



# Prediction of Polycyclic Aromatic Hydrocarbon Bioaccessibility to Earthworms in Spiked Soils by Composite Extraction with Hydroxypropyl- $\beta$ -Cyclodextrin and Organic Acids

ZHANG Yanan<sup>1,2</sup>, YANG Xinglun<sup>1</sup>, GU Chenggang<sup>1</sup>, BIAN Yongrong<sup>1</sup>, LIU Zongtang<sup>1</sup>, JIA Mingyun<sup>1</sup>, WANG Fang<sup>1</sup>, WANG Daizhang<sup>3</sup> and JIANG Xin<sup>1,\*</sup>

<sup>1</sup>Key Laboratory of Soil Environment and Pollution Remediation, Institute of Soil Science, Chinese Academy of Sciences, Nanjing 210008 (China)

<sup>2</sup>University of Chinese Academy of Sciences, Beijing 100049 (China)

<sup>3</sup>College of Resources and Environment, Henan Agricultural University, Zhengzhou 450002 (China)

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## ABSTRACT

Traditional exhaustive extraction methods often overestimate the risk of polycyclic aromatic hydrocarbon (PAH) bioaccessibility to biota. Therefore, reliable assessment methods need to be established. In this study, a composite extraction with hydroxypropyl- $\beta$ -cyclodextrin (HPCD) and three low-molecular-weight organic acids, oxalic acid (OA), malic acid (MA), and citric acid (CA), was used to predict the PAH bioaccessibility to earthworms, subjecting to two soils (red soil and yellow soil) spiked with selected PAHs, phenanthrene, pyrene, chrysene, benzo(*a*)anthracene, benzo(*b*)fluoranthene, benzo(*k*)fluoranthene, and benzo(*a*)pyrene. For both soils, concentrations of PAHs by composite extraction using HPCD-OA ( $R^2 = 0.89$ – $0.92$ , slope =  $1.89$ – $2.03$ ;  $n = 35$ ), HPCD-MA ( $R^2 = 0.92$ – $0.96$ , slope =  $1.43$ – $1.67$ ;  $n = 35$ ), and HPCD-CA ( $R^2 = 0.92$ – $0.96$ , slope =  $1.26$ – $1.56$ ;  $n = 35$ ) were significantly correlated with PAH accumulation in the *Eisenia fetida* earthworms. Moreover, the HPCD-CA- and HPCD-MA-extracted PAH concentrations were closer to the earthworm-accumulated PAH concentration than the extraction using just HPCD. The results indicated that the composite extraction could improve the prediction of PAH bioaccessibility, and therefore can serve as a reliable chemical method to predict PAH bioaccessibility to earthworms in contaminated soils.

**Key Words:** chemical extraction, citric acid, earthworm accumulation, low-molecular-weight organic acid, malic acid

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Polycyclic aromatic hydrocarbons (PAHs) are considered to be priority pollutants in the environment and are of major concern due to their recalcitrance and strong mutagenic/carcinogenic properties (Gao *et al.*, 2009). The total content of PAHs in soils is only weakly related to their actual threat to the environment, whereas the main determinant of their toxicity in the environment is their bioaccessibility (Alexander, 2000; Semple *et al.*, 2007). Therefore, it is necessary to assess PAH bioaccessibility.

There are many methods currently used to assess PAH bioaccessibility, including exhaustive and non-exhaustive/mild extraction techniques. There is considerable evidence that results obtained using exhaustive techniques, such as accelerated solvent extraction (ASE), are poorly correlated with actual environmental risk and overestimate the “true” fractions (*e.g.*,

phenanthrene (Phe) and pyrene (Pyr)) available to biota (Kelsey *et al.*, 1996; Reid *et al.*, 2000a; Harrison *et al.*, 2006). In contrast, non-exhaustive techniques, such as hydroxypropyl- $\beta$ -cyclodextrin (HPCD), resin adsorbents, and supercritical fluid extractions, are commonly recognized as important tools for the rational assessment of PAH bioaccessibility (*e.g.*, Phe and Pyr) due to their convenient extraction processes and the better correlation with actual environmental risk (Reid *et al.*, 2000b; Stokes *et al.*, 2005; Yang *et al.*, 2010; Khan *et al.*, 2011; Bernhardt *et al.*, 2013). However, these conventional mild extraction methods usually underestimate the bioaccessibility of target contaminants, even though they have a good relationship with the actual environment risk. For example, although the degradation efficiencies of all fungal microcosms are significantly correlated with bioaccessibility, certain PAHs,

\*Corresponding author. E-mail address: jiangxin@issas.ac.cn.

such as chrysene (Chry) and benzo(a)pyrene (BaP), are degraded by microorganisms from the polluted soil at amounts about 2.3 times higher than those extracted by a resin adsorbent (Covino *et al.*, 2010). For the higher-molecular-weight PAHs, the amount of biodegradation has been shown to be up to 3.3 times more than that extracted by HPCD, with the resulting slope of the best-fit line ranging from 1.0–1.9 to 2.0–3.3 (Dandie *et al.*, 2010). Therefore, not only the correlation coefficient but also the intercept and slope should be considered when assessing the applicability of the method (Reid *et al.*, 2000b; Rhodes *et al.*, 2008).

