

Sorptive protection of organic matter in soil

Preeti Roychand^A, Michael Angove^B and Judy Tisdall^A

^AFaculty of Sci Eng and Tech, La Trobe University, Bundoora, 3086, Australia, Email p8sharma@student.latrobe.edu.au

^BFaculty of Sci, Eng and Tech, La Trobe University, Bendigo, 3550, Australia, Email M.Angove@latrobe.edu.au

Abstract

Soils are a significant sink for organic carbon, which can be protected from chemical and biological change, and hence conversion into greenhouse gases, such as CO₂ and CH₄. In order to mitigate global climate change, and improve soil quality, the chemical mechanisms behind the long-term protection of organic matter must be understood, and strategies developed to improve this protection. Organic matter can be stabilised and protected in soil by a range of mechanisms, especially sorption. Sorption of organic matter to the surface of clay minerals via strong multiple complex bonds prevents hydrolytic enzymes approaching and decomposing the organic matter. We used clay minerals to study the sorption processes between organic matter and mineral phases, hence protection of the organic matter, that typically occur in soils. Initial results from sorption experiments show that humic acid was adsorbed more strongly to goethite than with kaolinite or montmorillonite. For all three mineral phases sorption was pH-dependent, with maximum sorption occurring at lower pH. XRD analysis in montmorillonite systems show that the sorbed humic acid decreased the 'd' spacing of the 2:1 clay.

Key Words

Preservation, organic compounds, bonding.

Introduction

A huge volume of organic carbon comes from anthropogenic sources, for example, from waste disposal, such as effluents from wastewater treatment, or biosolids used as crop manure. Storage of this organic carbon in soil is desirable in order to prevent rapid conversion to greenhouse gases; the organic matter could also add valuable plant nutrients to the soil. The extent to which a soil can store and protect carbon depends on the a) physicochemical properties of the organic matter, b) the nature of the minerals in soil, and c) on soil properties, such as pH, salinity and presence of natural organic matter. Colloidal clays and minerals abound in soils, and, through various processes, including sorption, can act as an ecological barrier for immobilization and protection of organic carbon. The organic matter can be adsorbed onto mineral phases by several different mechanisms.

Ion exchange

Organic ions can be adsorbed via ion-exchange mechanisms. For example, the exchangeable cations on the surface of clay minerals may be replaced by organic cations. Cation exchange is involved in the sorption of various aminated benzenes by montmorillonite. Anionic organics may be adsorbed via interaction with amphoteric Al-OH groups of clays and soil minerals at low pH when these functional groups carry a net positive charge.

Hydrogen bonding

Hydrogen bonding can occur between surface hydroxyl groups and hydrogen or electronegative atoms of sorbing molecules. For example, polar functional groups on hydrophobic compounds can enhance sorption with inorganic surfaces through non-hydrophobic bonding, including hydrogen bonding (Boily *et al.* 2000). Pyridine forms strong hydrogen bonds with water molecules coordinated with interlayer cations in montmorillonite (Kubicki *et al.* 1999).

Intercalation into the interlayer region of expanding clays

Organic molecules may intercalate between the layers of expanding clays (Schnitzer 1987), and thereby help to increase sorption of non-ionic hydrophobic organic compounds (Spark *et al.* 1997). Such sorption of organic molecules by expanding clays such as montmorillonite, can involve interaction with external surface sites and/or the interlayer regions. For example, Schnitzer and Kodama (1966) proposed that the sorption of some pyridine derivatives involves sites on the external surfaces, as well as those between layers of montmorillonite (Schnitzer and Kodama 1966). Intercalation may involve several pathways, including a)

cation exchange (Chen *et al.* 1987), b) dipole-dipole attractions, whereby organic molecules replace interlayer water molecules, or c) interaction with interlayer water molecules, via hydrogen bonding (Kubicki *et al.* 1999). When organic molecules penetrate the interlayers of expanding clays, the basal spacing of the clay is often increased (Chen *et al.* 1987), decreased, or remains unchanged. X-ray Diffraction studies can provide information about the extent of the change in basal spacing, and thereby provide conclusive evidence for intercalation.

