Organic matter coatings of soil minerals affect adsorptive interactions with phenolic and amino acids

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Summary

Phenolic (PAs) and amino acids (AAs) contribute potentially to the stabilization of organic matter (OM) in soil by forming mineral–organic associations (MOAs). However, little is known about how natural OM coating affects the adsorption of these compounds and their mutual interaction upon adsorption. Therefore, batch adsorption experiments were carried out to study how coatings of minerals with dissolved organic matter (DOM) obtained from forest leaf litter (L-DOM) and from the O horizon (O-DOM) affect the adsorption of phenolic acids (salicylic, syringic, ferulic and vanillic acid) and amino acids (lysine, glutamic acid, leucine and phenylalanine) at pH 6. Moreover, the adsorption of PAs on OM-coated minerals was tested after preconditioning by AAs and *vice versa*. Adsorption of DOM depended on the mineral (goethite ≫ kaolinite > montmorillonite) and sources of DOM (O-DOM > L-DOM for goethite). Coatings of all minerals with both DOM sources reduced the adsorption of PAs and the acidic glutamic acid but enhanced that of the basic lysine. The adsorption of PAs decreased with increasing OM coating of the minerals. Strong bonds between AAs and OM-coated minerals generally enhanced adsorption of PAs with preconditioning by AAs. This indirectly indicates a multilayer model of MOA. Adsorption of AAs, however, was rarely influenced by preconditioning with PAs. Competition between AAs and PAs generally suppressed the adsorption of AAs on coated minerals, whereas the PAs were hardly affected. These results emphasize that the amount and composition of OM coating must be considered when studying the adsorption of PAs and AAs in soil.

Highlights

- Adsorption of DOM on minerals followed the order: goethite ≫ kaolinite > montmorillonite.
- Adsorption of O-DOM (O horizon) on goethite was larger than that of L-DOM (leaf litter).
- Coatings of DOM reduced adsorption of PAs and acidic AAs and enhanced that of basic AAs.
- The amount and composition of OM coating affected the adsorption of PAs and AAs.

Introduction

Substantial efforts have been dedicated to understanding the formation of mineral–organic associations (MOAs) by adsorptive interaction between soil minerals and natural organic compounds (Kleber *et al.*, 2015). These interactions are decisive for the protection of soil organic matter (OM) against microbial decay (Mikutta *et al.*, 2007; Schneider *et al.*, 2010). At fresh mineral surfaces and small C loading, OM is strongly adsorbed through multidentate bonding,

whereas at larger C loading fewer functional groups of the organic molecules are involved (Kaiser & Guggenberger, 2007), which renders OM more susceptible to desorption and vulnerable to microbial decomposition.

Currently, there is no consensus on the processes and organic substances involved in the formation of MOAs. The classical view of a preferential bonding of lignin-derived components, such as phenolic acids (PAs), on many soil minerals (Kaiser & Guggenberger, 2000; Kalbitz *et al.*, 2005) is in contrast to the 'onion' or 'multilayer' model (Sollins *et al.*, 2006; Kleber *et al.*, 2007). This assumes that amphiphilic, N-rich molecules (e.g. amino acids, AAs) build up

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an inner layer directly linked to the negatively charged aluminosilicate surfaces and an outer layer of more loosely bound organic substances, probably including PAs. Thus, exploring the competitive adsorption of AAs compared with that of PAs is essential to advance our understanding of the formation and stabilization of MOAs.

The degradation products of lignin and proteins, PAs and AAs, respectively, are very active components in the cycling of C and N in soil. So far, knowledge about the adsorption patterns of aromatic and nitrogenous components including PAs and AAs on soil samples or model soil minerals has been obtained either in mono-component systems or by the changes in the composition of dissolved organic matter (DOM) following adsorption (Kalbitz *et al.*, 2005; Chefetz *et al.*, 2011; Yeasmin *et al.*, 2014). The consequences of interactions between PAs and AAs during adsorption for the formation of MOAs have rarely been studied, yet they are crucial for assessing the validity of the multilayer adsorption model. It can be expected that these interactions between PAs and AAs might not only be affected by the nature of the mineral surfaces (e.g. oxides with variable charge versus rarely charged 1:1 clay minerals versus permanently charged 2:1 clay minerals), but also by the surface adsorption of natural OM. Adsorption of DOM depends on its composition, and the DOM derived from decomposed OM usually has greater adsorption than that from fresh litter (Schneider *et al.*, 2010). Adsorption of OM can modify the surface properties of soil minerals, such as specific surface area, surface charge and hydrophilicity. Such changes in surface properties are important for DOM cycling because they modify qualitatively and quantitatively the adsorption and stabilization capacity of the mineral phase (Schneider *et al.*, 2010). However, the effects of these changes on the adsorption of PAs and AAs are not well understood.

Recently, we have shown that a preceding adsorption of both PAs and AAs on soil minerals enhanced the adsorption of the other group (Gao *et al.*, 2017). In other studies, the retention of non-polar organic compounds was greatly enhanced on minerals after coating with OM (Wang *et al.*, 2008; Polubesova *et al.*, 2009). However, whether that holds true for polar compounds such as PAs and AAs is unknown.

Therefore, the main objective of our study was to clarify how the coating of mineral surfaces with OM affects adsorptive interactions between PAs and AAs. Goethite (α-FeOOH), kaolinite and montmorillonite were chosen as model minerals, representing the most important fine-sized minerals in many soils (Fe oxides, and 1:1 and 2:1 clay minerals, respectively). These minerals have different surface properties: goethite, variable charge; kaolinite, little isomorphic substitution; montmorillonite, rich isomorphic substitution and permanent negative charge (Sposito, 2008). We studied (i) the adsorption behaviour of different AAs (glutamic acid, leucine, lysine and phenylalanine, representing acidic, neutral, basic and aromatic AAs, respectively) and PAs (salicylic, syringic, ferulic and vanillic acids, representing lignin degradation products) on minerals coated with OM, (ii) changes in the adsorption behaviour of PAs on OM-coated minerals after surface conditioning by AAs, (iii) changes in the adsorption behaviour of AAs on OM-coated minerals after surface conditioning by PAs and (iv) the competition

effects between PAs and AAs on their adsorption on OM-coated minerals. Herein, 'coating' and its derivatives refer to the adsorption of DOM on minerals, 'conditioning' and its derivatives refer to the adsorption of PAs and AAs on pure and OM-coated minerals. The terms as such are used consistently in the whole text.

