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## **Sorption and degradation of Nonylphenol: effect of soil organic matter conformation and substrate additions in soil**

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### **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 (Eschenbach 2001). The relative density and flexibility of SOM is affected by cations at the exchange sites (Schaumann 2006). Strongly hydrated monovalent cations (i.e. Na<sup>+</sup>) cause SOM to expand and thus make it more accessible to xenobiotics. Polyvalent cations (i.e. Ca<sup>2+</sup> or Al<sup>3+</sup>) reduce the volume and flexibility of SOM through cation bridging, which can thus limit diffusion of xenobiotics into the matrix and back out again (Clapp et al. 2001, Lu and Pignatello 2004). In our study, we wanted to 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 a soil organic carbon 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 water or solutions containing 0.1 M NaCl, CaCl<sub>2</sub> or AlCl<sub>3</sub> until a final soil:solution ratio of 1:50. After the treatment, samples were additionally washed with deionized water at ratio 1:15 and dried at 21 °C temperature.

#### *Chemicals*

The widespread endocrine-disrupting contaminant nonylphenol (NP) was used in this study (Erickson B.E. 2002). Ring <sup>14</sup>C-labelled and not radioactive nonylphenol [4-(3,5-dimethyl-3-heptyl)phenol] (NP) was obtained at 98% radiochemical purity from A. Schaeffer (RWTH Aachen) in methanol.

#### *Sorption and desorption batch experiment*

For the batch assays, 1.6 g of dry samples and 7 ml sodium azid solution (10 mg l<sup>-1</sup>) were added to 10 ml duplicate glass centrifuge vials (Novodirect, Kehl/Rhein) with Teflon-lined screw-cap. The acidity of all soil solutions was adjusted to pH 5 by 0.01 M hydrogen chloride. The solutions were then spiked with <sup>14</sup>C-labelled NP and enriched by not radioactive NP amount to four different concentrations 0.6, 1.4, 2.8 and 4.2 µg ml<sup>-1</sup>, which are below the water solubility of the compound. Final amount of liquid in the system was 8 ml and ratio between soil and solution was 1:5. Controls containing no soils were prepared in the same way. The samples were mixed on the over-head shaker with 20 rpm at room temperature. Based on the previously determined sorption kinetics (data not shown), equilibrium time was set to 20 h. After this time the samples were centrifuged for 30 min at 3000 rpm and 1 ml of supernatant was then removed to determine radioactivity by liquid scintillation counting.

Desorption experiments were carried out after then sorption equilibrium was reached by replacing the complete supernatant with

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deionized water and shaking the samples for 15 min. The radioactivity of solution was determined as described above.

### Mineralization assays

The cation-treated soils and original soil as a control were rewetted to 40% water holding capacity (WHC) and sterilized by  $\gamma$ -irradiation (30 kGy). After that the 40 g samples were mixed with 1 g of dried original soil and preincubated for 3 weeks at 20°C in the dark prior to spiking them with the labeled and unlabeled NP. For spiking, 1 g of contaminated pure sand was mixed into each soil sample. Contaminated soils with concentration of NP of  $1.2 \mu\text{g g}^{-1}$  were then wetted to 60% WHC and incubated in an automated respirometer Respicond-apparatus (Nordgren Innovations) that monitors  $\text{CO}_2$  production and collects respired  $\text{CO}_2$  in 0.6 m KOH solution. Periodically,  $^{14}\text{C}$ -activity was determined in the KOH solutions via liquid scintillation counting. To determine the effects of different substrate additions on the mineralization of NP, after 4 weeks of preincubation some samples were supplied with glucose, catechol or birch wood flour at concentrations of around 500, 300 and 10000  $\text{mg kg}^{-1}$  respectively and incubated 3 weeks more.

### Results

As determined in the batch equilibrium experiment the sorption isotherms for the investigated NP concentrations from 0.6 till  $4.2 \mu\text{g ml}^{-1}$  in soil-water system with ratio 1:5 fit well to the linear model (Fig. 1). The sorption and desorption of NP to the soil were significantly affected by the different cation treatments (Fig. 2). The lowest sorption was on soil treated by NaCl and the highest on soil treated by  $\text{AlCl}_3$ . The organic carbon normalized partitioning coefficient  $K_{oc}$  for  $\text{CaCl}_2$  treated soil was on the middle range and amount  $10566 \text{ g ml}^{-1}$  which was relatively close to the control original soil and water treated soil. There was no effect occurred with deionized water percolation of soil on sorption and desorption of NP. Clearly, the  $K_{oc}$  was higher for desorption than for sorption in all soils, reflecting a strong hysteresis.

