



Effects of sterile storage, cation saturation and substrate additions on the degradability and extractability of nonylphenol and phenanthrene in soil



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HIGHLIGHTS

- The long-term sterile aging increased respiration of re-inoculated soil.
- The negative aging effect on xenobiotics mineralization was evident in some soils.
- Na⁺ and Al³⁺ pre-treatment of soil significantly reduced xenobiotics mineralization.
- The p353-nonylphenol mineralization was enhanced by wood flour addition.
- The phenanthrene mineralization was retarded by wood flour addition.

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ABSTRACT

The main objective of this study was to determine the effects of long-term abiotic processes during aging of organic pollutants in soil on their microbial degradability and formation of non-extractable residues. The specific aims of our study were to investigate how the fate of p353-nonylphenol (NP) and phenanthrene (Phe) in soils might be affected by: (i) saturation of soil by cations with different valency (Na⁺, Ca²⁺ or Al³⁺), (ii) addition of organic substrate (wood flour) during incubation period and (iii) different soil moisture levels.

This study showed positive effect of long-term aging of sterilized samples on respiration of re-inoculated samples. However, the lack of aging effects on the mineralization of NP and Phe indicates that slow sorption processes by diffusion into less bioaccessible domains were not relevant in studied soils. Similarly, the lower respiration and xenobiotic mineralization rates in the Na⁺ and Al³⁺ treated soils indicate that this is due to toxic effects on microbial activity and not due to xenobiotic accessibility. Instead, the formation of non-extractable residues was strongly promoted by biological activity, most likely through formation of more reactive metabolites. The addition of wood flour greatly stimulated microbial respiration and enhanced NP mineralization while inhibiting that of Phe. Along with negligible effect of water addition after 4 weeks of incubation on kinetics of soil respiration, the soil moisture effect on xenobiotics mineralization indicates that most probably the bioavailability of NP and Phe increased due to bridging role of water films in soil.

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1. Introduction

Hydrophobic organic pollutants reaching the soil are generally strongly sorbed by soil constituents. Furthermore, xenobiotics can be transformed by microbial degradation and mineralization, which in turn may contribute to the formation of bound residues in soil. The intensity of these processes depends of bioaccessibility

and bioavailability of pollutant, which are governed by both sorbate and sorbent properties (Gevao et al., 2000; Semple et al., 2003).

One important factor which limits the bioaccessibility of pollutants is the strength of their sorption. Sorbing properties of soils are essentially conditioned by the properties of soil organic matter (SOM) (Alexander, 2000). Depending on the aromaticity and degree of condensation of SOM, sorption and desorption rates of pollutants may vary (Pan et al., 2007). One of the factors which can alter the SOM is the presence of strong complexing polyvalent cations. For example, in the presence of Al³⁺ and Ca²⁺ in solution the

Abbreviations: NP, nonylphenol; Phe, phenanthrene; SOM, soil organic matter.

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sorption of phenanthrene (Phe) was significantly increased in comparison to experiments with Na^+ (Lu and Pignatello, 2004). Another study showed that metals Cd, Cu, Pb, and Zn significantly increased Phe sorption to an agricultural soil (Saison et al., 2004). In contrast, cation saturation of soil with Na^+ , Ca^{2+} or Al^{3+} before mixing with xenobiotics did not show significant effect of cations on short-term sorption of nonylphenol (NP) or Phe (Shchegolikhina et al., 2013).

It is well-known that long-term interaction of xenobiotics with soil or so-called aging, causes its strong sorption and gradual increase of non-degradable and non-extractable fractions (Semple et al., 2003). One of the processes responsible for this has been proposed to be the slow diffusion of the compounds into poorly accessible micropores of soil organic macromolecules which by some authors is also attributed to sorption or entrapment within less flexible (“glassy”) structures (Lu and Pignatello, 2004; Pignatello, 2012). Our studies with aging of xenobiotics in a sterilized sandy soil for 9 months showed a decrease of the ethanol extractability of NP and Phe from 94.4% to 82.2% and from 77.0% to 59.5% respectively (Shchegolikhina et al., 2012). Investigation of soils with different properties showed decrease of Phe mineralization and extractability up to 9.6–35.0% and 14.1–54.3% respectively after 200 d of non-sterile aging (Chung and Alexander, 2002). Though the role of biotic and abiotic factors in the formation of bound residues was investigated using different materials and under various conditions (Kristensen et al., 2001; Chung and Alexander, 2002; Li et al., 2007; Ncibi et al., 2007), the processes occurred in soil during aging are still not well understood.

Besides the abiotic factors the fate of xenobiotics in soil depends on biotic factors, such as the activity of soil microorganisms. Microbial activity can enhance the formation of xenobiotics bound residues, most likely due to release of more reactive metabolites that covalently bind to SOM (Gevao et al., 2000; Li et al., 2007). On the other hand, the stimulation of microbial activity, through nutrient addition or organic substrates can also remobilize bound residues and thus increase their biodegradation (Wicke and Reemtsma, 2010). Along with availability of nutrients, the soil moisture is one of the essentially important soil properties for microbiological activity (Brockett et al., 2012). Water content in soil can limit the living space for microorganisms. The water films formed between soil particles play important transporting role for microbiology (Paradelo and Barral, 2009), which in turn can stimulate the bioaccessibility and bioavailability of water-solved chemicals in soil, including xenobiotics and their bound residues (Kottler et al., 2001).