Material and methods

Minerals

Goethite was synthesized according to the method of Atkinson *et al.* (1967) by alkaline hydrolysis of 0.5 M FeCl$_3$. Synthesis was terminated by adjusting pH to 6 with 1 M NaOH. Soluble salts were removed by washing with deionized H$_2$O and centrifugation. Finally, the suspension was freeze-dried. Montmorillonite was obtained by separating the < 2-μm fraction by sedimentation and decantation from Morocco bentonite (Ddani *et al.*, 2005). Exchange sites were saturated with Ca^{2+} by suspending the clay twice in 1 M CaCl$_2$ (1 g clay in 10 ml CaCl$_2$). Kaolinite (KGa-2) was purchased from the Clay Minerals Society (Warrenton, GA, USA). A suspension of kaolinite in deionized H$_2$O (1 g clay in 15 ml H$_2$O) was sonicated for 8 minutes (120 W) to break up the aggregates. Afterwards, exchange sites were also saturated with Ca^{2+} by suspending the clay three times in 1 M CaCl$_2$ (1 g clay in 5 ml CaCl$_2$). Finally, the montmorillonite and kaolinite were washed until salt free, then freeze-dried and passed through a 200-μm sieve. The X-ray diffraction patterns (Siemens, D500, Cu-Kα radiation, Karlsruhe, Germany) indicate the presence of well-crystallized goethite and a high purity of the <2-μm fraction of the Morocco bentonite and kaolinite (Figure S1). The specific surface area (SSA) and total pore volume (TPV) of minerals were derived from duplicate N$_2$ gas adsorption isotherms recorded with a Quantachrome Autosorb1-MP analyser (Quantachrome, Boynton Beach, FL, USA). For this purpose, 20–200 mg of each sample was weighed into the sample cell and degassed at 40°C until the pressure was < 0.12 Pa. The SSA was calculated from the linear Brunauer–Emmett–Teller (BET) plot (Brunauer *et al.*, 1938) with up to 10 adsorption points. The TPV was taken at P/P$_0$ ca. 0.995, where P and P$_0$ are the equilibrium and the saturation pressure of N$_2$ respectively. The results and other related properties are listed in Table 1.

Phenolic acids and amino acids

Salicylic (Sal), syringic (Syr), ferulic (Fer) and vanillic acids (Van), ethylvanillin (Eva), L-leucine (Leu), L-glutamic acid (Glu), L-lysine (Lys), DL-phenylalanine (Phe) and DL-norvaline (Nva) were purchased from Sigma-Aldrich (Zwijndrecht, the Netherlands). The purity was > 98%, except for Syr ($\geq$ 95%) and Van ($\geq$ 97%). The chemical structure and properties of these compounds are listed in Table S1 (Supporting Information). The Nva and Eva were used as the internal standards (ISs) for the measurement of AAs and PAs, respectively.

Preparation of PA and AA solutions

Stock standard solutions of each AA (2000 mg l^{-1}) were prepared in 0.1 M HCl, and those of the PAs were prepared in water

Table 1 Cation exchange capacity (CEC), specific surface area (SSA), total pore volume (TPV), average pore radius (APR), C content, organic carbon (OC) loading and ζ potential of pure and organic matter (OM)-coated minerals[a]

| Mineral | CEC / mmol$_c$ kg^{-1} | SSA / m^2 g^{-1} | TPV / mm^3 g^{-1} | APR / nm | C content / mg g^{-1} | OC loading[b] / % | ζ potential measurement | | |
							ζ potential / mV	EC / μS cm^{-1}	pH
G	13[c]	69.7 (1.1)	730 (3)	21.0 (0.2)	1.4 (0.1)		40.4 (1.7)	4.0 (0)	6.2 (0.1)
L-G	–	63.0 (2.4)	647 (36)	20.5 (0.4)	9.1 (0)	54	−6.8 (0.5)	5.3 (0.6)	6.0 (0.1)
O-G	–	69.3 (3.5)	702 (66)	20.2 (0.9)	17.9 (0)	53	−27.5 (2.1)	7.3 (0.6)	6.3 (0.1)
K	37[d]	25.0 (0.9)	315 (51)	25.2 (3.2)	0.5 (0)		−23.2 (1.3)	4.0 (0)	6.0 (0.1)
L-K	–	23.4 (1.1)	379 (6)	32.4 (1.0)	1.5 (0)	59	−37.9 (1.8)	4.0 (0)	6.1 (0)
O-K	–	23.6 (0.5)	403 (84)	34.1 (6.4)	1.6 (0)	54	−42.7 (0.3)	4.0 (0)	6.0 (0.1)
M	888[e]	94.7 (6.0)	187 (6)	4.4 (1.0)	1.1 (0)		−29.5 (3.5)	5.0 (0)	6.3 (0.1)
L-M	–	51.8 (0.2)	112 (4)	4.3 (0.2)	2.0 (0)	59	−49.3 (1.6)	6.0 (0)	6.2 (0.1)
O-M	–	48.6 (0.1)	110 (2)	4.5 (0.1)	2.2 (0)	74	−54.1 (2.8)	5.0 (0)	6.2 (0.1)

[a]The results are mean values with standard deviation ($n = 2$ except for the measurement of ζ potential, for which $n = 3$).
[b]Proportion of the maximum adsorption capacitiy for the respective dissolved organic matter (DOM).
[c]Calculated from the negative surface charge density at pH 6 in NaCl background electrolyte (Walsch & Dultz, 2010).
[d]Borden & Giese (2001).
[e]Daou *et al.* (2015).
CEC, cation exchange capacity; EC, electrical conductivity; G, goethite; L-G, goethite coated with dissolved organic matter obtained from forest leaf litter (L-DOM); O-G, goethite coated with dissolved organic matter obtained from the O horizon (O-DOM); K, kaolinite; L-K, kaolinite coated with L-DOM; O-K, kaolinite coated with O-DOM; M, montmorillonite; L-M, montmorillonite coated with L-DOM; O-M, montmorillonite coated with O-DOM.

at a concentration of 1000 mg l^{-1} for Sal, Syr and Van, and 500 mg l^{-1} for Fer. A smaller concentration was used for Fer because of its low solubility in water (Table S1). The stock solutions were stored at 4°C for no longer than 1 month. Working mixture solutions with equal concentrations for individual PAs and AAs were freshly prepared by mixing and diluting the stock standard solutions.

Dissolved organic matter

Dissolved OM was extracted from the Oi horizon (slightly decomposed organic material) and Oe + Oa horizon (intermediate and highly decomposed organic material) of a beech forest (Grinderwald, Germany) to represent DOM from the two most important sources percolating into the mineral soil. The leaf litter from the Oi horizon was dried and ground into small pieces. The field moist samples from the Oe + Oa horizon were sieved to < 4.8 mm and stored at 4°C. Suspensions of leaf litter in deionized H$_2$O (1 g litter in 10 ml H$_2$O) or of the Oe + Oa horizon sample in deionized H$_2$O (1 g litter in 5 ml H$_2$O) were stirred with a glass rod first and left at 20°C for 16 hours. The supernatant of the suspension was centrifuged (3500 *g*, 20 minutes) and filtered through a 0.45-μm mixed cellulose ester membrane (ME25, GE Healthcare Life Sciences, Whatman, Little Chalfont, UK). The DOM stock solutions were stored at 4°C before use. The dissolved organic carbon (DOC) concentration of the extracts derived from leaf litter (L-DOM) and the Oe + Oa horizon (O-DOM) were 1107 and 138 mg C l^{-1}, respectively. The pH of the L-DOM and O-DOM solution was 5.1 and 4.4, respectively. Extensive characterization of DOM derived from similar sources (i.e. Oi and Oa horizons of a beech forest) was carried out by Kalbitz *et al.* (2003).

