

Ferrihydrite enhances phenanthrene sorption to artificial soils

Geertje Pronk, Katja Heister, Ingrid Kögel-Knabner

Lehrstuhl für Bodenkunde, Technische Universität München, 85350 Freising-Weihenstephan, Germany, pronk@wzw.tum.de

Abstract

In order to investigate the effect of mineral composition on the sorption of hydrophobic organic chemicals in soil, phenanthrene sorption experiments were carried out to the <20 μ m fraction of artificial soils containing illite, ferrihydrite and both minerals. The sorption isotherms of the ferrihydrite containing samples show a significant increase in linearity and K'_f with respect to the sample containing only illite. This difference could not be explained by carbon content or BET-N₂ specific surface area as these parameters were very similar for the sample containing only illite and that containing illite and ferrihydrite. These results indicate that the presence of ferrihydrite increased the sorption capacity of the artificial soils. This could be due to sorption of phenanthrene to the ferrihydrite itself, but it is more probable that the presence of ferrihydrite changes the properties of the biogeochemical interfaces in the soil, thereby increasing the sorption capacity.

Key Words

Biogeochemical interfaces, sorption isotherm, K_{oc} , specific surface area, PAH

Introduction

The structure and properties of biogeochemical interfaces are an important factor controlling the fate and behaviour of organic chemicals in soil (Totsche *et al.* 2010). Recent studies show that next to organic matter composition, minerals in soil also have an important effect on the sorption of hydrophobic organic chemicals. However, how different minerals affect sorption capacity is not yet clear. At low organic carbon contents, chemicals may sorb directly onto mineral surfaces (Müller *et al.* 2007), but it is also possible that the association of organic matter with minerals changes its affinity for organic chemicals (Ahangar *et al.* 2008). One of the main groups of organic chemicals that are important to investigate are the polycyclic aromatic hydrocarbons (PAH) as they have a low solubility and therefore a high potential to be retained in soil. Phenanthrene is used as a model compound to represent this group of chemicals.

In order to gain more insight into the contribution of specific minerals to sorption of phenanthrene to soil, we carried out phenanthrene sorption experiments to artificial soils with different mineral compositions (quartz, illite and ferrihydrite). The artificial soils were composed in the laboratory from the main components that are present in most natural soils. They have a clearly defined composition and texture and the only difference between the different samples is mineral composition. Therefore these artificial soils give us the possibility to investigate the specific effect of mineral composition on phenanthrene sorption.

Methods

Materials

Artificial soils (Kögel-Knabner *et al.*, 2010) were produced from model materials, the minerals quartz, illite and ferrihydrite. Sterilized manure was added as an organic matter component. The soils were inoculated with the water extractable microbial community of a Eutric Cambisol. Soil texture was provided by adding sand and silt-sized quartz and was composed of 42% sand, 52 % silt and 6% clay. The soils were incubated for 3 months at 60% of the water holding capacity. Soil solution was composed of 0.01 M CaCl₂ in order to provide an ionic strength similar to that of natural soils.

For this study, soils with 3 different mineral compositions were used; illite (B), ferrihydrite (C) and illite + ferrihydrite (F). Quartz was present in all soils and in the soil without illite, clay-sized quartz was added to maintain the same texture. Illite and ferrihydrite were present at 8 and 1% mass respectively. The particle size fractions <20 μ m were obtained by sieving and consecutive freeze-drying of the soils. These fractions were used for the sorption experiments in order to concentrate the minerals of interest and to reduce the effect of the quartz sand and particulate organic matter present in the coarser fractions. Carbon and nitrogen content, C/N ratio and BET-N₂ specific surface area (SSA) of the samples were determined.

Sorption experiment

Phenanthrene sorption experiments were carried out in batch incubation experiments according to the guideline of the (OECD, 2000) in a concentration range from 10 to 50% of the water solubility of phenanthrene. One gram of sample was added to 75 ml of 0.01 M CaCl₂ solution, spiked with phenanthrene and incubated for 24 hours. The batches were centrifuged and phenanthrene was extracted from the supernatant using Bakerbond C18 material. Phenanthrene concentration was measured using GC-MS and quantified with deuterated phenanthrene as an internal standard.

Sorption isotherms were calculated using the solubility-normalized Freundlich isotherm (Carmo *et al.* 2000) according to equation 1:

$$\log C_{(a)s} = \log K'_f + n^{-1} \log(C_{(a)aq}/S) \quad (1)$$

Where $C_{(a)s}$ is the concentration of phenanthrene adsorbed to the sample, $C_{(a)aq}$ is the concentration of phenanthrene in solution at equilibrium, S is the super cooled liquid solubility of phenanthrene, n^{-1} is a measure of sorption linearity and K'_f is the Freundlich isotherm coefficient. The K'_{oc} was calculated by normalizing the K'_f to organic matter concentration and K'_{SSA} was calculated by dividing the K'_f by the specific surface area of the sample.