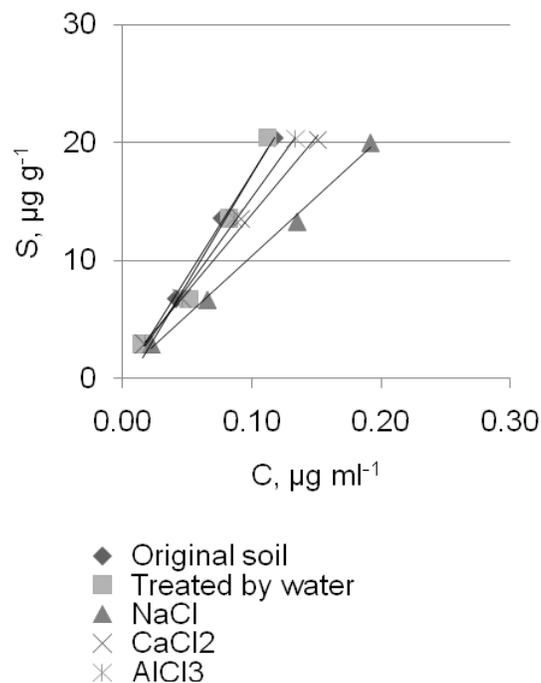


Fig. 1. Sorption isotherms for concentrations of nonylphenol 3, 7, 14 and  $21 \mu\text{g g}^{-1}$  and soil-solution ratio 1:5.  $S [\mu\text{g g}^{-1}]$  is the concentration of solute adsorbed on the soil matrix and  $C [\mu\text{g g}^{-1}]$  is the aqueous concentration in soil solution

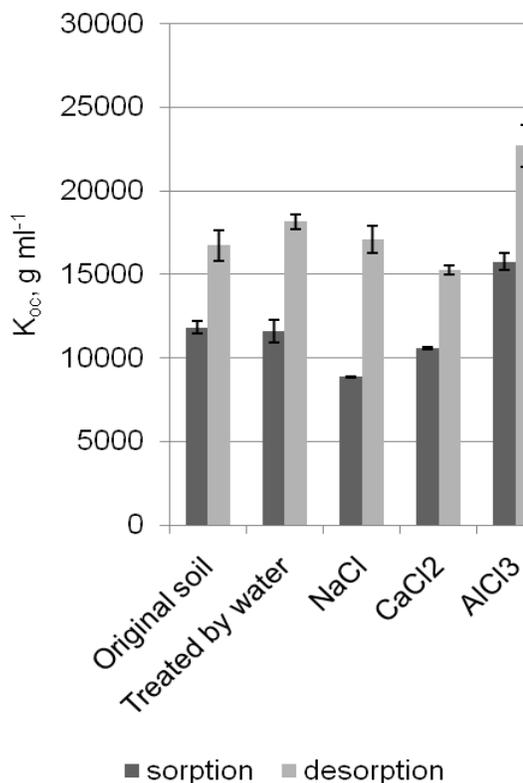


Fig. 2. Organic carbon normalized coefficient of sorption and desorption of nonylphenol on original and treated soils