Preparation of OM-coated minerals

To verify a similar coating efficiency for all minerals, adsorption isotherms for the two types of DOM and three minerals were first constructed in a batch adsorption experiment in duplicate at pH 6 (Schneider *et al.*, 2010). To inhibit microbial activity and assure a constant electrolyte background, NaN$_3$ was added to the solutions with a final concentration of 10 mM. The pH of the solution was adjusted to 6 to simulate a common natural condition before mixing with minerals by dropwise addition of 0.1 M NaOH or HCl. Based on the adsorption isotherms, we selected the solid-to-solution conditions under which 50% of the maximum DOM adsorption capacity was achieved. Fifty percent cover of the minerals was selected to reflect the situation in mineral subsoil horizons and to ensure that the minerals had sufficient remaining adsorption sites to interact with PAs and AAs. Briefly, goethite (20–700 mg), kaolinite (50–1200 mg) or montmorillonite (40–1500 mg) was suspended in 40 ml L-DOM or O-DOM solution adjusted to pH 6 (ca. 120 mg OC l^{-1} for goethite and ca. 50 mg OC l^{-1} for kaolinite and montmorillonite) and shaken horizontally (1.58 s^{-1}) for 16 hours in the dark at 4°C to achieve equilibrium, then centrifuged (3500 *g*, 20 minutes) and filtered as before. The UV absorbance of the filtrates at 280 nm was measured with a Spectroquant Pharo 300 spectrometer (Merck KGaA, Darmstadt, Germany). The pH was measured using a multi-channel analyser (CONSORT C831, Abcoude, the Netherlands). The DOC concentration was measured by a TOC analyser (TOC–V CPH Shimadzu, Kyoto, Japan). Adsorbed OC was calculated as the difference between the TOCs in the initial and equilibrium solutions.

The OM-coated minerals (L-DOM-coated goethite, L-goethite; L-DOM-coated kaolinite, L-kaolinite; L-DOM-coated montmorillonite, L-montmorillonite; O-DOM-coated goethite, O-goethite;

O-DOM-coated kaolinite, O-kaolinite; O-DOM-coated montmorillonite, O-montmorillonite) were freeze-dried, ground with an agate mortar and pestle and sieved to < 200 μm. The C contents (Table 1) were measured by a CN analyser (Elementar Vario EL, Hanau, Germany). The C loadings of the three minerals were between 45 and 67% of their maximum adsorption capacity, which is within an acceptable range of the desired 50%.

Adsorption experiments with PAs and AAs

Adsorption of PAs (mixed solution of Sal, Syr, Fer and Van) and AAs (mixed solution of Leu, Glu, Lys and Phe) was carried out with pure goethite, kaolinite and montmorillonite, and minerals coated with L-DOM and O-DOM. Experiments were conducted at three different initial concentrations of the individual adsorbates: 0.01 (small), 0.05 (intermediate) and 0.1 mM (large). The solutions were added to each OM-coated mineral separately (control experiment), together (competition experiment) and after preconditioning with PAs or AAs (conditioning experiment). For the latter, two conditioning experiments were performed: adsorption of PAs on OM-coated minerals after adsorption of AAs (conditioning experiment I) and adsorption of AAs on the OM-coated minerals after adsorption of PAs (conditioning experiment II). There were three replicates for each treatment. The initial pH conditions were set at 6 as before for all experiments and they increased to 6.2–6.7 after adsorption. Details of the adsorption procedure and the adsorption results of PAs and AAs on pure goethite and montmorillonite are given in Gao *et al.* (2017). The adsorption results on pure kaolinite are presented in Figures S2 and S3 (Supporting Information).

Measurement of PAs and AAs

The PAs in the filtrates were analysed directly by a Prominence high-performance liquid chromatography (HPLC) system equipped with a diode array detector (Shimadzu, Kyoto, Japan). The details are given in Measurement of PAs and Table S2 (Supporting Information). Hydrophilic interaction LC (Shimadzu, Kyoto, Japan) coupled with a 4000 QTRAP LC–MS/MS System (AB SCIEX, Milford, MA, USA) was used to analyse the AAs (Gao *et al.*, 2016; Gao *et al.*, 2017). Prior to measurement, the AAs in the filtrates were diluted 10 or 20 times in organic solvent (90% acetonitrile, 10% H_2O, 8 mM ammonium formate, 0.12% formic acid, v/v%) and spiked with Nva (IS) at a final concentration of 0.1 mg l^{-1}. Accuracy of the analytical methods of PAs and AAs were good when the measured concentrations of the mixture were compared with the calculated values (Table S3, Supporting Information). These results indicate that the measurements of PAs and AAs were not affected by each other. Typical chromatograms of PAs and AAs are shown in Figures S4 and S5 (Supporting Information).

Desorption experiments and potential flocculation of PAs or AAs with desorbed OM

The reversibility of adsorption of OM and the potential contribution of DOM-derived PAs and AAs was assessed by a desorption experiment using 10 mM NaN_3 (pH 6) at the same electrolyte background used in the adsorption experiment. Suspensions of OM-coated minerals in 40 ml NaN_3 solution (200 mg goethite, 600 mg kaolinite or montmorillonite) were shaken horizontally (1.58 s^{-1}) for 2 hours in the dark at 4°C, then centrifuged (3500 *g*, 20 minutes) and filtered as before. The minerals were resuspended by vortex before carrying out a second cycle of desorption. The DOC concentrations in the filtrates were analysed as before. Desorption was generally small for kaolinite and goethite (Table S4, Supporting Information). Strong mechanical force was needed to grind the OM-coated montmorillonite, which might explain the relatively large desorption of OM (22.2–26.7%). The PAs and AAs in the solutions of the first desorption cycle were generally undetectable except for small amounts of detected AAs for L-goethite (Table S5, Supporting Information). This indicates that the PAs and AAs measured in the adsorption experiments were almost exclusively derived from the added compounds.

The filtrate after the first desorption cycle was used further to test potential flocculation of PAs or AAs by possible desorbed OM because flocculation would result in extra loss of PAs and AAs in addition to adsorption, and therefore an overestimate of their adsorption. A certain amount of the solution with a mixture of PAs or AAs was added to 5 ml of the desorption solution to achieve final concentrations of 1, 4, 10 and 20 mg l^{-1}, respectively (the concentration was the same for individual compounds in each mixture). The samples were vortex mixed and measured for PAs or AAs. The large recoveries of the added PAs and AAs (91–93 and 86–101%, respectively; Table S6, Supporting Information) suggest negligible effects from flocculation.

Potential exchange of PAs or AAs with adsorbed OM

The solutions of PAs and AAs (intermediate initial concentration) in the control experiments were also analysed for TOC concentration. The differences between the measured TOC concentration and the calculated results from HPLC analysis were similar to the desorbed OC that was obtained from the desorption experiments (data not shown). In addition, the results of the desorption experiments showed that the majority of the adsorbed OM was irreversibly bound to the minerals (Table S4). Thus, the exchange of PAs or AAs with adsorbed OM was assumed to be negligible in this study.