Low-molecular-weight organic acids (LMWOAs), such as oxalic acid (OA), malic acid (MA), and citric acid (CA), have received attention in contaminated soil remediation. They are abundant in natural soil and water environments as a result of the microbial decomposition of organic matter and plant root exudates (Fox and Comerford, 1990). These LMWOAs always coexist with clay minerals and possess a strong chelating ability with multivalent cations, which occupy the adsorptive sites on mineral surfaces where PAHs are adsorbed (Semple *et al.*, 2004; Ding *et al.*, 2008), and therefore may enhance the desorption of organic pollutants in soils (White *et al.*, 2003). The retention of LMWOAs will unavoidably modify the surface properties and reactivity of clay minerals, and then influence the solubility and mobility of organic pollutants bound to them (Ling *et al.*, 2009; Ksiezopolska and Pazur, 2011). Theoretically, the action of LMWOAs working together with a conventional mild extraction, *e.g.*, HPCD, could improve the prediction of the bioaccessibility of organic pollutants in soil.

The predictive abilities of different extraction techniques were tested by earthworm accumulation in this study. The use of earthworms as a standard soil toxicity test organism has several advantages (Lanno *et al.*, 2004): i) earthworms can absorb contaminants not only through soil ingestion, but also directly through skin diffusion because their exterior epidermal surface is vascularized with no cuticle; ii) contaminant concentrations can be determined easily because of their large mass; and iii) some species, such as *Eisenia fetida*, can be cultured in the laboratory under controlled conditions and are tolerant of many soil types. In this study, it was hypothesized that a composite extraction method that incorporated HPCD with LMWOAs (OA, MA, and CA) would be suitable for assessing soil PAH bioaccessibility. The objective of this study was to verify the hypothesis and develop a reliable chemical extraction method to assess soil PAH bioaccessibility. This study can stimulate the development of methods

to assess soil PAH bioaccessibility, and will contribute to further environmental risk assessments.

## MATERIALS AND METHODS

### Chemicals

The following 7 priority PAHs, Phe (99%), Pyr (99%), Chry (99%), benzo(a)anthracene (BaA) (99%), benzo(b)fluoranthene (BbF) (99%), benzo(k)fluoranthene (BkF) (99%), and BaP (96%), were obtained from Sigma Aldrich (Augsburg, Germany). Acetone, *n*-hexane, dichloromethane, acetonitrile, HPCD (molecular weight (MW) 1 431–1 806, 99.7%), OA (MW 126.07, 99.5%), MA (MW 134.09, 99.5%), and CA (MW 210.14, 99.5%) were obtained from Shanghai Anpel Scientific Instrument Co., Ltd. (Shanghai, China). All reagents were of high performance liquid chromatography (HPLC) grade. Prior to use, anhydrous sodium sulfate, aluminum oxide, quartz sand, and diatomaceous earth, which were obtained from Sinapharm Chemical Reagent Co., Ltd. (Shanghai, China), were heated at 200 °C for 4 h, and silica gel (0.15 mm) was activated at 130 °C for 2 h.

### Soils

Two soils, a red soil and a yellow soil, were used in this study. The red soil was obtained from Hainan, China (19°46'16.6" N, 110°00'21.5" E) and the yellow soil was obtained from Baguazhou, Nanjing, China (32°12'46" N, 118°50'112.3" E). The two soils were not contaminated by PAHs and did not contain any PAHs at detectable levels. The basic physico-chemical properties of the soils are given in Table I. The soils were air dried, passed through a 2-mm sieve, and then stored under cool conditions until use.

### Soil spiking and aging

The polycyclic aromatic hydrocarbons (Phe, Pyr, Chry, BaA, BbF, BkF, and BaP) dissolved in acetone were added to each soil. The soil was then left uncovered in a fume hood for 24 h and then shaken with a mixer. All of the acetone was allowed to evaporate, and then the PAHs were mixed with the soil. The soil was then placed into amber glass jars for aging, and deionized water was added to each jar to keep the soil moisture at approximately 60% soil water-holding capacity. The jars were then placed in the dark at room temperature (about 20 °C). The spiked soil was rewetted to 60% soil water-holding capacity once per week. After aging for 0, 7, 15, 30, and 60 d, the aged soil samples were collected and freeze-dried to enable the use of earthworm bioassays (PAH accumulation in

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