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Comparing the desorption and biodegradation of low concentrations of phenanthrene sorbed to activated carbon, biochar and compost

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HIGHLIGHTS

- We compared phenanthrene desorption and biodegradation sorbed to carbonaceous sorbent.
- Activated charcoal and charcoal reduced phenanthrene dissolved concentrations.
- Activated charcoal and charcoal did not inhibit phenanthrene biodegradation.
- The data were modeled using a coupled desorption and biodegradation model.
- Desorption did not limit for biodegradation for any of the amendments.

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ABSTRACT

Carbonaceous soil amendments are applied to contaminated soils and sediments to strongly sorb hydrophobic organic contaminants (HOCs) and reduce their freely dissolved concentrations. This limits biouptake and toxicity, but also biodegradation. To investigate whether HOCs sorbed to such amendments can be degraded at all, the desorption and biodegradation of low concentrations of ^{14}C-labelled phenanthrene ($\leqslant$5 μg L^{-1}) freshly sorbed to suspensions of the pure soil amendments activated carbon (AC), biochar (charcoal) and compost were compared. Firstly, the maximum abiotic desorption of phenanthrene from soil amendment suspensions in water, minimal salts medium (MSM) or tryptic soy broth (TSB) into a dominating silicone sink were measured. Highest fractions remained sorbed to AC (84 ± 2.3%, 87 ± 4.1%, and 53 ± 1.2% for water, MSM and TSB, respectively), followed by charcoal (35 ± 2.2%, 32 ± 1.7%, and 12 ± 0.3%, respectively) and compost (1.3 ± 0.21%, similar for all media). Secondly, the mineralization of phenanthrene sorbed to AC, charcoal and compost by *Sphingomonas* sp. 10-1 (DSM 12247) was determined. In contrast to the amounts desorbed, phenanthrene mineralization was similar for all the soil amendments at about 56 ± 11% of the initially applied radioactivity. Furthermore, HPLC analyses showed only minor amounts (<5%) of residual phenanthrene remaining in the suspensions, indicating almost complete biodegradation. Fitting the data to a coupled desorption and biodegradation model revealed that desorption did not limit biodegradation for any of the amendments, and that degradation could proceed due to the high numbers of bacteria and/or the production of biosurfactants or biofilms. Therefore, reduced desorption of phenanthrene from AC or charcoal did not inhibit its biodegradation, which implies that under the experimental conditions these amendments can reduce freely dissolved concentration without hindering biodegradation. In contrast, phenanthrene sorbed to compost was fully desorbed and biodegraded.

1. Introduction

Soils and sediments accumulate hydrophobic organic pollutants (HOCs) to high levels, where they can serve as a long-term exposure source to the organisms inhabiting these sites as well as to the surrounding environment (Semple et al., 2003). The remediation of such contaminated soils and sediments poses considerable challenges, with treatment options including removal, capping or attenuation by microorganisms (Ghosh et al., 2011). However, the utility of these depends on numerous factors including the associated costs, undesired side-effects such as perturbation of the natural ecosystem, or limited remediation performance. Moreover, even after years of soil remediation a non-degradable fraction of the original HOC contamination persists, usually as a result of strong sorption and slow desorption. However, this also implies that this non-degradable fraction is poorly available to organisms and could even be considered as inert and as not posing a risk.

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Therefore, considerable efforts have been directed over the past years into developing alternative treatment technologies for ameliorating the detrimental effects of contaminated soils and sediments. One of these involves the *in situ* application of soil amendments (also called soil conditioners) such as carbonaceous materials (Kookana, 2010). These strongly sorb the HOCs, thus reducing their bioavailability and uptake into organisms as well as contaminant mass fluxes (Cornelissen et al., 2005). Obviously, reducing HOC uptake by organisms via soil amendment application is desirable in terms of limiting their toxicity. However, there is also a converse side to this. Biodegradation by microorganisms is the major mechanism of HOC removal, and here the reduction in dissolved concentrations due to any strong sorption to the soil amendments could potentially reduce bioavailability to the degraders leading to a concurrent decrease in biodegradation kinetics and high residual levels (Chung and Alexander, 1998; Bogan and Sullivan, 2003; Reichenberg et al., 2010). Indeed, in some studies the application of carbonaceous amendments, such as activated carbon (AC), to soils has been observed to reduce both the kinetics and the extent of HOC biodegradation (Rhodes et al., 2008, 2010). However, in other studies, whilst the addition of AC induced a reduction in the freely dissolved concentrations, the AC-amended soil still retained the potential to degrade the HOCs (Vasilyeva et al., 2010; Payne et al., 2011; Meynet et al., 2012). Uncertainties remain as to the mechanisms behind these different observations, with explanations including reduced HOC bioavailability due to the strong sorption, increased substrate heterogeneity or an inhibition of the development of HOC catabolic activity (Semple et al., 2003; Cornelissen et al., 2005; Rhodes et al., 2010).

The effects of such carbonaceous amendments on biodegradation are particularly relevant, as when residual HOC levels exceed the regulatory thresholds the land cannot be used as desired (Reichenberg et al., 2010). Since, regulatory thresholds are still based on total soil concentrations, even a documented reduction in risk through the application of carbonaceous amendments is not sufficient to permit unrestricted use (Latawiec and Reid, 2009). Incidentally, natural attenuation is also a treatment option for contaminated soils (Haritash and Kaushik, 2009), and here a more detailed understanding of how naturally occurring carbonaceous materials in soil influence HOC biodegradation is also needed.