Zeta potential measurement of OM-coated minerals

Zeta (ζ) potential measurements were carried out using phase-analysis light scattering (ZetaPALS, Brookhaven Instruments Corp., Holtsville, NY, USA). Mineral suspensions of 100 mg l^{-1} were prepared in ultrapure water in 25-ml flasks without further pH adjustment. After gentle shaking, 1.6 ml was sampled with a pipette, transferred into a cuvette and measured at 20°C. Zeta potentials of three replicates were determined for each sample in five repeated 'runs' and each run consisted of 20 measurements. The ζ potential was calculated from electrophoretic mobility using the Smoluchowski equation (Hunter, 1981). The electrical conductivity of the suspensions was determined simultaneously and

used to reflect electrolyte concentration. The pH was determined in the cuvette using a miniaturized electrode (BlueLine 16pH, Si Analytics, Mainz, Germany).

Statistics

Statistical analysis was performed with SIGMAPLOT (version 13.0). Two-way analysis of variance (ANOVA) was used to evaluate the effects of adsorbate concentration and each of the following factors, mineral types, OM coating, competition and surface conditioning, on the adsorption of PAs and AAs. Data were transformed if necessary to meet both the normality (Shapiro–Wilk) and homogeneity of variance tests (Brown–Forsythe) using appropriate methods. Fisher's least significant difference (LSD) was used for multiple comparisons of means. The significant level of difference was set at $P < 0.05$.

We introduced relative adsorbed amount to show the effects of OM coating, competition and conditioning more clearly on the adsorption of PAs and AAs. The relative adsorbed amount is the percentage value from the adsorption results relative to that obtained from the control experiments. The same mean values from the control experiments were used for each of the three replicates in calculating the relative values of adsorbed amounts.

Results

Adsorption of natural DOM on pure minerals

The adsorption of L-DOM and O-DOM on soil minerals followed the order of goethite ≫ kaolinite > montmorillonite on the basis of both mass and surface area in nearly neutral conditions (Figure 1 and Table S7, Supporting Information). Goethite retained more O-DOM than L-DOM, whereas a similar adsorption of both DOM solutions was observed for kaolinite and montmorillonite. The experiments with L-DOM showed a preferential adsorption of aromatic compounds to all minerals revealed by the decreasing specific UV absorbance at 280 nm (Figure S6, Supporting Information). For O-DOM, such a preferential adsorption to montmorillonite only was observed. The SSA of different minerals followed the order of montmorillonite > goethite > kaolinite, whereas a different order of goethite > kaolinite > montmorillonite was observed for the TPV (Table 1), which accords with the adsorption results. The SSA of montmorillonite was reduced by both types of DOM, whereas the effects on goethite and kaolinite were small (Table 1). The equilibrium pH after adsorption increased with the reduction of OC in solution, and the changes depended on the mineral and the type of DOM (Figure S7, Supporting Information). The ζ potential of goethite was reversed to negative by adsorption of both types of DOM, with a stronger effect for O-DOM (Table 1). Organic matter coatings led to more negative ζ potentials of kaolinite and montmorillonite, with similar effects for L-DOM and O-DOM. The increase in negative surface charge with DOM coating increased with the amount of C adsorbed (Figure S8). These changes were largest for goethite and differed between the two types of DOM because more O-DOM was adsorbed on goethite than L-DOM (Figure 1).
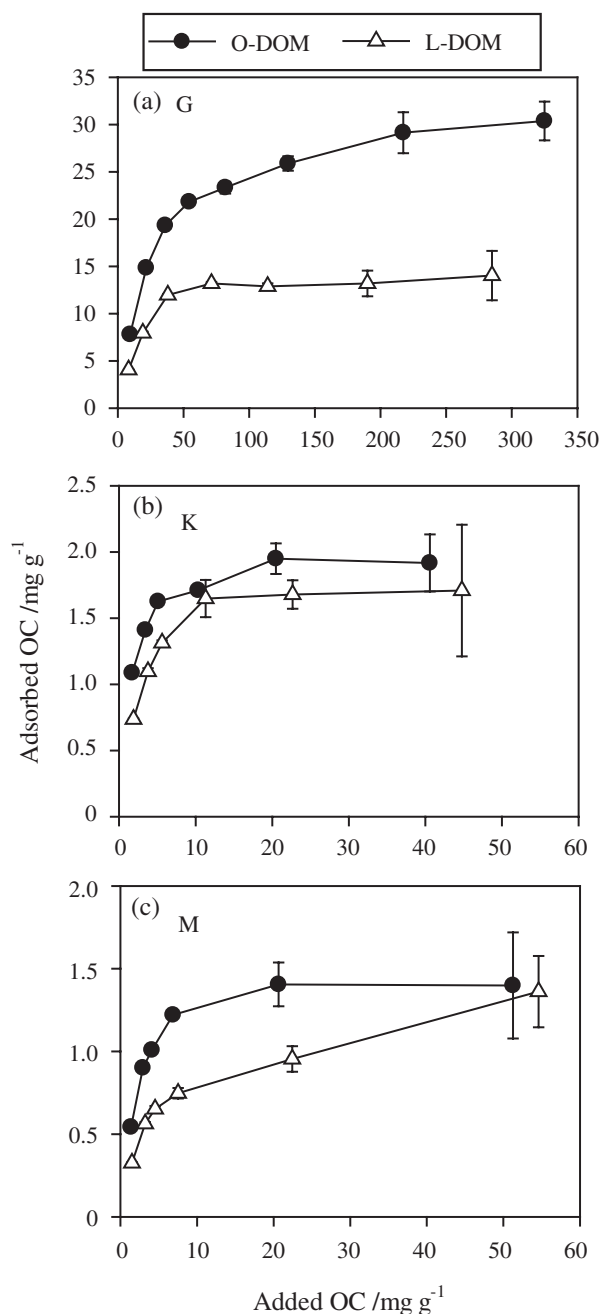

Figure 1 Adsorption isotherms of O-DOM and L-DOM on different minerals (G, goethite; K, kaolinite; M, montmorillonite). The results are mean values with standard errors ($n = 2$). L-DOM, organic matter obtained from forest leaf litter; O-DOM goethite coated with dissolved organic matter obtained from the O horizon.

Control experiment: adsorption of PAs or AAs on OM-coated minerals

Phenolic acids. The adsorption of PAs on pure minerals followed the order goethite ≫ kaolinite > montmorillonite in slightly acidic conditions (Figure S2a). This significant effect of minerals on adsorption was consistent for all concentrations ($P < 0.001$;

Table S8, Supporting Information). The adsorption of PAs on minerals was suppressed by the OM coating irrespective of the mineral and type of DOM (Figure 2a,b). For both types of DOM, the suppressing effect increased with increasing adsorption of DOM. The largest reduction was on goethite, which had the largest OM loading (Figure 2a,b). Consequently, the adsorption of PAs on the O-DOM-coated minerals followed the order montmorillonite > kaolinite > goethite (Figure S2c). No adsorption was observed on O-goethite and the differences between O-kaolinite and O-montmorillonite were significant for all concentrations ($P < 0.001$; Table S9, Supporting Information). That means the order of adsorption of PAs was reversed completely by O-DOM coatings compared with pure minerals. By comparison with L-DOM, O-DOM suppressed the adsorption of PAs to a larger extent, except for coated montmorillonite where both types of DOM had a similar effect (Figure 2a,b). Coatings of goethite with O-DOM were so large that it suppressed adsorption of all PAs completely. For the other minerals, Sal was the only adsorbed PA on their O-DOM-coated forms, and the other PAs (Syr, Fer and Van) were blocked completely by the O-DOM coating. Desorption of adsorbed PAs from OM-coated minerals was larger than that from pure minerals (Gao *et al.*, 2017) and larger from minerals coated with L-DOM than O-DOM (Table S5).