Hydrophobic interactions

Sorption of hydrophobic compounds can also occur through interaction with the more hydrophobic surfaces of mineral particles. The siloxane face of the clay mineral, for example, is more hydrophobic than are hydroxyl surfaces, and therefore the siloxane face interacts more readily with hydrophobic compounds. The sorption of hydrophobic compounds can depend on physicochemical properties, such as the hydrophobicity; a character that can be represented by the octanol-water partition coefficient (K_{ow} value). For example, sorption of some neutral hydrophobic compounds is directly correlated with their K_{ow} (Zhang *et al.* 1991)

Methods

The clay samples came from the Clay Minerals Society Source Clays Repository : a) Na-Montmorillonite (Wyoming) SWy-2 from Wyoming, USA, and b) Kaolin KGa-2 from Warren County, Georgia, USA. The surface areas (nitrogen adsorption) and cation exchange capacities (provided by the Clay Minerals Society) of these clay minerals were 31.8 m²/g and 76.4 cmol/kg respectively for SWy-2, and 23.5 m²/g, and 2.0 cmol/kg respectively for KGa-2.

Goethite was prepared by the modified method of Boily *et al.* (2000). Polycarbonate apparatus was used throughout to prevent silica contamination. To about 1.2 L of 1 M Fe(NO₃)₃, (prepared from boiled milli-Q water), 5 M carbonate-free NaOH was added dropwise, under an atmosphere of N₂, until the pH was 12.5. The dark brown precipitate was aged at 60 °C for 2 weeks. The suspension was then dialyzed against Milli-Q water under an atmosphere of N₂, with the water changed twice daily until the conductivity was less than 1.0 µS, after which the suspension was frozen before being freeze-dried.

Humic acid was purified from the sodium salt by a method similar to that of Susic and Boto (1989). Sodium humate was mixed with Milli-Q water, and the pH adjusted to about 10 by the addition of 25% aqueous NH₄OH. The mixture was centrifuged at 16 000 g for 10 min, and then concentrated HCl was added to precipitate the humic acid from the supernatant. The precipitate was collected by vacuum filtration (Whatman #1 filter paper), air-dried at 25 °C for 24 h, and oven-dried (80 °C) for 48 h.

Humic acid used in the experiments was added from a 5.0 g/L stock solution, prepared by dissolution of purified humic acid standard in water. Dissolution was assisted by the addition of a few drops of NH₄OH.

Measurement of pH

Great care was taken to ensure accurate measurement of pH in all experiments. Metrohm 691 pH meters with Orion Ross 'Sure Flow' and/or Metrohm combined pH-glass microelectrodes were used to measure pH. Before each experiment, the electrodes were calibrated at 25 ± 0.05 °C, with freshly-prepared NBS standard buffers at pH 4.01 and 6.86. The electrode calibration was checked at the end of each experiment to ensure that there had been no significant drift in the calibration during the experiment. Results were discarded if the re-calibration were outside 0.05 pH units. The pH electrodes were regularly checked and cleaned, according to manufacturer specifications.

Humic acid determination

Humic acid was determined by a method similar to that used by Susic and Boto (1989), by a Shimadzu HPLC system (SCL-10AVP) with fluorescence detection (RF-10AXL) at an excitation wavelength of 340 nm and an emission wavelength of 455 nm. The mobile phase was about 0.003% ammonium hydroxide at pH 10, at a flow rate of 1.0 mL/min. A 150 x 4.6-mm I.D., 4 µm Synergy Fusion Reverse column (Phenomenex, Australia) (protected by a guard column with matching stationary phase material) was used for separation of humic acid. A six-point linear calibration curve (0-100 mg/L) with a correlation coefficient > 0.99 was used to calculate the humic acid concentrations in samples.

Sorption experiments

Suspensions that contained sufficient substrate to give a BET surface area of 100 m²/L were prepared by an appropriate mass of solid (0.4800 ± 0.0005 g goethite, 0.9400 ± 0.0005 g montmorillonite, or 1.2800 ± 0.0005 g kaolinite) measured into 300 mL of 10 mM KNO₃. Suspensions were stirred with a magnetic stirring bar (covered with Pyrex) and equilibrated for about 20 h in a jacketed, borosilicate glass reaction vessel (maintained at 25.0 ± 0.5 °C). The suspensions were continuously purged with humidified nitrogen to eliminate carbon dioxide. Sorption experiments were conducted in triplicate. At the start of each experiment, the pH of the suspension was adjusted to the required value by the addition of 0.1 M HNO₃ or KOH, and then humic acid, to the required concentration. The suspension was periodically sampled over 48 h, and the concentration of HA determined as described above. The pH was continuously monitored, and the suspension continuously purged with nitrogen gas.

