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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 6

Synthesis

In this synthesis the findings of the overall research are compiled and interpreted within the context of the adsorptive interaction between soil minerals and natural organic compounds. In addition, efforts are devoted to linking the findings of this study to the multilayer conceptual model of mineral–organic associations (MOAs; Kleber *et al.*, 2007).

6.1 Analytical methods to measure free amino acids from soils

To test the conceptual multilayer model of MOAs using well defined phenolic acids (PAs) and amino acids (AAs), a first step was to obtain reliable analytical methods. For PAs, the quantification can be readily achieved by traditional HPLC coupled with ultraviolet (UV) detector. The situation is more complicated for AAs. Amino acids are zwitterionic compounds and lack specific chromophores for UV or fluorescence detection, thus derivatization is required in the traditional approaches to achieve clear separation of individual AAs and a high sensitivity (Kielland, 1995; Inagaki *et al.*, 2010; Sarazin *et al.*, 2011). However, these approaches suffer from low efficiency, poor reproducibility and lack of analyte specificity (Langrock *et al.*, 2006; Kaspar *et al.*, 2009). Although, direct analysis of underivatized AAs has been achieved by using capillary electrophoresis (CE) coupled with mass spectrometry (MS; Desiderio *et al.*, 2010) and ion-pairing liquid chromatography (LC) coupled with MS (Armstrong *et al.*, 2007; Le *et al.*, 2014), clear drawbacks still affect their application such as low throughput, reagents-induced retention time shift and contamination of reagents (Liu *et al.*, 2008; Kaspar *et al.*, 2009).

Previous research has demonstrated that hydrophilic interaction liquid chromatography (HILIC) coupled with MS is a reliable technique in measuring AAs without derivatization in various materials (Dell'mour *et al.*, 2010; Jandera, 2011; Buszewski & Noga, 2012; Guo *et al.*, 2013). However, the applicability of this technique in detecting free AAs from soils was unknown. Purification is often compulsory to eliminate the strong matrix effects. Moreover, the free AAs in soil extracts are generally present in concentrations lower than the detection limit. To overcome these issues, we developed a HILIC technique coupled with solid phase extraction (SPE) to quantify 20 free AAs extracted from soils (**chapter 3**). The method yielded good separation and accurate determination of 20 AAs without derivatization. Its applicability was validated by analysing the AAs extracted from 10 different soils spanning a wide range of matrix composition. The varied adsorption and desorption behaviour of AAs on SPE cartridge indicated the adsorptive immobilization of AAs in soils is controlled by

their specific properties. It is reasonable to separate the common soil AAs into three groups, i.e. acidic, basic and neutral, due to the analogous SPE recovery for each group. These laid the foundation for the rest of this study.

Our work greatly improved the previous SPE approach of Dell'mour *et al.* (2010) by including more natural AAs and increased the accuracies in quantifying free AAs from soils by using multiple H-labelled internal standards. Furthermore, this cost-efficient technique has promising application for the routine analysis of complex samples in soil and aquatic science. Apparently, more research is needed to address the difficulties in quantifying cysteine, Arg and Met. Cysteine was excluded in this study due to the poor peak shape. We observed the recovery of Arg and Met was affected strongly by the composition of soil, which blocks the application of the technique. More research is needed to address these issues. Finally, the method we developed also has potential to analyse amino sugars together with AAs.

6.2 Adsorption of PAs and AAs on pure minerals

With respect to the adsorption of AAs and PAs on soil minerals in the context of the multilayer model, until now the effects of interaction between these two groups of compounds were unclear. Some studies found a high affinity of carboxylated phenolic compounds to bulk soils and minerals (Kaiser & Guggenberger, 2000; Kalbitz *et al.*, 2005; Chefetz *et al.*, 2011), whereas other evidence supports a preferential retention of N-containing compounds (Kleber *et al.*, 2007). It was thus unclear whether PAs are preferentially adsorbed with respect to AAs or *vice versa*. In **chapters 4 and 5**, our results showed preferential adsorption of specific PAs and AAs on soil minerals. Compared with Syr, Fer and Van, Sal was adsorbed preferentially on mineral surfaces irrespective of the types of minerals. For AAs (Glu, Lys, Leu and Phe), acidic AA (Glu) was adsorbed preferentially on goethite while basic AA (Lys) on phyllosilicates (kaolinite and montmorillonite). For different minerals, larger total adsorption of PAs was observed on goethite than phyllosilicates, while the phyllosilicates were better adsorbent for AAs than goethite. This pattern remained the same when the PAs and AAs were present together. However, the adsorption of PAs (i.e. mainly Sal) on goethite and montmorillonite was partially suppressed in presence of AAs at intermediate and high initial concentrations. These results indicate the overall adsorption pattern of PAs and AAs depends strongly on the type of mineral and adsorbate properties, which is not affected by the competition between PAs and AAs.

