineral-organic-matter interface. Hence, from a heavy metal contamination perspective, it is not

clear whether the metal contaminants introduced into soils change the structure and composition of MOAs, whether they induce polarity at the mineral-organic matter interface, or whether polarity in MOAs pre-existed the sequestration of heavy metals.

Instead, almost all previous studies focused on the common occurrence of MOAs and metals in soils. X.Li et al. (2025) suggested that OM in metal-bearing MOAs contains a higher number of polar functional groups. This raises the question of whether polarity occurred prior to metal sequestration or whether the metal induced greater polarity in OM and along the mineral-organic-matter interface. Kleber et al. (2021) stated that certain transition metal ions, such as Fe, Ni, Mn, and Cu, at the mineral-water interface could be key drivers of changes in the electronic states of functional groups in OM. Still, the authors did not link any induced polarity changes to MOAs and the ability of MOAs to sequester metals. Hence, simplified experimental studies with a thorough characterization of the structure and composition of the MOAs are needed to understand whether MOAs can be treated as non-reactive entities during their sequestration of metals.

In this study, montmorillonite (Mt) and ferrihydrite (Fh) are the mineral components, fulvic acid (FA) is the organic component in the MOAs, and Cu and Ni are the cations to be sequestered.

Here, the use of fulvic acid as the organic matter component in MOAs seems unrealistic. However, most studies on the environmental and surface chemistry of mineral-organic matter associations used fulvic acid in their experiments (Dubbin et al., 2014; Theng, 1976; R. Yang et al., 2019; Zhang et al., 2023). Fulvic acid and humic acid are the primary components of natural organic matter in soil (Kou et al., 2022). Islam et al. (2020) suggested using fulvic acid as a model compound to study adsorption reactions on a wide range of mineral adsorbents. Both humic acid and fulvic acid are considered complex molecules, yet fulvic acid is known to have a lower molecular weight than humic acid (Tan, 2003). However, fulvic acid contains all the key functional groups observed in

soil organic matter, including carboxyl, alcoholic hydroxyl, phenolic hydroxyl, quinones, aliphatic, and aromatic groups (Smreczak & Ukalska-Jaruga, 2021; Song et al., 2016). Fulvic acid has more carboxylate and hydroxyl functional groups than humic acid, thereby having more oxygen content with an O/C ratio of 0.6 to 0.99 than humic acid with a O/C ratio ranging from 0.4 to 0.6 (Tan, 2003). Given its simple nature compared to other humic substances, fulvic acid is ideal for controlled laboratory experiments, with the ability to address various variables like pH and concentration.

Chen et al. (2023) conducted an adsorption study of fulvic acid on kaolinite and goethite. They analyzed their data using the Charge Distribution (CD)-Multisite Complexation (MUSIC) model, isothermal titration colorimetry, and acid-base titrations to understand and model the adsorption of organic ligands, protons, and oxyanions on mineral surfaces. They investigated the complexation mechanisms between FA and the mineral surfaces (kaolinite, goethite) and their adsorption behavior as pH increased. Maximum adsorption of FA on kaolinite occurred at $\text{pH} < 5.5$, where positively charged sites on the edge and O faces of kaolinite enhanced the binding of FA carboxylic groups, forming inner-sphere complexes. Adsorption of goethite decreased with increasing pH due to electrostatic repulsion, with complexation mostly in the outer sphere (Chen et al., 2023). Adsorption of FA on minerals such as kaolinite and muscovite surfaces occurs predominantly via hydrophobic interactions on siloxane surfaces (Kolchanova et al., 2021). In a study with ferrihydrite-FA composites, it was found that Fe-OH from ferrihydrite complexed with COOH groups in FA with the increase of C/Fe mole ratio (Zhang et al., 2023).

Some studies treated fulvic acid as a well-characterized group to understand interactions between OM and mineral nanoaggregates (Bai et al., 2024). Fulvic acid is considered a dominant fraction of DOM in surface waters, the open ocean, and soil solution, and also a component of organic

amendments that are added to soils. Most importantly, fulvic acid plays a key role in controlling heavy metal behavior in soil, where it binds contaminants upon adsorption, and in water and environmental environments, decreasing contaminant mobility in soil. Carboxylic and phenolic groups in fulvic acid primarily perform the complexation of metal ions more readily than other humic components in soil due to its high oxygen content, affecting metal ion migration and bioavailability in soil (Bai et al., 2024; Christl et al., 2001; Y. Peng et al., 2025; Song et al., 2016).

In soil, microbes can affect MOAs via extracellular oxidative enzymes that cleave complex organic molecules, releasing products that destabilize and degrade them (Jilling et al., 2021). When organic matter is adsorbed onto various minerals, it becomes, to a certain extent, more resistant to microbial decomposition (Mikutta et al., 2007). However, in laboratory adsorption studies involving MOAs and heavy metals, the synthesized MOAs can be considered stable against microbial degradation, given the short exposure times (24-48 h), use of sterilized centrifuge tubes, continuous shaking conditions, minimal headspace in the tubes, and their capped nature.

Previous studies (Kramer et al., 2012; Ndzana et al., 2022; Z. Xu & Tsang, 2024) considered MOAs (natural or synthetic) as stable macromolecules. On the contrary, other studies suggested that MOAs exhibit dynamic behavior in soils, undergoing different chemical reactions and processes at mineral-organic matter interfaces and boundaries (Bölscher et al., 2025). For example, OM adsorption on minerals like smectites is reversible, whereas adsorption on minerals such as Fe-(hydr)oxides and kaolinite is considered to be less reversible (Kleber et al., 2021).

To avoid complexity with respect to the structure, composition, and solubility of the OM and mineral components, the present study uses the well-defined fulvic acid as the organic matter component and the low-soluble, low-reactive minerals montmorillonite and ferrihydrite as mineral components. In contrast to fulvic acid, synthesizing MOAs with humic acid is challenging due to

their larger molecular size, greater hydrophobicity, and lower solubility (Güngör & Bekbölet, 2010; Sposito, 2008; Stevenson, 1994b). Similarly, Mn(IV)-oxides present in many soils are not suitable for the above adsorption experiments as they dissolve in the presence of FA due to the reduction of Mn^{4+} to Mn^{2+} on reduced functional groups (Shi et al., 2024). Additionally, basic metal-hydroxides such as $\text{Mg}(\text{OH})_2$ cannot be used either, as they react with atmospheric CO_2 to MgCO_3 (Botha & Strydom, 2001; Fagerlund & Zevenhoven, 2011).

The present study applies electron energy loss spectroscopy to characterize the fine structure of OM along the mineral-organic matter interface in synthesized MOAs and the changes in OM induced by the sequestration of Cu and Ni. The analog synchrotron method for EELS is near-edge X-ray absorption fine structure (NEXAFS), which is another method for measuring core-level excitations. However, we used EELS for this study as it provides structural information in site-specific nanometer-sized areas. This allowed the spatial resolution of structural changes at the mineral-OM interface, which could not be achieved by performing synchrotron or X-ray work.

1.12 Significance of the research

Contamination of soils by heavy metals is regarded as a significant environmental issue. A better understanding of the occurrences and associated forms of these metals in soils is needed before implementing any remediation measures. Determination of the speciation of metals within particulates or secondary phases helps us understand how these metals are sequestered and transported in the soils, allowing for better-designed targeted reclamation strategies (Mantha et al., 2019). Most importantly, comparisons between results of experimental studies and field observations allow for isolation and control of selected variables such as pH, metal ion concentration, and exposure time. This will provide precise measurements of all variables and,

therefore, produce valuable and replicable results. Hence, the studies of my thesis will provide a better understanding on the sequestration and mobility of Cu and Ni in organic-rich surficial soils impacted by contamination. This study assumes and provides evidence that MOAs are dynamic systems in which composition, structure, and interfacial chemistry change in response to changing Cu and Ni ion concentrations. Using a unique combination of ICP-MS, TOC analyzer, FTIR, XRD, STEM-EDS, EELS, and adsorption parameters, this study shows that MOAs (with M=montmorillonite and ferrihydrite, and O as Fulvic acid) undergo FA desorption, complexation, repolymerization, precipitation, Mt interlayer expansion, and an increase in polar functional groups upon exposure to these metal ions. Especially in the presence of Cu, it leads to alterations in the surface area, carbon chain structures, and specific surface binding sites of the MOAs. This suggests that adsorption behavior cannot be interpreted without accounting for ongoing structural and chemical changes and reorganization. These insights are important in predicting contaminant mobility and designing better-engineered remediation methods. Chapter 3 will discuss in greater detail how to use these results to characterize MOA colloids collected from surficial soils in contaminated industrial sites.

1.13 References

- Abollino, O., Aceto, M., Malandrino, M., Sarzanini, C., & Mentasti, E. (2003). Adsorption of heavy metals on Na-montmorillonite. Effect of pH and organic substances. *Water Research*, 37(7), 1619–1627. [https://doi.org/10.1016/S0043-1354\(02\)00524-9](https://doi.org/10.1016/S0043-1354(02)00524-9)
- Abollino, O., Giacomino, A., Malandrino, M., & Mentasti, E. (2008). Interaction of metal ions with montmorillonite and vermiculite. *Applied Clay Science*, 38(3–4), 227–236. <https://doi.org/10.1016/j.clay.2007.04.002>
- Adnan, M., Xiao, B., Xiao, P., Zhao, P., Li, R., & Bibi, S. (2022). Research Progress on Heavy Metals Pollution in the Soil of Smelting Sites in China. *Toxics*, 10(5), 231. <https://doi.org/10.3390/toxics10050231>
- Ahmad, A., & Martsinovich, N. (2022). Modelling the strength of mineral–organic binding: organic molecules on the α -Al₂O₃ (0001) surface. *RSC Advances*, 12(42), 27604–27615. <https://doi.org/10.1039/D2RA04742J>
- Al-Amin, K., Kawsar, Md., Mamun, Md. T. R. B., & Sahadat Hossain, Md. (2025). Fourier transform infrared spectroscopic technique for analysis of inorganic materials: a review. *Nanoscale Advances*, 7(21), 6677–6702. <https://doi.org/10.1039/D5NA00522A>
- Alloway BJ. (2013). Heavy metals in soils: trace metals and metalloids in soils and their bioavailability. *Choice Reviews Online*, 50(07), 50-3862-50–3862. <https://doi.org/10.5860/CHOICE.50-3862>
- Alvarez-Silva, M., Mirnezami, M., Uribe-Salas, A., & Finch, J. A. (2010). Point of Zero Charge, Isoelectric Point and Aggregation of Phyllosilicate Minerals. *Canadian Metallurgical Quarterly*, 49(4), 405–410. <https://doi.org/10.1179/cmqr.2010.49.4.405>
- Alvarez-Silva, M., Uribe-Salas, A., Mirnezami, M., & Finch, J. A. (2010). The point of zero charge of phyllosilicate minerals using the Mular–Roberts titration technique. *Minerals Engineering*, 23(5), 383–389. <https://doi.org/10.1016/j.mineng.2009.11.013>
- Angst, G., Potapov, A., Joly, F.-X., Angst, Š., Frouz, J., Ganault, P., & Eisenhauer, N. (2024). Conceptualizing soil fauna effects on labile and stabilized soil organic matter. *Nature Communications*, 15(1), 5005. <https://doi.org/10.1038/s41467-024-49240-x>
- Bai, Y., Weng, L., & Hiemstra, T. (2024). Interaction of fulvic acid with soil organo-mineral nano-aggregates and corresponding phosphate release. *Geoderma*, 441, 116737. <https://doi.org/10.1016/j.geoderma.2023.116737>
- Baldock, J. A., Masiello, C. A., G  linas, Y., & Hedges, J. I. (2004). Cycling and composition of organic matter in terrestrial and marine ecosystems. *Marine Chemistry*, 92(1–4), 39–64. <https://doi.org/10.1016/j.marchem.2004.06.016>

- Barreto, M. S. C., Elzinga, E. J., Ramlogan, M., Rouff, A. A., & Alleoni, L. R. F. (2021). Calcium enhances adsorption and thermal stability of organic compounds on soil minerals. *Chemical Geology*, 559, 119804. <https://doi.org/10.1016/j.chemgeo.2020.119804>
- Bates, S., Zografi, G., Engers, D., Morris, K., Crowley, K., & Newman, A. (2006). Analysis of Amorphous and Nanocrystalline Solids from Their X-Ray Diffraction Patterns. *Pharmaceutical Research*, 23(10), 2333–2349. <https://doi.org/10.1007/s11095-006-9086-2>
- Begum, W., Rai, S., Banerjee, S., Bhattacharjee, S., Mondal, M. H., Bhattarai, A., & Saha, B. (2022). A comprehensive review on the sources, essentiality and toxicological profile of nickel. *RSC Advances*, 12(15), 9139–9153. <https://doi.org/10.1039/D2RA00378C>
- Bernard, S. (1997). Removal of organic compounds by adsorption on pyrolusite (β -MnO₂). *Water Research*, 31(5), 1216–1222. [https://doi.org/10.1016/S0043-1354\(96\)00149-2](https://doi.org/10.1016/S0043-1354(96)00149-2)
- Bölscher, T., Cardon, Z. G., Garcia Arredondo, M., Grand, S., Griffen, G., Hestrin, R., Imboden, J., Jamoteau, F., Lacroix, E. M., Pérez Castro, S., Persson, P., Riley, W. J., & Keiluweit, M. (2025). Vulnerability of mineral-organic associations in the rhizosphere. *Nature Communications*, 16(1), 5527. <https://doi.org/10.1038/s41467-025-61273-4>
- Bonczek, J. L., Harris, W. G., & Nkedi-Kizza, P. (2002). Monolayer to Bilayer Transitional Arrangements of Hexadecyltrimethylammonium Cations on Na-Montmorillonite. *Clays and Clay Minerals*, 50(1), 11–17. <https://doi.org/10.1346/000986002761002612>
- Botha, A., & Strydom, C. A. (2001). Preparation of a magnesium hydroxy carbonate from magnesium hydroxide. *Hydrometallurgy*, 62(3), 175–183. [https://doi.org/10.1016/S0304-386X\(01\)00197-9](https://doi.org/10.1016/S0304-386X(01)00197-9)
- Brady, N., & Weil, R. (1996). *The Nature and Properties of Soil*.
- Brame, J., & Griggs, C. (2016). *Surface Area Analysis Using the Brunauer-Emmett-Teller (BET) Method Scientific Operating Procedure Series: SOP-C Environmental Laboratory*. www.erdc.usace.army.mil.
- Brunmayr, A. S., Hagedorn, F., Moreno Duborgel, M., Minich, L. I., & Graven, H. D. (2024). Radiocarbon analysis reveals underestimation of soil organic carbon persistence in new-generation soil models. *Geoscientific Model Development*, 17(15), 5961–5985. <https://doi.org/10.5194/gmd-17-5961-2024>
- Bu, H., Yuan, P., Liu, H., Liu, D., Liu, J., He, H., Zhou, J., Song, H., & Li, Z. (2017). Effects of complexation between organic matter (OM) and clay mineral on OM pyrolysis. *Geochimica et Cosmochimica Acta*, 212, 1–15. <https://doi.org/10.1016/j.gca.2017.04.045>
- Buss, W., Hasemer, H., Sokol, N. W., Rohling, E. J., & Borevitz, J. (2024). Applying minerals to soil to draw down atmospheric carbon dioxide through synergistic organic and inorganic

- pathways. *Communications Earth & Environment*, 5(1), 602.
<https://doi.org/10.1038/s43247-024-01771-3>
- Cameron, V., & Vance, D. (2014). Heavy nickel isotope compositions in rivers and the oceans. *Geochimica et Cosmochimica Acta*, 128, 195–211.
<https://doi.org/10.1016/j.gca.2013.12.007>
- Cao, H., Liu, X., Feng, B., Sun, J., Ma, D., Chen, X., & Li, H. (2024). Effect of pH on the surface charges of permanently/variably charged soils and clay minerals. *Scientific Reports*, 14(1), 23169. <https://doi.org/10.1038/s41598-024-74563-6>
- Carta, D., Casula, M. F., Corrias, A., Falqui, A., Navarra, G., & Pinna, G. (2009). Structural and magnetic characterization of synthetic ferrihydrite nanoparticles. *Materials Chemistry and Physics*, 113(1), 349–355. <https://doi.org/10.1016/j.matchemphys.2008.07.122>
- Chen, H., Hou, M., He, Z., Liang, Y., Xu, J., & Tan, W. (2023a). Adsorption behavior of soil fulvic acid on crystal faces of kaolinite and goethite: Described by CD-MUSIC model. *Science of The Total Environment*, 903, 165806.
<https://doi.org/10.1016/j.scitotenv.2023.165806>
- Chenu, C. (2006). Soil phases: the organic solid phase. In *Soils: Basic Concepts and Future Challenges* (pp. 45–56). Cambridge University Press.
<https://doi.org/10.1017/CBO9780511535802.005>
- Christl, I., & Kretzschmar, R. (2007). C-1s NEXAFS Spectroscopy Reveals Chemical Fractionation of Humic Acid by Cation-Induced Coagulation. *Environmental Science & Technology*, 41(6), 1915–1920. <https://doi.org/10.1021/es062141s>
- Christl, I., Milne, C. J., Kinniburgh, D. G., & Kretzschmar, R. (2001). Relating Ion Binding by Fulvic and Humic Acids to Chemical Composition and Molecular Size. 2. Metal Binding. *Environmental Science & Technology*, 35(12), 2512–2517.
<https://doi.org/10.1021/es0002520>
- Crowther, T. W., van den Hoogen, J., Wan, J., Mayes, M. A., Keiser, A. D., Mo, L., Averill, C., & Maynard, D. S. (2019). The global soil community and its influence on biogeochemistry. *Science*, 365(6455). <https://doi.org/10.1126/science.aav0550>
- Davidson, E. A., & Janssens, I. A. (2006). Temperature sensitivity of soil carbon decomposition and feedbacks to climate change. *Nature*, 440(7081), 165–173.
<https://doi.org/10.1038/nature04514>
- Demangeat, E., Pédrot, M., Dia, A., Bouhnik-Le-Coz, M., Davranche, M., & Cabello-Hurtado, F. (2020). Surface modifications at the oxide/water interface: Implications for Cu binding, solution chemistry and chemical stability of iron oxide nanoparticles. *Environmental Pollution*, 257, 113626. <https://doi.org/10.1016/j.envpol.2019.113626>

- Dollimore, D., Spooner, P., & Turner, A. (1976). The bet method of analysis of gas adsorption data and its relevance to the calculation of surface areas. *Surface Technology*, 4(2), 121–160. [https://doi.org/10.1016/0376-4583\(76\)90024-8](https://doi.org/10.1016/0376-4583(76)90024-8)
- Duan, S., Peng, L., Chen, W., Kwakye, K. K., Zhou, K., & Teng, C. (2024). Spectroscopic insights into the binding characteristics of heavy metals to dissolved organic matter in landfill leachate. *Chemosphere*, 352, 141433. <https://doi.org/10.1016/j.chemosphere.2024.141433>
- Dubbin, W. E., Vetterlein, J. P., & Jonsson, J. L. (2014). Fatty acids promote fulvic acid intercalation by montmorillonite. *Applied Clay Science*, 97–98, 53–61. <https://doi.org/10.1016/j.clay.2014.05.022>
- Dutton, M. D., Vasiluk, L., Ford, F., Bellantino Perco, M., Taylor, S. R., Lopez, K., Bolger, G. T., Gopalapillai, Y., & Hale, B. (2019). Towards an exposure narrative for metals and arsenic in historically contaminated Ni refinery soils: Relationships between speciation, bioavailability, and bioaccessibility. *Science of The Total Environment*, 686, 805–818. <https://doi.org/10.1016/j.scitotenv.2019.05.164>
- Egerton, R. F. (2009). Electron energy-loss spectroscopy in the TEM. *Reports on Progress in Physics*, 72(1), 016502. <https://doi.org/10.1088/0034-4885/72/1/016502>
- Egerton, R. F. (2011). *Electron Energy-Loss Spectroscopy in the Electron Microscope*. Springer US. <https://doi.org/10.1007/978-1-4419-9583-4>
- Essalmi, S., Lotfi, S., BaQais, A., Saadi, M., Arab, M., & Ait Ahsaine, H. (2024). Design and application of metal organic frameworks for heavy metals adsorption in water: a review. *RSC Advances*, 14(13), 9365–9390. <https://doi.org/10.1039/D3RA08815D>
- Essington. (2015). *Soil and Water Chemistry: An Integrative Approach*.
- Ettler, V., Mihaljevic, M., Sebek, O., & Strnad, L. (2005). Leaching of APC residues from secondary Pb metallurgy using single extraction tests: the mineralogical and the geochemical approach. *Journal of Hazardous Materials*, 121(1–3), 149–157. <https://doi.org/10.1016/j.jhazmat.2005.02.001>
- Evanko, C. R., & Dzombak, D. A. (1997). *Ground-Water Remediation Technologies Analysis Center Technology Evaluation Report Remediation of Metals-Contaminated Soils and Groundwater* (Number 412). <http://www.gwrtac.org>
- Fagerlund, J., & Zevenhoven, R. (2011). An experimental study of Mg(OH)₂ carbonation. *International Journal of Greenhouse Gas Control*, 5(6), 1406–1412. <https://doi.org/10.1016/j.ijggc.2011.05.039>
- Fan, J., Liu, F., Hu, Y., & Chen, J. (2015). Effects of pH and ionic composition on sorption/desorption of natural organic matter on zero-valent iron and magnetite