Amino acids. On pure minerals, adsorption of AAs generally followed the order montmorillonite ≥ kaolinite > goethite for the intermediate and large initial concentrations (Figure S3a). The differences were all significant ($P < 0.05$) except for that between kaolinite and montmorillonite at the intermediate concentration. Among the different AAs, goethite adsorbed only Glu, whereas montmorillonite adsorbed only Lys (Gao *et al.,* 2017). Both Glu and Lys were adsorbed on kaolinite, but with a dominant role for Lys (Figure S9, Supporting Information). No adsorption of Leu and Phe was observed on kaolinite. The adsorption of AAs responded very differently to the OM coatings compared with PAs. If effects occurred, they were mostly positive (i.e. increasing adsorption of AAs by OM coatings) (Figure 2c,d). Adsorption of AAs on L-goethite and L-montmorillonite increased by 56–145 and 24–40%, respectively, for different initial concentrations. All the differences were significant ($P < 0.05$) except for goethite at the small initial concentration (Figure 2c). Specifically, Lys, Leu and Phe, which did not show adsorption on pure goethite, were adsorbed on L-goethite in addition to Glu (Figure S10a, Supporting Information). Minor differences were observed between the adsorption of Glu on pure goethite and L-goethite (Figure S11a, Supporting Information). The adsorption of Lys on L-kaolinite increased significantly by 18–36% for different initial concentrations ($P < 0.05$; Figure S12a, Supporting Information), although the sum of various AAs did not change. Conversely, the adsorption of Glu on L-kaolinite decreased significantly by 74 or 60% for the small or intermediate initial concentration, respectively ($P < 0.05$), and it was entirely suppressed for the large initial concentration (Figure S11b).

Coating goethite with O-DOM did reduce the adsorption of AAs (Figure 2d) and changed the type of adsorbed AA (i.e. Glu was replaced by Lys). Nevertheless, the adsorption of Lys on O-goethite ($0.10–0.96\,\mu mol\,g^{-1}$) was much less than that on O-kaolinite ($0.57–3.29\,\mu mol\,g^{-1}$) and O-montmorillonite ($0.71–5.74\,\mu mol\,g^{-1}$). Similar to goethite, the coating of kaolinite with O-DOM entirely suppressed adsorption of Glu and increased concurrent adsorption of Lys (by 24–54%), resulting in no change in total adsorption of AAs on O-kaolinite (Figure 2d). Moreover, the adsorption of Lys, the only adsorbed AA on both pure montmorillonite and O-montmorillonite, increased significantly by 24–44% on O-montmorillonite ($P < 0.05$; Figure S12b).

In contrast to PAs, the presence of OM coatings reduced desorption of AAs from minerals. Percentages of desorbed AAs from OM-coated minerals were even smaller than those of PAs (Table S5).

Competition experiment: adsorption of PAs and AAs on OM-coated minerals

Phenolic acids. Competition with AAs was minor and resulted mainly in a slightly decreased adsorption of PAs on OM-coated minerals ($< 0.32\,\mu mol\,g^{-1}$; Figure 3a,b). Salicylic acid was the only adsorbed PA. There was a tendency for increased adsorption of PAs on O-kaolinite (significant for the intermediate and large initial concentrations, $P < 0.05$) compared with the situation without AAs (Figure 3b).

Amino acids. The presence of PAs resulted in significantly decreased adsorption of AAs on all L-DOM-coated minerals ($P < 0.05$; Figure 3c). Glutamic acid was the only adsorbed AA on L-goethite, and Lys the only adsorbed AA on L-kaolinite and L-montmorillonite under competition with PAs. The strongest reduction in adsorption was for L-goethite, with a decrease of 66–76% ($0.40–2.24\,\mu mol\,g^{-1}$; Figure 3c).

The adsorption of AAs on O-goethite increased significantly by 130% ($0.95\,\mu mol\,g^{-1}$) or 556% ($2.58\,\mu mol\,g^{-1}$) for the intermediate or large initial concentration ($P < 0.05$; Figure 3d). Little change ($0.02\,\mu mol\,g^{-1}$) was observed for the small initial concentration. Both Glu and Lys were adsorbed on O-goethite and O-kaolinite, whereas only Lys was adsorbed on O-montmorillonite under competition with PAs. There were no consistent effects on the adsorption of AAs on O-kaolinite. However, adsorption of Glu became detectable ($0.02–0.41\,\mu mol\,g^{-1}$) in addition to Lys. Competition resulted in reduced adsorption of AAs on O-montmorillonite by 9–30% ($0.21–0.54\,\mu mol\,g^{-1}$) for different initial concentrations ($P < 0.05$, Figure 3d).

Conditioning experiment I: adsorption of PAs on OM-coated minerals after adsorption of AAs

