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Summary

The bioavailability and dynamics of soil organic matter (SOM) depend largely on the association with mineral particles. However, no consensus exists on the formation, composition and structure of the mineral–organic associations (MOAs). A multilayer conceptual model was proposed ten years ago to clarify the role of SOM and minerals in the formation of MOAs and visualize their spatial structure. Although the multilayer model has seen extensive adoption as research motivation and theoretical explanation for the experimental results in soil science and related fields, the experimental evidence for this multilayer model was still lacking. Thus, the main objective of this study was to test the multilayer model with well-defined soil minerals and natural organic compounds via batch adsorption experiments. Goethite, kaolinite and montmorillonite were selected to represent important minerals derived from soils. Phenolic acids (PAs) and amino acids (AAs) were used to represent the degradation products of lignin and proteinaceous compounds respectively, which are widespread in the natural environment. The fate of these highly oxidized monomers was expected to be affected by the interaction with soil minerals to a larger extent than the original polymers.

First, this study summarized the applicability of the multilayer model and evaluated its validity based on current knowledge and experimental evidence (chapter 2). To date, the direct and reliable evidence for the multilayer model was still missing. The multilayer model was widely used to explain experimental observations in terms of the retention and turnover of OM in soils. In fact, many of these 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. The patchy distribution of adsorbed organic compounds on mineral surfaces has been visualized and verified using advanced submicron spectroscopy. However, this cannot be treated as direct evidence for the multilayer model. 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 be dependent on mineral surfaces. 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. Some state-of-the-art techniques have great potential to address these issues, including XPS depth profiling, NanoSIMS and STXM-NEXAFS. However, more works is needed to improve the feasibility and reliability of these techniques regarding the spatial resolution, sample preparation, control of radiation damage and spectral quantification.

We developed a HILIC-MS/MS technique to achieve precise quantification of free AAs in aqueous samples and subsequently applied it to measure 20 free AAs in soil extracts (chapter 3). A solid phase extraction (SPE) procedure was needed to clean up and concentrate the AAs in soil extracts. We achieved similar recoveries of individual AA over the SPE procedure within each group of acidic, basic and neutral AAs. This supported our selection strategy of the tested AAs in the adsorption experiments (chapters 4 and 5). The SPE recoveries of a few AAs (Arg and Met) were readily affected by the composition of soil extracts. Thus further study was needed to eliminate the varied SPE recoveries of Arg and Met for different soils. In brief, the method shows great promise for the routine analysis of free AAs extracted from soils.

In the batch adsorption experiments (chapter 4), we found selective adsorption of organic compounds depended largely on the properties of the soil minerals. Phenolic acids were preferentially adsorbed on goethite, whereas the phyllosilicates (kaolinite and montmorillonite) were a better adsorbent for AAs. Varied adsorption behaviour was also observed for some PAs and AAs. Among all tested PAs (Sal, Syr, Fer and Van), Sal was preferentially adsorbed on all minerals. For the AAs, Glu was preferentially adsorbed on goethite and Lys on phyllosilicates. Little adsorption of neutral AAs (Leu and Phe) was observed on all minerals. Similarly, in chapter 5 we demonstrated the adsorption of natural DOM depended on both the mineral and DOM sources. The adsorption of DOM on different minerals followed the order of goethite >> kaolinite > montmorillonite. Higher adsorption of O-DOM (derived from the O-horizon of forest soil) was observed on goethite than L-DOM (derived from forest leaf litter). Similar adsorption of O-DOM and L-DOM was observed on kaolinite and montmorillonite. Our findings contrasted with the general conclusion that aromatic compounds are preferentially adsorbed on soil particles, which is most likely controlled by soil mineralogy and composition of natural DOM.

Moreover, in chapter 4, we observed the AAs were more competitive than PAs and partially suppressed the adsorption of PAs on goethite and montmorillonite. The adsorption of PAs or AAs on both minerals was enhanced by surface conditioning with the other group, with larger effects for goethite than
montmorillonite. In chapter 5, the results illustrated that coating of various minerals with both DOM sources (O-DOM and L-DOM) reduced the adsorption of PAs and acidic AA (Glu), but enhanced the adsorption of basic AA (Lys). The effect of organic coating depended strongly on the amount of adsorbed OM. The strong bonds between AAs and OM-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 findings offer indirect evidence for the multilayer model of MOAs. The results suggest that the amount and composition of OM coatings affect the adsorption of PAs and AAs on soil particles and thus their dynamics in soils. Adsorbed organic matter on soil mineral phases might be subject to a self-strengthening effect via sequential adsorption of different classes of organic compounds. It is worthwhile to investigate the adsorbed PAs and AAs using advanced spectroscopy in future studies to unravel the adsorption mechanism and the molecular structure of the produced MOAs.

To conclude, our works increased the knowledge on the adsorption behaviour of natural organic compounds on soil minerals, especially the importance of the interplay between different OM components in the formation of MOAs. We propose that the adsorptive interaction with mineral phase should be perceived as an important factor in the cycling of SOM and the cycling of different components of SOM can affect each other via competitive or sequential adsorption on mineral phase. The experimental results of this study provide indirect evidence of the spatial multilayer organization of associated OM on mineral surfaces. More testing, however, remains necessary to verify the multilayer model. Since large uncertainties remain in the composition and spatial structure of MOAs, we suggest being more cautious in applying this model. More efforts remain needed to improve the feasibility and reliability of current techniques in examining the molecular composition of associated OM on mineral surfaces and the underlying mechanisms.