- nanoparticles. *Water Science and Technology*, 72(2), 303–310.
<https://doi.org/10.2166/wst.2015.219>
- Fariña, A. O., Peacock, C. L., Fiol, S., Antelo, J., & Carvin, B. (2018). A universal adsorption behaviour for Cu uptake by iron (hydr)oxide organo-mineral composites. *Chemical Geology*, 479, 22–35. <https://doi.org/10.1016/j.chemgeo.2017.12.022>
- Flemming, C. A., & Trevors, J. T. (1989). Copper toxicity and chemistry in the environment: a review. *Water, Air, and Soil Pollution*, 44(1–2), 143–158.
<https://doi.org/10.1007/BF00228784>
- Foley, S. F., & Fischer, T. P. (2017). An essential role for continental rifts and lithosphere in the deep carbon cycle. *Nature Geoscience*, 10(12), 897–902. <https://doi.org/10.1038/s41561-017-0002-7>
- Frederix, P. W. J. M., Patmanidis, I., & Marrink, S. J. (2018). Molecular simulations of self-assembling bio-inspired supramolecular systems and their connection to experiments. *Chemical Society Reviews*, 47(10), 3470–3489. <https://doi.org/10.1039/C8CS00040A>
- Funnell, N. P., Fulford, M. F., Inoué, S., Kletetschka, K., Michel, F. M., & Goodwin, A. L. (2020). Nanocomposite structure of two-line ferrihydrite powder from total scattering. *Communications Chemistry*, 3(1), 22. <https://doi.org/10.1038/s42004-020-0269-2>
- Galicía-Andrés, E., Escalona, Y., Oostenbrink, C., Tunega, D., & Gerzabek, M. H. (2021). Soil organic matter stabilization at molecular scale: The role of metal cations and hydrogen bonds. *Geoderma*, 401, 115237. <https://doi.org/10.1016/j.geoderma.2021.115237>
- Gao, J., Mikutta, R., Jansen, B., Guggenberger, G., Vogel, C., & Kalbitz, K. (2020). The multilayer model of soil mineral–organic interfaces—a review. *Journal of Plant Nutrition and Soil Science*, 183(1), 27–41. <https://doi.org/10.1002/jpln.201900530>
- Gougoulías, C., Clark, J. M., & Shaw, L. J. (2014). The role of soil microbes in the global carbon cycle: tracking the below-ground microbial processing of plant-derived carbon for manipulating carbon dynamics in agricultural systems. *Journal of the Science of Food and Agriculture*, 94(12), 2362–2371. <https://doi.org/10.1002/jsfa.6577>
- Griscom, B. W., Adams, J., Ellis, P. W., Houghton, R. A., Lomax, G., Miteva, D. A., Schlesinger, W. H., Shoch, D., Siikamäki, J. V., Smith, P., Woodbury, P., Zganjar, C., Blackman, A., Campari, J., Conant, R. T., Delgado, C., Elias, P., Gopalakrishna, T., Hamsik, M. R., ... Fargione, J. (2017). Natural climate solutions. *Proceedings of the National Academy of Sciences*, 114(44), 11645–11650. <https://doi.org/10.1073/pnas.1710465114>
- Güngör, E. B. Ö., & Bekbölet, M. (2010). Zinc release by humic and fulvic acid as influenced by pH, complexation and DOC sorption. *Geoderma*, 159(1–2), 131–138.
<https://doi.org/10.1016/j.geoderma.2010.07.004>

- Hayes, M. H. B., & Swift, R. (1978). The chemistry of soil organic colloids. *The Chemistry of Soil Constituents*, 179–320.
- Hayes, M. H. B., & Swift, R. S. (2020). Chapter One - Vindication of humic substances as a key component of organic matter in soil and water. In D. L. Sparks (Ed.), *Advances in Agronomy* (Vol. 163, pp. 1–37). Academic Press.
<https://doi.org/https://doi.org/10.1016/bs.agron.2020.05.001>
- Hayes, M. H. B., Tseng, T.-Y., & Wang, M.-K. (2007). Chemistry of Soil Organic Matter. In *Taiwan J For Sci* (Vol. 22, Number 3).
- Huang, X., Li, Y., Guggenberger, G., Kuzyakov, Y., Liu, B.-F., & Wu, J. (2020). Direct evidence for thickening nanoscale organic films at soil biogeochemical interfaces and its relevance to organic matter preservation. *Environmental Science: Nano*, 7(9), 2747–2758.
<https://doi.org/10.1039/D0EN00489H>
- Hug, S. J., & Bahnemann, D. (2006). Infrared spectra of oxalate, malonate and succinate adsorbed on the aqueous surface of rutile, anatase and lepidocrocite measured with in situ ATR-FTIR. *Journal of Electron Spectroscopy and Related Phenomena*, 150(2–3), 208–219.
<https://doi.org/10.1016/j.elspec.2005.05.006>
- Hur, J., & Schlautman, M. A. (2003). Molecular weight fractionation of humic substances by adsorption onto minerals. *Journal of Colloid and Interface Science*, 264(2), 313–321.
[https://doi.org/10.1016/S0021-9797\(03\)00444-2](https://doi.org/10.1016/S0021-9797(03)00444-2)
- Hutchinson, T. C., & Whitby, L. M. (1974). Heavy-metal Pollution in the Sudbury Mining and Smelting Region of Canada, I. Soil and Vegetation Contamination by Nickel, Copper, and Other Metals. *Environmental Conservation*, 1(2), 123–132.
<https://doi.org/10.1017/S0376892900004240>
- Ijagbemi, C. O., Baek, M.-H., & Kim, D.-S. (2009). Montmorillonite surface properties and sorption characteristics for heavy metal removal from aqueous solutions. *Journal of Hazardous Materials*, 166(1), 538–546. <https://doi.org/10.1016/j.jhazmat.2008.11.085>
- Islam, Md. A., Morton, D. W., Johnson, B. B., & Angove, M. J. (2020). Adsorption of humic and fulvic acids onto a range of adsorbents in aqueous systems, and their effect on the adsorption of other species: A review. *Separation and Purification Technology*, 247, 116949. <https://doi.org/10.1016/j.seppur.2020.116949>
- Jalali, M., & Moradi, F. (2013). Competitive sorption of Cd, Cu, Mn, Ni, Pb and Zn in polluted and unpolluted calcareous soils. *Environmental Monitoring and Assessment*, 185(11), 8831–8846. <https://doi.org/10.1007/s10661-013-3216-1>
- Jamoteau, F., Doelsch, E., Cam, N., Levard, C., Woignier, T., Boulineau, A., Saint-Antonin, F., Swaraj, S., Gassier, G., Duvivier, A., Borschneck, D., Pons, M.-L., Chaurand, P., Vidal, V.,

- Brouilly, N., & Basile-Doelsch, I. (2025). Interplay of coprecipitation and adsorption processes: deciphering amorphous mineral–organic associations under both forest and cropland conditions. *SOIL*, 11(2), 535–552. <https://doi.org/10.5194/soil-11-535-2025>
- 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>
- Kaiser, K., & Guggenberger, G. (2000). The role of DOM sorption to mineral surfaces in the preservation of organic matter in soils. *Organic Geochemistry*, 31(7–8), 711–725. [https://doi.org/10.1016/S0146-6380\(00\)00046-2](https://doi.org/10.1016/S0146-6380(00)00046-2)
- Kalbitz, K., & Kaiser, K. (2008). Contribution of dissolved organic matter to carbon storage in forest mineral soils. *Journal of Plant Nutrition and Soil Science*, 171(1), 52–60. <https://doi.org/10.1002/jpln.200700043>
- Kalev, S. D., & Toor, G. S. (2018). The Composition of Soils and Sediments. In *Green Chemistry* (pp. 339–357). Elsevier. <https://doi.org/10.1016/B978-0-12-809270-5.00014-5>
- Karathanasis, A. D. (2006). *SOIL MINERALOGY*.
- Katoh, M., Murase, J., Hayashi, M., Matsuya, K., & Kimura, M. (2004). Nutrient leaching from the plow layer by water percolation and accumulation in the subsoil in an irrigated paddy field. *Soil Science and Plant Nutrition*, 50(5), 721–729. <https://doi.org/10.1080/00380768.2004.10408528>
- 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(6), 588–595. <https://doi.org/10.1038/nclimate2580>
- Khalid, K., Ishak, R., & Chowdhury, Z. Z. (2024). UV–Vis spectroscopy in non-destructive testing. In *Non-Destructive Material Characterization Methods* (pp. 391–416). Elsevier. <https://doi.org/10.1016/B978-0-323-91150-4.00021-5>
- 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*, 2(6), 402–421. <https://doi.org/10.1038/s43017-021-00162-y>
- Kleber, M., Eusterhues, K., Keiluweit, M., Mikutta, C., Mikutta, R., & Nico, P. S. (2015a). *Mineral–Organic Associations: Formation, Properties, and Relevance in Soil Environments* (pp. 1–140). <https://doi.org/10.1016/bs.agron.2014.10.005>
- Kleber, M., Sollins, P., & Sutton, R. (2007). A conceptual model of organo-mineral interactions in soils: self-assembly of organic molecular fragments into zonal structures on mineral surfaces. *Biogeochemistry*, 85(1), 9–24. <https://doi.org/10.1007/s10533-007-9103-5>

- Kloster, N., Brigante, M., Zanini, G., & Avena, M. (2013). Aggregation kinetics of humic acids in the presence of calcium ions. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 427, 76–82. <https://doi.org/10.1016/j.colsurfa.2013.03.030>
- Kolchanova, K., Tolpeshta, I., & Izosimova, Y. (2021). Adsorption of Fulvic Acid and Water Extractable Soil Organic Matter on Kaolinite and Muscovite. *Agronomy*, 11(12), 2420. <https://doi.org/10.3390/agronomy11122420>
- Kollannur, N. J., & Arnepalli, D. N. (2019). Methodology for Determining Point of Zero Salt Effect of Clays in Terms of Surface Charge Properties. *Journal of Materials in Civil Engineering*, 31(12). [https://doi.org/10.1061/\(ASCE\)MT.1943-5533.0002947](https://doi.org/10.1061/(ASCE)MT.1943-5533.0002947)
- Kosmulski, M. (2023). The pH dependent surface charging and points of zero charge. X. Update. *Advances in Colloid and Interface Science*, 319, 102973. <https://doi.org/10.1016/j.cis.2023.102973>
- Kou, B., Hui, K., Miao, F., He, Y., Qu, C., Yuan, Y., & Tan, W. (2022). Differential responses of the properties of soil humic acid and fulvic acid to nitrogen addition in the North China Plain. *Environmental Research*, 214, 113980. <https://doi.org/10.1016/j.envres.2022.113980>
- Kramer, M. G., Sanderman, J., Chadwick, O. A., Chorover, J., & Vitousek, P. M. (2012). Long-term carbon storage through retention of dissolved aromatic acids by reactive particles in soil. *Global Change Biology*, 18(8), 2594–2605. <https://doi.org/10.1111/j.1365-2486.2012.02681.x>
- Kravchenko, A. N., & Guber, A. K. (2017). Soil pores and their contributions to soil carbon processes. *Geoderma*, 287, 31–39. <https://doi.org/10.1016/j.geoderma.2016.06.027>
- LaCroix, R. E., Walpen, N., Sander, M., Tfaily, M. M., Blanchard, J. L., & Keiluweit, M. (2021). Long-Term Warming Decreases Redox Capacity of Soil Organic Matter. *Environmental Science & Technology Letters*, 8(1), 92–97. <https://doi.org/10.1021/acs.estlett.0c00748>
- Lal, R. (2004). Soil carbon sequestration to mitigate climate change. *Geoderma*, 123(1–2), 1–22. <https://doi.org/10.1016/j.geoderma.2004.01.032>
- Lazar, S., Tiemeijer, P., Schnohr, C. S., Meledina, M., Patzig, C., Höche, T., Longo, P., & Freitag, B. (2025). Enabling electron-energy-loss spectroscopy at very high energy losses: An opportunity to obtain x-ray absorption spectroscopy-like information using an electron microscope. *Physical Review Applied*, 23(5), 054095. <https://doi.org/10.1103/PhysRevApplied.23.054095>
- Le Quéré, C., Andrew, R. M., Canadell, J. G., Sitch, S., Korsbakken, J. I., Peters, G. P., Manning, A. C., Boden, T. A., Tans, P. P., Houghton, R. A., Keeling, R. F., Alin, S., Andrews, O. D., Anthoni, P., Barbero, L., Bopp, L., Chevallier, F., Chini, L. P., Ciais, P., ... Zaehle, S.

- (2016). Global Carbon Budget 2016. *Earth System Science Data*, 8(2), 605–649. <https://doi.org/10.5194/essd-8-605-2016>
- Lehmann, J., & Kleber, M. (2015). The contentious nature of soil organic matter. *Nature*, 528(7580), 60–68. <https://doi.org/10.1038/nature16069>
- Li, B., Wang, S., Fessler, M., Zou, R., Su, Y., & Zhang, Y. (2024). Differential interactions between natural clay minerals and dissolved organic matter affect reactive oxygen species formation. *Water Research*, 249, 120984. <https://doi.org/10.1016/j.watres.2023.120984>
- Li, C., Li, M., Zeng, J., Yuan, S., Luo, X., Wu, C., & Xue, S. (2024). Migration and distribution characteristics of soil heavy metal(loid)s at a lead smelting site. *Journal of Environmental Sciences*, 135, 600–609. <https://doi.org/10.1016/j.jes.2023.02.007>
- Li, C., Zhou, K., Qin, W., Tian, C., Qi, M., Yan, X., & Han, W. (2019). A Review on Heavy Metals Contamination in Soil: Effects, Sources, and Remediation Techniques. *Soil and Sediment Contamination: An International Journal*, 28(4), 380–394. <https://doi.org/10.1080/15320383.2019.1592108>
- Li, Q., Wang, Y., Li, Y., Li, L., Tang, M., Hu, W., Chen, L., & Ai, S. (2022). Speciation of heavy metals in soils and their immobilization at micro-scale interfaces among diverse soil components. *Science of The Total Environment*, 825, 153862. <https://doi.org/10.1016/j.scitotenv.2022.153862>
- Li, W., Liao, P., Oldham, T., Jiang, Y., Pan, C., Yuan, S., & Fortner, J. D. (2018). Real-time evaluation of natural organic matter deposition processes onto model environmental surfaces. *Water Research*, 129, 231–239. <https://doi.org/10.1016/j.watres.2017.11.024>
- Li, X., Schindler, M., Zhou, J., Samaradiwakara, S., & Wu, L. (2025). Interaction between metal(loid)s and soil mineral-organic matter associations. *Critical Reviews in Environmental Science and Technology*, 55(9), 624–647. <https://doi.org/10.1080/10643389.2024.2434328>
- Li, Z., Liu, X., Chen, G., Liu, S., & Zou, J. (2025). Enhancing soil organic carbon stabilization by coupling microbial-mineral carbon pumps in agroecosystem. *Environmental Technology & Innovation*, 40, 104431. <https://doi.org/10.1016/j.eti.2025.104431>
- Liang, C., Schimel, J. P., & Jastrow, J. D. (2017). The importance of anabolism in microbial control over soil carbon storage. *Nature Microbiology*, 2(8), 17105. <https://doi.org/10.1038/nmicrobiol.2017.105>
- Liang, C., Wang, F., Fan, W., Zhou, W., & Tong, Y. (2017). Transmission electron microscopy analysis of some transition metal compounds for energy storage and conversion. *TrAC Trends in Analytical Chemistry*, 90, 62–79. <https://doi.org/10.1016/j.trac.2017.02.010>

- Liu, S., Wang, X., Guo, G., & Yan, Z. (2021). Status and environmental management of soil mercury pollution in China: A review. *Journal of Environmental Management*, 277, 111442. <https://doi.org/10.1016/j.jenvman.2020.111442>
- Liu, Z., Xu, P., Yang, C., Zhao, B., Gao, J., Shi, L., Dong, K., Zhao, X., Liu, F., & Xu, M. (2026). Soil organic carbon sequestration efficiency with biochar addition across the croplands of China: A perspective from particulate and mineral-associated organic carbon. *Environmental Research*, 293, 123777. <https://doi.org/10.1016/j.envres.2026.123777>
- Ma, H., Thompson, A., Hall, S. J., Wang, J., Xiao, Y., Liu, C.-Q., & Chen, C. (2025). Enrichment of metastable iron minerals in global coastal wetlands. *Nature Geoscience*, 18(9), 885–892. <https://doi.org/10.1038/s41561-025-01764-7>
- Machado, A. L., Garnier, J., Ratié, G., Guimaraes, E., Monvoisin, G., Cloquet, C., & Quantin, C. (2023). Nickel mass balance and isotopic records in a serpentinitic weathering profile: Implications on the continental Ni budget. *Chemical Geology*, 634, 121586. <https://doi.org/10.1016/j.chemgeo.2023.121586>
- Mantha, H., Schindler, M., & Hochella, M. F. (2019). Occurrence and formation of incidental metallic Cu and CuS nanoparticles in organic-rich contaminated surface soils in Timmins, Ontario. *Environmental Science: Nano*, 6(1), 163–179. <https://doi.org/10.1039/C8EN00994E>
- Manzoni, S., & Cotrufo, M. F. (2024). Mechanisms of soil organic carbon and nitrogen stabilization in mineral-associated organic matter – insights from modeling in phase space. *Biogeosciences*, 21(18), 4077–4098. <https://doi.org/10.5194/bg-21-4077-2024>
- Masion, A., Thomas, F., Tchoubar, D., Bottero, J. Y., & Tekely, P. (1994). Chemistry and Structure of Al(OH)/Organic Precipitates. A Small-Angle X-ray Scattering Study. 3. Depolymerization of the Al₁₃ Polycation by Organic Ligands. *Langmuir*, 10(11), 4353–4356. <https://doi.org/10.1021/la00023a069>
- McBride, M. B. (1989). *Reactions Controlling Heavy Metal Solubility in Soils* (pp. 1–56). https://doi.org/10.1007/978-1-4613-8847-0_1
- Mendez, J. C., & Hiemstra, T. (2020). Surface area of ferrihydrite consistently related to primary surface charge, ion pair formation, and specific ion adsorption. *Chemical Geology*, 532, 119304. <https://doi.org/10.1016/j.chemgeo.2019.119304>
- Mikutta, R., Mikutta, C., Kalbitz, K., Scheel, T., Kaiser, K., & Jahn, R. (2007). Biodegradation of forest floor organic matter bound to minerals via different binding mechanisms. *Geochimica et Cosmochimica Acta*, 71(10), 2569–2590. <https://doi.org/10.1016/j.gca.2007.03.002>

- Mikutta, R., Schaumann, G. E., Gildemeister, D., Bonneville, S., Kramer, M. G., Chorover, J., Chadwick, O. A., & Guggenberger, G. (2009). Biogeochemistry of mineral–organic associations across a long-term mineralogical soil gradient (0.3–4100kyr), Hawaiian Islands. *Geochimica et Cosmochimica Acta*, 73(7), 2034–2060. <https://doi.org/10.1016/j.gca.2008.12.028>
- Mikutta, R., Zang, U., Chorover, J., Haumaier, L., & Kalbitz, K. (2011). Stabilization of extracellular polymeric substances (*Bacillus subtilis*) by adsorption to and coprecipitation with Al forms. *Geochimica et Cosmochimica Acta*, 75(11), 3135–3154. <https://doi.org/10.1016/j.gca.2011.03.006>
- Moore, O. W., Curti, L., Woulds, C., Bradley, J. A., Babakhani, P., Mills, B. J. W., Homoky, W. B., Xiao, K.-Q., Bray, A. W., Fisher, B. J., Kazemian, M., Kaulich, B., Dale, A. W., & Peacock, C. L. (2023). Long-term organic carbon preservation enhanced by iron and manganese. *Nature*, 621(7978), 312–317. <https://doi.org/10.1038/s41586-023-06325-9>
- Mullet, M., Fievet, P., Szymczyk, A., Foissy, A., Reggiani, J.-C., & Pagetti, J. (1999). A simple and accurate determination of the point of zero charge of ceramic membranes. *Desalination*, 121(1), 41–48. [https://doi.org/10.1016/S0011-9164\(99\)00006-5](https://doi.org/10.1016/S0011-9164(99)00006-5)
- Nagaraju, P. T., & Amreen Sulthana, S. (2025). Review Article on FTIR Spectroscopy. | *IJIRT* |, 12.
- Ndzana, G. M., Zhang, Y., Yao, S., Hamer, U., & Zhang, B. (2022). The adsorption capacity of root exudate organic carbon onto clay mineral surface changes depending on clay mineral types and organic carbon composition. *Rhizosphere*, 23, 100545. <https://doi.org/10.1016/j.rhisph.2022.100545>
- Neubeck, A., & Kirschning, A. (2026). Nickel: Geochemistry, biochemistry and its role in chemical and biological evolutions. *Earth-Science Reviews*, 272, 105324. <https://doi.org/10.1016/j.earscirev.2025.105324>
- Ni, J., & Pignatello, J. J. (2018). Charge-assisted hydrogen bonding as a cohesive force in soil organic matter: water solubility enhancement by addition of simple carboxylic acids. *Environmental Science: Processes & Impacts*, 20(9), 1225–1233. <https://doi.org/10.1039/C8EM00255J>
- Noor, N., & Thompson, A. (2022). Localized alteration of ferrihydrite natural organic matter coprecipitates following reaction with Fe(II). *Soil Science Society of America Journal*, 86(2), 253–263. <https://doi.org/10.1002/saj2.20366>
- Nriagu, J. O., Wong, H. K. T., Lawson, G., & Daniel, P. (1998). Saturation of ecosystems with toxic metals in Sudbury basin, Ontario, Canada. *Science of The Total Environment*, 223(2–3), 99–117. [https://doi.org/10.1016/S0048-9697\(98\)00284-8](https://doi.org/10.1016/S0048-9697(98)00284-8)

- Omoike, A., & Chorover, J. (2006). Adsorption to goethite of extracellular polymeric substances from *Bacillus subtilis*. *Geochimica et Cosmochimica Acta*, 70(4), 827–838. <https://doi.org/10.1016/j.gca.2005.10.012>
- Oorts, K., Ghesquiere, U., Swinnen, K., & Smolders, E. (2006). Soil properties affecting the toxicity of CuCl₂ and NiCl₂ for soil microbial processes in freshly spiked soils. *Environmental Toxicology and Chemistry*, 25(3), 836–844. <https://doi.org/10.1897/04-672R.1>
- Paria, S., & Yuet, P. K. (2006). Solidification–stabilization of organic and inorganic contaminants using portland cement: a literature review. *Environmental Reviews*, 14(4), 217–255. <https://doi.org/10.1139/a06-004>
- Parvin, A., Moniruzzaman, M., Hossain, M. K., Saha, B., Parvin, A., Suchi, P. D., & Hoque, S. (2022). Chemical Speciation and Potential Mobility of Heavy Metals in Organic Matter Amended Soil. *Applied and Environmental Soil Science*, 2022, 1–13. <https://doi.org/10.1155/2022/2028860>
- Peng, X., Luan, Z., Chen, F., Tian, B., & Jia, Z. (2005). Adsorption of humic acid onto pillared bentonite. *Desalination*, 174(2), 135–143. <https://doi.org/10.1016/j.desal.2004.09.007>
- Peng, Y., Biswas, A., Adamowski, J. F., Zhang, X., Li, Y., Li, L., Peng, Y., & Cao, J. (2025). Sources and stability of particulate organic matter (POM) and mineral-associated organic matter (MAOM) on the Loess Plateau: Implications for soil carbon management. *Ecological Indicators*, 179, 114162. <https://doi.org/10.1016/j.ecolind.2025.114162>
- Persson, P., & Axe, K. (2005). Adsorption of oxalate and malonate at the water-goethite interface: Molecular surface speciation from IR spectroscopy. *Geochimica et Cosmochimica Acta*, 69(3), 541–552. <https://doi.org/10.1016/j.gca.2004.07.009>
- Piccolo, A., & Mbagwu, J. S. C. (1999). Role of Hydrophobic Components of Soil Organic Matter in Soil Aggregate Stability. *Soil Science Society of America Journal*, 63(6), 1801–1810. <https://doi.org/10.2136/sssaj1999.6361801x>
- Possinger, A. R., Zachman, M. J., Enders, A., Levin, B. D. A., Muller, D. A., Kourkoutis, L. F., & Lehmann, J. (2020). Organo–organic and organo–mineral interfaces in soil at the nanometer scale. *Nature Communications*, 11(1), 6103. <https://doi.org/10.1038/s41467-020-19792-9>
- Qiao, L., Wang, J., Wei, S., Ren, Y., Lichtfouse, E., & Han, J. (2025). The soil microbial carbon pump for carbon sequestration. *Environmental Chemistry Letters*, 23(5), 1145–1151. <https://doi.org/10.1007/s10311-025-01861-4>
- Qin, X., Liu, F., Wang, G., & Huang, G. (2015). Adsorption of humic acid from aqueous solution by hematite: effects of pH and ionic strength. *Environmental Earth Sciences*, 73(8), 4011–4017. <https://doi.org/10.1007/s12665-014-3686-7>

