Sorption-desorption behaviour of low molecular weight organic compounds on common soil minerals

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Abstract
Batch experiments were conducted to evaluate the sorption-desorption behaviour of ^{14}C-labelled carboxylic acids (oxalic and citric) and amino acids (glutamic acid, lysine, alanine and phenylalanine) on phyllosilicates (kaolinite, illite and montmorillonite) and Fe oxides (ferrihydrite and goethite). Sorption data fitted well with the non-linear Freundlich equation. Carboxylic and glutamic acid sorption was relatively higher on both types of minerals compared to other compounds (except basic lysine), indicating the significance of the carboxylic acid groups in OC sorption processes. Cationic lysine showed a stronger affinity to phyllosilicates than Fe oxides. Though the sorption of aliphatic alanine and aromatic phenylalanine was consistently low for all minerals, comparatively higher sorption of phenylalanine was observed. Overall, Fe oxides were more potent sorbents for carboxylic acids and amino acids than phyllosilicates. These differences are possibly mediated by the mineral properties (surface charge and specific surface area) and chemistry of the organic compounds along with the pH of the experimental system.

Key words: sorption, desorption, carboxylic acid, amino acids, clay minerals, iron oxides.

Introduction
Sorption is an important process that influences the fate, concentration, and bioavailability of low molecular weight (LMW) organic substances (e.g. amino acids, carbohydrates and carboxylic acids) in soil and soil solution (Hu et al., 2001). Generally, organic carbon (OC) compounds decompose more slowly and to a lesser extent than the free species when they are sorbed to mineral surfaces (Jones and Edwards, 1998). About 85% sorption of root-derived citric acid has been found on Fe oxide, imparting almost complete protection from microbial decomposition (Jones and Edwards, 1998). Jones and Brassington (1998) and van Hees et al. (2003) also reported 50-95% sorption of added LMW carboxylic acids and about 10% of amino acids to the solid phase. There is an increasing body of evidence that mineral-organic matter association, especially sorption of organic carbon on minerals, is a major potential process for OC preservation in soils (Guggenberger and Kaiser, 2003) and this process is influenced by both the properties of soil minerals and OC sorbate.

Clays, including layer and amorphous aluminosilicates, and sesquioxides, provide the major fraction of surface area in soils for the sorption of OC (Kaiser et al., 1996). The chemical (surface chemistry) and physical properties (specific surface area and porosity) of a mineral control organic matter-mineral interaction. Generally, non-expanding layer silicates are poor OC sorbents compared to the Al and Fe oxides/hydroxides (Kaiser and Zech, 2000). Minerals with different surface properties have particular affinities for specific functional moieties of OC (Kubicki et al., 1999).

The chemistry of OC (including pKa values, functional groups, aromaticities, hydrophobicity and molecular size) also has a strong influence in regulating the extent and stability of OC sorption. Certain OCs show a strong affinity for certain mineral surfaces, for example components rich in aromatic structures are generally hydrophobic and are sorbed more strongly than the hydrophilic LMW aliphatic compounds (Kaiser et al., 1996). In addition to the properties of the soil and OC, soil solution chemistry, including pH, solution composition and ionic strength, is an important factor for soil organo-mineral interactions.

Therefore, knowing the mineral-specific sorption patterns of definite organic compound group is must to understand the stabilisation of organic matter at mineral surface. Some studies have attempted to link soil mineralogy and chemical properties of OC to the sorption characteristics of OC; however a majority of the studies have dealt with a limited number of sorbates and/or sorbents. On the other hand, due to the inherent

complexities of natural OC properties it is crucial to evaluate the sorption-desorption behaviour of model compounds on different minerals that are likely to occur in natural soil systems. Thus, the overall objective of this study was to test the hypothesis that sorption-desorption behaviour of OC on soil minerals is influenced by mineralogy and OC chemistry.

Materials and Methods
Organic carbon compounds and minerals:
Six ^{14}C-labelled synthetic model OC compounds (organic acids: oxalic and citric acid; amino acids: L-glutamic acid, L-lysine, L-alanine and L-phenylalanine) were used as sorbates in this experiment. Five sorbents: kaolinite (KGa-2), illite (IMt-2), montmorillonite (SWy-2), goethite and ferrihydrite were chosen. Phyllosilicates were obtained from the Source Clays Repository of the Clay Minerals Society. Goethite and ferrihydrite were synthesized in the laboratory based on the procedure outlined by Atkinson et al. (1967) and Schwertmann and Cornell (2000), respectively. All minerals were oven dried at 40°C, ground, passed through a 0.63 mm sieve and characterized by powder X-ray diffraction analysis.