Results and discussion

The 3 month incubation has allowed for limited development of the soils (Kögel-Knabner *et al.*, 2010). Carbon concentrations (table 1) in all samples are relatively low although that of soil C is slightly higher than the others. The small difference in C/N ratio of the samples suggests that organic matter composition is relatively similar. The specific surface area of the two samples containing illite are similar while that of the sample containing only ferrihydrite is lower suggesting the presence of illite is an important factor determining SSA.

Table 1. Sample characterisation

name	major mineral	C content mg g ⁻¹	C/N	SSA m ² g ⁻¹
B	illite	8.8 ± 0.8	6.7	9.0 ± 0.4
C	ferrihydrite	12.8 ± 0.1	6.7	6.8 ± 0.4
F	illite+ferrihydrite	7.8 ± 0.2	6.4	9.6 ± 0.4

The phenanthrene sorption isotherms are presented in figure 1. The isotherms for the two samples containing ferrihydrite have the same slope with slightly higher sorption in sample C than sample F.

The isotherm for sample B has a lower slope and although sorption at the two lowest concentrations is higher than in samples C and F, it is lower at the other concentrations.

These differences are reflected in the calculated Freundlich isotherm coefficients and nonlinearity constants (table 2). R^2 of all three isotherms is 0.99 which shows that the Freundlich isotherm model can be used to explain the data. The calculated distribution coefficients K'_f (table 2) for samples C and F are rather similar while that for soil B is much lower. Furthermore it can be seen clearly that the phenanthrene sorption to samples C and F was linear with a nonlinearity constant close to 1 while that of sample B was nonlinear with an n of 0.64.

The K'_{oc} values (table 2) show no clear pattern and cannot be used to explain the difference in sorption behaviour between sample B and samples C and F. This can also be concluded from the carbon concentrations (table 1). The carbon concentration for sample B and F is very similar while phenanthrene sorption is significantly different. It is possible that the slightly higher sorption to sample C relative to F is due to its higher carbon content. However, there is a significant difference in the K'_{oc} of these two samples. This may be due to the calculation method because differences in carbon content could have a disproportionately large effect on the K'_{oc} at these low concentrations. It may also indicate that other differences between the samples are also important for phenanthrene sorption. It is possible that during the 3 months of incubation, the artificial soils developed differently leading to a difference in organic matter composition between the 3 soils. Several studies have shown that organic matter composition has an effect on phenanthrene sorption and this might explain the differences in K'_{oc} values.

Table 2. Freundlich isotherm parameters; the solubility normalized distribution coefficient K'_f , the isotherm linearity constant n , correlation coefficient R^2 , the distribution constant normalized to organic carbon content in $\text{g g}^{-1} K'_{oc}$ and the distribution constant normalized to specific surface area in $\text{g m}^{-2} K'_{SSA}$

sample	K'_f	n	R^2	K'_{oc}	K'_{SSA}
B	174	0.64	0.99	$2.0 \cdot 10^4$	19
C	589	0.97	0.99	$4.6 \cdot 10^4$	87
F	646	1.03	0.99	$8.3 \cdot 10^4$	67

The K'_{SSA} values (table 2) also show no clear relation between the samples. Again, specific surface area was very similar for sample B and F indicating that their difference in sorption behaviour cannot be explained by differences in SSA.

As organic matter content and specific surface area cannot be used to explain the significant difference in sorption behaviour between samples C and F which contain ferrihydrite and sample B which does not, we must conclude that the presence of ferrihydrite itself affects sorption behaviour. The presence of illite is of low importance in this experiment. It might be that some sorption of phenanthrene to ferrihydrite itself takes place. However, it is also possible that the ferrihydrite affected the development of biogeochemical interfaces in the soil during the 3 months of incubation. The association of organic matter with ferrihydrite could have given it a different structure, providing an interface with a higher affinity towards phenanthrene.