- Ramamoorthy, S., & Rust, B. R. (1978). Heavy metal exchange processes in sediment-water systems. *Environmental Geology*, 2(3), 165–172. <https://doi.org/10.1007/BF02430670>
- Ramos-Tejada, M. M., Ontiveros, A., Viota, J. L., & Durán, J. D. G. (2003). Interfacial and rheological properties of humic acid/hematite suspensions. *Journal of Colloid and Interface Science*, 268(1), 85–95. [https://doi.org/10.1016/S0021-9797\(03\)00665-9](https://doi.org/10.1016/S0021-9797(03)00665-9)
- Rancourt, D. G., Thibault, P.-J., Mavrocordatos, D., & Lamarche, G. (2005). Hydrous ferric oxide precipitation in the presence of nonmetabolizing bacteria: Constraints on the mechanism of a biotic effect. *Geochimica et Cosmochimica Acta*, 69(3), 553–577. <https://doi.org/10.1016/j.gca.2004.07.018>
- Ransom, B., Bennett, R. H., Baerwald, R., & Shea, K. (1997). TEM study of in situ organic matter on continental margins: occurrence and the “monolayer” hypothesis. *Marine Geology*, 138(1–2), 1–9. [https://doi.org/10.1016/S0025-3227\(97\)00012-1](https://doi.org/10.1016/S0025-3227(97)00012-1)
- Riedel, T., Zak, D., Biester, H., & Dittmar, T. (2013). Iron traps terrestrially derived dissolved organic matter at redox interfaces. *Proceedings of the National Academy of Sciences*, 110(25), 10101–10105. <https://doi.org/10.1073/pnas.1221487110>
- Riemer, D. N., & Toth, S. J. (1970). Adsorption Of Copper By Clay Minerals, Humic Acid And Bottom Muds. *Journal (American Water Works Association)*, 62(3), 195–197. <http://www.jstor.org/stable/41266170>
- Rowley, M. C., Grand, S., & Verrecchia, É. P. (2018). Calcium-mediated stabilisation of soil organic carbon. *Biogeochemistry*, 137(1–2), 27–49. <https://doi.org/10.1007/s10533-017-0410-1>
- Saito, T., Koopal, L. K., van Riemsdijk, W. H., Nagasaki, S., & Tanaka, S. (2004). Adsorption of Humic Acid on Goethite: Isotherms, Charge Adjustments, and Potential Profiles. *Langmuir*, 20(3), 689–700. <https://doi.org/10.1021/la034806z>
- Samota, R., Senthamizhkumaran, V. R., Verma, L. P., Kumar, K., & Agarwal, S. (2024). *INTRODUCTION TO SOIL SCIENCE EDITORS*. www.npapublishing.in
- Scheel, T., Jansen, B., Van Wijk, A. J., Verstraten, J. M., & Kalbitz, K. (2008). Stabilization of dissolved organic matter by aluminium: a toxic effect or stabilization through precipitation? *European Journal of Soil Science*, 59(6), 1122–1132. <https://doi.org/10.1111/j.1365-2389.2008.01074.x>
- Schneider, M. P. W., Scheel, T., Mikutta, R., van Hees, P., Kaiser, K., & Kalbitz, K. (2010). Sorptive stabilization of organic matter by amorphous Al hydroxide. *Geochimica et Cosmochimica Acta*, 74(5), 1606–1619. <https://doi.org/10.1016/j.gca.2009.12.017>

- Schnitzer, M., & Kodama, H. (1972). Reactions between Fulvic Acid and Cu²⁺ - Montmorillonite. *Clays and Clay Minerals*, 20(6), 359–367.
<https://doi.org/10.1346/CCMN.1972.0200603>
- Schnitzer, M., & Monreal, C. M. (2011). *Quo Vadis Soil Organic Matter Research? A Biological Link to the Chemistry of Humification* (pp. 143–217). <https://doi.org/10.1016/B978-0-12-386473-4.00003-8>
- Schroth, B. K., & Sposito, G. (1996). Surface Charge Properties Of Kaolinite. *MRS Proceedings*, 432, 87. <https://doi.org/10.1557/PROC-432-87>
- Schwarzenbach, R. P. ., Gschwend, P. M. ., & Imboden, D. M. . (2017). *Environmental organic chemistry*. John Wiley & Sons.
- Setia, R., Dhaliwal, S. S., Singh, R., Singh, B., Kukal, S. S., & Pateriya, B. (2023). Ecological and human health risk assessment of metals in soils and wheat along Sutlej river (India). *Chemosphere*, 312, 137331. <https://doi.org/10.1016/j.chemosphere.2022.137331>
- Shahid, M., Dumat, C., Khalid, S., Schreck, E., Xiong, T., & Niazi, N. K. (2017). Foliar heavy metal uptake, toxicity and detoxification in plants: A comparison of foliar and root metal uptake. *Journal of Hazardous Materials*, 325, 36–58.
<https://doi.org/10.1016/j.jhazmat.2016.11.063>
- Shaker, A. M., Komy, Z. R., Heggy, S. E. M., & El-Sayed, M. E. A. (2012). Kinetic Study for Adsorption Humic Acid on Soil Minerals. *The Journal of Physical Chemistry A*, 116(45), 10889–10896. <https://doi.org/10.1021/jp3078826>
- Shi, Y., Wang, Z., Jia, H., & Li, C. (2024). Insights into the transformation of dissolved organic matter and carbon preservation on a MnO₂ surface: Effect of molecular weight of dissolved organic matter. *Science of The Total Environment*, 945, 174022.
<https://doi.org/10.1016/j.scitotenv.2024.174022>
- Shuman, L. M. (1991). *Chemical Forms of Micronutrients in Soils* (pp. 113–144).
<https://doi.org/10.2136/sssabookser4.2ed.c5>
- Smreczak, B., & Ukalska-Jaruga, A. (2021). Dissolved organic matter in agricultural soils. *Soil Science Annual*, 72(1), 1–10. <https://doi.org/10.37501/soilsa/132234>
- Sollins, P., Swanston, C., Kleber, M., Filley, T., Kramer, M., Crow, S., Caldwell, B. A., Lajtha, K., & Bowden, R. (2006). Organic C and N stabilization in a forest soil: Evidence from sequential density fractionation. *Soil Biology and Biochemistry*, 38(11), 3313–3324.
<https://doi.org/10.1016/j.soilbio.2006.04.014>
- Song, X., Li, L., Zhang, X., Zheng, J., Zheng, J., Hussain, Q., & Pan, G. (2016). Molecular changes of ferric oxide bound soil humus during the decomposition of maize straw.

- Chemical and Biological Technologies in Agriculture*, 3(1), 27.
<https://doi.org/10.1186/s40538-016-0060-x>
- Sparks, D. L. ., & Antanasovic, Svetlana. (2015). *Advances in agronomy. Volume 130*. Academic Press.
- Sposito, Garrison. (2008). *The chemistry of soils*. Oxford University Press.
- Stevenson, F. J. . (1994a). *Humus chemistry : genesis, composition, reactions*. Wiley.
- Stewart, C. E., Plante, A. F., Paustian, K., Conant, R. T., & Six, J. (2008). Soil Carbon Saturation: Linking Concept and Measurable Carbon Pools. *Soil Science Society of America Journal*, 72(2), 379–392. <https://doi.org/10.2136/sssaj2007.0104>
- Stiff, M. J. (1971). The chemical states of copper in polluted fresh water and a scheme of analysis to differentiate them. *Water Research*, 5(8), 585–599. [https://doi.org/10.1016/0043-1354\(71\)90114-X](https://doi.org/10.1016/0043-1354(71)90114-X)
- Strawn, D. G. (2021). Sorption Mechanisms of Chemicals in Soils. *Soil Systems*, 5(1), 13. <https://doi.org/10.3390/soilsystems5010013>
- Su, D. (2017). Advanced electron microscopy characterization of nanomaterials for catalysis. *Green Energy & Environment*, 2(2), 70–83. <https://doi.org/10.1016/j.gee.2017.02.001>
- Sutton, R., & Sposito, G. (2005). Molecular Structure in Soil Humic Substances: The New View. *Environmental Science & Technology*, 39(23), 9009–9015. <https://doi.org/10.1021/es050778q>
- Swindle, A. L., Madden, A. S. E., Cozzarelli, I. M., & Benamara, M. (2014). Size-Dependent Reactivity of Magnetite Nanoparticles: A Field-Laboratory Comparison. *Environmental Science & Technology*, 48(19), 11413–11420. <https://doi.org/10.1021/es500172p>
- Sylva, R. (1976). The environmental chemistry of copper (II) in aquatic systems. *Water Research*, 10(9), 789–792. [https://doi.org/10.1016/0043-1354\(76\)90097-X](https://doi.org/10.1016/0043-1354(76)90097-X)
- Taioli, S., Simonucci, S., Calliari, L., & Dapor, M. (2010). Electron spectroscopies and inelastic processes in nanoclusters and solids: Theory and experiment. *Physics Reports*, 493(5), 237–319. <https://doi.org/10.1016/j.physrep.2010.04.003>
- Tan, K. H. (2003). *Humic Matter in Soil and the Environment*. CRC Press. <https://doi.org/10.1201/9780203912546>
- Tan, K. H. (2014). *Humic Matter in Soil and the Environment*. CRC Press. <https://doi.org/10.1201/b17037>

- Tang, Z., Zhao, X., Zhao, T., Wang, H., Wang, P., Wu, F., & Giesy, J. P. (2016). Magnetic Nanoparticles Interaction with Humic Acid: In the Presence of Surfactants. *Environmental Science & Technology*, 50(16), 8640–8648. <https://doi.org/10.1021/acs.est.6b01749>
- Temminghoff, E. (1998). *Chemical Speciation of Heavy Metals in Sandy Soils in Relation to Availability and Mobility*.
- Theng, B. K. G. (1976). Interactions between montmorillonite and fulvic acid. *Geoderma*, 15(3), 243–251. [https://doi.org/10.1016/0016-7061\(76\)90078-1](https://doi.org/10.1016/0016-7061(76)90078-1)
- Tombácz, E., Dobos, Á., Szekeres, M., Narres, H. D., Klumpp, E., & Dékány, I. (2000). Effect of pH and ionic strength on the interaction of humic acid with aluminium oxide. *Colloid & Polymer Science*, 278(4), 337–345. <https://doi.org/10.1007/s003960050522>
- Tong, Y., Xiang, H., Jiang, J., & Chen, W. (2024). Interfacial interactions between minerals and organic matter: Mechanisms and characterizations. *Chemosphere*, 359, 142383. <https://doi.org/10.1016/j.chemosphere.2024.142383>
- Violante, A., Cozzolino, V., Perelomov, L., Caporale, A. G., & Pigna, M. (2010). Mobility And Bioavailability Of Heavy Metals And Metalloids In Soil Environments. *Journal of Soil Science and Plant Nutrition*, 10(3). <https://doi.org/10.4067/S0718-95162010000100005>
- Wagai, R., & Mayer, L. M. (2007). Sorptive stabilization of organic matter in soils by hydrous iron oxides. *Geochimica et Cosmochimica Acta*, 71(1), 25–35. <https://doi.org/10.1016/j.gca.2006.08.047>
- Wan, Y., Liu, J., Zhuang, Z., Wang, Q., & Li, H. (2024). Heavy Metals in Agricultural Soils: Sources, Influencing Factors, and Remediation Strategies. *Toxics*, 12(1), 63. <https://doi.org/10.3390/toxics12010063>
- Warren, J., & Spiers, G. (2021). Soil mineralogy. In D. A. Lobb (Ed.), *Soil science* (Chapter 14). Saskatchewan Open Educational Resources. <https://www.saskoer.ca/soilscience/chapter/soil-mineralogy/>
- Wei, S., & Xiang, W. (2013). Adsorption removal of Pb(II) from aqueous solution by fulvic acid-coated ferrihydrite. *Journal of Food, Agriculture and Environment*, 11, 1376–1380.
- Weng, L., Temminghoff, E. J. M., Lofts, S., Tipping, E., & Van Riemsdijk, W. H. (2002). Complexation with Dissolved Organic Matter and Solubility Control of Heavy Metals in a Sandy Soil. *Environmental Science & Technology*, 36(22), 4804–4810. <https://doi.org/10.1021/es0200084>
- Wershaw, R. (1993). Model for Humus in Soils and Sediments. *Environmental Science & Technology*, 27(5), 814–816. <https://doi.org/10.1021/es00042a603>

- Wild, A., & Keay, J. (1964). Cation-Exchange Equilibria With Vermiculite. *Journal of Soil Science*, 15(2), 135–144. <https://doi.org/10.1111/j.1365-2389.1964.tb02214.x>
- Willemsen, J. A. R., Myneni, S. C. B., & Bourg, I. C. (2019). Molecular Dynamics Simulations of the Adsorption of Phthalate Esters on Smectite Clay Surfaces. *The Journal of Physical Chemistry C*, 123(22), 13624–13636. <https://doi.org/10.1021/acs.jpcc.9b01864>
- Woodcroft, B. J., Singleton, C. M., Boyd, J. A., Evans, P. N., Emerson, J. B., Zayed, A. A. F., Hoelzle, R. D., Lamberton, T. O., McCalley, C. K., Hodgkins, S. B., Wilson, R. M., Purvine, S. O., Nicora, C. D., Li, C., Frolking, S., Chanton, J. P., Crill, P. M., Saleska, S. R., Rich, V. I., & Tyson, G. W. (2018). Genome-centric view of carbon processing in thawing permafrost. *Nature*, 560(7716), 49–54. <https://doi.org/10.1038/s41586-018-0338-1>
- Wu, J., Pjevac, P., & Kraemer, S. M. (2026). *Coupled Dynamics of Mineral Transformation and Mineral-Associated Organic Matter (MAOM) Degradation*. <https://doi.org/10.5194/egusphere-egu26-21317>
- Wu, M., Jia, Y., Zhang, Y., Wen, R., Guo, J., Wang, N., Liu, W., Qiu, H., Wang, H., Xian, Y., Yu, C., & Yang, T. (2021). Heavy metal pollution from copper smelting during the Shang Dynasty at the Laoniupo site in the Bahe River valley, Guanzhong Basin, China. *Journal of Geographical Sciences*, 31(11), 1675–1693. <https://doi.org/10.1007/s11442-021-1917-x>
- Wu, S., Konhauser, K. O., Chen, B., & Huang, L. (2023). “Reactive Mineral Sink” drives soil organic matter dynamics and stabilization. *Npj Materials Sustainability*, 1(1), 3. <https://doi.org/10.1038/s44296-023-00003-7>
- Wuddivira, M. N., & Camps-Roach, G. (2007). Effects of organic matter and calcium on soil structural stability. *European Journal of Soil Science*, 58(3), 722–727. <https://doi.org/10.1111/j.1365-2389.2006.00861.x>
- Xiao, K.-Q., Zhao, M., Moore, O., Zhao, Y., Li, X.-N., Woulds, C., Babakhani, P., Mills, B. J. W., Homoky, W. B., Johnson, K., Tagliabue, A., Liang, C., Zhu, Y.-G., & Peacock, C. (2025). Mineral carbon pump in the Earth system. *The Innovation*, 6(1), 100737. <https://doi.org/10.1016/j.xinn.2024.100737>
- Xiao, K.-Q., Zhao, Y., Liang, C., Zhao, M., Moore, O. W., Otero-Fariña, A., Zhu, Y.-G., Johnson, K., & Peacock, C. L. (2023). Introducing the soil mineral carbon pump. *Nature Reviews Earth & Environment*, 4(3), 135–136. <https://doi.org/10.1038/s43017-023-00396-y>
- Xiao, M., Guo, J., Zhao, S., & Li, S. (2023). Adsorption of As(V) at Humic Acid-Kaolinite-Bacteria Interfaces: Kinetics, Thermodynamics, and Mechanisms. *Agronomy*, 13(2), 611. <https://doi.org/10.3390/agronomy13020611>

- Xu, Z., & Tsang, D. C. W. (2022). Redox-induced transformation of potentially toxic elements with organic carbon in soil. *Carbon Research*, 1(1), 9. <https://doi.org/10.1007/s44246-022-00010-8>
- Xu, Z., & Tsang, D. C. W. (2024). Mineral-mediated stability of organic carbon in soil and relevant interaction mechanisms. *Eco-Environment & Health*, 3(1), 59–76. <https://doi.org/10.1016/j.eehl.2023.12.003>
- Yan, Y., Wan, B., Mansor, M., Wang, X., Zhang, Q., Kappler, A., & Feng, X. (2022). Co-sorption of metal ions and inorganic anions/organic ligands on environmental minerals: A review. *Science of The Total Environment*, 803, 149918. <https://doi.org/10.1016/j.scitotenv.2021.149918>
- Yang, K., Lin, D., & Xing, B. (2009). Interactions of Humic Acid with Nanosized Inorganic Oxides. *Langmuir*, 25(6), 3571–3576. <https://doi.org/10.1021/la803701b>
- Yang, R., Li, Z., Huang, M., Luo, N., Wen, J., & Zeng, G. (2019). Characteristics of fulvic acid during coprecipitation and adsorption to iron oxides-copper aqueous system. *Journal of Molecular Liquids*, 274, 664–672. <https://doi.org/10.1016/j.molliq.2018.11.030>
- Yruela, I. (2009). Copper in plants: acquisition, transport and interactions. *Functional Plant Biology*, 36(5), 409–430. <https://doi.org/10.1071/FP08288>
- Yu, H., Li, C., Yan, J., Ma, Y., Zhou, X., Yu, W., Kan, H., Meng, Q., Xie, R., & Dong, P. (2023). A review on adsorption characteristics and influencing mechanism of heavy metals in farmland soil. *RSC Advances*, 13(6), 3505–3519. <https://doi.org/10.1039/D2RA07095B>
- Zhang, J., Wu, Y., & Xu, Y. (2017). Factors Affecting the Levels of Pb and Cd Heavy Metals in Contaminated Farmland Soils. *Proceedings of the 2016 International Conference on Biological Engineering and Pharmacy (BEP 2016)*. <https://doi.org/10.2991/bep-16.2017.85>
- Zhang, Y., Chen, Y., An, J., Zhao, X., & Zu, B. (2023). Adsorption-Reduction Behavior of Cr(VI) by Ferrihydrite-Fulvic Acid Complexes with Different C/Fe Mole Ratios. *Adsorption Science & Technology*, 2023. <https://doi.org/10.1155/2023/5716199>
- Zhao, C., Yao, J., Knudsen, T. Š., Liu, J., Zhu, X., & Ma, B. (2023). Effect of goethite-loaded montmorillonite on immobilization of metal(loid)s and the micro-ecological soil response in non-ferrous metal smelting areas. *Science of The Total Environment*, 865, 161283. <https://doi.org/10.1016/j.scitotenv.2022.161283>
- Zheng, Z., Liu, B., Fang, X., Fa, K., & Liu, Z. (2022). Dryland farm soil may fix atmospheric carbon through autotrophic microbial pathways. *CATENA*, 214, 106299. <https://doi.org/10.1016/j.catena.2022.106299>

- Zhu, T., Herath, S., Newton, P., Hou, F., & Bowatte, S. (2021). Distribution of physiochemically defined soil organic carbon pools and their relationship to the soil microbial community in grasslands. *Pedobiologia*, 84, 150704. <https://doi.org/10.1016/j.pedobi.2020.150704>
- Zhu, W., Li, Z., Li, P., Yu, B., Lin, C.-J., Sommar, J., & Feng, X. (2018). Re-emission of legacy mercury from soil adjacent to closed point sources of Hg emission. *Environmental Pollution*, 242, 718–727. <https://doi.org/10.1016/j.envpol.2018.07.002>
- Zhuang, Y., Zhu, J., Shi, L., Fu, Q., Hu, H., & Huang, Q. (2022). Influence mechanisms of iron, aluminum and manganese oxides on the mineralization of organic matter in paddy soil. *Journal of Environmental Management*, 301, 113916. <https://doi.org/10.1016/j.jenvman.2021.113916>

Chapter 2: The Dynamic Nature of Mineral Organic Matter Associations in Adsorption Experiments

Abstract

Mineral-organic matter associations (MOAs) are predominant in soil environments and encompass a range of soil minerals and organic matter. This study characterizes changes in the structure and chemical composition of MOAs in the presence of metal ions of high (Cu) and low (Ni) affinity towards organic matter. It shows that MOAs are highly dynamic in terms of size, composition, and structure during their interactions with Cu- and Ni-bearing solutions. MOAs are synthesized using montmorillonite and ferrihydrite as the mineral components and polymerized fulvic acid (FA) as the organic component. Adsorption isotherms and Total Organic Carbon (TOC) analysis indicate that desorbed FA complexes both metal ions at lower metal ion concentrations and that the polymerization of Cu- and Ni-FA complexes occurs at higher metal concentrations. Structural characterization of MOAs using electron microscopy, spectroscopy, and X-ray diffraction indicates that Cu induces greater structural and compositional changes than Ni, owing to its higher affinity for polar organic functional groups. Here, the formation of Cu-carboxylate complexes in ferrihydrite-FA-OA increases with the concentrations of Cu, and the interaction of Cu with montmorillonite-FA-OA follows a 2-step intercalation with the formation of higher polymerized Cu-FA complexes at higher Cu concentrations. Additionally, the formation and polymerization of Cu-FA complexes increased the number of polar functional groups, thereby increasing the number of binding sites. Future adsorption studies involving MOAs and metal ions with a high affinity for organic functional groups need to consider that neither the surface area, composition, nor the

number of binding sites in MOAs remains constant as the metal ion concentration in solution increases.

Keywords: Mineral organic matter associations, desorption, complexation, polymerization, polar groups, surface area

2.1 Introduction

Minerals and organic matter (OM), such as humic and fulvic acids, coexist in soils, forming mineral-organic matter associations (MOAs) (Kleber et al., 2015). Humic substances promote soil aggregation through linkages with soil minerals (Deng & Dixon, 2002). Microaggregates formed by interactions between OM and minerals serve as the primary repository of the most stable carbon pool in soils (Chia et al., 2012). In soils, fulvic or low-molecular-weight fractions of humic acids commonly participate in OM-clay and OM-Fe-oxide interactions (Nikishina et al., 2022). Here, Fe-oxide nanoparticles form nanoaggregates with humic substances, providing chemical stabilization at the organic–mineral interface and offering reactive sites for metal sequestration (Di Iorio et al., 2022). Organic matter sorbs to the interlamellar surfaces of swelling clay or onto edge surfaces, increasing negative surface charge and thus promoting reactions with positively charged metal species (Dubbin et al., 2014). OM often polymerizes as multilayers on mineral surfaces with a first-generation monolayer (Kleber et al., 2007). Here, polar functional groups of the OM, mainly carboxylic and carbonyl carbon and N-containing groups, define the organic–mineral interface (Possinger et al., 2020), whereas hydrophobic interactions are prevalent in the zonal structure of the OM (Kleber et al., 2021). MOAs in the rhizosphere are vulnerable to disruption, undergoing destabilization mechanisms such as OM desorption, mineral dissolution, or OM depolymerization, depending on the effects of climate and land-use change (Bölscher et al., 2025). Several

biogeochemical changes in the rhizosphere, such as redox status, solute concentrations, and soil pH, also control the (de-)stabilization of MOAs.