Sorption experiments
Batch experiments were carried out in triplicate in 1.5 ml Eppendorf tubes. One ml of ^{14}C-labelled solution (in a background electrolyte of 0.01M NaN_3 to prevent microbial activity) from different concentrations (ranging from 10-1000 $\mu mol\ L^{-1}$) was added to 20 mg of each of the clay minerals. The tubes were mechanically shaken in an end over end shaker at room temperature for four hours, which was sufficient time to reach an apparent equilibrium (according to preliminary kinetics results). The equilibrium mixtures were then centrifuged at 14,000 rpm for five minutes and pH was measured. The supernatant was collected and radioactivity was measured by using a liquid scintillation counter (Tri-Carb 3110TR PerkinElmer) using OptiPhase HiSafe3 scintillation cocktail. In the case of montmorillonite unlabelled compounds were used and same experimental steps have been taken except for using a high solid: solution ratio and a TOC analyser to quantify OC samples.

Desorption experiments
The reversibility of organic compounds was determined using a single-step desorption. Desorption was determined immediately after sorption by replacing all the added labelled solution with 1 ml fresh 0.01 M NaN_3. Then the tubes were shaken overnight, centrifuged and the supernatant was analysed the same as in the sorption experiment.

Following batch equilibrations, sorption isotherms were generated using the Freundlich isotherm equation:
$$X = kC^n$$
where X is the amount sorbed ($\mu moles\ g^{-1}$), C is the equilibrium concentration ($\mu mol\ L^{-1}$) and k and n are the Freundlich coefficients. Sorption data were fitted to the nonlinear Freundlich equation using a computer program R.

Results
The sorption isotherms of all OC compounds are shown in Figure 1 and Freundlich coefficients are given in Table 1. Freundlich equation fitted the sorption data well for all OC compounds with high correlation coefficients (0.94-1.00).The equilibrium solution pH for all OC-mineral systems (except illite) varied between 5.5 and 7.4. In case of illite the equilibrium solution pH was much higher with a value from 5.8 to 8.8.

The amount of carboxylic acids (oxalic and citric) sorbed on Fe oxides was greater than on the phyllosilicates, which was also designated by higher value of the Freundlich constant k (Table 1). The value of k suggests the number of sorbent sites on clay mineral and other surfaces that contribute to OC sorption (Singh and Gilkes, 1990). It also shows the relative sorption capacity of the sorbent, i.e. the higher the sorption site greater the sorption. The sorption capacity for carboxylic acid was in the sequence ferrihydrite > goethite > kaolinite > montmorillonite > illite, and in all cases k values for citric acid sorption were comparatively higher than oxalic acid, especially for Fe oxides. The value of the Freundlich constant n for carboxylic acids ranged from 0.4 to 1.0. A value of n close to unity represents a linear isotherm, which indicates that the number of active sites remains constant up to saturation of sorption sites (Giles et al., 1974). After a one step desorption (data not shown), Fe oxides retained almost all of the initially sorbed oxalic and citric acids (85-100%), indicating strong fixation of carboxylic acid. However among