Therefore, this study investigates the extent to which HOCs freshly sorbed to different types of carbonaceous soil amendments in suspension are abiotically desorbed, and whether they can be biodegraded at all under optimum conditions. Phenanthrene was selected as a model HOC belonging to the relevant and widespread class of PAH contaminants that pollute soils either through oil spills or via continuous diffuse atmospheric deposition. AC, charcoal (as an example of biochar) and compost were selected as model carbonaceous soil amendments. AC displays a very strong sorption propensity for HOCs, and has already been used in pilot studies to reduce their risks in soils and sediments (Ghosh et al., 2011; Hale et al., 2012). Charcoal is receiving increasing interest as an alternative sorbent to AC because of its lower cost and potential for CO_2 sequestration (Lehmann et al., 2006), and it has also been shown to inhibit pesticide biodegradation (Kookana, 2010). Compost was selected because it has been shown to stimulate PAH degradation (Kästner and Mahro, 1996). As a model bacterial degrader, *Sphingomonas* sp. 10-1 (DSM 12247) was used. *Sphingomonas* sp. has been used in the removal and degradation of several pollutants under natural and bioreactor conditions (Willumsen et al., 1998; van Herwijnen et al., 2003; Zhong et al., 2007).

Firstly, the maximum extent of abiotic desorption of low concentrations of phenanthrene ($\leqslant 5\ \mu g\ L^{-1}$) freshly sorbed to pure suspensions of AC, biochar or compost were measured. These were then compared to the mineralization of phenanthrene sorbed to suspensions of the pure soil amendments by the bacterium *Sphingomonas* sp. 10-1 (DSM 12247). In order to analyze and explain the key processes involved and to determine kinetic parameters, modeling was carried out considering abiotic desorption from soil amendment and adsorption to silicone as well as coupled desorption and biodegradation.

2. Materials and methods

2.1. Chemicals and materials

All chemicals were of analytical grade or better, and all media and aqueous solutions prepared using Milli-Q water (Super Q treated, Millipore, MA). Food-grade silicone O-rings with an outer diameter of 14.4 mm, inner diameter of 9.6 mm, mass of 231 mg (C.V. 1%, $n = 10$) and volume of 0.171 mL (Order No. ORS-0096-24., Altec, Cornwall, United Kingdom) were used as a dominating sink in the abiotic desorption experiments. Ethylacetate (p.a. grade) and methanol (HPLC grade) were obtained from Merck (Darmstadt, Germany), and acetone (HPLC grade) from Rathburn (Walkerburn, UK). Stock solutions of radiolabelled [9-^{14}C]-phenanthrene (specific activity 2.04×10^9 Bq mmol^{-1}, >99% radiochemical purity. American Radiolabeled Chemicals Inc., St. Louis, USA) and non-labelled phenanthrene (99.5%, Aldrich, St. Louis, USA) were prepared in methanol and acetone, respectively. Glass scintillation vials (Mikrolab Aarhus A/S, Aarhus, Denmark) were used as supplied. Ready Gel™ and Ready Safe™ scintillation cocktails were obtained from Beckman Coulter (Fullerton, USA). Bacterial culturing media were: tryptic soy broth (TSB) (3 g L^{-1}) and tryptic soy agar (TSA) consisting of 3 g L^{-1} TSB and 15 g L^{-1} bacteriological agar (both from Scharlau microbiology, Barcelona, Spain). Minimal salts medium (MSM) was prepared as described in Table S1. Acridine orange was obtained from Sigma (St. Louis, USA) and used to stain bacterial cells for direct cell counting. As model carbonaceous soil amendments, AC (untreated powder, 100–400 mesh; Sigma–Aldrich, St. Louis, USA), charcoal wood powder (Merck, Darmstadt, Germany) and compost, made from garden waste by a municipal composting company (Solum Gruppen, Roskilde, Denmark), were selected.

2.2. Preparation of the soil amendment suspensions

AC and charcoal were used as supplied. Compost was stored at 4 °C in sealed plastic bags until required. Then it was air dried for 4 d, passed through a 2 mm sieve to remove large objects such as wood, leaves and roots, and homogenized by hand. The homogenized compost was ground with a mortar and passed through a 0.125 mm sieve to obtain the same particle size range as the AC and charcoal (10–100 μm). The compost powder was stored in a glass bottle at room temperature until use.

For the abiotic desorption assays, suspensions of each amendment at a concentration of 10 mg L^{-1} were prepared in either MilliQ-water, TSB or MSM. These were spiked with ^{14}C-labelled phenanthrene (volume of acetone 0.005% v/v) to give a nominal concentration of 1.6 μg L^{-1} at a specific radioactivity of 11.4 MBq mg^{-1} of phenanthrene. The suspensions were shaken for 24 h before use in the abiotic desorption experiments to allow a surface equilibration between aqueous and soil amendment phases.

For the mineralization assays, suspensions of each amendment at a concentration of 10 mg L^{-1} were prepared in either TSB or MSM. For the mineralization assays, the MSM suspensions were supplemented with 100 mg L^{-1} of glucose to sustain a minimal bacterial growth. The suspensions were autoclaved and subsequently sonicated for 15 min in a water bath (Metason 200 (5210E-MT), Struers, Denmark) to break up any aggregates. Finally, they were spiked with ^{14}C-labelled phenanthrene (volume of