As major constituents in organic-rich soils, MOAs control the retention, release, and mobilization (as colloids) of metals (Jadoon & Schindler, 2022). Their interaction with metals, however, is complex and involves adsorption, coprecipitation, occlusion, redox processes, catalysis, and dissolution (Tong et al., 2024). For example, the interaction of metal ions with MOAs can result in ternary complexes, such as mineral-metal ion-OM or mineral-OM-metal ion associations, or in metal nanoparticles within OM or along the OM-mineral interface (X. Li et al., 2025). Despite the instability of MOAs in certain soil environments and the complexity of their interactions with metal ions, previous adsorption studies involving metal ions and MOAs assumed that the composition and structure of MOAs remained unchanged throughout the experiments (Komy et al., 2014; Zhang et al., 2023). Here, we show that MOAs exhibit dynamic behavior, including de- and re-attachment, de- and re-polymerization, and polarization of the organic components, in adsorption studies with metal ions. Most previous studies have focused on adsorption kinetics, adsorption capacities, adsorption edge studies, and adsorption thermodynamics (Fariña et al., 2018; Öztürk Er et al., 2026; Xiao et al., 2023; L. Xu et al., 2022) with synthetic and natural organic matter. Still, studies on structural and compositional changes in response to changes in the metal ion concentrations are scarce.

Monitoring structural and chemical changes in complex metal ion-MOA adsorption studies, however, requires simplified model systems with an initially well-defined organic component, a relatively insoluble mineral, a relevant pH, and a single cationic metal species to facilitate analysis and better understanding. It also requires that the MOAs be thoroughly characterized prior to the

adsorption experiments and that changes in their structure and composition be monitored alongside changes in the metal ion concentration.

The objectives of this study are therefore to characterize structural changes in MOAs in adsorption experiments with metal ions of high toxicity, high and low affinity for OM, and with well-known interactions with OM and the mineral component. This allows us to determine whether structural changes in MOAs are cation-dependent and whether they enhance the sequestration of toxic elements. Cu^{2+} and Ni^{2+} follow the above requirements. Cu^{2+} exhibits a high affinity for OM and is commonly sequestered by surface complexation on synthetic OM and Fe-(hydr)oxides. Cu^{2+} is also sequestered via complex redox reactions and precipitation mechanisms on natural analogs of the latter components (Manceau & Matynia, 2010; Mantha et al., 2019; R. Yang et al., 2018). Ni^{2+} has a higher affinity for minerals than for OM and is mainly retained via surface complexation and ion exchange by minerals and OM (Esfandiar et al., 2022; Lee & Jonasson, 1983; D.Xu et al., 2008). We expect to observe compositional and structural changes in MOAs in adsorption experiments with Cu and Ni ions and hypothesize that Cu and Ni are more abundant at mineral-OM interfaces than in organic matter alone due to surface-induced polarization.

In this study, montmorillonite (Mt) and ferrihydrite (Fh) are the mineral components, and fulvic acid (FA) is the organic component in the MOAs. Structural and compositional changes in the Mt-FA-OA and Fh-FA-OA associations with increasing concentrations of Cu^{2+} and Ni^{2+} are monitored using a unique combination of Scanning-Transmission (STEM) and Transmission Electron Microscopy (TEM), Total Organic Carbon analyzer (TOC analyzer), Ultraviolet-Visible spectroscopy (UV-Vis), X-ray powder diffraction (XRD), Fourier Transform Infrared (FT-IR) spectroscopy, and Electron Energy Loss spectroscopy (EELS).

2.2 Materials and methods

The synthesis of two-line Fh followed the method by Schwertmann and Cornell (Schwertmann & Cornell, 2000) and the one for Fh-FA association (Fh-OA) was modified from previous literature (Wei & Xiang, 2013; Zhang et al., 2023). Synthetic Mt was purchased from Nanochemazone (Alberta, Canada), and Mt-FA associations (Mt-OA) were synthesized using previously reported methods (Dubbin et al., 2014; Schnitzer & Kodama, 1967; Zhou et al., 2024). Analysis of FA abundance in supernatant solutions was performed using TOC analyzer. Further details on materials and methods are listed in the supplementary data (Figure S1).

2.2.1. Synthesis of Fh-OAs and Mt-OAs

Twenty mg of Fh and Mt powder were mixed with 20 mL of a 200 mg L⁻¹ FA solution containing 0.02 mM CaCl₂ · 2H₂O. The ionic strength was adjusted to 0.01 M with 0.01 M NaNO₃ in both solutions. The Fh-OA and Mt-OA solutions were maintained at pH 6.0 ± 0.1 and pH 3.5 ± 0.1 by adding 0.01 M HNO₃ and 0.01M NaOH, respectively. The resulting suspensions were shaken at room temperature for 48 h and centrifuged at 3,500 rpm for 5 min and at 3,000 rpm for 10 min. After the supernatant was removed, the residue was rinsed with Milli-Q water. The precipitates were dried and stored under dry conditions.

2.2.2 Adsorption Experiments

Many contaminated soils, especially those impacted by smelters, have elevated concentrations of metals in the bulk soil as well as in the leachable mobile fraction (Han & Gu, 2023; Sutherland, 2000). For example, Cu-concentrations in the surficial soils and their leachable fractions in the smelter-impacted area of Rouyn-Noranda, Canada, are in the range of 2600-7900 mg kg⁻¹ and 8-19 mg L⁻¹ (Jadoon & Schindler, 2022). The latter leachate concentration occurred in a saturated system, whereas those in nanoscale-to-microscale surface films on mineral surfaces in unsaturated conditions can be much higher (Nishiyama & Yokoyama, 2021; Tokunaga, 2011). Hence, the

chosen concentration range for the adsorption experiments, 10-200 mg L⁻¹ for Cu and Ni, occurs most likely within surface films of highly contaminated soil.

Hundred mg of Fh, Mt, and Mt-OAs, and Fh-OAs were placed in 50 mL polypropylene centrifuge tubes and mixed with 20 mL of Cu²⁺ and Ni²⁺ -bearing solutions with varying concentrations (10, 20, 50, 80, 100, 150, 180, and 200 mg L⁻¹ Cu or Ni). The pH was adjusted to pH = 6 with 0.01 M NaOH and 0.01 M HNO₃, and NaNO₃ (0.01 M) was used to maintain a constant ionic strength. Resulting suspensions were shaken at room temperature for 24 h and centrifuged at 3,000 rpm for 10 min. All adsorption experiments were conducted in triplicate. Following the adsorption experiments (Table S3), the amounts of absorbed metal ions were calculated as the difference between the initial concentration of Cu²⁺/Ni²⁺ and the Cu²⁺/Ni²⁺ equilibrium concentration in the supernatant measured with an Agilent 8900 Triple Quadrupole ICP-MS. Langmuir and the Freundlich equations were used to characterize the adsorption of Cu²⁺ and Ni²⁺ on the MOAs (Figure S2). The abundance of FA in supernatant solutions was monitored with a TOC analyzer (Shimadzu TOC-L series) (Figure S3).

2.2.3 Characterization of treated and untreated MOAs

BET surface area analysis was conducted with a Micromeritics 3Flex, using Nitrogen gas, and a 12mm flat-bottom sample tube with a check seal valve.

Powder XRD patterns were recorded at room temperature using a Bruker D5000 powder diffractometer equipped with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) operating at 40 kV and 40 mA. Data were collected with a step size of 0.02° and a step time of 1 s over an angular range of 2–60° (2 θ).

FTIR spectroscopy was used to characterize the surface functional groups of the synthesized complexes using a Bruker Tensor 27 FTIR spectrometer equipped with a KBr beam splitter and a DLATGS detector. Spectra over the range 4000–400 cm⁻¹ were collected by averaging 100 scans

at an operating resolution of 4 cm^{-1} . The resulting spectra were fitted with Gaussian curves, with the constraints that the bands for the components at 1705 cm^{-1} (C=O), 1390 cm^{-1} ($\text{COO}^-_{\text{sym}}$), and 1585 cm^{-1} ($\text{COO}^-_{\text{asym}}$) had the same full width at half maximum (FWHM) and occurred at previously reported wavenumbers (Fu & Quan, 2006).

MOAs deposited on a 300-mesh holey carbon TEM grid (gold) were characterized with TEM, Scanning TEM (STEM), and STEM-EDS (FEI Talos F200X) at 200 kV in bright-field mode, a Fischione high-angle annular dark-field (HAADF) detector, and with 4 SDD detectors, at the Manitoba Institute of Materials, University of Manitoba, Canada.

Electron energy-loss spectroscopy (EELS) measures the energy loss of high-energy electrons as they pass through a material (Taioli et al., 2010). This energy loss can provide information about an element's valence and bonding environment in a TEM sample (Lazar et al., 2025). The fine structure of the C 1s spectrum in EELS allows for the determination of the proportions of the aromatic C=C, aliphatic C-H, carboxylic/carbonyl, and C-O components in a nanometer-sized area. As the presence of mineral surfaces and metal ions can change the proportions of these components through the formation of metal-oxygen-carbon bonds, this study investigates whether their proportions differ between the OM matrix and the Mt-OA and Fh-OA interfaces in the presence and absence of adsorbed Cu- and Ni-species (Tables S1, S2). Previous NEXAFS studies provided information on the speciation and bonding environments of Fe, Ni, and Cu with FA at the bulk scale (Christl & Kretzschmar, 2007; Strathmann & Myneni, 2005; van Schaik et al., 2008; Xia et al., 1997). Contrary, EELS could not resolve in this study the speciation of Cu and Ni in the MOAs as accurate peak fittings of EELS spectra require metal concentrations in the weight% range. A total of 48 EELS spectra were recorded from Mt-OA, Fh-OA, and Cu and Ni-bearing Mt-OAs and Fh-OAs with a TFS Spectra Ultra, a double-corrected HRTEM/STEM equipped with

both image and probe correctors at the Canadian Center for Electron Microscopy, McMaster University, Canada. Experiments were performed at 200 kV with a probe current of approximately 70 pA, a convergence angle of 28 mrad, and a collection angle of approximately 90 mrad (Fig. S2). To minimize beam damage and carbon contamination while ensuring precise elemental detection at relevant scales, the analysis time per pixel was minimized. Regions of interest (ROIs) for high-resolution imaging and analysis were selected based on sample position relative to the vacuum and electron transparency. Changes in the chemical bonding in Fh- and Mt-OAs were determined by comparing C 1s spectra recorded before and after the adsorption experiments. Here, the fine structure of the C 1s spectra was extracted using the empirical model proposed by Tenailleu(Pal et al., 2020, 2021; Tenailleu & Martin, 1992) . The resulting spectra were fitted with the constraint that the bands of the various C-components (Table S1) had the same FWHM and occurred at energies similar to those previously reported (Ivanova et al., 2019; Pal et al., 2021; Pelaez-Fernandez et al., 2021; Possinger et al., 2020).

2.3 Results and Discussion

2.3.1 Characterization of MOA Complexes

The Fh nanoparticles (NPs) are predominantly spherical with diameters ranging from 5 to 12 nm (Figure S4). The Mt NPs exhibit platelets with a thickness of 1 nm and lateral dimensions of 80-500 nm (Figure S5). In the MOAs (Figure 1), Fh-NPs occur in larger aggregation states and Mt-NPs in smaller grain sizes. Aggregation of the Fh NPs is promoted by neutralizing their positive surface charge under weakly acidic conditions via attachment of negatively charged FA

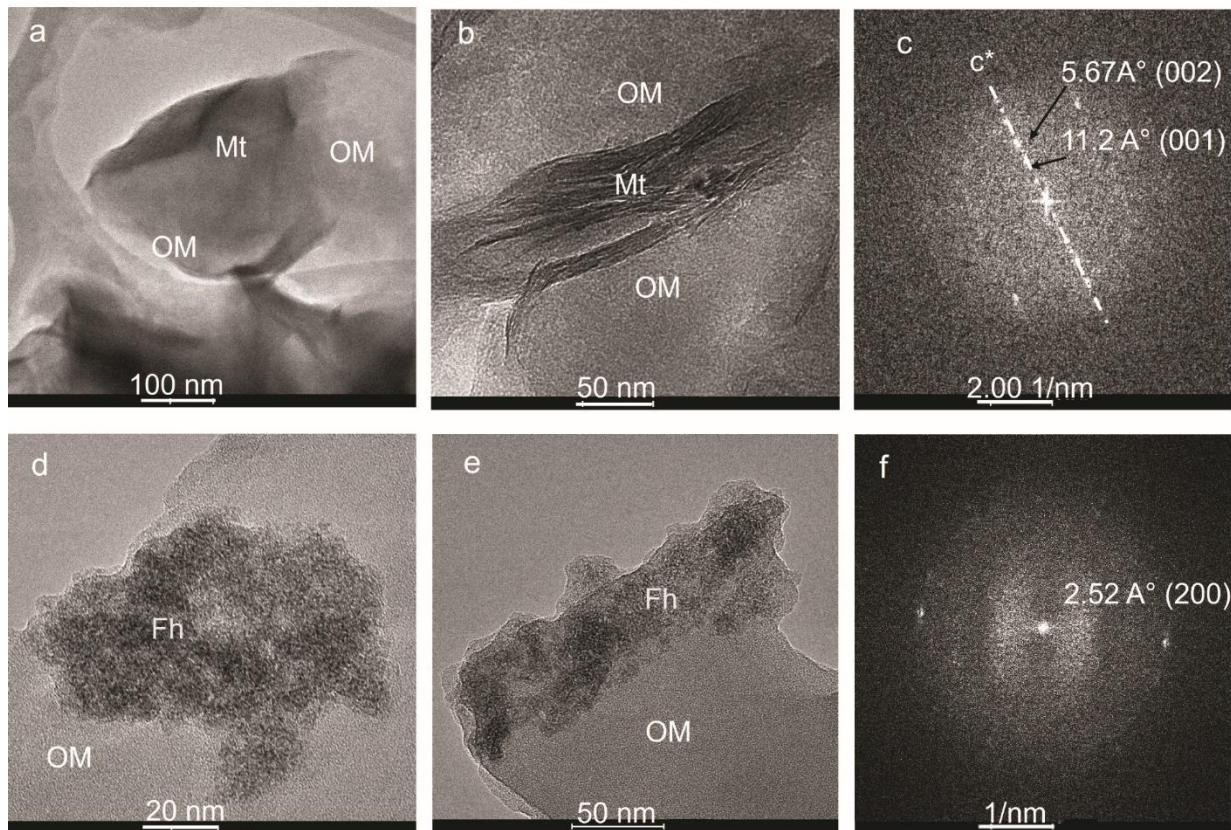


Figure 1. (a)-(f) High-resolution TEM images and FFT pattern of montmorillonite (Mt)- and ferrihydrite (Fh)-organic matter (OM) associations: (a) Platy Mt crystal with a prominent basal surface, (b) Mt fibers displaying the characteristic layered structure, (c) FFT patterns with the characteristic d-spacings parallel to c^* ; (d)-(e) Fh aggregates and (f) FFT pattern of a single Fh domain.

(Wei & Xiang, 2013). The size reduction of the Mt NPs is most likely caused by the defragmentation of the Mt sheets in the presence of Cu^{2+} and Ni^{2+} species (Zeng et al., 2024). Consequently, the specific surface areas decrease and increase during the formation of the Fh-OAs

and Mt-OAs from $114.55 \pm 0.4 \text{ m}^2\text{g}^{-1}$ (Fh) to $106.1 \pm 0.3 \text{ m}^2\text{g}^{-1}$ and from $54.95 \pm 0.4 \text{ m}^2\text{g}^{-1}$ (Mt) to $64.4 \pm 0.6 \text{ m}^2\text{g}^{-1}$, respectively.

2.3.2 Adsorption Isotherms

The adsorption isotherms for Cu^{2+} and Ni^{2+} on Fh, Mt, Fh-OA, and Mt-OA follow the empirical adsorption model and show a decrease in vacant binding sites with increasing equilibrium metal concentration in solution (Figure 2a-b). At low metal ion loadings, inner-sphere surface complexes are predominant (Gupta & Bhattacharyya, 2006; Malamis & Katsou, 2013), whereas at higher loadings, the driving force for ions to reach adsorption sites increases, leading to the formation of low-energy, non-specific binding sites (multilayer adsorption) or mineral surface precipitations (Shirvani et al., 2015). The adsorption isotherms further indicate that the formation of Cu- and Ni-MOA networks (Figure 2a, b) results in a higher adsorption capacity for the MOAs than for Fh and Mt, in accordance with results from previous studies (Komy et al., 2014). Here, Fh-OA, Fh, and Mt-OA depict a higher binding affinity towards Cu^{2+} than Ni^{2+} , which follows the Irving–Williams series, where the adsorption affinity of most substrates increases in the sequence $\text{Mn}^{2+} < \text{Fe}^{2+} < \text{Co}^{2+} < \text{Ni}^{2+} < \text{Cu}^{2+} < \text{Zn}^{2+}$ (Guan et al., 2019; Halmos et al., 2015; J. Wang et al., 2025). Contrary to Fh and the MOAs, the adsorption capacity of Mt is higher for Ni than for Cu. This may be explained by the lower ability of Ni vs. Cu to hydrolyze; i.e., Ni^{2+} with a lower degree of hydrolysis can bond more effectively to Mt surface than Cu^{2+} due to its higher charge density and the higher desolvation energy penalty to shed off a $\text{H}_2\text{O}/\text{OH}$ group in its hydration sphere (Abollino et al., 2008; Ali et al., 2019; Wild & Keay, 1964).

Regression analyses of the adsorption isotherms for Cu and Ni on Fh, Mt, Fh-OA, and Mt-OA complexes indicate higher R^2 values for the Freundlich- than the Langmuir model (Table S4,6) (Komy et al., 2014), in accordance with previous studies (L.Xu et al., 2022).

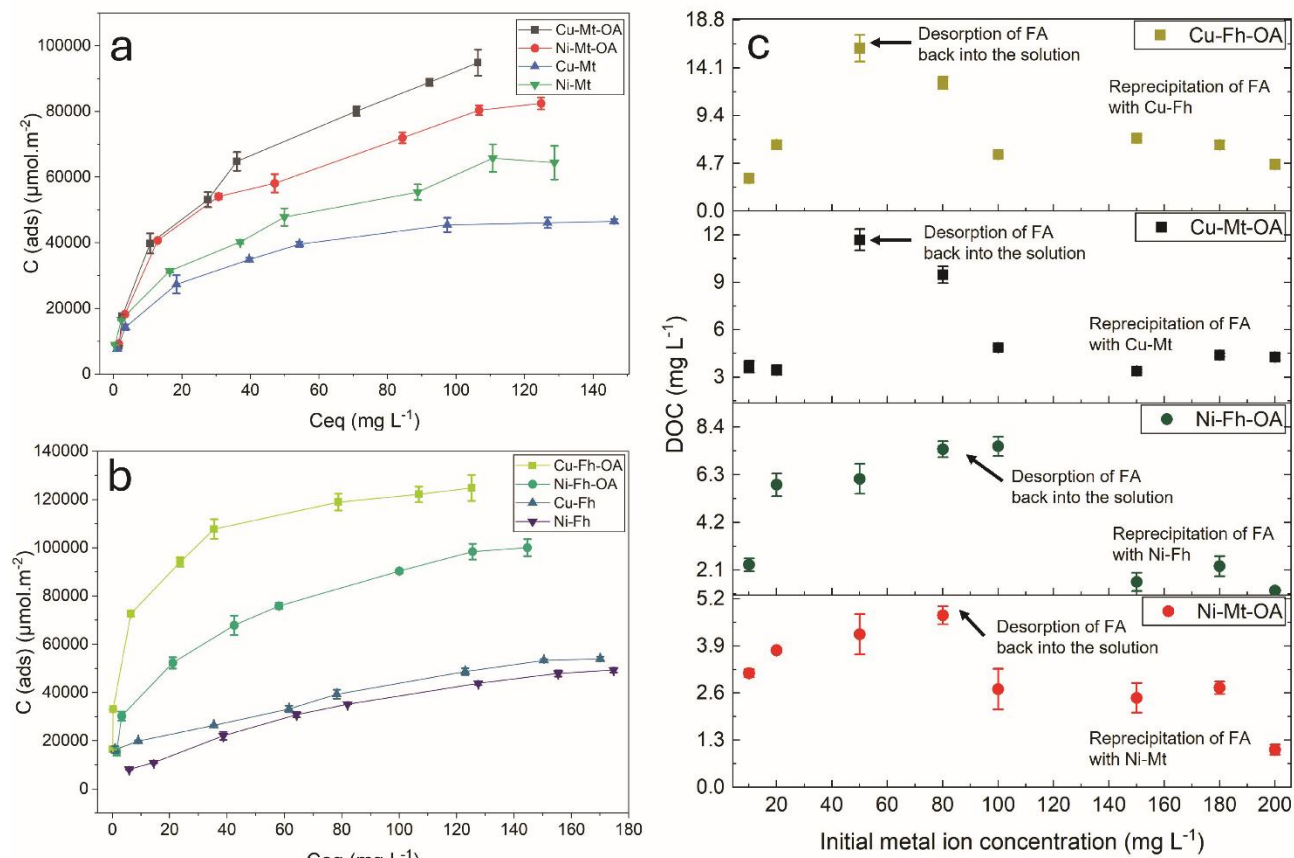


Figure 2. (a) The adsorption isotherms for Cu^{2+} and Ni^{2+} on Mt and Mt-OA, (b) The adsorption isotherms for Cu^{2+} and Ni^{2+} on Fh and Fh-OA, (c) DOC content in supernatant solutions versus the initial concentrations of Cu^{2+} and Ni^{2+} in the Fh-OA and Mt-OA adsorption experiments

2.3.3 Dynamic nature of MOAs

Previous studies(Kramer et al., 2012; Ndzana et al., 2022; Z.Xu & Tsang, 2024) considered MOAs (natural or synthetic) stable macromolecules, where,

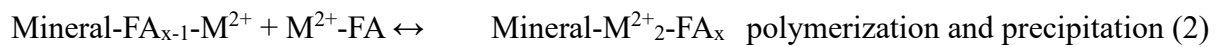
- a. The amount and composition of organics bound to the surface of mineral remains unchanged during the adsorption experiment or with the concentration of the cation in solution(Komy et al., 2014; Mikutta et al., 2007)
- b. They were final products rather than dynamic entities incapable of undergoing structural changes due to metal exposure.

The latter was evaluated by quantifying the ratio of polar to non-polar functional groups in the organic fraction of selected Cu- and Ni-bearing Mt-OA and Fh-OA before and after the adsorption experiment (*see section 3.7*).