phyllosilicates, kaolinite was more effective in retaining carboxylic acids (77-98%) than illite and montmorillonite, which retained on an average of 46-82%.
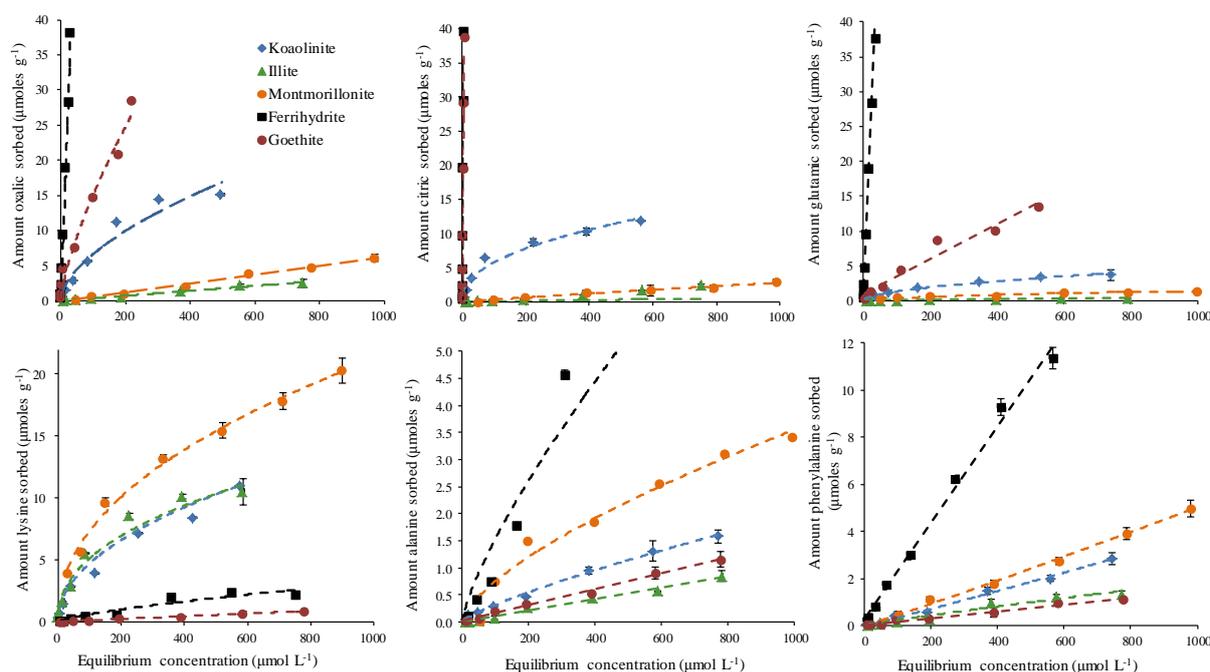

Figure 1. Sorption isotherms of oxalic, citric, glutamic, lysine, alanine and phenylalanine on clay minerals. Symbols denote experimental points (mean±S.E., *n*=3) while dotted lines represent Freundlich isotherm fitted data.

Among the amino acids, glutamic acid sorption followed the sorption pattern of the carboxylic acids at an equilibrium pH of 5.6-8.4. After desorption, about 52-98 and 22-48% of glutamic acid was retained by Fe oxides and phyllosilicates, respectively. Sorption of lysine on phyllosilicates (montmorillonite > illite > kaolinite) was higher than on Fe oxides at equilibrium pH (6.1-7.0). The Freundlich n value was lower than unity (0.43-0.71) for all sorbent-lysine combinations. Initially sorbed lysine was retained about 41-98% by phyllosilicates and 13-50% by Fe oxides after desorption. Low sorption of alanine and phenylalanine to all clay minerals was represented by the lower k values (Table 1). In most cases, less than half of the sorbed alanine was retained by the sorbents. Phenylalanine retention capacity on phyllosilicates was comparatively higher (33-81%) than on Fe oxides (16-51%).

Table 1. Freundlich sorption parameters and coefficient of determination (R^2) for each combination of mineral and organic carbon compounds.

Minerals	Oxalic			Citric			Glutamic			Lysine			Alanine			Phenylalanine		
	k	n	R^2	k	n	R^2	k	n	R^2	k	n	R^2	k	n	R^2	k	n	R^2
Kaolinite	0.46	0.58	0.96	0.78	0.44	0.94	0.11	0.54	0.96	0.26	0.59	0.97	0.01	0.80	0.99	2.51^{-3}	1.04	1.00
Illite	3.05^{-3}	1.00	0.99	5.78^{-4}	0.98	0.99	5.87^{-4}	0.98	1.00	0.70	0.43	0.92	1.19^{-3}	0.98	1.00	3.48^{-3}	0.91	1.00
Montmorillonite	3.07^{-3}	1.01	1.00	4.61^{-3}	0.93	1.00	0.04	0.53	0.98	0.88	0.46	0.96	0.03	0.67	0.99	3.36^{-3}	1.04	1.00
Ferrihydrite	1.02	1.03	1.00	17.01	1.02	1.00	2.23	0.79	0.99	0.02	0.71	0.99	0.05	0.77	0.99	0.04	0.90	1.00
Goethite	0.55	0.72	0.99	9.57	0.76	0.99	0.16	0.70	0.99	1.58^{-3}	0.95	0.99	1.99^{-3}	0.96	1.00	3.04^{-3}	0.89	1.00