Surface conditioning by AAs on OM-coated minerals resulted mainly in significantly increased adsorption of PAs ($P < 0.05$; Figure 4a,b). A large effect was observed for L-montmorillonite (increase of 25–86%) and little change was obtained for both
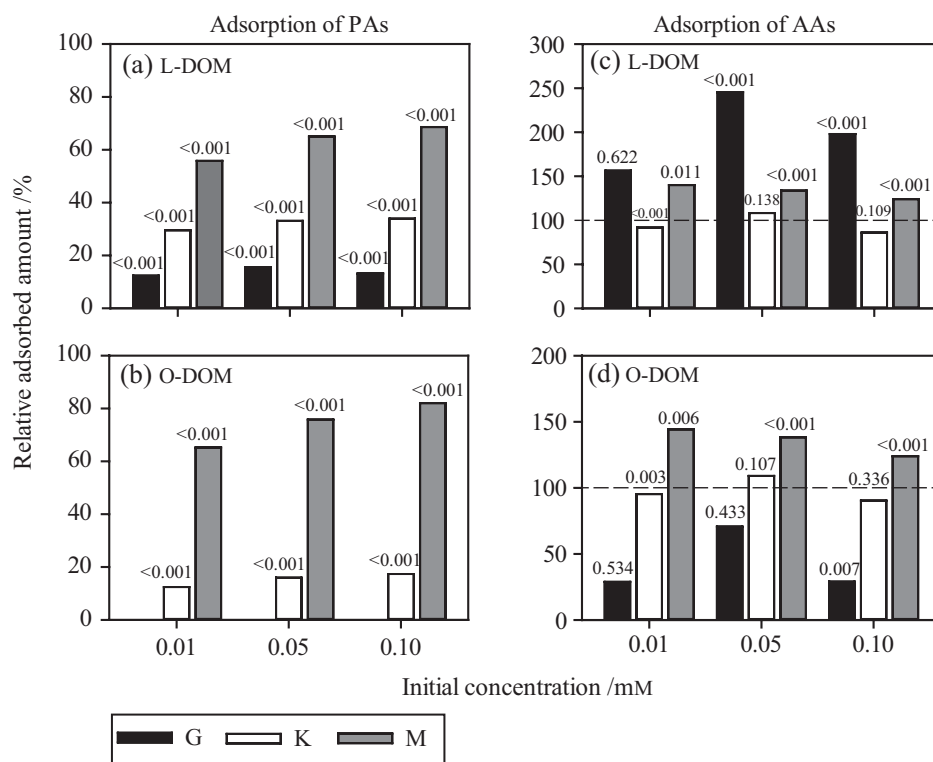
Figure 2 Relative adsorption of: (a) PAs on coated minerals with L-DOM, (b) PAs on coated minerals with O-DOM, (c) AAs on coated minerals with L-DOM and (d) AAs on coated minerals with O-DOM in the control experiment. Dotted lines in (c) and (d) refer to the reference values (absolute adsorption results on pure minerals). The results are mean values ($n = 3$). P values above each column are from the analysis of variance of the absolute adsorption results; they indicate the significance of the difference from the corresponding reference (i.e. the adsorption results on pure minerals). G, goethite; K, kaolinite; M, montmorillonite. PAs, phenolic acids; L-DOM, organic matter obtained from forest leaf litter; O-DOM goethite coated with dissolved organic matter obtained from the O horizon; AAs, amino acids.

L-goethite and L-kaolinite ($< 0.13 \, \mu mol \, g^{-1}$). Surface conditioning by AAs on O-goethite resulted in an increased adsorption of PAs from 0 to $0.20-1.22 \, \mu mol \, g^{-1}$ at different initial concentrations (Figure S13, Supporting Information), and for both O-montmorillonite and O-kaolinite the adsorption of PAs increased significantly by 24–70% ($P < 0.05$; Figure 4b). Salicylic acid was the only adsorbed PA on L-goethite, L-kaolinite and O-kaolinite, regardless of whether surface conditioning of AAs took place or not. Even though little adsorption of Syr, Fer and Van was observed for L- and O-montmorillonite following surface conditioning, Sal still dominated the adsorption of PAs.

Conditioning experiment II: adsorption of AAs on OM-coated minerals after adsorption of PAs

In general, surface conditioning by PAs on OM-coated minerals did not result in significant changes in the adsorption of AAs (Figure 4c,d). The large relative increase in adsorbed AAs on O-goethite at the small initial concentration was very small in absolute terms ($0.2 \, \mu mol \, g^{-1}$). Lysine remained the predominantly adsorbed AA on OM-coated kaolinite and montmorillonite after adsorption of PAs.

Discussion

Adsorption of natural DOM on pure minerals

The stronger adsorption of DOM on goethite than kaolinite and montmorillonite (Figure 1) corroborated the results of Mikutta *et al.* (2007) and Meier *et al.* (1999). This related mainly to the positive charge of the goethite, whereas kaolinite and montmorillonite are negatively charged (Table 1). The more negative ζ potential with DOM adsorption illustrates the predominant negative charge provided by both types of DOM. The positively charged functional groups of DOM enable binding to negatively charged sites. However, these compounds are a minority group in natural DOM solution (Kalbitz *et al.*, 2003). The stronger adsorption of DOM on kaolinite than on montmorillonite could be attributed to the larger pore volume and size (Mikutta *et al.*, 2014). A consistent increase in equilibrium solution pH after DOM adsorption (Figure S7) suggests ligand exchange of DOM with hydroxyl groups of the mineral surface as an important binding mechanism (Chorover & Amistadi, 2001; Polubesova *et al.*, 2008). Moreover, the large uncharged and less hydrophilic regions on kaolinite surfaces can attract strongly hydrophobic moieties of DOM (Sposito, 2008).

The greater adsorption of O-DOM on goethite than L-DOM (Figure 1 and Table S7) could be attributed to the larger content
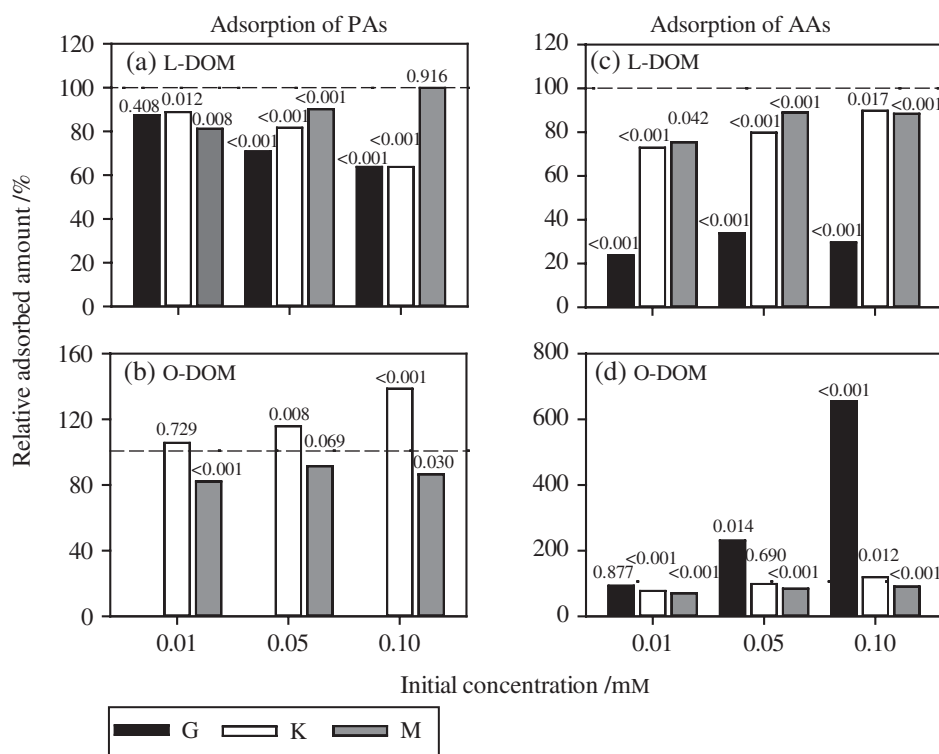
Figure 3 Effects of competition on the adsorption of: (a) PAs on coated minerals with L-DOM, (b) PAs on coated minerals with O-DOM, (c) AAs on coated minerals with L-DOM and (d) AAs on coated minerals with O-DOM. Dotted lines refer to the reference values (control experiments). The results are mean values ($n = 3$). *P* values above each column are from the analysis of variance of the absolute adsorption results; they indicate the significance of the difference from the corresponding reference (i.e. the adsorbed amount of PAs or AAs in the control experiments). The adsorption of PAs on O-goethite (b) is not displayed because the values of the reference were zero. G, goethite; K, kaolinite; M, montmorillonite; PAs, phenolic acids; L-DOM, organic matter obtained from forest leaf litter; O-DOM goethite coated with dissolved organic matter obtained from the O horizon; AAs, amino acids.

of aromatic compounds in O-DOM (Kalbitz *et al.*, 2003). This was confirmed by the measured UV absorbance (Figure S6). Moreover, dissolved OM from the O horizon is more strongly oxidized, has a smaller pH value and has larger negative charges than that from leaf litter. Many studies have shown the preferential adsorption of aromatic compounds on mineral surfaces (Kaiser & Guggenberger, 2000; Kalbitz *et al.*, 2005). Our results, however, do not confirm this for the adsorption of O-DOM on goethite and kaolinite (Figure S6). Aliphatic and nitrogenous components might also be adsorbed preferentially (Aufdenkampe *et al.*, 2001; Wang & Xing, 2005).

