Effect of different cation saturations on the sorption and mineralization of the hydrophobic organic compounds nonylphenol and phenanthrene in soils

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Abstract

Based on the assumption that the relative density and flexibility of SOM is affected by cations at the exchange sites, nonylphenol (NP) and phenanthrene (PHE) sorption and mineralization experiments were conducted with a sandy soil that had been treated with solutions of NaCl, $CaCl_2$ or $AlCl_3$. Sorption and desorption of the ^{14}C-labelled compounds was determined in batch equilibrium assays. Moneralization was determined by monitoring $^{14}CO_2$ efflux from samples that were additionally supplemented with organic substrates. For NP, organic carbon normalized sorption and desorption coefficients were increased in Na- and Al-treatments, for PHE in the Na-treatment and a water-washed control soil. Mineralization of NP was enhanced by addition of glucose and wood flour, indicating that it is substrate limited and most likely co-metabolic. At high mineralization rates, bioavailability of NP is limited in the Ca- and Al-treatments.

Key Words

Xenobiotics, SOM conformation, cations, sorption, mineralization

Introduction

Bound residues of hydrophobic organic compounds develop mainly through interactions with soil organic matter (SOM), either through sorption to specific sites (i.e. hydrophobic cavities) or through slow diffusion into less accessible domains. The relative density and flexibility of SOM is affected by cations at the exchange sites (Schaumann *et al.* 2006). Strongly hydrated monovalent cations (i.e. Na^+) cause SOM to expand and thus make it more accessible to xenobiotics. Polyvalent cations (i.e Ca^{2+} or Al^{3+}) reduce the volume and flexibility of SOM through cation bridging, which can thus limit diffusion of xenobiotics into the matrix and back out again. The higher rigidity of Ca^{2+} or Al^{3+}-saturated humic acids has been shown to reduce atrazine sorption, while it increased with Na^+ relative to the H-saturated humic acid (Clapp *et al.* 2001). Yuan and Xing (2001) showed that an Al-saturated humic acid strongly increased the non-linearity and irreversibility (hysteresis) of PAH sorption. Lu and Pignatello (2004) made similar observations for naphthalene and trichlorbenzene and explain this by the restricted access of sorption sites in the more rigid Al-saturated humic acid. In our study, we test two hypotheses: (1) the structural conformation of SOM affects sorption and desorption kinetics of xenobiotics and thus influences the formation of "bound residues". (2) The addition of substrates can enhance the biodegradation of bound residues, either through co-metabolism or through enhanced degradation of the sorbent (priming effects).

Methods

Soil sampling and treatment

Soil was sampled from a permanent pasture near Hannover, Germany. The sandy gleyic podzol with a pH of 5.7 had an SOC content of 3.2% and a clay content of 2.3%. After sieving to 2 mm and air drying, subsamples of the soil were percolated under saturated conditions with solutions containing 0.1 M NaCl, $CaCl_2$ or $AlCl_3$ until a final soil:solution ratio 1:50. After the cation treatment, samples were washed with deionized water at 1:15.

Chemicals

Ring ^{14}C-labelled nonylphenol [4-(3,5-Dimethyl-3-heptyl)phenol] (NP) was obtained at 98% radiochemical purity from A. Schaeffer (RWTH Aachen) in petrolether. Uniformly-^{14}C-labelled phenanthrene (PHE) with radiochemical purity 99.7% was purchased from Campo Scientific GmbH, Germany in methanol.

Sorption and desorption

Two g soil samples were placed into one half of a 10 ml double-cell Teflon chamber separated by a dialysis membrane with MWCO 1000 Da. After filling both halves with deionized water, the ^{14}C-labelled NP and Phe were injected into the soil-free half of the chamber at concentrations 5.5 µg/g and 1.2 µg/g respectively, which is below the water solubility of the compounds. To prevent the microbial activity, NaN_3 at 5 mg/l was added to the system. The acidity of all soil solutions was reduced to pH of 5 by addition of 0.01 M HCl. Ratio between solid and liquid parts in system was 1:5. Sorption kinetics were determined by removing 200 µl samples from the soil free half-cell and analysing ^{14}C-activity by liquid scintillation counting (LSC). Desorption experiments were carried out after sorption equilibrium was reached (generally after 72-110 hr) by replacing the complete aqueous solution of the soil-free half-cell with deionized water repeatedly.

Mineralization assays

The cation-treated and control soil samples of 40 g were re-wetted to 40% water holding capacity and preincubated for 2 weeks at 20°C in the dark prior to spiking them with the ^{14}C-labelled NP. For spiking, NP dissolved in petrolether was added to 1 g acid washed quartz sand, left to dry and then mixed into the soil sample. Contaminated soils with concentration of NP of 1.2 µg/g were then wetted to 60% WHC and incubated in an automated respirometer Respicond-apparatus (Nordgren Innovations) that monitors CO_2 production and collects respired CO_2 in 0.6 m KOH solution. Periodically, ^{14}C-activity was determined in the KOH solutions via LSC. To determine the effects of different substrate additions on the mineralization of NP, after 3 weeks of preincubation some samples were supplied with glucose, catechol or beech wood flour at concentrations of around 500, 300 and 10000 mg/kg respectively and incubated 3 weeks more.

