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Interactive adsorption of phenolic acids and amino acids on soil minerals

Implications for the formation and properties of soil mineral–organic associations

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Chapter 1

General introduction

Soil as the interface between lithosphere, hydrosphere and atmosphere and hosting most of the biosphere, makes great contributions by maintaining the stability of various ecosystem on earth, e.g. (i) providing food, biomass and raw material, (ii) storing, filtering and transforming water, nutrients and carbon, (iii) playing a central role as a biodiversity pool and (iv) serving as archive of geological and archaeological heritage (European Commission (EC), 2006; Keesstra *et al.*, 2016). Among these functions, the significance of soil as the largest terrestrial carbon pool (Lal, 2004; FAO and ITPS, 2015) is of particular importance in a world with a changing climate.

1.1   Importance of SOM

The global soil carbon pool (2500 Pg) is much larger than the atmospheric pool (760–829 Pg) and vegetation pool (420–620 Pg) combined (Lal, 2004; Lehmann & Kleber, 2015). The soil carbon pool can be divided into a pool of soil organic carbon (SOC) and a pool of soil inorganic carbon (SIC). The former accounts for > 60% of the total soil carbon pool (Lal, 2004). Given the vast size of the SOC pool and its role in global carbon cycling, processes regulating SOC dynamics have a great and direct influence on the concentration of greenhouse gases (e.g. CO_2 and CH_4) in the atmosphere and thus on global climate change (Lal, 2004; Schmidt *et al.*, 2011; FAO and ITPS, 2015; Luo *et al.*, 2015).

Due to land use change (e.g. expansion of agriculture), the global decrease of the SOC pool over the last two centuries was estimated at 136–160 Pg, which was the second-largest source of CO_2 emission to the atmosphere following combustion of fossil fuel (Ruddiman, 2003; Lal, 2004; Le Quéré *et al.*, 2009). Although the global carbon sequestration potential in soils is supposed to be finite in capacity and time, many studies have showed that the decreasing trend of SOC was reversible and soils have great potential to mitigate climate change via sustainable soil management and sequestration of more carbon in the soil (Lal, 2004; Fischlin *et al.*, 2007; Smith *et al.*, 2008; Stockmann *et al.*, 2013; Minasny *et al.*, 2017). Therefore, great efforts need to be taken to mitigate soil carbon loss and increase SOC storage on a global scale. In order to achieve these targets and predict the changes of soil carbon under climate change, one of the prerequisites is to understand the mechanisms underlying the retention of soil organic matter (SOM) that protect them against decomposition and increase the turnover time (Schmidt *et al.*, 2011).

1.2   Retention mechanism of SOM

The traditional theory argues that humic substances, operationally extracted OM in alkaline solution, make up the majority of SOM and they are thought to be the most stable OM fraction because of the large molecular size and complex molecular structure (Stevenson, 1994; Swift, 1999). However, this theory is increasingly questioned due to lack of evidence to verify the existence of humic substances by modern techniques and their formation process in natural environments (Schmidt *et al.*, 2011; Lehmann & Kleber, 2015). Recently, substantial evidence leads to an emerging view on SOC dynamics that progressive decomposing of SOM is primarily controlled by the surrounding environment rather than the intrinsic properties of these compounds (Schmidt *et al.*, 2011; Lehmann & Kleber, 2015). The mechanisms currently proposed to govern the protection of SOM against decomposition include: (i) selective preservation of recalcitrant OM, such as lignin-derived aromatic carbons, tannins and black carbon, (ii) physical protection via occlusion, intercalation, hydrophobicity and encapsulation to achieve spatial inaccessibility of microbes and enzymes to OM and a shortage of O_2 and (iii) stabilization by interaction with mineral surfaces (Fe-, Al-, Mn-oxides and phyllosilicates) and metal ions (Six *et al.*, 2004; Lützow *et al.*, 2006; Mikutta *et al.*, 2006). Although, the relative contribution of these mechanisms is still under debate, there is a consensus that adsorption of OM on mineral surfaces plays an important role in stabilizing SOM (Lützow *et al.*, 2006; Paul, 2016). Many researchers have reported a positive correlation between the contents of fine mineral particles and SOC (Burke *et al.*, 1989; Mayer & Xing, 2001; Kögel-Knabner *et al.*, 2008 and citations). The strongly associated OM with minerals can account for the major fraction of the SOC pool, especially for the subsoil deeper than 10–15 cm (John *et al.*, 2005; Kögel-Knabner *et al.*, 2008; Herold *et al.*, 2014; Schrumpf & Kaiser, 2015). On the global scale the majority of SOC is stored in the subsoil (below 20 cm; Stockmann *et al.*, 2013). Therefore, the dynamics of SOM could be primarily controlled by the association with minerals and metal ions. However, this assumption deserves more tests on a larger spatial and temporal scale.