Effects of OM coatings on the adsorption of PAs and AAs on minerals

The reversed surface charge of goethite from positive to negative and increased negative charge of the phyllosilicates after coating with OM (Table 1) can explain the reduced adsorption of PAs by enhancing repulsion effects. This is supported because both the strongest changes in surface charge coincided with the largest decrease in PA adsorption (goethite) and O-DOM had a stronger effect than L-DOM (Table 1, Figure 2a,b). This combination led to complete suppression of PA adsorption on O-goethite (Figure 2b). This was unexpected because the OM loading of the mineral

surface was about 50% of the adsorption capacity (Table 1). The most likely explanation is that when DOM molecules are adsorbed, the hydrophilic portions associate directly with the mineral surface and hydrophobic portions are exposed outwards (Kleber *et al.*, 2007). This would create organo–mineral surfaces with strong hydrophobicity, thus preventing adsorption of polar organic compounds. These results suggest that the overall charge characteristics are more important for adsorption of PAs than the theoretical number of adsorption sites.

Our results probably indicate that PAs were still primarily attached to the adsorption sites of the mineral surface not yet occupied by DOM, but the bonds were weaker, as indicated by a larger desorption than for pure minerals (Gao *et al.*, 2017 and Table S5). The association of PAs with adsorbed OM might occur through polar-π interactions (Keiluweit & Kleber, 2009), but its contribution should be negligible. Therefore, metal (hydr)oxides play a dominant role in the adsorption of PAs rather than organic components (Huang *et al.*, 1977; Cecchi *et al.*, 2004). Our results show clearly that OM coatings have a distinctly different effect on the adsorption of PAs from that for non-polar organic compounds, for which adsorption is enhanced by such coatings (Wang *et al.*, 2008; Polubesova *et al.*, 2009).
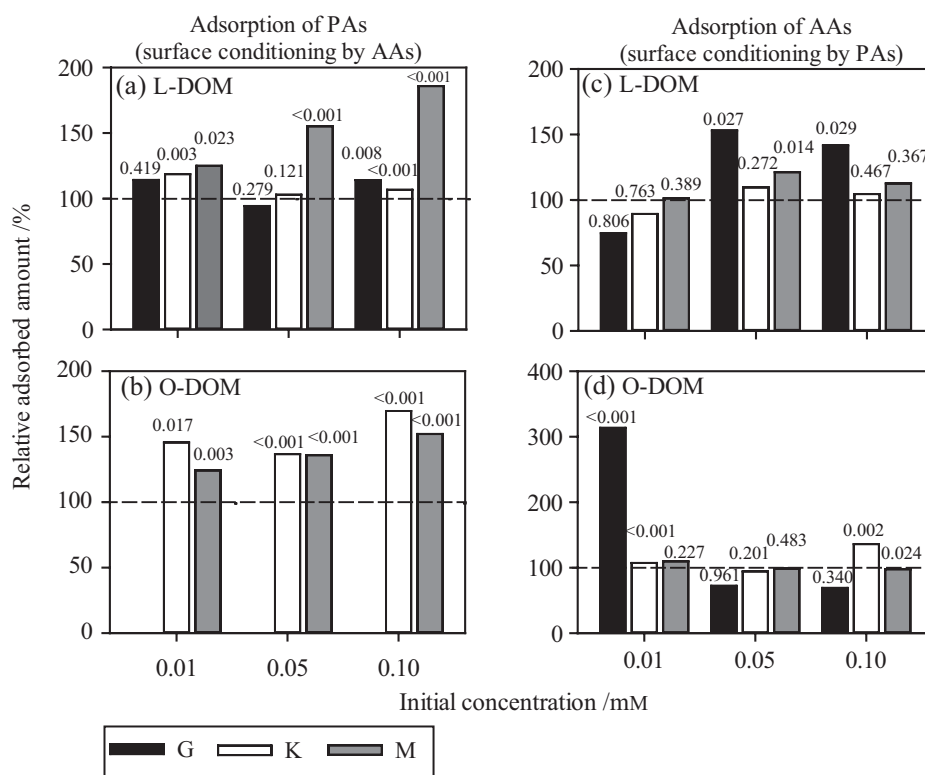
Figure 4 Effects of surface conditioning on the adsorption of: (a) PAs on coated minerals with L-DOM, (b) PAs on coated minerals with O-DOM, (c) AAs on coated minerals with L-DOM and (d) AAs on coated minerals with O-DOM. Dotted lines refer to the reference values (control experiments). The results are mean values ($n = 3$). *P* values above each column are from the analysis of variance of the absolute adsorption results; they indicate the significance of the difference from the corresponding reference. The adsorption of PAs on O-goethite (b) is not displayed because the values of the reference were zero. G, goethite; K, kaolinite; M, montmorillonite; PAs, phenolic acids; L-DOM, organic matter obtained from forest leaf litter; O-DOM goethite coated with dissolved organic matter obtained from the O horizon; AAs, amino acids.

An increase in negative charge by the OM coating can explain the increased adsorption of Lys on all minerals (Figure S12) and decreased or no adsorption of Glu on L- and O-kaolinite and O-goethite (Figure S11). The large negative charge of montmorillonite probably caused non-adsorption of Glu that was independent of adsorbed OM. The small changes in adsorption of Glu on L-goethite might be related to the small adsorption of L-DOM (Table 1 and Figure 1). Many studies also reported that natural soil and sediments have a much larger adsorption capacity for basic AAs (Lys) than acidic (Glu) and neutral ones (Henrichs & Sugai, 1993; Jones & Hodge, 1999). Mikutta *et al.* (2010) found a stronger association (larger abundance) of acidic AAs with metal–organic precipitates and minerals with variable charge obtained by separating bulk soil samples. Therefore, we propose that soil OM and negatively charged minerals contribute to the immobilization of basic AAs, whereas the retention of acidic AAs is controlled primarily by soil minerals with positive charges (i.e. metal oxides and hydroxides). This rationale would underpin the varied dynamics and patterns of distribution of PAs and AAs across soil profiles characterized by large differences in soil OM contents.