The main objective of this study was to determine the effects of long-term abiotic processes during aging of organic pollutants in soil on their microbial degradability and formation of non-extractable residues. Two model compounds, with different chemical structure and properties were used in our study: the hydrophobic phenanthrene comprised of three aromatic rings ($\log K_{ow}$ 4.5, S_w 1.3 mg L^{-1}) (Montgomery and Welkom, 1990) and the branched nonylphenol isomer 4-(3,5-dimethyl-3-heptyl)-phenol with both hydrophobic (aliphatic) and polar (phenolic-OH) subunits ($\log K_{ow}$ 4.7, S_w 6 mg L^{-1}) (Porter and Hayden, 2002). The Phe is a representative compound of the large group of polycyclic aromatic hydrocarbons, which can be formed in the environment during incomplete burning of oil, gas, coal or other organic substances; and due to decay and decomposition of some dyes, plastics and pesticides (Van der Perk, 2006). The NP is a primary breakdown product of nonylphenol ethoxylates. These chemicals are non-ionic surfactants, which are used in agricultural and industrial applications (Guenther et al., 2002). The specific aims of our study were to investigate how the fate of NP and Phe in soils might be affected by: (i) saturation of soil by cations with different valency, (ii) addition of organic substrate (wood flour) during incubation period and (iii) different soil moisture levels.

2. Materials and methods

2.1. Soil preparation

The sandy soil was collected from the upper 0–20 cm layer of a gleyic podzol from the Fuhrberger Feld (Lakwiese), Fuhrberg, Lower Saxony, Germany. It was dried at 20 °C and sieved (≤ 2 mm). The content of sand, silt and clay in the original soil was 68.6%, 29.0% and 2.4% respectively, pH (determined in water solution) was 5.0 (Shchegolikhina et al., 2012).

To obtain soil material with a dominance of one cation at the exchange sites, the original soil was placed into percolation cylinders and leached with aqueous solutions of 0.1 M NaCl, CaCl_2 , or AlCl_3 at a ratio of 1:50 (w/w) during 18 h. Then samples were leached with deionized water at a ratio 1:15 (w/w) until electric conductivity of the leachate reached constant values. An additional reference sample was obtained by leaching the original soil with water instead of salt solutions. After the percolation treatment, the soils were dried at room temperature and humidity around 40%.

In accordance with the determined soil–water potential values (Shchegolikhina et al., 2012), the soil samples were moistened to pF 2.8 (–630 hPa) and then sterilized 3 times by γ -radiation with a total radiation dose of 75 kGy. After sterilization, all further treatments and experiments were performed under sterile conditions. The pH of the samples was altered by the salt solution and water percolation. To adjust the pH of the samples to the same value (4.6), the soils were mixed with certain amounts of 0.05 M HCl. The final matric potential of all samples corresponded to pF 2 (–100 hPa), which is equal to water content 10.5% in original soil, 9.0% in H_2O -treated soil, 11.8% in Na-treated soil, 11.6% in Ca-treated soil, 11.3% in Al-treated soil. The preliminary incubation experiments with original soil moistened to different levels (5–15%) showed that the soil moisture corresponded to pF 2 is optimal for microbial activity (data not shown).

The sterilized soils were spiked with ^{14}C -ring-labeled and unlabeled NP or Phe. ^{14}C -U-ring-labeled and unlabeled *p*353-nonylphenol (NP) (98% purity, RWTH Aachen, Aachen, Germany) was dissolved in methanol. 9- ^{14}C -labeled phenanthrene (Phe) (99.7% purity, Campro Scientific GmbH, Berlin, Germany) and unlabeled Phe (99% purity, Sigma-Aldrich Chemie GmbH, Steinheim, Germany) were separately dissolved in ethanol. The chemicals were applied to the dry sea sand (washed, untreated by acid, Sigma-Aldrich Chemie GmbH, Steinheim, Germany), solvents were evaporated and then the spiked sand was mixed into the moist soils (1%, d/w) to achieve the concentration of 10 $\mu\text{g g}^{-1}$ soil for both compounds. Radioactivity of the spiked soils was 1800 Bq g^{-1} .

The concentrations of ^{14}C -labeled NP and Phe in soils were determined by dry combustion. Dried homogenized soil was placed in a crucible and burned for 4 min in an oxygen stream at 900 °C (OX-300, Zinsser Analytic GmbH, Frankfurt, Germany). Released $^{14}\text{CO}_2$ was trapped in an alkaline scintillation cocktail and measured by liquid scintillation counting with background correction. The determined recovery rate was 88–94%.

The sterility of the irradiated samples was tested after 7 months of storage of soils under sterile conditions. The test was carried out by incubation of aliquots in liquid cultures using 0.1x Luria-Bertani medium after Miller (Atlas, 1993). Cultures were incubated under aerobic and anaerobic conditions at 25 °C for 72 h. In addition, soil extracts obtained with 0.9% NaCl were spread onto 0.1x Luria-Bertani agar plates and incubated aerobically at 25 °C for 2 weeks. Since no microbial growth was observed in any sample, it was assumed that the microbial activity in the irradiated samples was negligible.

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