Moreover, we observed AAs were more competitive than PAs in binding on mineral surfaces such as goethite and montmorillonite, and surface conditioning with AAs enhanced the adsorption of PAs. These results illustrate the important role of free acidic and basic AAs for surface conditioning in relation to adsorption and probably stabilization of SOM by soil minerals, irrespective of the surface charges of the mineral. Our results also showed that aromatic structures in PAs can enhance the adsorption of AAs and probably of other organic components, independently of net charge characteristics. The PAs resulted in a larger increase in the adsorption of AAs than AAs did for PAs. These findings improved our understanding of the adsorptive process of natural organic compounds on mineral surfaces by mimicking the complex composition of the organic material and the mineral phase. The adsorption of one class of SOM components might alter the adsorption, and potential preservation, of other classes. Thus, we assume that the cycling of different components of SOM possibly affect each other. Nevertheless, the true molecular-scale arrangements of individual compounds on mineral surfaces are still unknown. Elucidation of such arrangements could be achieved by nanoscale spectroscopy (e.g. synchrotron-based mass spectrometry or X-ray photoelectron spectroscopy) and quantum chemical modelling approaches. We also recommend further batch adsorption experiments to assess possible altered adsorption site availabilities induced by mineral dispersion.

6.3 Adsorption of PAs and AAs on OM-coated minerals

Organic matter coating on mineral surfaces can alter the surface properties and thus the remaining adsorption and stabilization capacity of the mineral phase (Sanderman *et al.*, 2008; Kaiser & Kalbitz, 2012). However, the effects of these changes induced by OM coating on the adsorption of AAs and PAs were not well understood. In **chapter 5**, we observed the coating of OM reversed the surface charge of goethite from positive to negative and increased the negative charge of the phyllosilicates. Moreover, the O-DOM (from the O horizon) with a larger negative charge had a stronger effect than L-DOM (from forest leaf litter) with a smaller negative charge. These results support the observations that natural DOM coating reduced the adsorption of PAs and the acidic AA (Glu), but enhanced the adsorption of the basic AA (Lys). This trend proved consistent for all minerals (goethite, kaolinite and montmorillonite). These results further support the observation that the strongest changes in surface charge coincided with the largest decrease in PAs adsorption (goethite). Thus, we proposed that

the effect of DOM coating on the adsorption of PAs and AAs is strongly dependent on the amount and composition of adsorbed OM. Our results support the conclusion that metal (hydr)oxides play a dominant role in the adsorption of PAs rather than organic components (Huang *et al.*, 1977; Cecchi *et al.*, 2004). By contrast, soil OM and negatively charged minerals contribute to the immobilization of basic AAs, while the retention of acidic AAs is primarily controlled by soil minerals with positive charges, i.e. oxides and hydroxides.

Furthermore, we found DOM coating changed the adsorption behaviour of PAs and AAs under competition. Competition between AAs and PAs generally suppressed the adsorption of AAs on OM-coated minerals, while it had little influence on the adsorption of PAs. The strong bonds between AAs and DOM-coated minerals resulted in generally enhanced adsorption of PAs with surface conditioning by AAs. This is in accordance with the results for pure minerals. These results indicate that N-rich organic material bound on mineral surfaces may offer more reactive binding sites for other organic compounds. We found Lys was selectively adsorbed on OM-coated minerals, thus only basic AAs possibly could perform this bridging function. This provides indirect evidence for the multilayer model of MOAs (Kleber *et al.*, 2007). These results demonstrated that the amount and composition of the OM coating on mineral surfaces were more important for adsorption of PAs and AAs than the competition between single molecules. They also support the strong influence of OM coating on the properties of mineral phase and the cycling of fresh SOM. The turnover of carboxylated aromatic compounds and acidic AAs in OM-rich soils could be faster than that in mineral soils. Conversely, the accumulation of OM can enhance the residence time of basic AAs in soils. These results highlight the controlling role of surface adsorbed OM in the cycling of fresh SOM and indicate that labile organic compounds can also possess long residence time. Future studies should focus on clarifying the mechanisms involved in the adsorptive interaction between organic compounds and mineral phase, and between free and bound organic compounds on mineral surfaces. More research is needed to visualize the spatial structure of associated OM using molecular spectroscopy techniques.