The changes in the chemical composition of Mt-OA and Fh-OA as a function of Cu and Ni concentrations during adsorption experiments were monitored by measuring DOC in the supernatant. In all Ni/Cu-MOA systems, the DOC (i.e. FA) concentrations are lower at low initial Cu and Ni concentrations. The DOC concentrations peak for Cu-Fh-OA and Cu-Mt-OA at 50 mgL⁻¹ initial Cu-concentration, and for Ni-Fh-OA at 80-100mg L⁻¹ and Ni-Mt-OA at 80 mgL⁻¹ initial Ni concentration. At initial Cu and Ni concentrations above 100 mg L⁻¹, the DOC decreases towards the concentration observed in the experiments with low initial metal ion concentrations.

The low DOC concentrations at low initial metal concentrations can be explained by the bridging effect of polyvalent cations (Cu²⁺ and Ni²⁺) between the mineral surface and organic molecules. Especially in the montmorillonite system, metal ions reduce the electrostatic repulsion between the negatively charged clay surface and organic molecules, thereby enhancing adsorption strength

at initial low metal concentrations (Allard et al., 2017; Z. Xu & Tsang, 2024). Multivalent cations can promote the sorption of organic molecules onto minerals, forming intra- and intermolecular linkages with organic matter (Mikutta et al., 2007). Higher initial Cu and Ni concentrations in solution can lead to two competitive processes: competition between (1) aqueous Cu^{2+} and Ni^{2+} species and FA to adsorption sites on the mineral surface (Sutton & Sposito, 2006; Yan et al., 2022b) and (2) aqueous Cu^{2+} and Ni^{2+} species and metal-surface terminations to bond to FA species (Dorfman et al., 2023; Du et al., 1999). Both processes most likely led to the desorption of FA from the MOA at moderate initial concentrations of Cu and Ni in solution (Figure 2c). The delay in the maximum desorption of FA for the Ni (80-100 mg L⁻¹) compared to the Cu system (50 mg L⁻¹) can be explained by the higher affinity of Cu for OM, forming stronger Cu-FA complexes in solution (Du et al., 1999; R. Yang et al., 2018). Hence, higher initial Ni concentrations were required to achieve maximum FA desorption from MOA. The observed decrease in DOC at very high initial Cu and Ni concentrations in solution was likely due to the repolymerization of metal ions with FA, thereby promoting the formation of surface metal ion (M)-FA precipitates on mineral-FA surfaces. Desorption of FA and repolymerization and precipitation of Metal ion-FA complexes on the mineral-OA surfaces may be expressed with the following equations:



Here, repolymerization occurs with an excess of M^{2+} , shifting equilibrium (2) towards the product side. The repolymerization of FA requires, however, structural changes in the FA, as the linkage of FA by a higher proportion of M^{2+} demands an increase in the number of polar functional groups. In this regard, plots of DOC versus initial metal ion concentration (Figure 2c) indicate that

- (I) a greater fulvic acid desorption from MOAs in the presence of Cu than Ni;
- (II) a greater fulvic acid desorption in Fh-MOAs than Mt-MOAs for both Cu and Ni;

Observation I is in accord with the reported higher dissociation constants of Ni-FA than Cu-FA complexes (Eshwar, 2017; Mandal et al., 1999; Sekaly et al., 1999). Observation II can be explained by the strong binding ability of fulvic acid towards $\text{Fe}^{2+/3+}$ (Zhang et al., 2023), causing the formation of FA- $\text{Fe}^{2+/3+}$ complexes (Pullin & Cabaniss, 2003). The presence of these complexes in solutions could not be verified, but the repolymerization of potential M-FA- $\text{Fe}^{2+/3+}$ complexes is evident in minor concentrations of Fe in the organic matrices of the M-Fh-OA (as determined by STEM-EDS; Figure S6). Although the particle size (average hydrodynamic diameter) of the colloidal fraction in the supernatant solution does not provide direct evidence for the size of the Cu- and Ni-bearing MOAs, it offers insights into how the size of the colloids is linked to the stability of the MOAs. Here, the maximum colloid sizes in the Cu- and Ni-MOA systems occur prior to the peak of DOC concentrations (i.e., prior to the peak of FA desorption, Fig. 2c), whereas smaller-sized colloids are predominant at very high initial metal ion concentrations (Figure S7). These trends suggest that I. High polymerization degrees of minerals, FA, and metal ions in solution stabilize metal-bearing MOAs at low metal-ion concentrations; II. repolymerization at high initial metal-ion concentrations involves smaller-sized metal-ion-mineral-FA colloids.

2.3.4 Characterization of the Cu- Ni-carboxylate environments in Mt- and Fh-OAs

The differences in the binding affinities of Cu and Ni to the functional groups of FA were investigated using FT-IR spectroscopy of Fh-OAs, thereby linking molecular-level observations to desorption and repolymerization at the bulk scale. The Cu- and Ni-bearing Fh-OAs show clear differences in the bonding environment of FA functional groups from the initial, unreacted Fh-

OAs (Figure 3a). Here, two prominent peaks and one shoulder at wavenumbers 1390, 1585 and 1705 cm^{-1} serve as key spectral markers for metal binding to FA in the FT-IR spectra (Fu & Quan, 2006). Note that these spectral features overlap with the bands for OH-bending components in the FT-IR spectra of Mt and thus cannot be used to monitor the change in bonding environments of the Cu- and Ni-Mt-OA systems.

The band for the shoulder at 1705 cm^{-1} is associated with the C=O component, and the bands for the peaks at 1390 cm^{-1} and 1585 cm^{-1} with symmetric ($\text{COO}^-_{\text{sym}}$) and asymmetric ($\text{COO}^-_{\text{asym}}$) stretching frequencies of the COO^- component (Figure 3b).

Upon adsorption of Cu and Ni, the area of the $\text{COO}^-_{\text{sym}}$ band at 1390 cm^{-1} increases, and the band shifts to lower wavenumbers (1382–1384 cm^{-1} , Table S7)(Gu et al., 1994; Heckman et al., 2011; Kaiser & Guggenberger, 2007). These changes are consistent with carboxylate-metal bond formation via a ligand exchange mechanism (Gu et al., 1994). Adsorption also leads to a significant decrease in the area of the $\text{COO}^-_{\text{asym}}$ band at 1585 cm^{-1} (Figure 3a), indicating that asymmetric stretching becomes suppressed when Cu and Ni adsorb to carboxyl functional groups via inner-sphere complexes (Byler et al., 1987; Chen, 2013; R. Yang et al., 2019). These intensity variations between symmetric ($\text{COO}^-_{\text{sym}}$) and asymmetric ($\text{COO}^-_{\text{asym}}$) stretching vibrations are initiated by the deprotonation of carboxyl groups (Terkhi et al., 2008) and are followed by Cu complexation with carboxylate anions.

A plot of the initial concentration of Cu (Cu_{in}) in solution versus the area ratios of the 1390/1585 cm^{-1} bands shows an increase in the 1390/1585 cm^{-1} band ratio with increasing Cu_{in} , indicating progressive coordination of Cu to carboxylates (Figure 3c). As intensity is considered proportional to the number of the COO^- groups coordinating to Cu ions (Mizuguchi et al., 1997) the increase in the intensity of ($\text{COO}^-_{\text{sym}}$), indicates an increase in the Cu-carboxylate bonding environments.

Unlike the Cu system, increasing amounts of adsorbed Ni do not result in a continuous increase in the area ratios of the COO^- bands (Figure 3d). The initial increase in this ratio relative to the spectrum of the untreated Fh-OA indicates formation of Ni-carboxylate bonding environments. The constant area ratios of the COO^- bands with increasing amounts of adsorbed Ni suggest a lower total number of Ni-carboxylate bonding environments in the Ni- than Cu-Fh-OA system (Figure 3c vs. 3d).

Previous studies showed that adsorption of Cu^{2+} to Fh-OA can lead to ligand-bridging ternary surface complexes (Cu-FA-Fh), metal ion-bridging ternary surface complexes (FA-Cu-Fh), as well as surface complexes where Cu remains directly bonded to Fe-OH groups (Fariña et al., 2018; R. Yang et al., 2019). For Ni, while it can theoretically form the same types of complexes (Strathmann & Myneni, 2004, 2005), binary Ni-Fh or metal ion-bridging ternary surface complexes (FA-Ni-Fh) may be more prevalent due to Ni's lower affinity for OM compared to Cu.

2.3.5 Intercalation of metal ions and metal ion-FA complexes in Mt

Structural changes caused by increasing amounts of adsorbed Cu and Ni on Mt and Mt-OA were monitored by changes in the d-spacing between the Tetrahedral-Octahedral-Tetrahedral layers (diffraction peak (001)).

In systems containing only Mt and Cu or Ni, the d-spacings of Mt remain nearly constant across all concentrations, fluctuating between 12.3 Å and 12.7 Å for Cu and 13.8 Å to 14.1 Å for Ni (Figure 3f). The differences in these d-spacings can be explained by the presence of a second hydration shell around Ni^{2+} (Oueslati et al., 2009), which leads to a greater expansion of the Mt interlayer (Karmous et al., 2006). The similarities in the d-spacings for Ni-Mt and Ni-Mt-OA

(Figure 3f) indicate that the presence of FA did not result in an increase in d-spacings, ruling out the intercalation of Ni-FA complexes.

Cu Mt-OA (Figure 3e) exhibits a two-step interlayer expansion (1st step- from 13.02 Å to 13.84 Å at 10-130 mg L⁻¹ Cu²⁺, 2nd step from 13.84 Å to 15 Å at 150-200 mg L⁻¹ Cu²⁺). During the first step, modified Cu-FA complexes may form, as the FA molecule itself is most likely too large to intercalate into the Mt interlayer. However, previous studies (Dubbin et al., 2014; Schnitzer & Kodama, 1967) claimed FA intercalation in the Mt interlayer, with Mt interlayer d-spacings ranging from 12.56 Å to 14.35 Å and from 10 Å to 15.1 Å. Here, interlayer expansion through intercalation of FA is affected by steric effects arising from the length of the C chains and the orientation of the functional groups. For example, chains oriented perpendicular and parallel to the silicate plane resulted in larger or similar d-spacings, respectively (Deng & Dixon, 2002; Theng, 1976).

A two-step interlayer expansion also occurred in the Na-montmorillonite-hexadecyltrimethylammonium system (Bonczek et al., 2002b), where the first and second steps were caused by the intercalation of a monolayer and a bilayer of organo-cation complexes, respectively. Similarly, we propose here that the two-step layer expansion results from the intercalation of mono- and bilayers of Cu-FA complexes with FA modified through dissociation into simpler molecular structures (Deng & Dixon, 2002), or by alteration of the fulvic acid polymer conformation, thereby favoring the reaction between C=O groups and metal ions (Nikishina et al., 2022). As the two-step interlayer expansion is not observed in the absence of FA (Figure 3e, f), the formation of gibbsite-type layers with polymerized (CuO_n) polyhedra in Mt-OA can be ruled out.

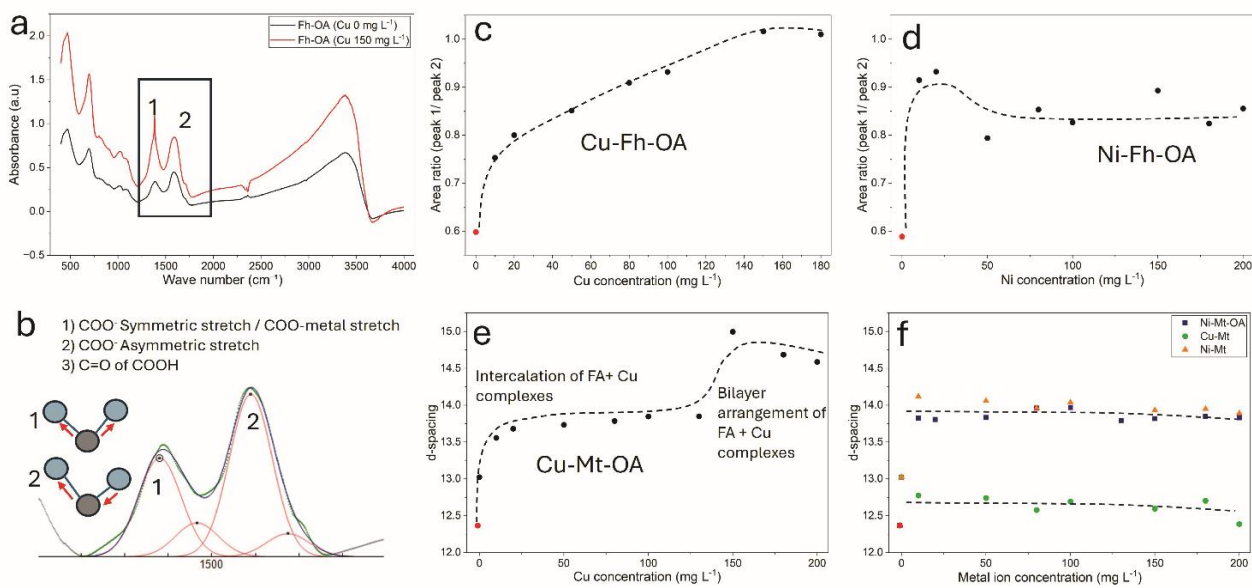


Figure 3. a) FTIR spectra of Fh-OA treated with Cu (red) and without Cu (black), indicating the difference in peak intensities of (1) COO⁻ symmetric stretch and, (2) COO⁻ asymmetric stretch, b) Fitted spectra indicating distinct bands (1)-(3) below peak envelope for Fh-OA, with an illustration showing asymmetric and symmetric stretching for (1) and (2), respectively; (c)-(d) Plot of the initial concentrations of (c) Cu and (d) Ni in the adsorption experiment in the Fh-OA system versus the area ratios of the 1390/1585 cm^{-1} bands (the untreated Fh-OA is labelled with a red sphere) ; (e)-(f) Plot of the initial Cu and Ni concentrations in solution in the Mt and Mt-OA system versus the (001) d spacings of Mt; the symbols for the d-spacings of the untreated Mt are coloured in red. Dashed lines in (c),(d),(e), and (f) represent the general trend of each plot.

2.3.6 Distribution of Cu- and Ni- at the nanoscale and changes in the crystallinity of Mt

Comparison between the STEM-EDS chemical distribution maps for Cu, Si, and C in Cu-treated Mt-OA and Fh-OA (Figure 4b, d) indicates that Cu occurs in a higher fraction in the OM matrix of Mt-OA (yellow in Figure 4b) than in Fh-OA. On the contrary, the distribution maps for Ni, Fe, and C in Ni-bearing Mt-OA and Fh-OA show that Ni is predominantly associated with Mt and Fh or with their interfaces towards OM (Figure 4f, h).

These distributions of Cu and Ni in the MOAs are consistent with the FT-IR spectra, which suggested higher numbers of Cu- than Ni-carboxylate bonding environments in Fh-OA. The predominant occurrence of Ni in the mineral component (Figure 4f, h) in combination with a lower abundance of Ni-FA complexes (FT-IR) is most likely the reason for the absence of intercalated Ni-FA complexes in the interlayer of Mt (Figure 3f).

Electron diffraction patterns of individual Cu-bearing Mt-OA indicate an increase in nano-crystallinity of Mt (from sharp diffraction spots to diffraction rings) during the treatment with Cu-bearing solutions (Figure S8). Similarly, bulk XRD patterns depict broadening of the (001) peak and a loss of intensity after treatment with Cu-bearing solutions (Figure S9). Previous SEM and XRD studies (Zeng et al., 2024) suggested that enhanced Mt dissolution by FA broadened the (001) diffraction peak. However, TEM images of the Cu Mt-OAs indicate the occurrence of smaller Mt NPs in the FA matrix (Figure S1), suggesting that defragmentation rather than dissolution increases the nano-crystallinity of Mt during exposure to Cu- and FA-bearing solutions.

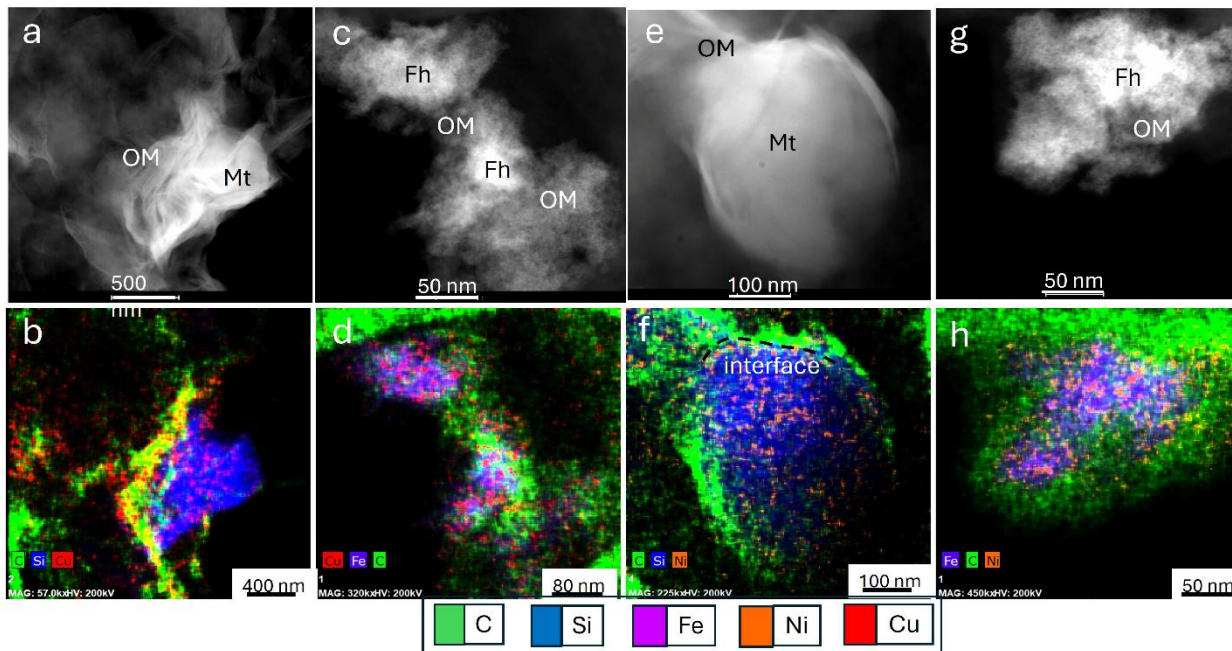


Figure 4. STEM images and corresponding STEM-EDS chemical distribution maps of (a)-(b) Cu-Mt-OA, (c)-(d) Cu-Fh-OA, (e)-(f) Ni-Mt-OA, (g)-(h) Ni-Fh-OA with C in green, Si in blue, Fe in purple, Cu in red, and Ni in orange.

2.3.7 Abundance of polar and non-polar carbon groups in Cu-bearing Mt-MOAs

Adsorption isotherms, FT-IR spectra, STEM chemical distribution maps, and XRD patterns indicate that exposure of Mt- and Fh-OAs to higher Cu-concentrations results in the enhanced repolymerization of FA, an increase in Cu-carboxylate bonding environments (Fh-OAs), the intercalation of bilayers of modified Cu-FA complexes (Mt-OAs), and a higher abundance of Cu in the OM fraction of Mt-OA than in Fh-OA. These observations suggest that higher concentrations of Cu cause structural changes to FA. These changes may be explored by examining the difference in the C 1s envelopes of EELS spectra before and after treatments of the MOAs with Cu and Ni.

The EELS spectra of the untreated Mt-OA and Fh-OA indicate a higher abundance of polar groups along the interfaces between the mineral and the OM matrix (Figure 5a,b), suggesting that FA

molecules depolymerize and orient themselves in such a fashion that carboxylic or carbonyl groups predominantly bond to polar groups along the Mt edges (note that this is not the case for the Fh-OA interface). These observations are in accord with EELS data obtained from natural-occurring organic–mineral interfaces (Possinger et al., 2020), which provided direct evidence for the involvement of polar carbon compounds in interactions with mineral surfaces. This can be explained by preferential polar-polar interactions between hydrophilic organic functional groups and the mineral hydroxyls mediated by mechanisms such as strong ligand exchange (Kleber et al., 2007).

The change in the abundance of polar functional groups may be expressed with the term *polarity*, which we define here as the ratio of the polar C to non-polar C components in the spectra. (Figure 5):

$$Polarity = \frac{(Area\ of\ C(1s \rightarrow \pi^*)C=O\ Carboxyl, Carbonyl + C(1s \rightarrow \sigma^*)C-O)}{(C(1s \rightarrow \pi^*)aromatic\ C=C + C(1s \rightarrow \sigma^*)\ aliphatic\ C-H)}$$

In the presence of Cu (150 mgL⁻¹), the magnitude and range of polarity increase in the Cu-bearing OM matrices and along the interfaces Cu (Figure 5c, d). This increase in polarity suggests Cu-mediated oxidation, also known as oxidative degradation (Allara & White, 1978; Li et al., 2024). and may be attributed to the ability of Cu to catalyze (Kim et al., 2020), the breaking of aliphatic C-C bonds (Agterberg, 1994; Wang et al., 2024). In comparison to Cu, the polarity in the Ni-bearing OM matrices and along the Fh-OA and Mt-OA interfaces (treated with a 150 mgL⁻¹ Ni-solution) does not show any increase in the polarity, in accordance with the predominant association of Ni with Fh and Mt (Fig. 5e and f and 4e and h).

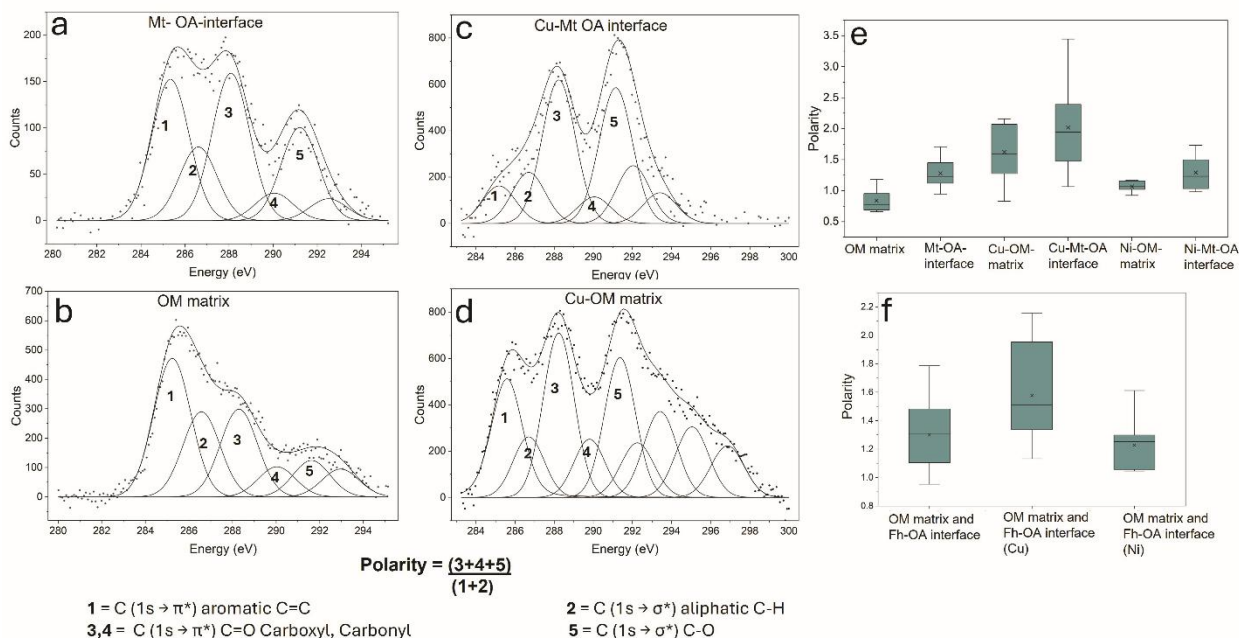


Figure 5. (a) The fitted EELS spectra of the Mt-OA interface and (b) adjacent FA region before treatment with Cu, (c) The fitted EELS spectra of the Mt-OA interface and (d) adjacent FA region after treatment with Cu; The corresponding polar (3,4,5) and non-polar bands (1,2) are labeled accordingly; note that the bands 3 and 4 are polar functional groups corresponding to carboxyl/carbonyl functional groups, which can be either part of aromatic rings or not; (e) Box plot indicating polarity differences between the OM matrix and Mt-OA interfaces in the presence (and absence of adsorbed Cu- and Ni-species. (f) Box plot indicating polarity differences between untreated Fh-OA and those treated with Cu- and Ni-species (OM matrix and interfaces combined).