Results

Sorption experiments

The sorption of humic acid to goethite, kaolinite and montmorillonite is pH-dependent, with maximum sorption at low pH (Figure 1). This behaviour is typical for the sorption of humic and fulvic substances by mineral phases. At low pH, mineral surfaces may carry a positive charge, which can interact with a) ionized negatively-charged groups of dissolved organic matter, or b) by hydrogen bonding with –C=O from carboxylic acids. The sorption of humic acid on goethite was the highest of the three substrates. This is not surprising because the goethite surface is known to have a higher surface charge density than do phyllosilicate minerals. The point of zero charge (PZC) for the goethite sample used in this study was about 8.5, so the surface had a net positive charge below this pH. The lower sorption of the dissolved organic material observed for the clay minerals is probably because of the lower concentration of positive charged sites on their surfaces. Lower sorption of organic anions onto clays has often been observed. For example, various benzene carboxylates (simple analogues of complex humic and fulvic structures) were adsorbed significantly less to kaolinite than to goethite (Spark *et al.* 1997). The decrease in sorption at higher pH results from repulsion between the increasingly negative surface charge, and the negatively charged carboxylate groups on the humic acid.

The XRD data for the sorption of humic acid to montmorillonite (Figure 2) shows that the basal spacing of the montmorillonite decreases significantly when humic acid is present. Changes in basal spacing for swelling clays have often been used as diagnostic evidence for intercalation of solutes. However, the change in basal spacing observed with added humic acid is in the opposite direction to that expected for the intercalation of such bulky molecules. Furthermore, sorption of humic acid to montmorillonite was fully reversible, which was unexpected with the large molecules that intercalated into the clay structure. This suggests that the humic acid did not intercalate, but was rather adsorbed to the external surfaces of the montmorillonite.

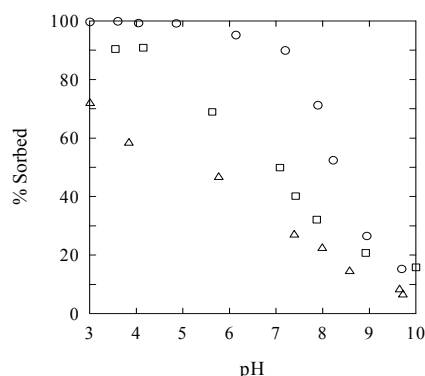


Figure 1. Sorption of humic acid at 25 °C to 100 m²/L to goethite (○), kaolinite (□) and montmorillonite (△). Initial concentration of the humic acid was 50 mg/ L. Background electrolyte 10 mM KNO₃.

Error! Objects cannot be created from editing field codes.

Figure 2. X-ray diffractograms of dried samples of montmorillonite suspensions at pH 4.5: (a) without humic acid, (b) with added humic acid; and pH 10.5: (c) without humic acid, and (d) with added humic acid.

Conclusion

Sorption is pH-dependent, with more humic acid adsorbing to the iron oxide compared with the clay minerals, probably because of the higher surface charge density on goethite compared with the clays. The sorption of humic acid to montmorillonite decreased the 'd' spacing, perhaps suggesting that intercalation was not the primary mechanism for uptake of humic acid on that clay. This may be significant, because surface-bound organic matter is generally thought to be more prone to degradation than is that which diffuses into micro porous clay structures.

References

- Beckett R (1990) Surface and Colloid Chemistry in Natural Waters and Water Treatment. (Plenum: New York).
- Boily JF, Persson P, Sjöberg S (2000) Benzene carboxylate surface complexation at the goethite/water interface *Geochim. Cosmochim. Acta* **64**, 3453–3470.
- Chen S, Low PF, Cushman JH, Roth CB (1987) Organic compound effects on swelling and flocculation of Upton montmorillonite *Soil Science Society of America Journal* **51**, 1444-1450.
- Kubicki JD, Schroeter LM, Itoh, MJ, Nguyen BN, Apitz SE (1999). Attenuated total reflectance Fourier-transform infrared spectroscopy of carboxylic acids adsorbed into mineral surfaces. *Geochim. Cosmochim. Acta* **63**, 2709–2725.
- Schnitzer M (1986) Binding of humic substances by soil mineral colloids. In 'Interactions of Soil Minerals with Natural Organics and Microbes'. pp. 77-102.
- Schnitzer M, Kodama H (1966) Montmorillonite: Effect of pH on its adsorption of a soil humic compound. *Science* **15**, 70-71.
- Spark KM, Wells JD, Johnson BB (1997) Characteristics of the sorption of humic acid by soil minerals *Australian Journal of Soil Research* **35**, 103-112.
- Susic M, Boto KG (1989) Performance liquid chromatographic determination of humic acid in environmental samples. *Journal of Chromatography* **482**, 175-187.
- Zhang Y, Gan H, Low PF (1991) Effect of sodium-humate on the rheological characteristics of montmorillonite suspensions *Soil Science Society of America Journal* **55**, 989-993.