Despite the fact that the emerging view tends to focus more on the effects of environmental factors on turnover of the SOM, there is no consistent evidence for the contribution of inherent properties of OM to their stabilization. Because the adsorption of organic compounds is highly dependent on their molecular composition and preferential adsorption of specific compounds is a widespread phenomenon (see section 1.3), we propose that the molecular properties of OM largely affect the storage of SOM through indirectly governing the interaction

with soil minerals rather than a direct effect on the turnover time by the inherent chemical recalcitrance.

1.3   Interaction of SOM with soil minerals and metal ions

Theoretically, the interaction of OM with soil minerals is dominated by adsorption and the involved mechanisms include: ligand exchange, electrostatic interaction, Van der Waals forces, hydrophobic forces, H-bonding, cation bridging and surface ion chelation (Schlautman & Morgan, 1994; Feng *et al.*, 2005; Mikutta *et al.*, 2007; Philippe & Schaumann, 2014). The prevailing mechanisms involved in the formation of mineral–organic associations (MOAs) in the natural environment include: (i) ligand exchange, i.e. displacement of superficial hydroxyl/water groups of minerals by organic carboxyl groups; (ii) cation bridging, i.e. bridging polar functional groups of OM to permanently negative-charged siloxane surface or to hydroxyls of oxides and phyllosilicates via polyvalent metal ions; (iii) electrostatic and Van der Waals interactions and (iv) hydrophobic interactions (Gu *et al.*, 1994; Mikutta *et al.*, 2007; Philippe & Schaumann, 2014; Kleber *et al.*, 2015). The varied adsorption energy for these mechanisms would produce MOAs with different stability and the larger adsorption energy of chemisorption than physisorption indicates a weaker desorbability and thus a smaller bioavailability of OM bound through ligand exchange and cation bridging (Gatta, 1985; Gu *et al.*, 1994; Kleber *et al.*, 2015). Not only the properties of soil minerals and OM, such as mineral surface charge, reactive surface area, crystalline phase, surface coating, OM molecular structure, hydrophobicity and conformation, but also the surrounding environmental conditions, such as soil moisture, solution pH, ionic strength, temperature and valence of ions can influence the adsorption process (Hunter, 2001; Sposito, 2008; Kleber *et al.*, 2015). Several modes of interaction can operate simultaneously in a system (Kleber *et al.*, 2014). In order to fully understand the stabilization of OM adsorbed on the mineral surface, it is pivotal to identify the dominant mechanisms involved in the adsorptive protection of SOM.

In general, soil mineral surfaces can be divided into three categories: uncharged, permanently charged and variable-charge surfaces (Sposito, 2008; Kleber *et al.*, 2015). Uncharged siloxane surfaces, typically derived from kaolin group minerals, are expected to adsorb nonpolar organic molecules or moieties such as alkyl and aromatic compounds via Van der Waals forces and hydrophobic interactions (Sposito, 2008; Kleber *et al.*, 2015). These interactions

were suggested to play an important role in the adsorption of proteins, hydrophobic organic compounds from soil dissolved organic matter (DOM) and polymers such as cutin and carboxymethyl cellulose (Jardine *et al.*, 1989; Servagent-Noinville *et al.*, 2000; Feng *et al.*, 2005; Cuba-Chiem *et al.*, 2008). Negatively charged siloxane surfaces triggered by isomorphic substitution, can promote the adsorption of organic compounds via cation bridging and electrostatic interaction (Barré *et al.*, 2014). For example, the adsorbed polyvalent cations on negatively charged siloxane can link negatively charged functional groups (amino, carbonyl, carboxyl, or hydroxyl groups) with mineral surfaces to form inner-sphere or outer-sphere complexes (Sposito, 2008). Cation bridging could also be established between charged siloxane surfaces and aromatic π-systems (Keiluweit & Kleber, 2009). Moreover, the negatively charged siloxane surfaces can attract positively charged functional groups (e.g. amines) and organic cations (e.g. quaternary ammonium and pyridinium) via electrostatic interaction (Yeasmin *et al.*, 2014; Kleber *et al.*, 2015). This process may be coupled with a process of cation exchange, i.e. replacement of the bound metal ions such as Na^+ and Ca^{2+} (Kleber *et al.*, 2014). Variable-charge surfaces, derived from metal oxides and broken edge sites of phyllosilicates, can facilitate ligand exchange reactions between hydroxyl groups of mineral surfaces and carboxyl or hydroxamate groups of organic compounds, resulting in formation of inner-sphere complexes via covalent metal–O–C bonds (Liu *et al.*, 2008; Kleber *et al.*, 2015). Outer-sphere complexation and H-bonding may also contribute to the adsorption of organic compounds to the edge sites of phyllosilicates (Liu *et al.*, 2008).

