



# Evaluating bioavailability of organic pollutants in soils by sequential ultrasonic extraction procedure



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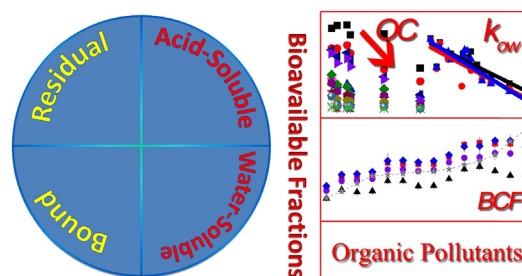
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## HIGHLIGHTS

- SUEP is used to evaluate bioavailability of organic pollutants in soils.
- Bioavailable fraction includes water and acid-soluble fractions.
- Bioavailable fraction is negatively correlated with  $\log K_{ow}$  and SOM.
- Amount of plant uptake is highly correlated with bioavailable fraction.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Under current retrospective risk assessment framework, the total concentrations of organic pollutants in soils have been employed as the standard for over 30 years. The total concentrations reflect the overall accumulation in soils but tend to be overly conservative for assessing the ecological risks, where the bioavailability plays an important role. In this study, the bioavailability of organic pollutants in soils was evaluated using a stepwise and tiered classification method, namely the sequential ultrasonic extraction procedure (SUEP). The water-soluble and acid-soluble fractions extracted by the SUEP were the bioavailable fractions. The reliability and environmental relevance of the speciation method were examined with representative organic pollutants using the root uptake methods and the semipermeable membrane devices (SPMDs). The plant uptake amounts corrected with weight were highly correlated with the bioavailable fractions ( $R^2 > 0.75$ ). The amounts of the bioavailable fractions were negatively correlated with the  $\log K_{ow}$  values ( $R^2$  ranging from 0.71 to 0.77) of the organic pollutants and the contents of soil organic matter ( $R^2$  ranging from 0.68 to 0.96). As a refinement of the current risk assessment framework, the SUEP that has proved to be a reliable and convenient is thus highly recommended for evaluating the bioavailability of organic pollutants in soils.

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## 1. Introduction

Organic pollutants in arable lands of China are seriously

endangering the safety of agricultural products. Long and Chapman (1985) proposed the sediment quality triad to measure the pollution level and toxicity to infaunal communities in sediment. Under the current retrospective risk assessment framework, the total concentrations of organic pollutants has been employed as the standard for over 30 years, which however tend to be overly conservative (Semple et al., 2004; Clarke and Smith, 2011). For

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instance, the concentrations of organochlorine pesticides (OCPs) in carrots and other crops were found to be insignificantly correlated with the total concentrations in the soils (Harris and Sans, 1967). It is thus important to prioritize organic polluted soils based on the bioavailable rather than the total concentrations (Ortega-Calvo et al., 2015). While the total concentrations of organic pollution in soils reflect the accumulation, the bioavailable concentrations should be employed for environmental risk assessment.

Bioavailability, initially used in medicine, was used as the evaluation standard for risk assessment in environmental science since 2004 (Ehlers and Luthy, 2003; Semple et al., 2004). In numerous studies regarding toxicology or agricultural sciences, the most common definition of bioavailability is the amount of pollutants entering organisms. These pollutants, usually adsorbed by soils or sediments, can only be accumulated in organisms while being released via desorption. It was found that with higher content of soil organic matter (SOM), the phenanthrene (PHEN) had lower bioavailability in soils. With 155d of aging, the earthworm-uptake ratio of PHEN in the dissimilar soils is 0.7% (with SOM of 4.5%) and 3.3% (with SOM of 1.1%), respectively (White et al., 1997). The polychlorinated biphenyls (PCBs) with relatively lower hydrophobicity were found to have higher bioavailability (Mayer et al., 2000). Thus, the bioavailability is affected by properties of soil and pollutants.

For measuring the bioavailability, various of chemical and biological methods have been developed, including Tenax (Morrison et al., 2000; Harmsen et al., 2007; Congiu and Ortega-Calvo, 2014), cyclodextrin extraction (Cuypers et al., 2002; Doick et al., 2005; Cai et al., 2014, 2015), semipermeable membrane device-assisted (SPMDs) (Huckins et al., 1990; Petty et al., 2000; Sun et al., 2008), uptake by earthworm (Paris, 2004) and plant (Laperche et al., 1997; Chojnacka et al., 2005; Kidd et al., 2007; Misra and Chaturvedi, 2007). The choice of method depends on the objectives and may differ for scientific research. The existing methods have limitations in the evaluation of bioavailability. The risk assessment data used for decision making was not clearly and understandably connected to the presence of organic chemicals in the soil or sediment environment (Ortega-Calvo et al., 2015). Standardized methods should be suitable for all soils/sediments and chemicals. The soil quality procedure for site-specific ecological risk assessment of soil contamination (TRIAD approach), which consists of three lines of evidence, standardized by the International Organization for Standardization (ISO) is neither practical nor economically feasible (Standardization, 2014). Therefore, a stepwise and tiered approach, similar to that used for metals, is required. The migration, transformation and bioavailability of soil organic pollutants largely depends on their chemical speciation. Therefore, it is important to understand the speciation of soil organic pollutants for efficiently regulating the migration of organic pollutants.