6.4 Implication for and assessment of the multilayer model

In **chapter 2**, we summarized the applicability and validity of the conceptual multilayer model of Kleber *et al.* (2007). This model suggests that the associated OM on mineral surfaces is arranged in a discrete zonal structure

(Figure 1.1, **chapter 1**) consisting of the following three zones: (1) the polar functional groups of organic compounds interact with mineral hydroxyls via ligand exchange to form the contact zone, or form association via electrostatic force; (2) an entropically driven membrane-like bilayer structure is developed via hydrophobic interacting with other amphiphilic compounds, forming the so-called hydrophobic zone and exposing the hydrophilic portions towards aqueous solution, and (3) more organic compounds possibly interact with the hydrophilic moieties in the hydrophobic zone via cation bridging, hydrogen bonding and other interactions to form an outer region (kinetic zone).

The multilayer model has been extensively used to underpin experimental observations and develop new theory in soil science and related fields across various spatial and temporal scales. However, to date, the hypothesized multilayer structure and its coupled interaction between different types and classes of molecules that together constitute SOM still lack rigorous testing. In fact, many of the experimental findings can be explained by simpler explanations instead of the multilayer model, like aggregation effects for the storage of SOM and differences in the availability of reactive mineral surfaces for the positive relationship between SOC content and the content of specific minerals.

Although a patchy distribution of associated OM on mineral surfaces was proved recently by analysing the surface elemental composition of soil particle (Vogel *et al.*, 2014; Hatton *et al.*, 2015), its existence cannot be treated as direct evidence for the multilayer model. The significance of proteinaceous compounds has often been overestimated and misused in literature. The current evidence does not support the idea that N-rich organic compounds are generally enriched on mineral surfaces by preferential adsorption. The enrichment of N could depend on mineral surfaces. To date, it is still challenging to directly visualise the spatial organization of associated OM on mineral surfaces at the molecular scale and unravel the mechanisms involved due to the heterogeneous SOC forms and mineral composition and the lack of suitable analytical techniques (Lehmann *et al.*, 2008; Liu *et al.*, 2013). Some state-of-the-art techniques have great potential to address these issues, including XPS depth profiling, NanoSIMS and STXM-NEXAFS. However, many challenges still affect their performance. Thus, more work is needed to improve the feasibility and reliability of these techniques regarding the spatial resolution, sample preparation, control of radiation damage and spectral quantification (Lehmann & Solomon, 2010). Our results as described in **chapter 5**, provide indirect evidence for the multilayer structure of the associated organic compounds, i.e.

that the adsorption of basic AAs can be enhanced by OM coating on mineral surfaces and OM-coated minerals generally resulted in enhanced adsorption of PAs with surface conditioning by AAs. Integrating nanoscale spectroscopy into batch adsorption experiments is required in the future research to clarify the adsorption mechanisms and spatial organization of well-defined organic compounds on mineral surfaces.

6.5 Conclusions

This thesis provides an analytical method to quantify free AAs in soils and increased our understanding of the adsorptive protection and cycling of PAs and AAs in soils. Our findings highlight the controlling role of surface adsorbed OM in the cycling of fresh SOM and indicate that labile organic compounds can also possess long residence time. Thus it provides new, direct evidence that adsorptive interaction with mineral phase should be perceived as an important factor in the cycling of SOM. Moreover, our results demonstrated that the cycling of different components of SOM can affect each other via competitive or sequential adsorption on mineral phase. The direct and reliable experimental evidence for the multilayer conceptual model is still missing. Indirect evidence was showed in this research. The role of proteinaceous compounds in the formation of MOAs was generally overestimated and misused. The enrichment of N-rich OM on mineral surfaces possibly depends on types of minerals. The patchy distribution of adsorbed OM and enrichment of N-rich organic compounds on mineral surfaces cannot be used as direct evidence of the multilayer model. Therefore, we suggest being more cautious in applying this multilayer model.