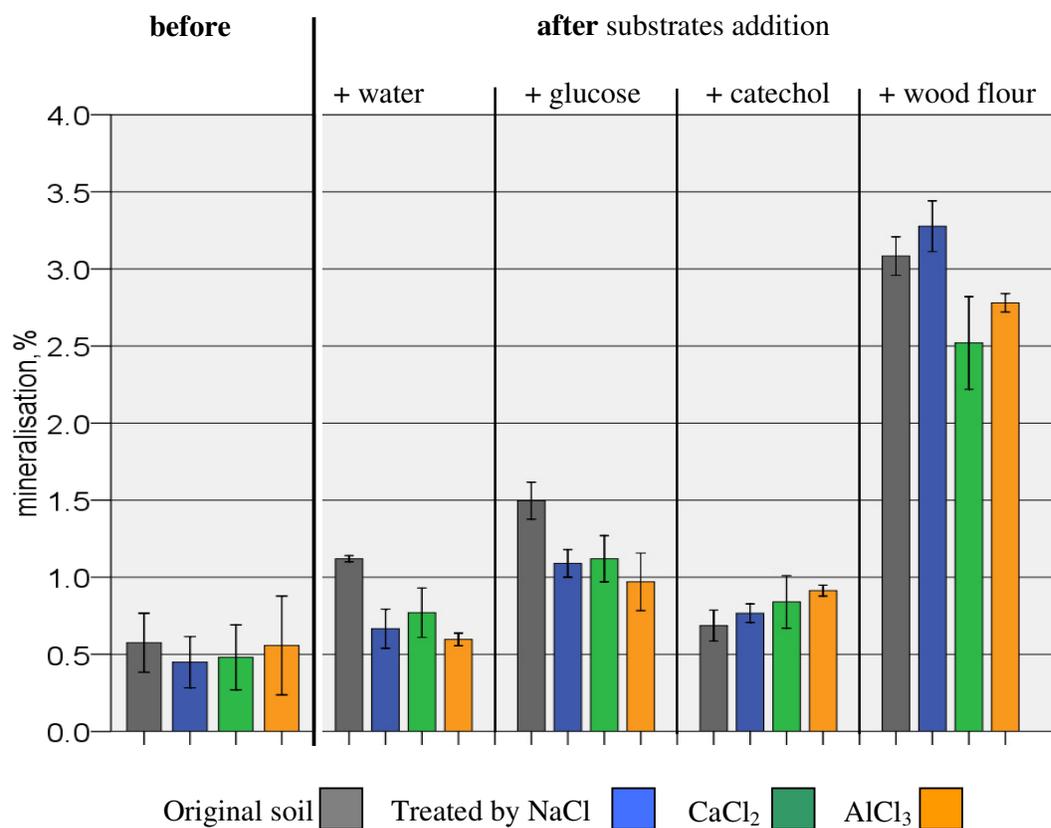


Fig. 3. Mineralization of nonylphenol in original and treated by different salts soils before and after substrates addition

Mineralization rates of NP were very low, reaching only 0.4 to 0.5% within the first two weeks before substrate additions (Fig. 3). 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<sub>2</sub> release was not markedly affected by the treatments, this indicates that NP bioavailability may be reduced in the treatments with the higher charged cations.

## Conclusions

The differences in NP mineralization in the test soils with substrate additions showed that certain chemical or biological soil properties seem to strongly affect the degradation processes, which still are poorly understood. It is expected that one factor influencing sorption and bioaccessibility of NP is the structural conformation of soil organic matter that can be altered by different cations

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## References

Eschenbach A., Mescher H., Wienberg R., Mahro B. 2001. Humification of PAH and TNT during bioremediation – evaluation of long term risk and sustainability. In: R. Stegmann, G. Brunner, W. Calmano, G. Matz, Treatment of contaminated soil: fundamental analysis applications. Springer, Berlin, pp. 212-219.

Schaumann, G.E., 2006. Soil organic matter beyond molecular structure Part I: Macromolecular and supramolecular characteristics. Journal of Plant Nutrition and Soil Science - Zeitschrift Fur Pflanzenernahrung Und Bodenkunde, 169(2): 145-156.

Clapp, C.E., Hayes, M.H.B. and Mingelgrin, U., 2001. Measurements of sorption –desorption and isotherm analyses. In: C.E. Clapp, M.H.B. Hayes, N. Senesi, P. Bloom and P.M. Jardine (Editors), Humic Substances and Chemical Contaminants. Soil Science Society of America, Madison, pp. 205-240.

Lu, Y.F. and Pignatello, J.J., 2004. Sorption of apolar aromatic compounds to soil humic acid particles affected by aluminum(III) ion cross-linking. Journal of Environmental Quality, 33(4): 1314-1321.

Erickson, B. E. 2002 Endocrine-disrupting nonylphenols detected in wide range of food. Environmental Science Technology, 36(9):178A-179A.