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A novel bioaccessibility prediction method for PAHs in soil: Composite extraction with hydroxypropyl-β-cyclodextrin and extracellular polymer substances

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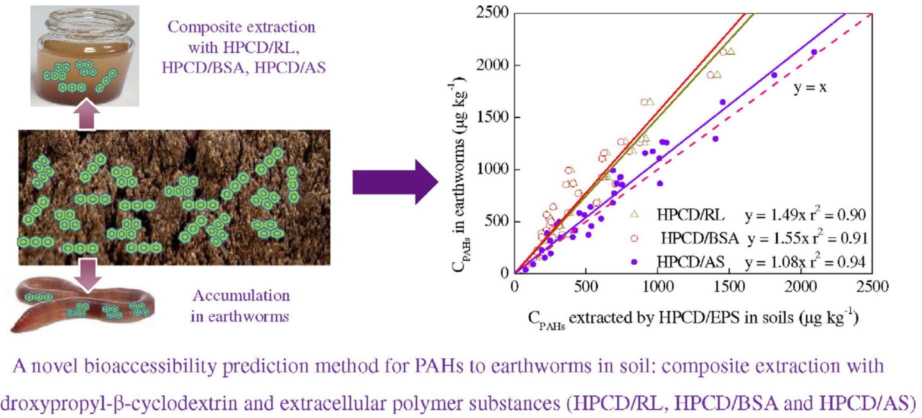
HIGHLIGHTS

- PAH bioaccessibility is often underestimated by traditional mild solvent extraction.
- Exogenous substances should be considered in the PAH bioaccessibility assessment.
- HPCD combined with EPS can improve PAH bioaccessibility assessment.
- Rhamnolipid, BSA and AS were chosen as models of the main components of EPS.
- HPCD/AS extraction performed best on assessing PAH bioaccessibility to earthworms.

GRAPHICAL ABSTRACT



A novel bioaccessibility prediction method for PAHs to earthworms in soil: composite extraction with hydroxypropyl-β-cyclodextrin and extracellular polymer substances (HPCD/RL, HPCD/BSA and HPCD/AS).

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ABSTRACT

Hydroxypropyl-β-cyclodextrin (HPCD) extraction has been widely used to estimate bioaccessibility of polycyclic aromatic hydrocarbons (PAHs) in soil, but it often underestimates the actual risk due to lack of information regarding the exogenous active substances, such as extracellular polymer substance (EPS) secreted by microorganisms. In this study, a novel technique, composite extraction of HPCD each with rhamnolipid (RL), bovine serum albumin (BSA) and alginate sodium (AS), models of lipopolysaccharide, proteins and polysaccharides, was developed to assess PAHs bioaccessibility to earthworms. In addition, comparisons were conducted with accelerated solvent extraction (ASE) and individual HPCD extraction. The results demonstrated that all chemical extractions were linearly correlated with earthworm accumulation, and individual HPCD extraction underestimated PAH bioaccessibility by about two times. However, the overall performances of the three composite chemical extractions (HPCD/AS, HPCD/RL, HPCD/BSA) were better than individual HPCD extraction, among which, HPCD/AS was best at estimating the earthworm accumulation (considering both correlation coefficient and fitted linear slope).

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Bovine serum albumin
Alginate sodium

Therefore, all observations implied that HPCD/AS extraction could be used as a fast and reliable method to predict PAH bioaccessibility to earthworms in contaminated soils.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a class of persistent organic pollutants, which are by-products of incomplete combustion of fossil fuels and biomass that are ubiquitous in the environment. The sorption and desorption of PAHs are significantly influenced by soil physicochemical properties such as soil texture, as well as dissolved organic matter (DOM) (Ortega-Calvo et al., 2015; Tang et al., 2016). In soil, PAHs may bind with soil organic matter or enter into soil micropores, resulting in difficulty of desorption and reduced risk. Therefore, PAH bioaccessibility, instead of total concentration, needs to be considered in the risk assessment and remediation of contaminated soils (Semple et al., 2004; Ding et al., 2008).

The bioaccessible fraction of a contaminant is denoted as being accessible for biological uptake or degradation (Reid et al., 2000a). Recently, a series of methods to estimate bioaccessibility have been developed with regard to microbial biodegradation (Sun et al., 2014; Ma et al., 2012), plant accumulation and animal uptake (Gomez-Eyles et al., 2010, 2012; Krauss et al., 2000; Liste and Alexander, 2002; Jonker et al., 2007). Most of these methods aim at simulating or accelerating the mobilization of the bioaccessible pollutant fraction without attacking the soil matrix. Such techniques include solid phase micro extractions (SPME) (Jonker et al., 2007), supercritical fluid extraction (Kreitinger et al., 2007), and extraction with surfactants such as hydroxypropyl-β-cyclodextrin (HPCD) (Bennett, 2000), as well as persulfate oxidation (Cuypers et al., 2000) and sub-critical water methods (Latawiec and Reid, 2009; Khan et al., 2015; Freddo et al., 2012; Waqas et al., 2014, 2015.) and mild solvent extraction (Oleszczuk, 2009). These methods have certain disadvantages – they usually under – or overestimate the bioaccessibility of target contaminants to some extent, and they do not take pollutant specific and organism specific characteristics into consideration. For example, although the fraction of PAHs degraded by microorganism is highly correlated with chemical extraction, the amount of PAHs degraded by microorganisms from the polluted soil is about 2.3-fold higher than that extracted by resin adsorbent (Covino et al., 2010). For the higher molecular weight hydrocarbons, biodegradation is up to 3.3 times higher than that extracted by HPCD (Dandie et al., 2010). To curtail these disadvantages, not only the correlation coefficient, but also the slope should be considered when modeling the relationship between bioassays and chemical extraction (Reid et al., 2000b; Rhodes et al., 2008). Therefore, there is a great need to develop improved chemical extraction methods for monitoring the bioaccessible PAHs in the soil ecosystem.