2.4. Conclusion

This study showed that increasing concentrations of Cu and Ni during the recording of adsorption isotherms for MOAs (with M = ferrihydrite or montmorillonite and O = fulvic acid) led to the desorption of FA and the repolymerization of Cu-FA and Ni-FA complexes. Furthermore, it showed that Cu, with a higher affinity towards polar organic functional groups than Ni, altered the surface area, carbon chain structures, porosity, and specific surface binding sites of MOAs. These results suggest that (1) the interaction of MOAs with metal ions in contaminated environments can be highly complex and varies with the concentration and affinity of metal ions towards organic matter; (2) conventional approaches to recording adsorption isotherms may be inadequate when characterizing the interaction of MOAs with metal ions exhibiting a strong affinity for organic matter. We recommend that future experimental adsorption studies of metal ions on MOAs account for substantial structural changes in MOAs as metal-ion concentration increases.

2.5 References

- Abollino, O., Giacomino, A., Malandrino, M., & Mentasti, E. (2008). Interaction of metal ions with montmorillonite and vermiculite. *Applied Clay Science*, 38(3–4), 227–236. <https://doi.org/10.1016/j.clay.2007.04.002>
- Ali, S. Y., Reddy, K. D., & Manna, A. K. (2019). Structural, Electronic, and Spectral Properties of Metal Dimethylglyoximate $[M(DMG)_2; M = Ni^{2+}, Cu^{2+}]$ Complexes: A Comparative Theoretical Study. *The Journal of Physical Chemistry A*, 123(42), 9166–9174. <https://doi.org/10.1021/acs.jpca.9b06762>
- Allard, S., Gutierrez, L., Fontaine, C., Croué, J.-P., & Gallard, H. (2017). Organic matter interactions with natural manganese oxide and synthetic birnessite. *Science of The Total Environment*, 583, 487–495. <https://doi.org/10.1016/j.scitotenv.2017.01.120>
- Bölscher, T., Cardon, Z. G., Garcia Arredondo, M., Grand, S., Griffen, G., Hestrin, R., Imboden, J., Jamoteau, F., Lacroix, E. M., Pérez Castro, S., Persson, P., Riley, W. J., & Keiluweit, M. (2025). Vulnerability of mineral-organic associations in the rhizosphere. *Nature Communications*, 16(1), 5527. <https://doi.org/10.1038/s41467-025-61273-4>
- Bonczek, J. L., Harris, W. G., & Nkedi-Kizza, P. (2002). Monolayer to Bilayer Transitional Arrangements of Hexadecyltrimethylammonium Cations on Na-Montmorillonite. *Clays and Clay Minerals*, 50(1), 11–17. <https://doi.org/10.1346/000986002761002612>
- Byler, D. M., Gerasimowicz, W. V., Susi, H., & Schnitzer, M. (1987). FT-IR Spectra of Soil Constituents: Fulvic Acid and Fulvic Acid Complex with Ferric Ions. *Applied Spectroscopy*, 41(8), 1428–1430. <https://doi.org/10.1366/0003702874447185>
- Chia, C. H., Munroe, P., Joseph, S. D., Lin, Y., Lehmann, J., Muller, D. A., Xin, H. L., & NEVES, E. (2012). Analytical electron microscopy of black carbon and microaggregated mineral matter in Amazonian dark Earth. *Journal of Microscopy*, 245(2), 129–139. <https://doi.org/10.1111/j.1365-2818.2011.03553.x>
- Christl, I., & Kretzschmar, R. (2007). C-1s NEXAFS Spectroscopy Reveals Chemical Fractionation of Humic Acid by Cation-Induced Coagulation. *Environmental Science & Technology*, 41(6), 1915–1920. <https://doi.org/10.1021/es062141s>
- Deng, Y., & Dixon, J. B. (2002). *Soil Organic Matter and Organic-Mineral Interactions* (pp. 69–107). <https://doi.org/10.2136/sssabookser7.c3>
- Di Iorio, E., Circelli, L., Angelico, R., Torrent, J., Tan, W., & Colombo, C. (2022). Environmental implications of interaction between humic substances and iron oxide nanoparticles: A review. *Chemosphere*, 303, 135172. <https://doi.org/10.1016/j.chemosphere.2022.135172>

- Dorfman, A., Wanhala, A., Eng, P., Stubbs, J., Colon, O., Donetian, M., & Bracco, J. N. (2023). Inhibition of Strontium Adsorption and Desorption by Ethylenediaminetetraacetic Acid at the Barite (001)–Water Interface. *The Journal of Physical Chemistry C*, 127(19), 9049–9058. <https://doi.org/10.1021/acs.jpcc.3c01092>
- Du, Q., Sun, Z., Forsling, W., & Tang, H. (1999). Complexations in illite–fulvic acid–Cu²⁺ systems. *Water Research*, 33(3), 693–706. [https://doi.org/10.1016/S0043-1354\(98\)00263-2](https://doi.org/10.1016/S0043-1354(98)00263-2)
- Dubbin, W. E., Vetterlein, J. P., & Jonsson, J. L. (2014). Fatty acids promote fulvic acid intercalation by montmorillonite. *Applied Clay Science*, 97–98, 53–61. <https://doi.org/10.1016/j.clay.2014.05.022>
- Esfandiar, N., Suri, R., & McKenzie, E. R. (2022). Competitive sorption of Cd, Cr, Cu, Ni, Pb and Zn from stormwater runoff by five low-cost sorbents; Effects of co-contaminants, humic acid, salinity and pH. *Journal of Hazardous Materials*, 423, 126938. <https://doi.org/10.1016/j.jhazmat.2021.126938>
- Eshwar, M. (2017). Complexation Behavior of Humic and Fulvic Acids with Metal Ions and their Assessment by Stability Constants. *International Journal of Pure & Applied Bioscience*, 5(6), 899–907. <https://doi.org/10.18782/2320-7051.5461>
- Fariña, A. O., Peacock, C. L., Fiol, S., Antelo, J., & Carvin, B. (2018). A universal adsorption behaviour for Cu uptake by iron (hydr)oxide organo-mineral composites. *Chemical Geology*, 479, 22–35. <https://doi.org/10.1016/j.chemgeo.2017.12.022>
- Fu, H., & Quan, X. (2006). Complexes of fulvic acid on the surface of hematite, goethite, and akaganeite: FTIR observation. *Chemosphere*, 63(3), 403–410. <https://doi.org/10.1016/j.chemosphere.2005.08.054>
- Gu, Baohua., Schmitt, Juergen., Chen, Zhihong., Liang, Liyuan., & McCarthy, J. F. (1994). Adsorption and desorption of natural organic matter on iron oxide: mechanisms and models. *Environmental Science & Technology*, 28(1), 38–46. <https://doi.org/10.1021/es00050a007>
- Guan, J., Wang, J., Wang, Z., Zhuang, J., Dong, D., Luo, M., Lu, N., & Yuan, X. (2019). Comparison of Pb(II), Cu(II), Cd(II), and Ni(II) adsorption onto surficial sediment components from aquatic environments in the Phaeozem zone of Northeast China. *Journal of Geochemical Exploration*, 197, 220–227. <https://doi.org/10.1016/j.gexplo.2018.12.005>
- Gupta, S. Sen, & Bhattacharyya, K. G. (2006). Adsorption of Ni(II) on clays. *Journal of Colloid and Interface Science*, 295(1), 21–32. <https://doi.org/10.1016/j.jcis.2005.07.073>
- Halmos, L., Bozsó, G., & Pál-Molnár, E. (2015). Adsorption properties of Ni, Cu, and Zn in young alkaline lake sediments in south Hungary (Lake Fehér, Szeged). *Soil and Water Research*, 10(4), 244–251. <https://doi.org/10.17221/165/2014-SWR>

- Han, Y., & Gu, X. (2023). Enrichment, contamination, ecological and health risks of toxic metals in agricultural soils of an industrial city, northwestern China. *Journal of Trace Elements and Minerals*, 3, 100043. <https://doi.org/10.1016/j.jtemin.2022.100043>
- Heckman, K., Vazquez-Ortega, A., Gao, X., Chorover, J., & Rasmussen, C. (2011). Changes in water extractable organic matter during incubation of forest floor material in the presence of quartz, goethite and gibbsite surfaces. *Geochimica et Cosmochimica Acta*, 75(15), 4295–4309. <https://doi.org/10.1016/j.gca.2011.05.009>
- Ivanova, A., Mitiurev, N., Cheremisin, A., Orekhov, A., Kamyshinsky, R., & Vasiliev, A. (2019). Characterization of Organic Layer in Oil Carbonate Reservoir Rocks and its Effect on Microscale Wetting Properties. *Scientific Reports*, 9(1), 10667. <https://doi.org/10.1038/s41598-019-47139-y>
- Jadoon, S., & Schindler, M. (2022). The role of organic colloids in the sequestration and mobilization of copper in smelter-impacted soils. *Environmental Science: Processes & Impacts*, 24(6), 945–959. <https://doi.org/10.1039/D1EM00539A>
- Kaiser, K., & Guggenberger, G. (2007). Sorptive stabilization of organic matter by microporous goethite: sorption into small pores vs. surface complexation. *European Journal of Soil Science*, 58(1), 45–59. <https://doi.org/10.1111/j.1365-2389.2006.00799.x>
- Karmous, M. S., Rhaiem, H. Ben, Naamen, S., Oueslati, W., & Amara, A. B. H. (2006). The interlayer structure and thermal behavior of Cu and Ni montmorillonites. *Zeitschrift Für Kristallographie Supplements*, 2006(suppl_23_2006), 431–436. https://doi.org/10.1524/zksu.2006.suppl_23.431
- 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*, 2(6), 402–421. <https://doi.org/10.1038/s43017-021-00162-y>
- Kleber, M., Eusterhues, K., Keiluweit, M., Mikutta, C., Mikutta, R., & Nico, P. S. (2015). *Mineral–Organic Associations: Formation, Properties, and Relevance in Soil Environments* (pp. 1–140). <https://doi.org/10.1016/bs.agron.2014.10.005>
- Kleber, M., Sollins, P., & Sutton, R. (2007). A conceptual model of organo-mineral interactions in soils: self-assembly of organic molecular fragments into zonal structures on mineral surfaces. *Biogeochemistry*, 85(1), 9–24. <https://doi.org/10.1007/s10533-007-9103-5>
- Komy, Z. R., Shaker, A. M., Heggy, S. E. M., & El-Sayed, M. E. A. (2014). Kinetic study for copper adsorption onto soil minerals in the absence and presence of humic acid. *Chemosphere*, 99, 117–124. <https://doi.org/10.1016/j.chemosphere.2013.10.048>
- Kramer, M. G., Sanderman, J., Chadwick, O. A., Chorover, J., & Vitousek, P. M. (2012). Long-term carbon storage through retention of dissolved aromatic acids by reactive particles in

- soil. *Global Change Biology*, 18(8), 2594–2605. <https://doi.org/10.1111/j.1365-2486.2012.02681.x>
- Lazar, S., Tiemeijer, P., Schnohr, C. S., Meledina, M., Patzig, C., Höche, T., Longo, P., & Freitag, B. (2025). Enabling electron-energy-loss spectroscopy at very high energy losses: An opportunity to obtain x-ray absorption spectroscopy–like information using an electron microscope. *Physical Review Applied*, 23(5), 054095. <https://doi.org/10.1103/PhysRevApplied.23.054095>
- Lee, J., & Jonasson, I. R. (1983). Contribution of organic complexation to Ni, Co and Cu speciation in surface waters: Implications for hydrogeochemical surveys. *Journal of Geochemical Exploration*, 18(1), 25–48. [https://doi.org/10.1016/0375-6742\(83\)90079-1](https://doi.org/10.1016/0375-6742(83)90079-1)
- Li, X., Schindler, M., Zhou, J., Samaradiwakara, S., & Wu, L. (2025). Interaction between metal(loid)s and soil mineral-organic matter associations. *Critical Reviews in Environmental Science and Technology*, 55(9), 624–647. <https://doi.org/10.1080/10643389.2024.2434328>
- Malamis, S., & Katsou, E. (2013). A review on zinc and nickel adsorption on natural and modified zeolite, bentonite and vermiculite: Examination of process parameters, kinetics and isotherms. *Journal of Hazardous Materials*, 252–253, 428–461. <https://doi.org/10.1016/j.jhazmat.2013.03.024>
- Manceau, A., & Matynia, A. (2010). The nature of Cu bonding to natural organic matter. *Geochimica et Cosmochimica Acta*, 74(9), 2556–2580. <https://doi.org/10.1016/j.gca.2010.01.027>
- Mandal, R., L.R. Sekaly, A., Murimboh, J., Hassan, N. M., Chakrabarti, C. L., Back, M. H., Grégoire, D. C., & Schroeder, W. H. (1999). Effect of the competition of copper and cobalt on the lability of Ni(II)–organic ligand complexes, Part II: in freshwaters (Rideau River surface waters). *Analytica Chimica Acta*, 395(3), 323–334. [https://doi.org/10.1016/S0003-2670\(99\)00351-7](https://doi.org/10.1016/S0003-2670(99)00351-7)
- Mantha, H., Schindler, M., & Hochella, M. F. (2019). Occurrence and formation of incidental metallic Cu and CuS nanoparticles in organic-rich contaminated surface soils in Timmins, Ontario. *Environmental Science: Nano*, 6(1), 163–179. <https://doi.org/10.1039/C8EN00994E>
- Mikutta, R., Mikutta, C., Kalbitz, K., Scheel, T., Kaiser, K., & Jahn, R. (2007). Biodegradation of forest floor organic matter bound to minerals via different binding mechanisms. *Geochimica et Cosmochimica Acta*, 71(10), 2569–2590. <https://doi.org/10.1016/j.gca.2007.03.002>

- Mizuguchi, M., Nara, M., Kawano, K., & Nitta, K. (1997). FT-IR study of the Ca^{2+} -binding to bovine α -lactalbumin. *FEBS Letters*, 417(1), 153–156. [https://doi.org/10.1016/S0014-5793\(97\)01274-X](https://doi.org/10.1016/S0014-5793(97)01274-X)
- Ndzana, G. M., Zhang, Y., Yao, S., Hamer, U., & Zhang, B. (2022). The adsorption capacity of root exudate organic carbon onto clay mineral surface changes depending on clay mineral types and organic carbon composition. *Rhizosphere*, 23, 100545. <https://doi.org/10.1016/j.rhisph.2022.100545>
- Nikishina, M., Perelomov, L., Atroshchenko, Y., Ivanova, E., Mukhtorov, L., & Tolstoy, P. (2022). Sorption of Fulvic Acids and Their Compounds with Heavy Metal Ions on Clay Minerals. *Soil Systems*, 6(1), 2. <https://doi.org/10.3390/soilsystems6010002>
- Nishiyama, N., & Yokoyama, T. (2021). Water Film Thickness in Unsaturated Porous Media: Effect of Pore Size, Pore Solution Chemistry, and Mineral Type. *Water Resources Research*, 57(6). <https://doi.org/10.1029/2020WR029257>
- Oueslati, W., Benrhaïem, H., Lanson, B., & Benhajamara, A. (2009). Selectivity of Na–montmorillonite in relation with the concentration of bivalent cation (Cu^{2+} , Ca^{2+} , Ni^{2+}) by quantitative analysis of XRD patterns. *Applied Clay Science*, 43(2), 224–227. <https://doi.org/10.1016/j.clay.2008.09.010>
- Öztürk Er, E., Gürsoy, S., & Bakırdere, S. (2026). Equilibrium modelling and kinetic studies on adsorption of cadmium from lake water by a magnetic covalent organic framework. *Scientific Reports*, 16(1), 4838. <https://doi.org/10.1038/s41598-025-34851-1>
- Pal, R., Bourgeois, L., Weyland, M., Sikder, A. K., Saito, K., Funston, A. M., & Bellare, J. R. (2020). Chemical fingerprinting of polyvinyl acetate and polycarbonate using electron energy-loss spectroscopy. *Polymer Chemistry*, 11(34), 5484–5492. <https://doi.org/10.1039/D0PY00771D>
- Pal, R., Bourgeois, L., Weyland, M., Sikder, A. K., Saito, K., Funston, A. M., & Bellare, J. R. (2021). Chemical Fingerprinting of Polymers Using Electron Energy-Loss Spectroscopy. *ACS Omega*, 6(37), 23934–23942. <https://doi.org/10.1021/acsomega.1c02939>
- Pelaez-Fernandez, M., Bermejo, A., Benito, A. M., Maser, W. K., & Arenal, R. (2021). Detailed thermal reduction analyses of graphene oxide via in-situ TEM/EELS studies. *Carbon*, 178, 477–487. <https://doi.org/10.1016/j.carbon.2021.03.018>
- Possinger, A. R., Zachman, M. J., Enders, A., Levin, B. D. A., Muller, D. A., Kourkoutis, L. F., & Lehmann, J. (2020). Organo–organic and organo–mineral interfaces in soil at the nanometer scale. *Nature Communications*, 11(1), 6103. <https://doi.org/10.1038/s41467-020-19792-9>
- Pullin, M. J., & Cabaniss, S. E. (2003). The effects of pH, ionic strength, and iron–fulvic acid interactions on the kinetics of non-photochemical iron transformations. I. Iron(II) oxidation

- and iron(III) colloid formation. *Geochimica et Cosmochimica Acta*, 67(21), 4067–4077.
[https://doi.org/10.1016/S0016-7037\(03\)00366-1](https://doi.org/10.1016/S0016-7037(03)00366-1)
- Schnitzer, M., & Kodama, H. (1967). Reactions Between a Podzol Fulvic Acid and Na-montmorillonite. *Soil Science Society of America Journal*, 31(5), 632–636.
<https://doi.org/10.2136/sssaj1967.03615995003100050009x>
- Schwertmann, U., & Cornell, R. M. (Eds.). (2000). *Iron Oxides in the Laboratory*. Wiley-VCH Verlag GmbH. <https://doi.org/10.1002/9783527613229>
- Sekaly, A. L. R., Mandal, R., Hassan, N. M., Murimboh, J., Chakrabarti, C. L., Back, M. H., Grégoire, D. C., & Schroeder, W. H. (1999). Effect of metal/fulvic acid mole ratios on the binding of Ni(II), Pb(II), Cu(II), Cd(II), and Al(III) by two well-characterized fulvic acids in aqueous model solutions. *Analytica Chimica Acta*, 402(1–2), 211–221.
[https://doi.org/10.1016/S0003-2670\(99\)00534-6](https://doi.org/10.1016/S0003-2670(99)00534-6)
- Shirvani, M., Rafiei, H. R., Bakhtiary, S., Azimzadeh, B., & Amani, S. (2015). Equilibrium, kinetic, and thermodynamic studies on nickel removal from aqueous solutions using Ca-bentonite. *Desalination and Water Treatment*, 54(2), 464–472.
<https://doi.org/10.1080/19443994.2014.887037>
- Strathmann, T. J., & Myneni, S. C. B. (2004). Speciation of aqueous Ni(II)-carboxylate and Ni(II)-fulvic acid solutions: Combined ATR-FTIR and XAFS analysis. *Geochimica et Cosmochimica Acta*, 68(17), 3441–3458. <https://doi.org/10.1016/j.gca.2004.01.012>
- Strathmann, T. J., & Myneni, S. C. B. (2005a). Effect of Soil Fulvic Acid on Nickel(II) Sorption and Bonding at the Aqueous-Boehmite (γ -AlOOH) Interface. *Environmental Science & Technology*, 39(11), 4027–4034. <https://doi.org/10.1021/es0481629>
- Strathmann, T. J., & Myneni, S. C. B. (2005b). Effect of Soil Fulvic Acid on Nickel(II) Sorption and Bonding at the Aqueous-Boehmite (γ -AlOOH) Interface. *Environmental Science & Technology*, 39(11), 4027–4034. <https://doi.org/10.1021/es0481629>
- Sutherland, R. A. (2000). Bed sediment-associated trace metals in an urban stream, Oahu, Hawaii. *Environmental Geology*, 39(6), 611–627. <https://doi.org/10.1007/s002540050473>
- Sutton, R., & Sposito, G. (2006). Molecular simulation of humic substance–Ca-montmorillonite complexes. *Geochimica et Cosmochimica Acta*, 70(14), 3566–3581.
<https://doi.org/10.1016/j.gca.2006.04.032>
- Taioli, S., Simonucci, S., Calliari, L., & Dapor, M. (2010). Electron spectroscopies and inelastic processes in nanoclusters and solids: Theory and experiment. *Physics Reports*, 493(5), 237–319. <https://doi.org/10.1016/j.physrep.2010.04.003>

