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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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.

Samenvatting

De bio-beschikbaarheid en dynamiek van organisch materiaal in de bodem (SOM) is grotendeels afhankelijk van de associatie met minerale deeltjes. Er is echter geen consensus over de formatie, compositie en de structuur van de resulterende mineraal-organische deeltjes (MOAs). Tien jaar geleden is er een multilayer conceptueel model voorgesteld welke de rol van SOM en mineralen in de formatie van MOAs zou moeten verduidelijken, en daarnaast hun ruimtelijke structuur zou moeten visualiseren. Hoewel het multilayer model al wel veelvuldig is geadopteerd als onderzoeksmotivatie en theoretische onderbouwing voor experimentele resultaten in bodemkunde en gerelateerde velden, blijft de experimentele onderbouwing voor dit multilayer model incompleet.

Het doel van deze studie was het testen van het multilayer model met behulp van goed gedefinieerde bodemmineralen en natuurlijke organische verbindingen in een set adsorptie experimenten. Goethiet, Kaoliniet en Montmorilloniet zijn geselecteerd als goede representanten van belangrijke bodemmineralen. Fenolzuren (PAs) en aminozuren (AAs) representeerden de afbraakproducten van Lignine en andere proteïneverbindingen, welke veelvuldig aanwezig zijn in natuurlijke bodemomstandigheden. De verwachting was dat deze zwaar geoxideerde monomeren eerder beïnvloed zouden worden door interactie met bodemmineraleren dan de oorspronkelijke polymeren.

Als eerste hebben we de toepasbaarheid van het multilayer model samengevat, en vervolgens de validiteit van het model geëvalueerd op basis van de huidige kennis en het huidige beschikbare experimentele bewijs (Hoofdstuk 2). Tot op heden ontbreekt direct en betrouwbaar bewijs voor het multilayer model. Het multilayer model is veelvoudig gebruikt voor het onderbouwen van experimentele observaties in betrekking tot het vasthouden en het omzetten van OM in de bodem. Veel van de experimentele bevindingen kunnen echter ook verklaard worden met simpelere theorieën dan het multilayer model, zoals de aggregatie effecten voor de opslag van SOM, en de verschillen in de beschikbaarheid van reactieve minerale oppervlakten voor de positieve relatie tussen de hoeveelheid bodemorganisch koolstof en de hoeveelheid specifieke mineralen.

De onregelmatige verdeling van geadsorbeerde organische verbindingen op minerale oppervlaktes is gevisualiseerd en geverifieerd door middel van geavanceerde submicron spectroscopie. Echter, de resultaten hiervan kunnen niet worden gezien als direct bewijs voor het multilayer model. Het idee dat stikstofrijke organische verbindingen verrijkt worden op de minerale oppervlakten door preferentiële adsorptie wordt niet ondersteund door het huidige beschikbare bewijs. De verijking van stikstof is mogelijk afhankelijk van minerale oppervlaktes. Het is nog steeds een uitdaging om de ruimtelijke organisatie van geassocieerd OM op minerale oppervlaktes op een moleculair niveau direct te visualiseren en de betrokken mechanismes te ontrafelen. De nieuwste technieken, zoals XPS depth profiling, NanoSIMS en STXM-NEXAFS, kunnen mogelijk toegepast worden om deze barrières te slechten. Om dit ook werkelijk te bewerkstelligen zal echter de haalbaarheid en de betrouwbaarheid van deze technieken op het gebied van ruimtelijke resolutie, monstervoorbewerking, beperking van stralingsschade, en spectrale kwantificatie moeten worden verbeterd.

We hebben een HILIC-MS/MS techniek ontwikkeld voor precieze kwantificatie van vrije AAs in watermonsters en deze vervolgens toegepast op 20 vrije AAs in bodemextracten (Hoofdstuk 3). Een solid phase extraction (SPE) procedure was nodig om de extracten op te schonen en de AAs in de extracten te concentreren. Met de SPE procedure hebben we voor de individuele AAs, binnen de verschillende milieus, zuur, basisch en neutraal, vergelijkbare opbrengsten weten te realiseren. Dit resultaat ondersteunde onze geselecteerde strategie van de geteste AAs in de adsorptie experimenten (Hoofdstuk 4 en 5). De SPE opbrengst van een aantal AAs (Arg en Met) werd duidelijk beïnvloed door de samenstelling van de bodemextracten. Het vereiste verder onderzoek om de variatie in SPE opbrengst voor Arg en Met in verschillende bodems te elimineren. Tot slot, toont deze methode grote potentie voor de routine analyse van vrije AAs geëxtraheerd uit bodems.