Discussion

The charge properties of carboxylic acids and the sorbent surface at equilibrium pH could explain their sorption pattern on clay minerals. Within the range of equilibrium pH carboxylic acids are fully dissociated and exist in deprotonated states, while Fe oxides carry a net positive charge and phyllosilicates have predominately negative charge on their surface. The opposite charge between Fe oxides and oxalic and citric acids induces electrostatic attraction between the sorbent and sorbate. Though possessing negative charge, phyllosilicates, especially kaolinite possibly have some positive charge on their edge sites where sorption of anionic carboxylic acids may have occurred. Higher citrate sorption capacity could be explained by a greater number (three) of dissociable carboxyl ligands of citric acid, which give a possibility of three negative

charges in the system. The strong affinity of citric to Fe oxides has also been indicated by Bowden et al. (1980). Within Fe oxides, ferrihydrite sorbed comparatively more than goethite, possibly due to its high specific surface area and poor crystallinity that provide more sorption sites for OC sorption. Illite shows the lowest affinity towards carboxylic acids, which could be explained by highest pH along with its surface charge properties (Lackovic et al., 2003). The sorption of anions normally decreases with increasing pH as it relates to the dissociation constant of the organic anions involved (Jones and Brassington, 1998). Differences in the Freundlich constant n value may be caused by different sorbent properties. Retention of sorbed acids after desorption varied between and within sorbent groups, which might be related to the sorption mechanism. Some past studies have suggested that oxalic and citric acids sorption to mineral surfaces was primarily through formation of inner-sphere (a direct bond between carboxylate and a surface metal ion) or outer-sphere surface (attraction between the positively charged surface and the negatively charged carboxylate) complexes (Persson and Axe, 2005). Generally, inner surface complexes are more protected from microbial degradation than outer surface complexes.

In comparison with carboxylic acids, the amount and pattern of amino acid sorption was different for both phyllosilicates and Fe oxides, with the exception of glutamic acid. The solution pH enhanced glutamic acid sorption since there were two deprotonated carboxylic and one protonated amino groups. Relatively higher sorption of this amino acid might be described by the higher affinity of anionic carboxylic groups towards positively charged Fe oxides and attraction of positively charged amino group to the negatively charged phyllosilicates. Greater sorption of carboxylic and glutamic acids might indicate the importance of carboxylic acid groups in OC sorption. In case of lysine, higher sorption and retention after desorption on phyllosilicates (montmorillonite > illite > kaolinite) was expected. At experimental pH levels, there was a strong possibility of having predominantly cationic lysine which would enhance sorption on phyllosilicates. Montmorillonite with greater layer charge and specific surface area sorbed more lysine than illite and kaolinite. This sorption was primarily driven by electrostatic interactions with negatively charged mineral surface and may be supplemented by hydrophobic interaction in case of zwitterionic lysine (Kitadai et al., 2009). Though, the sorption of both alanine and phenylalanine was relatively small on all sorbents, phenylalanine sorption and retention percentages were slightly higher than alanine. The equilibrium pH was higher than isoelectric point (pI) (6.02 and 5.48 for alanine and phenylalanine) in both cases, which can be one of the reasons for the overall low sorption. Maximum sorption of a protein on solid matrix near to pI and lower sorption under a higher/lower pH was reported (Li and Lu, 2006). However, comparatively high sorption of phenylalanine could be favoured by its aromatic side chain, while alanine has an aliphatic structure with a non-polar side chain (Kaiser et al., 1996).

Conclusions

Sorption and desorption of oxalic, citric, glutamic, lysine, alanine and phenylalanine were influenced by the chemical and physical properties of the minerals and chemistry of these compounds. The results of such experiments will allow an understanding of the effects of mineralogical and chemical factors that affect soil organic matter sorption under field conditions. In addition, it is necessary to study the sorption mechanisms, which could explain more details about sorption-desorption behaviour of these organic compounds.

Acknowledgements

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Notes