- Tenailleau, H., & Martin, J. M. (1992). A new background subtraction for low-energy EELS core edges. *Journal of Microscopy*, 166(3), 297–306. <https://doi.org/10.1111/j.1365-2818.1992.tb01529.x>
- Terkhi, M. C., Taleb, F., Gossart, P., Semmoud, A., & Addou, A. (2008). Fourier transform infrared study of mercury interaction with carboxyl groups in humic acids. *Journal of Photochemistry and Photobiology A: Chemistry*, 198(2–3), 205–214. <https://doi.org/10.1016/j.jphotochem.2008.03.018>
- Theng, B. K. G. (1976). Interactions between montmorillonite and fulvic acid. *Geoderma*, 15(3), 243–251. [https://doi.org/10.1016/0016-7061\(76\)90078-1](https://doi.org/10.1016/0016-7061(76)90078-1)
- Tokunaga, T. K. (2011). Physicochemical controls on adsorbed water film thickness in unsaturated geological media. *Water Resources Research*, 47(8). <https://doi.org/10.1029/2011WR010676>
- Tong, Y., Xiang, H., Jiang, J., & Chen, W. (2024). Interfacial interactions between minerals and organic matter: Mechanisms and characterizations. *Chemosphere*, 359, 142383. <https://doi.org/10.1016/j.chemosphere.2024.142383>
- van Schaik, J. W. J., Persson, I., Kleja, D. B., & Gustafsson, J. P. (2008). EXAFS Study on the Reactions between Iron and Fulvic Acid in Acid Aqueous Solutions. *Environmental Science & Technology*, 42(7), 2367–2373. <https://doi.org/10.1021/es072092z>
- Wang, J., Kaiyum, Y. A., Wang, S., Li, X., Lei, H., Johnson, P. E., & Liu, J. (2025). A general transition metal binding aptamer following the Irving–Williams series. *Chemical Science*, 16(31), 14286–14294. <https://doi.org/10.1039/D5SC02436F>
- Wei, S., & Xiang, W. (2013). Adsorption removal of Pb(II) from aqueous solution by fulvic acid-coated ferrihydrite. *Journal of Food, Agriculture and Environment*, 11, 1376–1380.
- Wild, A., & Keay, J. (1964). Cation-Exchange Equilibria With Vermiculite. *Journal of Soil Science*, 15(2), 135–144. <https://doi.org/10.1111/j.1365-2389.1964.tb02214.x>
- Xia, K., Bleam, W., & Helmke, P. A. (1997). Studies of the nature of Cu²⁺ and Pb²⁺ binding sites in soil humic substances using X-ray absorption spectroscopy. *Geochimica et Cosmochimica Acta*, 61(11), 2211–2221. [https://doi.org/10.1016/S0016-7037\(97\)00079-3](https://doi.org/10.1016/S0016-7037(97)00079-3)
- Xiao, M., Guo, J., Zhao, S., & Li, S. (2023). Adsorption of As(V) at Humic Acid-Kaolinite-Bacteria Interfaces: Kinetics, Thermodynamics, and Mechanisms. *Agronomy*, 13(2), 611. <https://doi.org/10.3390/agronomy13020611>
- Xu, D., Zhou, X., & Wang, X. (2008). Adsorption and desorption of Ni²⁺ on Na-montmorillonite: Effect of pH, ionic strength, fulvic acid, humic acid and addition sequences. *Applied Clay Science*, 39(3–4), 133–141. <https://doi.org/10.1016/j.clay.2007.05.006>

- Xu, L., Xing, X., Peng, J., & Ji, M. (2022). Effects of In Situ Remediation on Copper Distribution and Soil Aggregate Adsorption–Desorption Characteristics in Smelter-Impacted Soil. *Frontiers in Environmental Science*, 10. <https://doi.org/10.3389/fenvs.2022.816361>
- Xu, Z., & Tsang, D. C. W. (2024). Mineral-mediated stability of organic carbon in soil and relevant interaction mechanisms. *Eco-Environment & Health*, 3(1), 59–76. <https://doi.org/10.1016/j.eehl.2023.12.003>
- Yan, Y., Wan, B., Mansor, M., Wang, X., Zhang, Q., Kappler, A., & Feng, X. (2022). Co-sorption of metal ions and inorganic anions/organic ligands on environmental minerals: A review. *Science of The Total Environment*, 803, 149918. <https://doi.org/10.1016/j.scitotenv.2021.149918>
- Yang, R., Li, Z., Huang, B., Luo, N., Huang, M., Wen, J., Zhang, Q., Zhai, X., & Zeng, G. (2018). Effects of Fe(III)-fulvic acid on Cu removal via adsorption versus coprecipitation. *Chemosphere*, 197, 291–298. <https://doi.org/10.1016/j.chemosphere.2018.01.042>
- Yang, R., Li, Z., Huang, M., Luo, N., Wen, J., & Zeng, G. (2019). Characteristics of fulvic acid during coprecipitation and adsorption to iron oxides-copper aqueous system. *Journal of Molecular Liquids*, 274, 664–672. <https://doi.org/10.1016/j.molliq.2018.11.030>
- Zeng, L., Peng, T., Sun, H., Zhang, X., & Zhao, D. (2024). Comparative study on ionic dissolution and structural changes of montmorillonite, kaolinite and muscovite during interfacial reactions with oxalic acid solution. *Mineralogical Magazine*, 88(5), 546–556. <https://doi.org/10.1180/mgm.2024.31>
- Zhang, Y., Chen, Y., An, J., Zhao, X., & Zu, B. (2023). Adsorption-Reduction Behavior of Cr(VI) by Ferrihydrite-Fulvic Acid Complexes with Different C/Fe Mole Ratios. *Adsorption Science & Technology*, 2023. <https://doi.org/10.1155/2023/5716199>
- Zhou, W., Wang, Z., Wu, Q., Nie, Q., & Wang, Y. (2024). The Effects of Montmorillonite–Humic Acid Composite Particles on the Photolysis of Tetracycline in Water. *Crystals*, 14(10), 896. <https://doi.org/10.3390/cryst14100896>

Chapter 3

The research questions raised in Chapter One can be answered one by one as follows.

1. How are the composition and structure of MOAs affected by the presence of different concentrations of Cu and Ni?

Fulvic acid bound to the Mt and Fh was observed to change with increasing metal ions in solution, as evidenced by the TOC analysis in supernatant solutions. At lower initial metal ion concentrations, FA desorption into solution was minimal, supporting the idea of enhanced adsorption strength due to the bridging effect of Cu and Ni ions. Further increasing the initial metal ion concentration led to competition among adsorbate species in solution, resulting in desorption of bound Fulvic acid from MOAs into solution, followed by complexation with Cu and Ni ions, as evidenced by the observed peak in DOC concentration. The observed decrease in DOC at very high initial Cu and Ni concentrations in solution was likely due to the repolymerization of metal ions with FA, thereby promoting the formation of surface metal-ion (M)-FA precipitates on mineral-FA surfaces.

With increasing Cu concentration, the Mt interlayer in the Mt-OA system showed an increase in spacing, leading to a two-step expansive pattern, whereas in Ni-bearing Mt-OA, the presence of FA did not increase d-spacings, ruling out intercalation of Ni-FA complexes.

2. How are Cu and Ni sequestered by synthesized MOAs with M being either montmorillonite (Mt) or ferrihydrite (Fh) and O being fulvic acid (FA)?

Adsorption isotherms for Cu and Ni on Fh-OA, Mt-OA, Fh, and Mt show higher adsorption capacities for MOAs than for the minerals (Fh and Mt). These complexes indicate higher R^2 values for the Freundlich model, suggesting heterogeneous multilayer adsorption and possible surface precipitation and repolymerization at higher metal ion concentrations. Here, MOAs depict a higher binding affinity towards Cu than Ni, suggesting formation of Cu and Ni MOA networks, thus increasing additional binding sites for metal intake.

Along with the above observations, the sequestration of Cu and Ni at the molecular scale and structural changes were evident in the FTIR and XRD results. On Fh-OA, a progressive increment of symmetric/asymmetric COO⁻ peaks with increasing Cu and Ni concentration indicated the formation of inner-sphere Cu-carboxylate complexes with ligand exchange. On Mt-OA, modified Cu-FA complexes intercalate via a two-step expansion, first forming mono- and then bilayer structures, thereby increasing the number of available binding sites.

Whereas Ni-carboxylate bonding environments were found to be less pronounced compared to the Cu system, suggesting less progressive carboxylate bond formation with increasing Ni concentration. At higher Ni loadings, STEM-EDS maps indicated that Ni predominantly associated with Mt or Fh or along their interfaces, which is in accordance with mineral surface complexation with Ni.

3. How do their distribution and speciation change with different concentrations of Ni and Cu?

Nanoscale distribution at higher metal loadings can be explained as follows. Cu bearing Mt-OA shows Cu concentrated in the OM matrix, indicating incorporation into organic domains and suggesting Cu-FA complexation, whereas Fh-OA showed more Cu localization along Fh-OM interfaces as well. Ni-bearing Fh-OA and Mt-OA show Ni predominantly associated with Mt and Fh, or at their interfaces, and less dispersed in the OM matrix, reflecting Ni affinity for minerals.

The abundance of Cu-Carboxylate complexes increases with increasing Cu concentration in Fh-OA, whereas those for Ni-carboxylate initially increase but then remain with increasing Ni loading.

In Mt-OA, two-step layer expansion results from intercalation of mono- and bilayers of Cu-FA complexes, with FA modified through dissociation into simpler molecular structures or by alteration of the fulvic acid polymer conformation, thereby favoring reactions between C=O groups and Cu and Ni ions.

4. What is the role of polar surfaces on the surfaces of montmorillonite and ferrihydrite, and what is the role of the polar organic functional groups along the mineral-OM interfaces in the sequestration of Cu and Ni by MOAs?

The EELS spectra of the untreated Mt-OA and Fh-OA indicate a higher abundance of polar groups along the interfaces between the mineral and the OM matrix, suggesting that FA molecules depolymerize and orient themselves in such a fashion that carboxylic or carbonyl groups predominantly bond to polar groups along the mineral.

In the presence of Cu, the magnitude and range of polarity increase in the Cu-bearing OM matrices and along the interfaces Cu. This increase in polarity suggests Cu-mediated oxidation and generation of additional polar groups, which in turn create more binding sites for further Cu complexation and polymerization.

The main hypotheses in this study, that Cu and Ni are more abundant at mineral-OM interfaces than in organic matter alone due to surface-induced polarization of the OM along the latter interfaces, is supported by higher polarity at Mt-OA and Fh-OA interfaces and the preferential localization of Ni at Mt-OA and Fh-OA interfaces rather than in the adjacent OM matrix. Polar-polar interactions, which are interactions between mineral hydroxyl terminations and hydrophilic groups in FA, lead to strong ligand exchange and inner-sphere complex formation with increasing metal sequestration relative to nonpolar regions.

3.1 Summary

This thesis emphasized the structural and compositional changes in MOAs during adsorption experiments with increasing concentrations of Cu and Ni metal ions, using a combination of bulk and nanoscale analytical techniques. Desorption of FA in MOAs was observed in both Cu and Ni systems at moderate initial metal-ion concentrations, with a delay in the maximum FA desorption in the Ni system relative to the Cu system, which can be explained by the higher affinity of Cu for OM, forming stronger Cu-FA complexes in solution. FTIR spectroscopy provided evidence for progressive coordination of Cu to carboxylates in Cu-Fh-OA, indicating an increase in the Cu-carboxylate bonding environments. In contrast, adsorbed Ni indicated a lower total number of Ni-carboxylate bonding environments in the Ni- than in the Cu-Fh-OA system. Cu Mt-OA showed a two-step interlayer expansion. In contrast, Ni Mt-OA did not indicate that the presence of FA

increased d-spacings, ruling out intercalation of Ni-FA complexes. STEM-EDS maps indicated that Cu occurs at a higher fraction in the OM matrix of Mt-OA than in that of Fh-OA. On the contrary, the distribution maps for Ni, Al, Si, Fe, and C in Ni-bearing Mt-OA and Fh-OA show that Ni is predominantly associated with Mt and Fh or with their interfaces towards OM. These distributions of Cu and Ni in the MOAs are consistent with the FT-IR spectra, which suggest higher numbers of Cu- than Ni-carboxylate bonding environments in Fh-OA. The predominant occurrence of Ni in the mineral component, in combination with a lower abundance of Ni-FA complexes (FT-IR) is most likely the reason for the absence of intercalated Ni-FA complexes in the interlayer of Mt. These observations suggest that higher concentrations of Cu cause structural changes to FA; in the presence of Cu, the magnitude and range of polarity increase in the Cu-bearing OM matrices and along the interfaces with Cu. Compared with Cu, the polarity in the Ni-bearing OM matrices and along the Fh-OA and Mt-OA interfaces does not show the same degree of increase. Yet, the polarity is slightly higher than in untreated MOAs, suggesting that Ni induces polarity, however, to a lesser extent than Cu. Hence, these results showed that Cu, with a higher affinity towards polar organic functional groups than Ni, altered the structure and composition of the OM in the MOAs. Hence, there are two main sub-conclusions based on this thesis,

- 1) The interaction of MOAs with metal ions in contaminated environments can be highly complex and varies with the concentration and affinity of metal ions towards organic matter;
- 2) Conventional approaches to recording adsorption isotherms may be inadequate when characterizing the interaction of MOAs with metal ions exhibiting a strong affinity for organic matter.

When comparing the results of this study with previous recordings of adsorption isotherms of metals on MOAs, it becomes clear that they treated the synthesized (or natural) MOAs as stable entities, as they did not monitor changes in compositional and structural changes of the organic matter components bound to MOAs throughout the experiment with changing parameters. Despite the instability of MOAs in certain soil environments and the complexity of their interactions with metal ions, previous adsorption studies involving MOAs and metal ions assumed that the MOA composition and structure remained unchanged throughout the experiments. Previous studies considered MOAs (natural or synthetic) stable macromolecules, where the amount and composition of organics bound to the surface of the mineral remain unchanged during the adsorption experiment or with the concentration of the cation in solution, and as they were final products rather than dynamic entities incapable of undergoing structural changes due to metal exposure.

3.2 Recommendations for future research

I recommend that future experimental adsorption studies of metal ions on MOAs account for substantial structural changes in MOAs as metal-ion concentration increases. Also, it is recommended to perform future experimental adsorption studies of other metal(loid)s on MOAs to examine changes in adsorption over time, pH, and temperature. Previous studies have examined the adsorption of metal ions onto mineral-organic matter associations, focusing on changes in adsorption over time and with pH. These studies, however, did not monitor any structural and compositional changes in MOAs. Hence, it is important to address these changes in MOAs with different metal ions, with or without higher-affinity metal ions towards OM, with a focus on adsorption kinetics, adsorption capacities, adsorption edge studies, and adsorption

thermodynamics. Future studies may include other metals of high and low affinity towards such as Pb^{2+} and Zn^{2+} or oxy-anion species such as $(\text{AsO}_4)^{3-}$ and $(\text{PO}_4)^{3-}$. While similar results are expected for the former cations, adsorption and spectroscopic studies of the latter anions should yield different outcomes. Here, adsorption should follow an anion-specific mechanism, in which ligand-exchange interactions with mineral surfaces dominate. The anion species could act as a competitive agent for organic matter (OM) adsorption on minerals, thereby enhancing the desorption of OM components from minerals and directly binding to the mineral surface rather than to OM, since it creates strong repulsive forces due to negative charges arising from both OM and the anion species.

Future studies of MOAs in the environment should also consider the results of this study. For example, studies of MOAs in soils should couple adsorption measurements with other characterization techniques, such as a TOC analyzer (to monitor changes in OM composition) and a BET analyzer (to monitor changes in surface area), at each concentration. Also, future studies should consider analyzing the data using more complex adsorption models, rather than the Langmuir and Freundlich models, which may not capture multi-site adsorption given the changing nature of the adsorbent.

For example, the results of this study could be used to characterize the MOA colloids collected from surficial soils in the Sudbury area, highly impacted by Cu- and Ni-bearing smelter emissions. Leaching experiments to extract the colloids could be conducted on acidic and limed surficial soils. The solid (MOA fraction) and liquid phases (desorbed OM component) of the leachates could then be characterized using various techniques to understand any structural or compositional changes induced by varying levels of contamination. Also, the results of this study could be used to characterize surficial, non-contaminated soil samples collected in the Sudbury area by exposing

them to varying Cu and Ni concentrations and conducting adsorption experiments. Characterizing these treated soils using a range of analytical techniques would provide insights into how natural mineral-OM soil aggregates control the adsorption of Cu and Ni.

Appendices

Appendix : Chapter 2

Supplementary Information

Figure S1. More details on methods and methodology

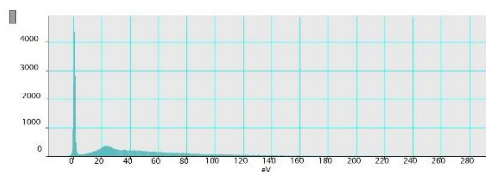
a) Materials

The montmorillonite Nps $((\text{Na}, \text{Ca})_{0.33} (\text{Al}, \text{Mg})_2 [\text{Si}_4\text{O}_{10}] (\text{OH})_2 \cdot n\text{H}_2\text{O})$ (Purity: 99%) employed in this study were purchased from Nanochemazone (Alberta, Canada). All the chemical reagents used to synthesize ferrihydrite and MOAs, and for the batch adsorption experiments, Iron (III) chloride hexahydrate, Sodium hydroxide, Nitric acid concentrate, calcium chloride dihydrate, Copper (II) nitrate trihydrate, Nickel (II) nitrate hexahydrate were 99+% pure, for analysis, and purchased from Thermo Fisher Scientific Chemicals, Canada. Fulvic acid powder (99%) was supplied by Mark Nature, CA, USA. All aqueous solutions were prepared with Milli-Q water.

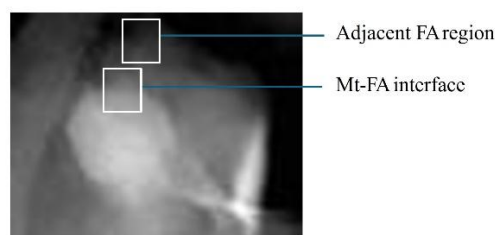
b) Details on EELS analysis

The measured energy resolution was 1 eV, and a 0.09 eV/channel dispersion was used for the core-loss EELS acquisition of the C-K edge at 284 eV. EELS spectra were collected with the Gatan GIF Continuum spectrometer and the K3 direct-detection camera in Dual EELS counting mode. The dwell time was set to 50 ms, with 5 ms for the low-loss region and 45 ms for the core-loss region.

a) The energy alignment

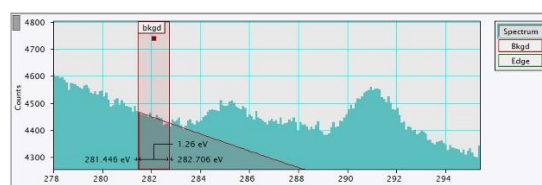
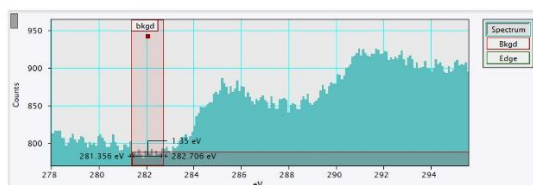


b) Selecting the analysis region



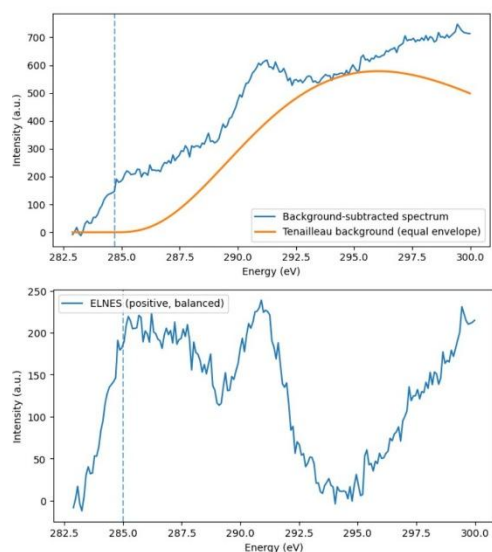
c) The background in the EELS spectrum was removed in 2 steps:

1st step: an inverse-power-law fit was performed in the Gatan Digital Micrograph software on extracted EELS spectra.

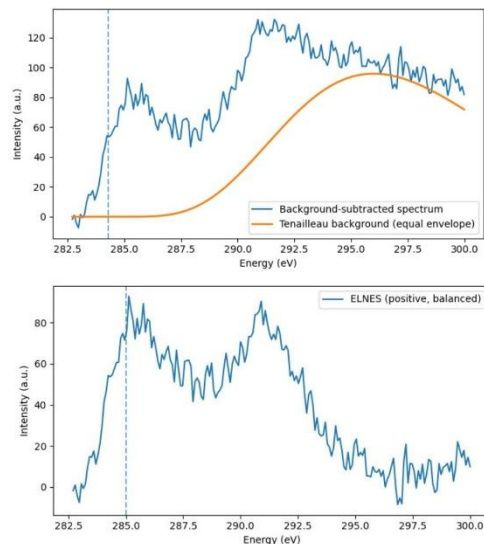


2nd step: the fine structure of the C 1s spectra was extracted using the empirical model proposed by Tenailleau. The resulting spectra after the background subtraction using the Python script are provided below for one example ROI.

Interface



Adjacent FA region



d) Then, all the spectra were fitted using the Fityk software, keeping the FWHM the same. Peak parameters were then extracted and plotted in Origin Pro 2026 for comparison.

Figure S2. a) Langmuir and the b) the Freundlich equations, used to characterize the adsorption of Cu^{2+} and Ni^{2+} on the MOAs

$$\text{a) } \frac{1}{y} = \left(\frac{1}{y_m \cdot K} \right) \cdot \frac{1}{x} + \frac{1}{y_m} \quad \text{b) } \log q_e = \log Kf + \log C_e/n$$

Figure S3. TOC analyzer procedure

Supernatant solutions were analyzed for DOC measurements by Shimadzu TOC-L analyzer in non-purgeable organic carbon (NPOC) mode.