1.4 Distribution and structure of bound organic matter on mineral surfaces

Some studies display that OM can homogenously coat mineral surfaces (e.g. Heister *et al.*, 2012). However, most studies reveal a patchy distribution of OM on mineral surfaces. This was observed via both direct approaches (e.g. microscopy and mass spectrometry) and indirect approaches (e.g. specific surface area (SSA) measurements (Arnarson & Keil, 2001; Mayer & Xing, 2001; Kaiser & Guggenberger, 2003; Dümig *et al.*, 2012; Ransom *et al.*, 1997; Chenu & Plante, 2006; Heister *et al.*, 2012; Vogel *et al.*, 2014). This is in line with the interactions between OM and the mineral phase as described in the previous paragraph. Based on those, adsorption of OM would be expected to occur at specific reactive sites of mineral surfaces. As a result, the discrete distribution of organic compounds on mineral surfaces could be ascribed to the
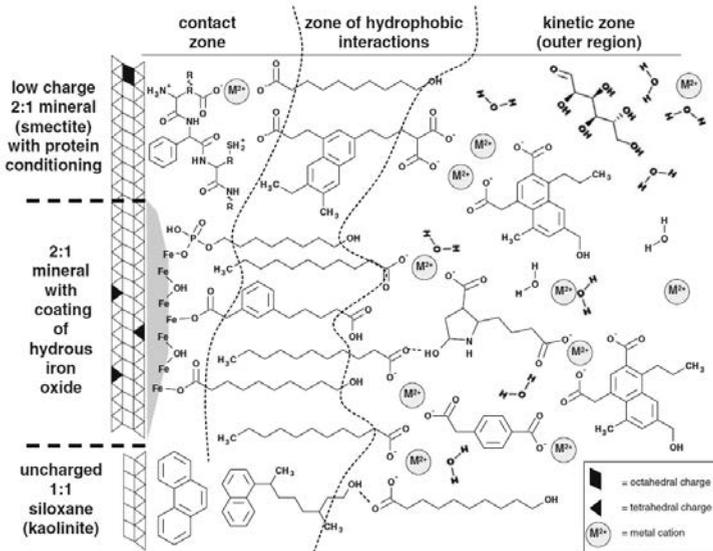
Figure 1.1 The multilayer structure model of mineral-organic associations. Figure adapted from Kleber *et al.* (2007) with reused permission.

heterogeneous distribution of reactive surface hydroxyl groups in phyllosilicates or oxyhydroxide mineral structures and uneven distribution of isomorphic substitution sites in 2:1 clay mineral structures (Kaiser & Guggenberger, 2003; Sposito, 2008).

An important advancement in our understanding of the interactions between SOM and minerals is the introduction of a layer-structure adsorption theory, as first proposed by Schmidt *et al.* (1990). Then a bilayer model of associated OM was suggested by Wershaw (1993). The second important advancement came with the improvement into a multilayer conceptual model (Figure 1.1) by Kleber *et al.* (2007). In this model the structure of bound OM can be self-organized and separated into three layers: (i) the contact zone, i.e. the OM that directly contacts with mineral surfaces; (ii) the intermediate region or zone of hydrophobic interaction and (iii) the outer or kinetic zone. This model reconciles all the prevailing mechanisms that potentially govern the association of OM with soil minerals. It is widely used as the research motivation and explanation for experimental findings (see **chapter 2**). However, there is still no direct and reliable evidence to support this conceptual model.

1.5 Adsorptive protection of phenolic and amino compounds

Substantial evidence supports the preferential adsorption of carboxylated phenolic compounds to various soil minerals (Kaiser & Guggenberger, 2000; Kalbitz *et al.*, 2005; Kothawala *et al.*, 2012). This contradicts the assumption that N-containing amphiphilic compounds are selectively immobilized to form the so called inner layer in the model of Kleber *et al.* (2007). Experimental information about the adsorption of carboxylated phenolic and N-containing compounds to different mineral surfaces and their interaction with respect to competition and surface conditioning is lacking. The proposed multilayer structure regulating the adsorption of organic compounds on mineral surfaces has not yet been tested experimentally, nor has the potentially important role of N-containing compounds therein been tested for the development of a multilayer adsorption structure. This may be achieved by using model compounds, representing nitrogenous and lignin-derived SOM species.