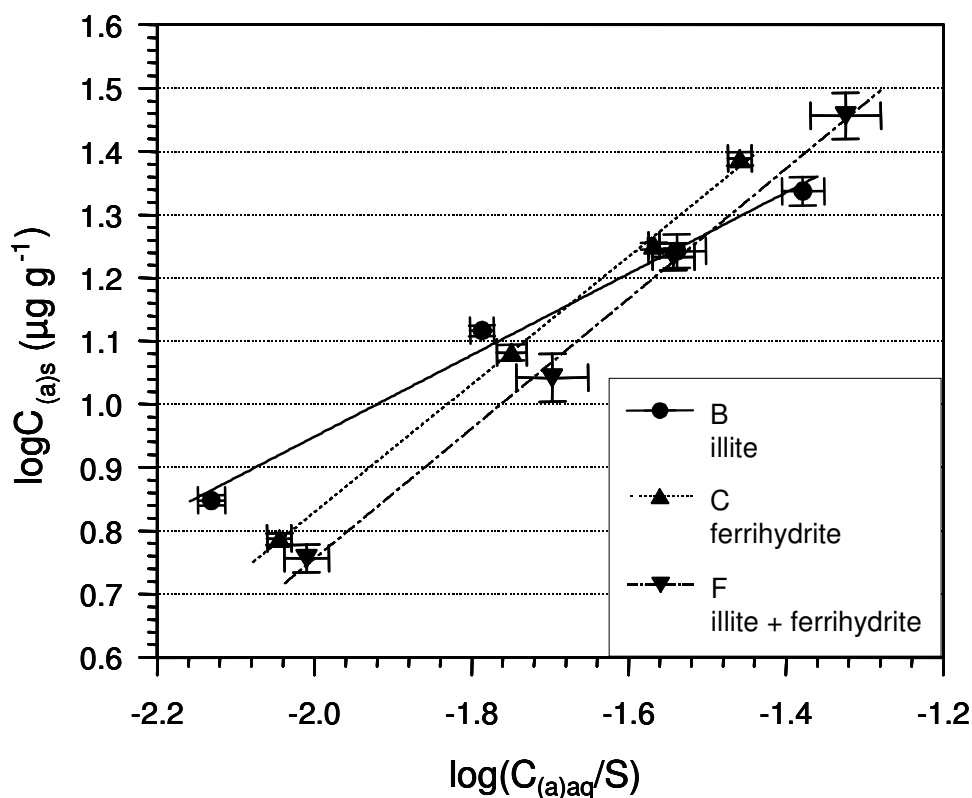


Figure 1. Phenanthrene sorption isotherm, $C_{(a)s}$ is the equilibrium concentration of adsorbed phenanthrene in the solid phase in $\mu\text{g g}^{-1}$, $C_{(a)aq}$ is the equilibrium concentration of phenanthrene in the aqueous phase in $\mu\text{g ml}^{-1}$ and S is the supercooled liquid solubility of phenanthrene in $\mu\text{g ml}^{-1}$. The error bars represent the standard deviation of the three replicates for each sample.

Conclusions

1. The presence of ferrihydrite lead to an increase in sorption capacity and sorption linearity compared to the soil containing only illite.
2. This difference cannot be explained by carbon content or specific surface area.
3. Overall, either significant sorption of phenanthrene to ferrihydrite itself occurs or, most probably, ferrihydrite has affected the properties and structure of the biogeochemical interfaces in the soil formed during the 3 month incubation, increasing its affinity to phenanthrene.

References

- Ahangar AG, Smernik RJ, Kookana RS, Chittleborough DJ (2008) Separating the effects of organic matter-mineral interactions and organic matter chemistry on the sorption of diuron and phenanthrene. *Chemosphere* **72**, 886-890.
- Carmo AM, Hundal LS, Thompson ML (2000) Sorption of Hydrophobic Organic Compounds by Soil Materials: Application of Unit Equivalent Freundlich Coefficients, doi:10.1021/es000968v. *Environmental Science & Technology* **34**, 4363-4369.
- Kögel-Knabner I, Ding GC, Heister K, Pronk GJ, Schaumann GE, Schloter M, Schulz S, Schwarz J, Smalla K (2010) Formation of biogeochemical interfaces in soils as controlled by mineral and organic components. *World Congress of Soil Science, Soil Solutions for a Changing World*, 1-6 August 2010, **accepted**
- Müller S, Totsche KU, Kögel-Knabner I (2007) Sorption of polycyclic aromatic hydrocarbons to mineral surfaces, doi:10.1111/j.1365-2389.2007.00930.x. *European Journal of Soil Science* **58**, 918-931.
- OECD (2000) Adsorption/desorption using a batch equilibrium method, test guideline 106. *OECD guidelines for testing chemicals, OECD publications, Paris*.
- Totsche KU, Rennert T, Gerzabek MH, Kögel-Knabner I, Smalla K, Spiteller M, Vogel HJ (2010) Biogeochemical interfaces in soil: The interdisciplinary challenge for soil science. *Journal of Plant Nutrition and Soil Science* **173**, 88-99.