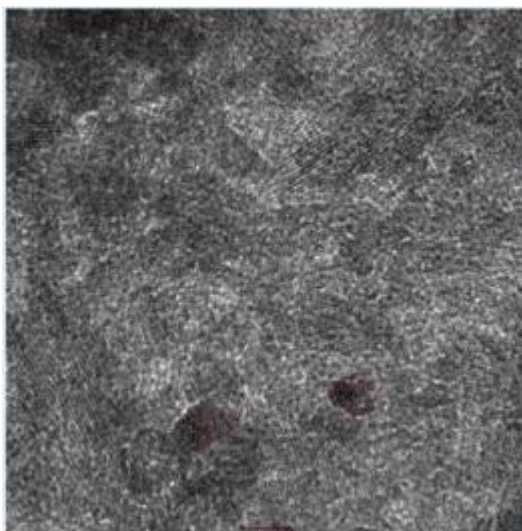


Figure S4. The synthesized ferrihydrite (Fh) NPs

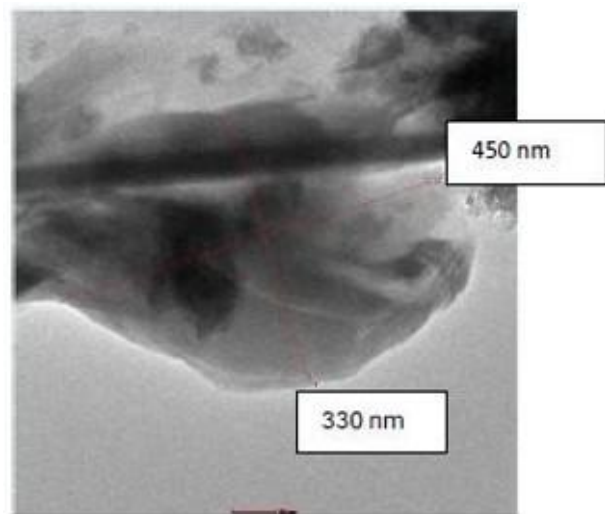


Figure S5. The purchased montmorillonite (Mt)

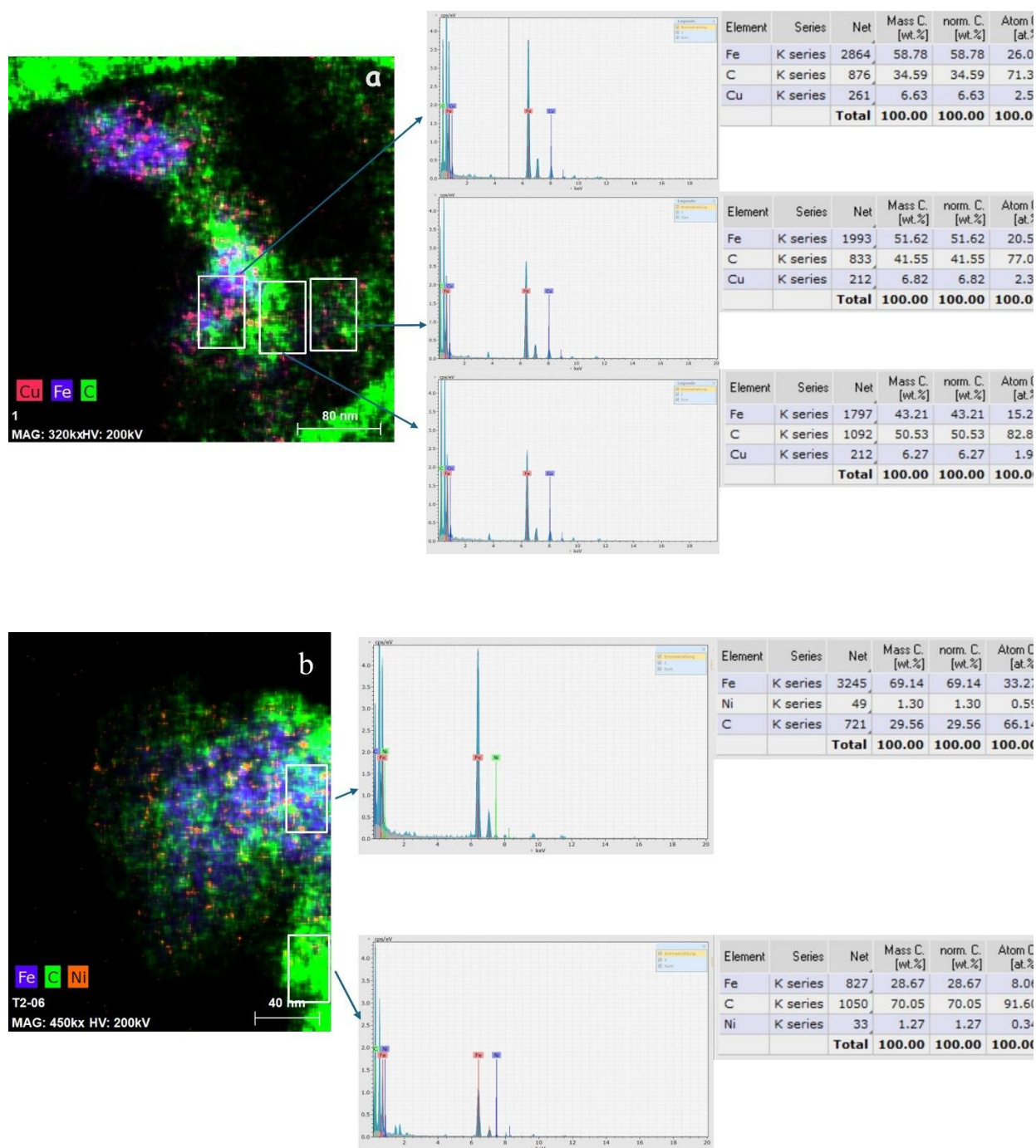


Figure S6. EDS spectra for the organic matrix for a) Cu-Fh-OA and b) Ni-Fh-OA

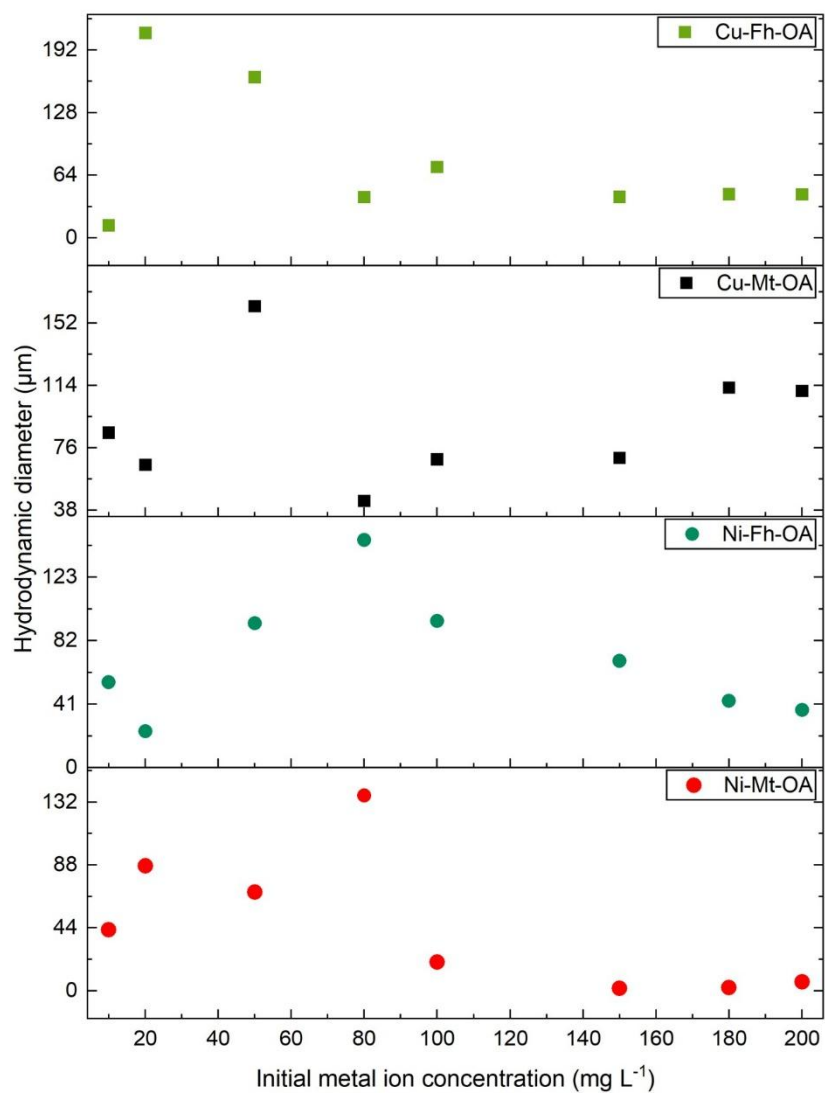


Figure S7. Particle size (hydrodynamic diameter) vs initial metal ion concentration in supernatant solutions

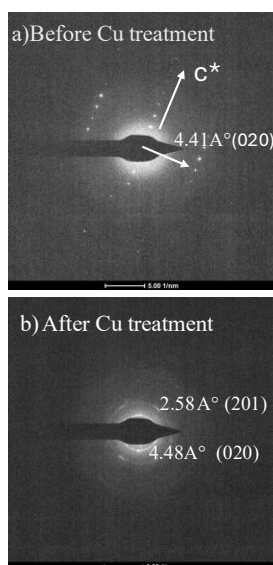


Figure S8. Selected area electron diffraction patterns of individual Mt-OA (a) before and (b) after the Cu treatment.

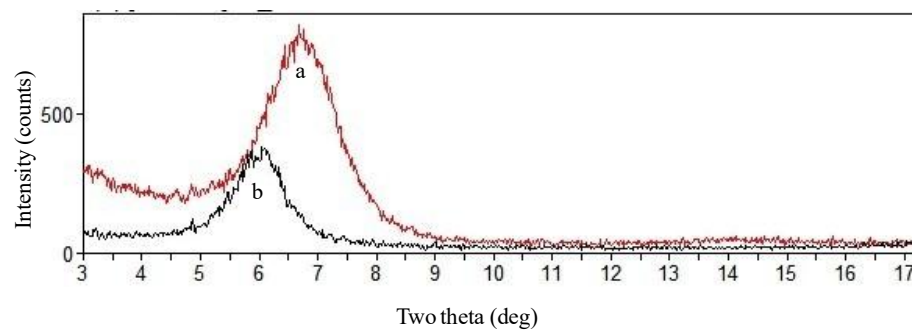


Figure S9. Bulk XRD patterns (001) peak (a) before and (b) after treatment with a solution containing $150 \text{ mg L}^{-1} \text{ Cu}$

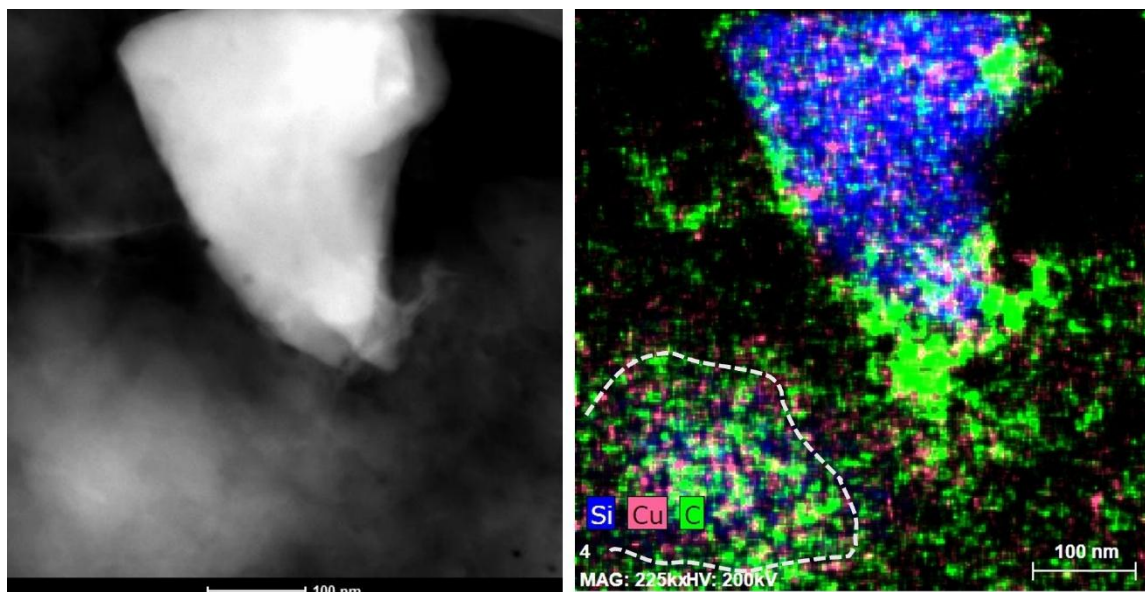


Figure S10. STEM images and corresponding EDS maps that indicate the occurrence of smaller Mt NPs in the FA matrix

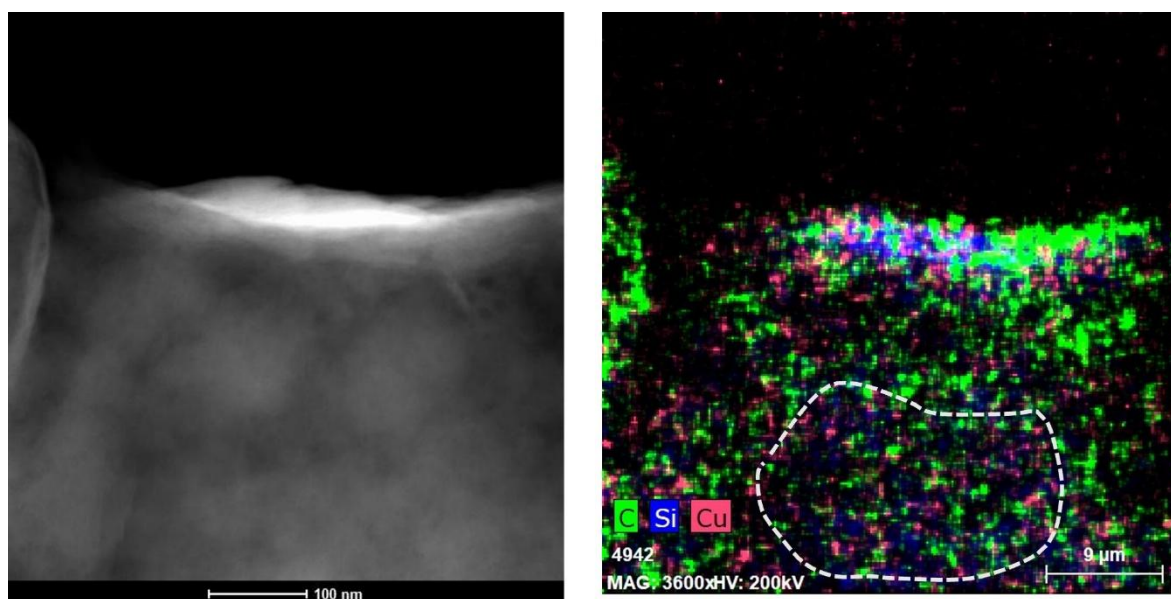


Figure S10. STEM images and corresponding EDS maps that indicate the occurrence of smaller Mt NPs in the FA matrix

Table S1. Major bands used in EELS peak ratio calculations and peak parameters of figure 5a,b,c,d

Center (eV)	Bands
285±0.4	C (1s → π^*) aromatic C=C
286.8±0.4	C (1s → σ^*) aliphatic C-H
288.1±0.4	C (1s → π^*) C=O Carboxyl, Carbonyl
290±0.4	
291±0.4	C (1s → σ^*) C-O

Table S1a. Peak parameters of Mt-OA interface (figure 5a)

Center	Height	Area	FWHM		Polarity
285.34	152.6	324.875	2	C (1s → π^*) aromatic C=C	1.2464465
286.605	79.5	169.25	2	C (1s → σ^*) aliphatic C-H)	
288.085	159.1	338.713	2	C (1s → π^*) C=O	
290.05	29.7	63.2293	2	Carboxyl, Carbonyl	
291.209	100.5	213.958	2	C (1s → σ^*) C-O	
292.514	23.6	50.2428	2		

Table S1b. Peak parameters of OM matrix (figure 5b)

Center	Height	Area	FWHM		Polarity
285.233	472.3	1005.5	2	C (1s $\rightarrow$ π^*) aromatic C=C	0.689743
286.574	290.3	618.03	2	C (1s $\rightarrow$ σ^*) aliphatic C-H)	
288.294	299.1	636.764	2	C (1s $\rightarrow$ π^*) C=O Carboxyl,	
290.036	102.8	218.854	2	Carbonyl	
291.321	124.1	264.201	2	C (1s $\rightarrow$ σ^*) C-O	
292.955	95	202.249	2		

Table S1c. Peak parameters of Cu-Mt-OA interface (figure 5c)

Center	Height	Area	FWHM		Polarity
285.184	162.2	345.313	2	C (1s $\rightarrow$ π^*) aromatic C=C	3.447002
286.694	220.8	470.069	2	C (1s $\rightarrow$ σ^*) aliphatic C-H)	
288.229	619.7	1319.3	2	C (1s $\rightarrow$ π^*) C=O Carboxyl,	
290.047	114.5	243.763	2	Carbonyl	
291.145	586	1247.56	2	C (1s $\rightarrow$ σ^*) C-O	
293.402	132.8	282.722	2		
292.038	249.6	531.382	2		

Table S1d. Peak parameters of Cu-OM matrix (figure 5d)

Center	Height	Area	FWHM		Polarity
285.381	513.1	1116.12	2	C (1s $\rightarrow$ π^*) aromatic C=C	1.90203
286.694	262.1	520.608	2	C (1s $\rightarrow$ σ^*) aliphatic C-H)	
288.229	710.4	1411.06	2	C (1s $\rightarrow$ π^*) C=O Carboxyl,	
289.802	252.1	500.745	2	Carbonyl	
291.364	604.8	1201.31	2	C (1s $\rightarrow$ σ^*) C-O	
292.251	236.1	502.641	2		
293.416	371.7	791.325	2		

Table S2. Polarity differences between the OM matrix and Mt-OA and Fh-OA interfaces in the presence and absence of adsorbed Cu- and Ni-species

Mt group	Polarity range	Mean	Median
OM Matrix	0.66-1.18	0.84	0.78
Mt-OA-interface	0.94-1.70	1.27	1.22
Cu-OM-matrix	0.83-2.15	1.62	1.58
Cu-Mt-OA interface	1.06-3.44	2.02	1.94
Ni-OM matrix	0.92-1.16	1.06	1.06
Ni-Mt-OA interface	0.98-1.73	1.29	1.23

n (total number of spectra fitted) =52

Fh group	Polarity range	Mean	Median
OM matrix and Fh-OA interface	0.95-1.78	1.30	1.30
OM matrix and Fh-OA interface (Cu)	1.13-2.15	1.57	1.50
OM matrix and Fh-OA interface(Ni)	1.04-1.61	1.22	1.25

n (total number of spectra fitted) =30

Table S3. Cu/Ni ion concentration in equilibrium solution and mean adsorption capacity of Mt- OA, Fh-OA, Mt, and Fh

Ceq mg L ⁻¹	C (ads) μmol.m ⁻²		Ceq mg L ⁻¹	C (ads) μmol.m ⁻²		Ceq mg L ⁻¹	C (ads) μmol.m ⁻²		Ceq mg L ⁻¹	C (ads) μmol.m ⁻²
	Cu-Mt-OA			Ni-Mt-OA			Cu-Mt			Ni-Mt
1.58675	8525.7797		1.55575	9265.79826		1.0875	7706.40244		0.4595	8932.53493
2.56725	17665.918		3.36175	18256.999		3.47675	14287.216		2.27125	16598.992
10.718	39807.408		12.88925	40721.286		18.3885	27333.626		16.43225	31428.657
27.55925	53142.161		30.67375	54125.2428		39.63175	34905.355		37.01125	40249.307
36.046	64809.404		47.04025	58112.249		54.27175	39540.005		49.904	47839.925
70.949	80108.330		84.394	71988.864		97.44625	45441.834		88.80625	55421.649
92.25325	88920.389		106.73825	80389.448		126.72025	46069.587		110.73325	65789.0256
106.39575	94856.234		124.83875	82473.752		146.17625	46539.970		128.72675	64390.698

Ceq mg L ⁻¹	C (ads) μmol.m ⁻²		Ceq mg L ⁻¹	C (ads) μmol.m ⁻²		Ceq mg L ⁻¹	C (ads) μmol.m ⁻²		Ceq mg L ⁻¹	C (ads) μmol.m ⁻²
	Cu-Fh-OA			Ni-Fh-OA			Cu-Fh			Ni-Fh
0.126	16485.152		1.469	15422.373		0.93525	16339.372		5.81425	8169.6654
0.23325	33001.608		3.2545	30272.5771		8.98325	19857.8869		14.38725	10954.856
6.45575	72699.3694		21.0515	52333.206		35.36025	26388.409		38.68775	22079.029
23.63225	94108.863		42.45925	67866.3073		61.58425	33194.715		64.2015	30835.205
35.466	107742.84		58.021	75889.792		78.205	39285.873		81.9965	35138.881
78.7645	118931.34		100.0305	90335.048		122.9785	48706.732		127.5455	43826.256
106.82625	122167.35		125.56725	98403.728		150.424	53311.264		155.45075	47914.748
125.2395	124816.51		144.64325	100074.14		170.0655	53957.466		174.73875	49304.416

Table S4. Isotherm parameters for Cu adsorption on Mt-OA, Fh-OA complexes, Mt, and Fh as determined by the Freundlich and Langmuir models

	Langmuir			Freundlich		
	R ²	K	Y _m (mol·m ⁻²)	R ²	K _F	n
Montmorillonite MOA	0.96595	0.056	0.102	0.97293	0.008	1.818
Ferrihydrite MOA	0.96089	1.571	0.112	0.94916	0.039	3.816
Montmorillonite	0.9738	0.169	0.039	0.97909	0.007	2.579
Ferrihydrite	0.69393	0.444	0.037	0.91962	0.012	3.596

Table S5. Isotherm parameters for Ni adsorption on Mt-OA, Fh-OA complexes, Mt, and Fh as determined by the Freundlich and Langmuir models

	Langmuir			Freundlich		
	R ²	K	Y _m (mol·m ⁻²)	R ²	K _F	n
Montmorillonite MOA	0.99605	0.086	0.0802	0.97051	0.009	2.045
Ferrihydrite MOA	0.97464	0.301	0.0783	0.98075	0.019	3.048
Montmorillonite	0.90596	0.618	0.0428	0.99318	0.012	2.859
Ferrihydrite	0.91752	0.034	0.0439	0.98843	0.003	1.723

Table S6. Area, Intensity, and position of COO⁻_{sym} and COO⁻_{asym} bands and the respective area and intensity ratios upon adsorption of Cu/Ni with increasing initial Cu/Ni concentration.

[Cu] mg/L	Center	Height	Area	Center	Height	Area	Intensity ratio	Area ratio
0	1380.49	0.21474	27.1535	1590.07	0.359082	45.4052	0.598025	0.598026
10	1375.32	0.329304	41.6398	1594.36	0.437421	55.311	0.752831	0.75283
20	1376.32	0.437517	55.3232	1595.66	0.546863	69.1498	0.800049	0.800049
50	1375.09	0.389424	49.2419	1596.9	0.457471	57.8463	0.851254	0.851254
80	1377.05	0.652983	82.5684	1596	0.718307	90.8285	0.909058	0.909058
100	1375.31	0.730379	92.355	1596.46	0.783924	99.1256	0.931696	0.931697
150	1377.91	0.618672	78.2299	1597.16	0.60874	76.974	1.016316	1.016316
180	1377.7	0.783668	99.0933	1595.68	0.775736	98.0903	1.010225	1.010225
200	1377.04	0.605674	76.5863	1595.48	0.638667	80.7582	0.948341	0.948341

[Ni] mg/L	Center	Height	Area	Center	Height	Area	Intensity ratio	Area ratio
0	1380.52	0.213595	27.0792	1590.61	0.362899	46.0076	0.58858	0.588581
10	1376.46	0.471673	59.7977	1594.55	0.515551	65.3605	0.914891	0.91489
20	1376.17	0.401016	50.84	1593.02	0.430148	54.5334	0.932274	0.932273
50	1379.1	0.549632	69.6812	1591.93	0.692315	87.7703	0.793905	0.793904
80	1379.44	0.544575	69.0402	1584.55	0.638064	80.8925	0.85348	0.853481
100	1378.65	0.788396	99.9513	1589.49	0.953994	120.946	0.826416	0.826413
150	1379.45	0.552525	70.048	1586.93	0.618836	78.4548	0.892846	0.892845
180	1382.16	0.514759	65.2601	1584.7	0.624466	79.1686	0.824319	0.824318
200	1380.5	0.723215	91.6878	1587.52	0.845311	107.167	0.855561	0.85556