Phenolic acids (PAs) and amino acids (AAs) as degradation products of lignin and organic nitrogen, respectively, play a central role in our current understanding how MOA is formed. Interaction of AAs with soil minerals has been recognized as an important process that may influence the bioavailability of AAs in the soil (Yeasmin *et al.*, 2014). Competitive interaction between AAs and other organic compounds during adsorption on mineral surfaces are, however, not well understood. Numerous studies have shown a high affinity of PAs for soil or soil minerals (Cecchi *et al.*, 2004; Chefetz *et al.*, 2011). However, we do not know whether these monomeric aromatic acids are preferentially adsorbed with respect to N-containing compounds. Furthermore, experimental evidence is lacking for the idea that the proposed surface conditioning by AAs would increase the adsorption of aromatic moieties.

Organic compounds are strongly adsorbed on new mineral surfaces with low C loading through multidentate bonding (Kaiser & Guggenberger, 2007). At larger C loading less functional groups of the organic molecules are involved (Kaiser & Guggenberger, 2007), which renders OM more susceptible to desorption and thus vulnerable to microbial decomposition. Adsorption of natural DOM on mineral surfaces modifies their surface properties, such as SSA and surface charge, consequently altering the adsorption behavior of organic contaminants and phosphate (Zhuang & Yu, 2002; Weng *et al.*, 2008). Such changes in surface properties are important for DOM cycling in the soil profile, which is the result of continuous adsorption (i.e. the formation of MOAs), desorption and microbial production of organic compounds (Sanderman *et al.*, 2008; Kaiser & Kalbitz, 2012). However, effects of these changes in surface properties on the

adsorption of AAs and PAs and their interactions in the soil profile are not well understood, besides the above mentioned decrease in chemical bonds of organic compounds on mineral surfaces with increasing C loading.

1.6 Research objectives and outline

Therefore, the aim of this study was to test Kleber's multilayer conceptual model in general, and in particular with respect to the role of nitrogen containing SOM constituents by investigating the interactive adsorption of AAs and PAs on pure and coated soil minerals with natural DOM in batch adsorption experiment. The outcomes would increase our understanding of the stabilization mechanisms involved in soil C cycling and provided inspirations in modelling and predicting the fate of soil C pool under climate change. To this purpose, the following specific objectives were proposed.

In **chapter 2**, we aimed to critically review and summarize the current state of knowledge with respect to the applicability of the multilayer adsorption model by Kleber and the implications for the model and SOM retention in general.

In **chapter 3**, a robust technique was developed to quantify free AAs in soil extracts using hydrophilic interaction liquid chromatography coupled with electrospray tandem mass spectrometry. The goal was to ensure the precise detection of all the model AAs (lysine, glutamic acid, leucine and phenylalanine) used in the batch adsorption experiments.

In **chapter 4**, batch adsorption experiments were conducted to study the interaction between PAs (salicylic, syringic, ferulic and vanillic acid) and AAs (lysine, glutamic acid, leucine, and phenylalanine) during adsorption on goethite and Ca^{2+}-montmorillonite at pH 6 by applying adsorbate concentrations of 0.01, 0.05 and 0.1 mM. The competition experiments aimed to identify the adsorptive competitiveness of PAs and AAs. The conditioning experiments allowed uncovering the potential role of them in developing a multilayer structure of mineral-associated OM.

In **chapter 5**, batch adsorption experiments were conducted to study how the coating of mineral surfaces with DOM (derived from forest leaf litter (L-DOM) and the underlying O horizon (O-DOM)) affects adsorptive interactions of PAs (salicylic, syringic, ferulic and vanillic acid) and AAs (lysine, glutamic acid, leucine and phenylalanine) on goethite, kaolinite, and montmorillonite at pH 6. This experiment aimed to increase our understanding of the influence of natural

DOM coating of mineral surface on the interactive adsorption of AAs and PAs and add first experimental evidence of the existence of a multilayer structure of associated OM on mineral surfaces.

In **chapter 6**, a synthesis of the thesis is given where the findings of this study were discussed within the context of the multilayer model of Kleber.