The weak desorbability of AAs bound to OM-coated minerals (Table S5) possibly hints at the formation of stable inner sphere

complexes, in particular for Lys. This mechanism needs to be verified by further research, given the relatively short time (2 hours) taken for desorption.

This study was carried out at pH 6. The observed effects would probably be even more pronounced at lower pH because of larger adsorption of DOM to mineral surfaces at acidic pH (Davis, 1982; Feng *et al.*, 2005). In contrast, increasing pH to neutral or alkaline values should result in less DOM adsorption, less positive surface charge of goethite and increased negative variable charge of kaolinite. These changes should result in less effect from OM coatings on PAs and AAs in general, whereas the adsorption of Lys should be enhanced to pure minerals until the isoelectric point of Lys (i.e. pH 9.8). When the pH is larger than 9.8, Lys becomes negatively charged and expels mineral with the same charge.

Competitive adsorption of PAs and AAs on OM-coated minerals

According to Gao *et al.* (2017), the greater competitiveness of AAs compared with PAs reduced the adsorption of PAs. This was explained by the different number of bonds between the organic acid and the mineral surface. Bidentate complexes between mineral

surfaces and Sal, which dominated the adsorbed PAs, require two adjacent adsorption sites (Yost *et al.*, 1990; Kubicki *et al.*, 1997), whereas the AAs probably need only one binding site (Kitadai *et al.*, 2009; Yang *et al.*, 2016). Taking into account the less favourable conditions for adsorption of PAs on organically coated minerals (Figure 2a,b), the slightly decreased adsorption of PAs under competitive conditions (Figure 3a,b) seems to be reasonable. Enhanced adsorption of PAs on O-kaolinite countered the decreased adsorption for PAs alone (Figure 3b). This could be attributed to surface conditioning by AAs, which promoted the adsorption of PAs (Figure 4b).

The hypothesis of greater competitiveness of AAs must be refuted based on this study. In contrast to pure minerals (Gao *et al.*, 2017), competition reduced adsorption of AAs on OM-coated minerals, except for O-goethite and O-kaolinite (Figure 3d). The reduction was larger for AAs than for PAs. It seems that coating of mineral surfaces is quantitatively more important for adsorption than competition between single molecules.

Adsorption of PAs and AAs on OM-coated minerals with conditioning by AAs and PAs

Surface conditioning by AAs generally enhanced the adsorption of PAs on all OM-coated minerals, except at some concentrations for L-goethite and L-kaolinite (Figure 4a,b). This accords with the results for pure minerals (Gao *et al.,* 2017), which indicate that N-rich organic material bound on mineral surfaces might provide more reactive binding sites for other organic compounds (e.g. PAs). The strength of the effects seems to depend on the amount of adsorbed AAs and is greater for phyllosilicates than for Fe oxides. Because PAs are negatively charged in slightly acidic conditions, the amino groups of adsorbed AAs could provide additional binding sites for PAs. This can also explain the increased adsorption of PAs (mainly Sal). Earlier we showed that Lys was adsorbed selectively on OM-coated minerals; therefore, possibly only basic AAs could perform this bridging function.

Surface conditioning by PAs generally had little effect on the adsorption of AAs on OM-coated minerals (Figure 4c,d). The larger reduction in adsorption of PAs on OM-coated minerals than for pure minerals prevented any effects of PAs on the subsequent adsorption of AAs.

Conclusions

This study has shown that the adsorption of natural DOM on soil minerals depended largely on both the charge characteristics of mineral surfaces and the composition of natural DOM. Organic matter coatings on mineral surfaces had a marked influence on the surface charge properties and on the adsorption of PAs and AAs. Coating of various kinds of mineral surfaces (goethite, kaolinite and montmorillonite) by natural DOM consistently increased their negative charges and consequently altered the adsorption of PAs and AAs, promoting adsorption of basic AAs and suppressing the PAs and acidic AAs under slightly acidic conditions. Binding sites on metal

oxides not yet occupied by OM (positive charges) were particularly important for adsorption of PAs and acidic AAs, whereas the retention of basic AAs depended strongly on the amount of negative charges of clay minerals, which can be increased further by adsorption of DOM. The binding of basic AAs such as Lys was particularly strong on OM-coated mineral surfaces. These stable bonds of adsorbed Lys on OM-coated mineral surfaces resulted in enhanced adsorption of PAs, thus providing indirect evidence for the multilayer model. Coating mineral surfaces with DOM changes the competition between different organic components and the more competitive strength of AAs disappears. The amount and composition of OM coatings on mineral surfaces were quantitatively more important for adsorption of PAs and AAs than the competition between single molecules or effects of surface conditioning by the other class of compounds. Future studies should focus on direct evidence of the formation of a multilayer structure and the functions of specific compound classes using molecular spectroscopy (e.g. infrared or X-ray photoelectron spectroscopy) and modelling approaches (molecular dynamics).

Supporting Information

The following supporting information is available in the online version of this article:

Table S1. Structure and properties of PAs and AAs.

Table S2. Range of linear regression line and coefficients of determination of the PAs.

Table S3. Accuracies (%) of the analytical methods for PAs and AAs.

Table S4. Desorption of adsorbed OC from OM-coated minerals.

Table S5. Desorption of adsorbed PAs and AAs in the conditioning experiment.

Table S6. Recovery of PAs and AAs added to the desorption solutions of OM-coated minerals.

Table S7. Langmuir parameters from the adsorption isotherms of L-DOM and O-DOM.

Table S8. Summary results of the analysis of variance (ANOVA) for the adsorption of PAs on different pure minerals.

Table S9. Summary results of ANOVA for the adsorption of PAs on coated minerals with O-DOM (kaolinite and montmorillonite).

Figure S1. The XRD patterns of (a) goethite, (b) montmorillonite and (c) kaolinite.

Figure S2. Adsorption of PAs on (a) pure minerals, (b) coated minerals with L-DOM and (c) coated minerals with O-DOM.

Figure S3. Adsorption of AAs on (a) pure minerals, (b) coated minerals with L-DOM and (c) coated minerals with O-DOM.

Figure S4. Typical chromatograms of the targeted PAs and IS (Eva) obtained from a mixed solution of PAs and AAs.

Figure S5. Typical chromatograms of the targeted AAs and IS (Nva).

Figure S6. Changes in UV absorbance (280 nm) of the equilibrium solution with reduced OC in solution for all combinations of minerals and DOM.

Figure S7. Changes in equilibrium solution pH with reduced OC in the solution for all combinations of minerals and DOM.

Figure S8. Relation between the increased C content of all OM-coated minerals and the changes in ζ potential.

Figure S9. Adsorption of Glu and Lys on kaolinite.

Figure S10. Adsorption of individual AAs on (a) L-goethite and (b) L-goethite with preconditioning by PAs.

Figure S11. Adsorption of Glu on (a) pure and coated goethite and (b) pure and coated kaolinite.

Figure S12. Relative adsorption of Lys on (a) coated minerals with L-DOM and (b) coated minerals with O-DOM.

Figure S13. Adsorption of PAs on O-goethite (OG) and after preconditioning by AAs (OG-AAs).

Acknowledgements

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