A sequential ultrasonic solvent extraction procedure (SUEP) has been developed for separating different fractions of polycyclic aromatic hydrocarbons (PAHs), presented in one of our previous studies (Wang et al., 2015). The PAHs in soils are classified into four fractions, including water-soluble fraction, acid-soluble fraction, bound fraction and residual fraction. PAHs in the water-soluble fraction can be desorbed by water, directly bioavailable to plants. The acid-soluble fraction which can be desorbed by root exudates or organic acids was also bioavailable. In contrast, the bound and residual fractions are hard or impossible for plants to uptake which meant little or no bioavailability. This method had proved to be accurate and repetitive with an isotope experiment. For our previous studies, the tested categories of organic pollutants and soil types should be expanded. While, the correlation between the bioavailability and the speciation of organic pollutants in soils need

to be further investigated.

The aim of this study is to validate the SUEP, a stepwise and tiered classification method, against a more extensive set of organic pollutants and soils. The correlations between the evaluation results by this method and the bioavailability measured using the root uptake methods and the SPMDs in the soils for the pollutants were explored. The relationships of the bioavailable fraction with the properties of soil and organic pollutants were also investigated. This study provides a practical, convenient and reliable method for predicting the concentration of pollutants accumulated in crops in order to accurately evaluate the ecological risk of organic pollutants in farmland soils.

## 2. Materials and methods

### 2.1. Soil samples

Six typical soils were used in this experiment, with main properties provided in Table S1 of the supplementary material (SM). All the soils were collected from the top layer of the ground (0–20 cm). The sandy soil (soil A) was collected from the edge of Kubuqi desert in Inner Mongolia. The soils from Zhejiang province (soil B and C) were used for rice plantation and the soil from Jiangxi province (Soil D) was used in tea plantation. The soil E from Jilin province and the soil F from Heilongjiang province were planted with sorghum and maize. The soil samples were transported and stored at  $-20\text{ }^{\circ}\text{C}$  under  $\text{N}_2$  in a sealed aluminum foil tube to minimize microbial activity immediately after collection.

### 2.2. Chemicals

For the quantitative analysis of the concentration of pollutants in the extraction from soil samples and plants, standards of 6 kinds of PAHs, 5 kinds of phthalate esters (PAEs), one kind of OCP, polybrominated diphenyl ethers (PBDEs), PCB, phenol, and xylene homologue were used in the experiment. The detailed information about the pollutants is provided in the SM (Table S2). The stock standards were purchased from AccuStandard (NewHaven, USA). All solvents were of HPLC grade or pesticide grade. For the spiking of the pollutants in the soils, analytical grade of listed pollutants were used. Florisil, silica gel and anhydrous sodium sulfate for clean-up procedure were activated or pretreated in advance (Niu et al., 2013). Others chemicals used in this study were purchased from the Aladdin<sup>®</sup> Chemical Reagent Co., Ltd., China.

### 2.3. Soil contamination

All the soil samples were freeze-dried, ground and passed through a stainless steel 75-mesh (0.5 mm) sieve. The concentrations of the 17 organic pollutants were measured in all the samples, and all of them were lower than the limit of detection (LOD). One soil sample (50 g) was spiked with pollutant dissolved in acetone through dropwise addition, one kind at a time, and thoroughly shaken for even distribution. Then, 50 g of spiked soil and the aqueous solution of sodium azide ( $\text{NaN}_3$ ) with a concentration of  $200\text{ mg kg}^{-1}$  were added into 950 g of clean soil. The mixed samples were exposed in the ambient air ( $10\text{ }^{\circ}\text{C}$ ) overnight to evaporate acetone. 17 kinds of organic pollutants (Table S2) followed the contamination procedure at a concentration of  $100\text{ mg kg}^{-1}$  and the BaP at a level of  $20\text{ mg kg}^{-1}$ . The soils were then stored in the dark at room temperature ( $25 \pm 1\text{ }^{\circ}\text{C}$ ) and aged for 30d.

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