It is well known that some exogenous substances such as root exudates and extracellular polymer substance (EPS) secreted by plant roots or microorganisms heavily influence the migration, transformation and metabolism of some compounds (e.g., heavy metals and organic contaminants) in soils (Song et al., 2014; Sun et al., 2009; Henriques and Love, 2007). Polysaccharides, lipopolysaccharide and proteins are the main components of EPS (Herzberg et al., 2009), which accumulate on the surface of microbial cells or in soil matrix, provide binding sites for nutrients from the environment and promote the transformation of metal ions or organic compounds (Sheng et al., 2008). These compounds are able to improve the desorption of organic contaminants from soils and enhance their adsorption by other organisms such as plants or earthworms (Pan et al., 2010). Therefore, when exogenous substances such as EPS are involved in the chemical extraction method, the extraction amount of organic contaminants would be closer to the actual exposure of organisms. However, the effects of EPS on predicting PAH bioaccessibility have not yet been reported. Hypothetically, the composite extraction method that combined mild solvents with EPS would have good performance at assessing soil organic pollutants bioaccessibility. To test this hypothesis, rhamnolipid (RL), bovine serum albumin (BSA) and alginate sodium (AS) were selected as a model lipopolysaccharide, protein and polysaccharide, respectively, and combined with HPCD as a composite extraction agent for assessment of soil PAH bioaccessibility. The ASE extraction was set as the total portion and the earthworm uptake of PAHs in soil was used as the bioaccessible fraction. The results of this study will be useful for the development of soil PAH bioaccessibility assessment and will contribute to further environmental risk assessment.

2. Materials and methods

2.1. Chemicals

The following PAHs were selected: phenanthrene (Phe, 99%), pyrene (Pyr, 99%), chrysene (Chry, 99%), benzo(*a*)anthracene (BaA, 99%), benzo(*b*)fluoranthene (BbF 99%), benzo(*k*)fluoranthene (BkF, 99%), and benzo(*a*)pyrene (BaP, 96%) were obtained from Sigma Aldrich (Augsburg, Germany). Reagents of acetone, *n*-hexane, dichloromethane and acetonitrile were of HPLC grade, while HPCD (>98%), RL (>90%), AS (>90%) and BSA (>98%) were of analytical reagents. All of the aforementioned reagents were obtained from Shanghai Anpel Scientific Instrument Co., Ltd., China. Prior to use, anhydrous sodium sulfate, aluminum oxide, quartz sand, and diatomaceous earth (obtained from Sinopharm Chemical Reagent Co., Ltd., China) were heated at 200 °C for 4 h, and silica gel (100 mesh) was activated at 130 °C for 2 h.

2.2. Soil samples

Clean natural Yellow Soil was collected from the 10–20 cm depth zone of an agriculture field near Baguazhou of Nanjing, China (32°12′46″N,118°50′112.3″E). The physical and chemical characteristics were as follows: pH 7.6, organic matter 3%, sand 14%, silt 63%, clay 23%. The texture of the soil was silt loam, and it contained no detectable levels of PAHs. The soil was air dried and passed through a 2 mm sieve, then stored under cool conditions until use.

2.2.1. Soil spiking and aging

A stock solution of Phe (3-ringed PAH), Pyr, Chry, BaA, BbF and BkF (4-ringed PAHs), and BaP (5-ringed PAH) in acetone was mixed with 500 g soil in a glass beaker under a fume hood. The glass beaker was then put on a shaker in the hood for 24 h to evaporate all of the acetone. Next, the soil was transferred into amber glass jars, after which deionized water was added to bring the soil moisture to approximately 60% of the water holding capacity. The soil was incubated at 20 °C in the dark for aging, during which time the loss of water was determined by weighing, and replenished once a week. After 0, 7, 15, 30 and 60 days, the aged soils were collected and freeze-dried for different chemical extractions and bioassays. A non-spiked soil was used as the control. Initial PAH concentrations in the spiked soil measured with ASE and HPLC were as follows: Phe 924 ± 9 μg kg^{-1}, Pyr 1132 ± 29 μg kg^{-1}, Chry 1019 ± 21 μg kg^{-1}, BbF 906 ± 11 μg kg^{-1}, BaA 2148 ± 40 μg kg^{-1}, BkF 1046 ± 16 μg kg^{-1}, BaP 428 ± 17 μg kg^{-1}.

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