Results

The sorption of NP to the soil as determined in the batch equilibrium experiments was slightly enhanced in the Al-treatment, but differences to the control were not significant (Figure 1). For desorption, the organic carbon normalized partitioning coefficient K_{oc} was much higher than for sorption in all soils, reflecting a strong hysteresis. Here, the Na- and Al-treated soils showed significantly higher Koc-values than the control and Ca-treatments.

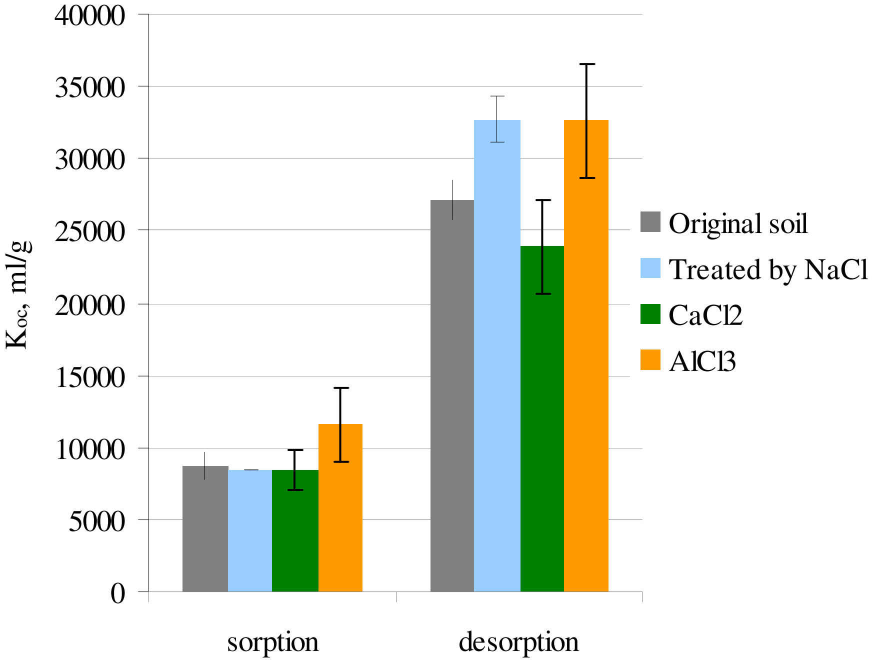

Figure 1. Organic carbon normalized coefficient of sorption and desorption of nonylphenol at the equilibrium time in soils treated with different salt solutions

Mineralisation rates of NP were very low, reaching only 0.4 to 0.5% within the first two weeks before substrate additions (Figure 2). After this period, the addition of water stimulated mineralization in all treatments but most markedly in the untreated control soil. Glucose additions stimulated NP mineralization to an even greater degree, reaching up to 1.5% in the original soil, which again showed the highest values. The strongest stimulation of NP mineralization occurred after the addition of wood flour. This treatment also increased soil respiration to the highest degree, showing that this organic substrate was readily utilized by the soil microorganisms. Here, the mineralization of NP was significantly higher in the original soil and in the

Na-treatment than in the Ca- and Al-treatments. Since total CO_2 release was not markedly affected by the treatments, this indicates that at high degradation rates, NP bioavailability may be limited in the treatments with the higher charged cations.