In de adsorptie experimenten (Hoofdstuk 4) vonden we dat de selectieve adsorptie van organische verbindingen grotendeels afhankelijk is van de karakteristieken van de bodemmineralen. Fenolzuren werden preferentieel geadsorbeerd op Goethiet, terwijl de AAs preferentieel adsorbeerden op de phyllosilicaten (Kaoliniet en Montmorilloniet). Gevarieerd adsorptie gedrag voor PAs en AAs werd ook geobserveerd. Onder alle geteste PAs (Sal, Syr, Fer en Van) werd Sal preferentieel geadsorbeerd door alle mineralen. Onder de AAs adsorbeerde Glu preferentieel op Goethiet, en Lys op phyllosilicaten. Neutrale AAs (Leu en Phe) werden weinig geadsorbeerd op de mineralen. In Hoofdstuk

5 demonstreerden we de adsorptie van natuurlijke DOM, afhankelijk van de oorsprong van het mineraal en de DOM. De adsorptie van DOM op verschillende mineralen verliep met de volgorde Goethiet >> Kaoliniet >> Montmorilloniet. Bij O-DOM (afkomstig uit de O-horizon van een bosbodem) werd een hogere adsorptie op Goethiet waargenomen dan bij L-DOM (afkomstig uit boomblad litter). Vergelijkbare adsorptie van O-DOM en L-DOM is waargenomen op Kaoliniet en Montmorilloniet. Onze bevindingen contrasteren met de algemene conclusie dat aromatische verbindingen preferentieel adsorberen op bodemdeeltjes. De reden is hoogstwaarschijnlijk een afhankelijkheid van de bodemmineralogie en de compositie van het aangewende natuurlijke DOM.

In Hoofdstuk 4 vonden we dat AAs in grotere mate competitief zijn dan PAs en leiden tot gedeeltelijke onderdrukking van de adsorptie van PAs op Goethiet en Montmorilloniet. De adsorptie van PAs of AAs op beide mineralen werd versterkt door het conditioneren van het oppervlakte met de andere groep, met grotere effectiviteit voor Goethiet dan bij Montmorilloniet. In hoofdstuk 5 illustreerden de resultaten dat door de mineralen te voorzien van een coating van DOM (O-DOM of L-DOM) de adsorptie van PAs en zure AA (Glu) wordt gereduceerd, maar de adsorptie van basische AA (Lys) versterkt wordt. Het effect van de organische coating is sterk afhankelijk van de hoeveelheid geadsorbeerd OM. De sterke verbindingen tussen AAs en OM-gecoate mineralen resulteren in het algemeen in versterkte adsorptie van PAs bij oppervlakte conditionering door AAs. Dit is in overeenstemming met de resultaten voor pure mineralen. Deze bevindingen bieden indirect bewijs voor het multilayer model van MOAs. Het resultaat suggereert dat de hoeveelheid en compositie van OM coatings de adsorptie van PAs en AAs op bodemmineralen beïnvloed en daarbij ook hun dynamiek in bodems. De adsorptie van organisch materiaal op bodemmineralen is mogelijk onderhevige aan een zelfversterkend effect via een sequentiële adsorptie van verschillende klassen van organische verbindingen. In toekomstig onderzoek zou het waardevol zijn om de geadsorbeerde PAs en AAs met behulp van geavanceerde spectroscopie te onderzoeken om zo het adsorptiemechanisme en de moleculaire structuur van de geproduceerde MOAs beter te begrijpen.

Ter conclusie, draagt ons onderzoek bij aan de kennis over adsorptiegedrag van natuurlijke organische verbindingen op bodemmineralen, en dan met name met betrekking tot het belang van de wisselwerking tussen verschillende OM componenten in de formatie van MOAs. We stellen voor dat de adsorptie wisselwerking met de minerale fase zou moeten worden gezien als een

belangrijke factor in de omzetting van SOM en dat de omzetting van verschillende componenten van SOM elkaar kan beïnvloeden door middel van competitie of sequentiële adsorptie op de minerale fase. De experimentele resultaten van dit onderzoek leveren indirecte bewijzen voor de ruimtelijke organisatie van geassocieerde OM op minerale oppervlaktes in laagjes. Verder onderzoek blijft echter nodig om het multilayer model verder te verifiëren. Aangezien er grote onzekerheden blijven ten opzichte van de samenstelling en ruimtelijke structuur van MOAs raden we voorzichtigheid aan bij het toepassen van dit model. Er zal verder onderzoek nodig zijn om de bruikbaarheid en de betrouwbaarheid van de huidige technieken in het bestuderen van de moleculaire samenstelling van geassocieerd OM op minerale oppervlaktes en de onderliggende mechanismen te verbeteren.

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