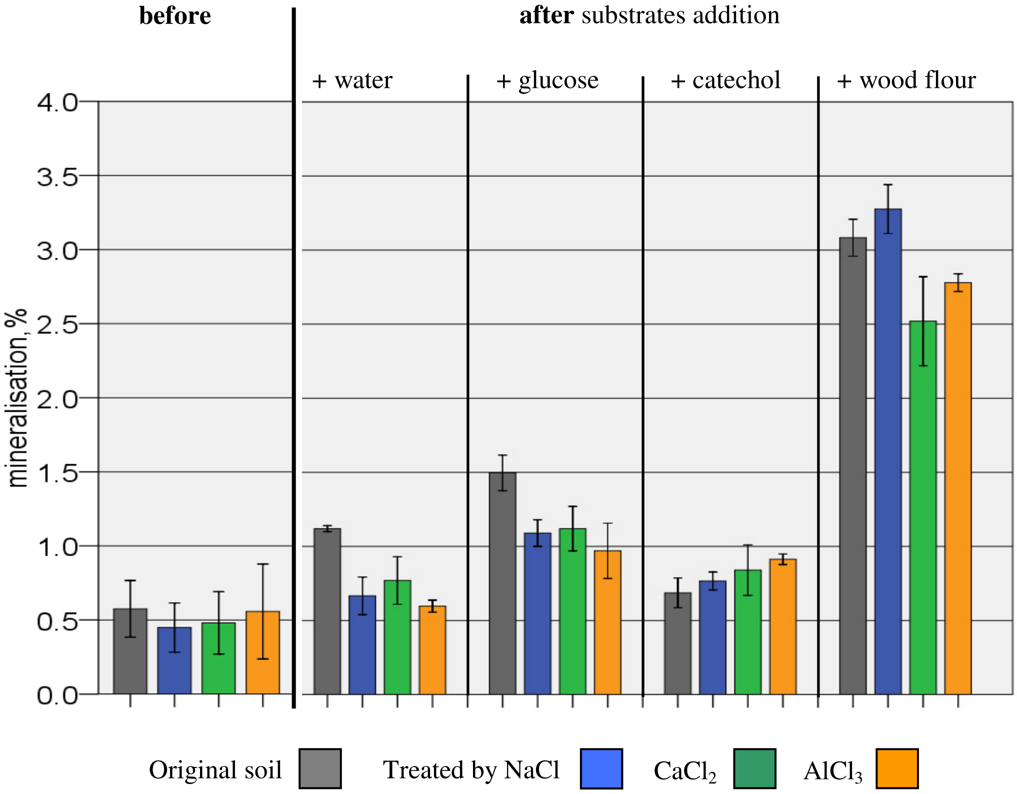

Figure 2. Total mineralisation of nonylphenol with and without substrate additions in soils treated with different salt solutions

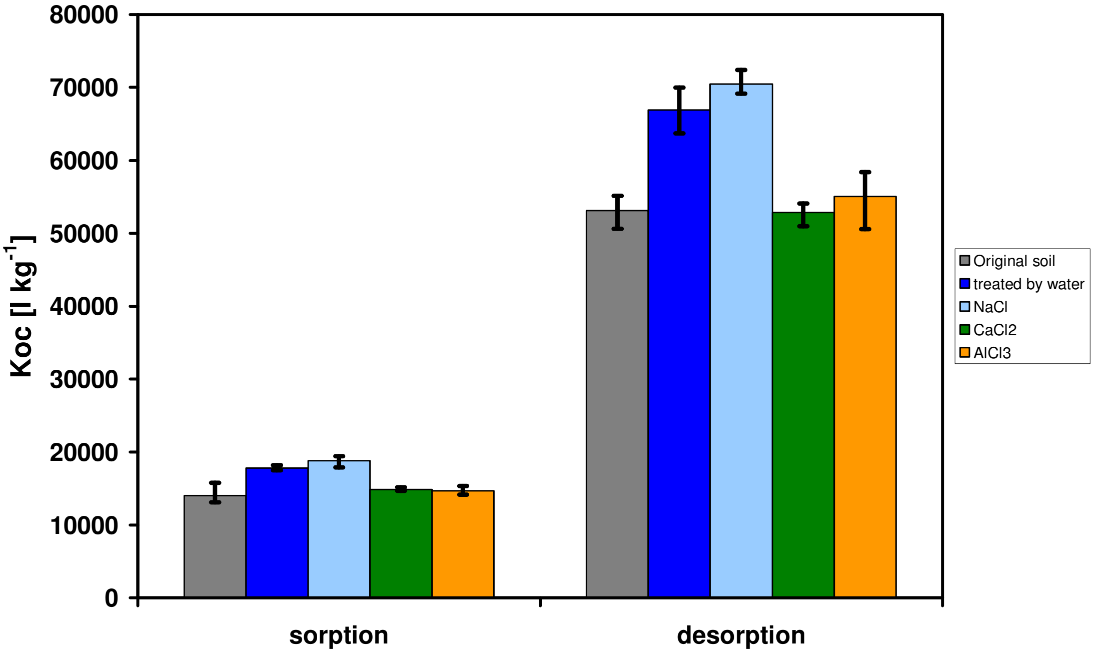

Figure 3. Organic carbon normalized coefficient of sorption and desorption of phenanthrene at the equilibrium time in the soils treated with different salt solutions

For the sorption experiments with PHE, an additional control treatment was included where the same amount of deionized water was percolated through the samples as in the cation treatments. As shown in Figure 3, the water and Na-treatments increased the carbon-normalized partition coefficients for sorption and desorption of PHE compared to the original soil and the Ca- and Al-treatments. If this is due to the leaching of hydrophilic low molecular organic compounds, leaving more hydrophobic sorption domains accessible for PHE or due to better accessibility of sorption sites due to swelling and expansion of the SOM matrix is unclear at the moment.

Conclusion

Our results show that the saturation of exchange sites with different cations affects the sorption/desorption and mineralization of the hydrophobic test compounds. However, there is no general trend for higher sorption or lower bioavailability in soils treated with multivalent cations as we had expected. We are currently conducting longer-term aging experiments to investigate, if the observed effects persist or even are amplified if the compounds have more time to interact with the sorbent matrix.

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