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Short communication

Adsorption of phenanthrene by earthworms - A pathway for understanding the fate of hydrophobic organic contaminants in soil-earthworm systems

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ABSTRACT

The fate of hydrophobic organic contaminants (HOCs) in soil-earthworm systems is an important foundation for soil pollution risk assessment and pollution control. Equilibrium partitioning is considered to be the main mechanism by which HOCs enter earthworms and, as such, a mechanistic model has been developed to estimate the earthworm-water partition coefficients ($K_{w\text{-}w}$). In the present study, the adsorption of phenanthrene (PHE) by earthworm tissue was investigated to evaluate the validity of the mechanistic models. Results revealed that $K_{w\text{-}w}$ derived from the mechanistic model (346.90) was lower than that derived from the sorption experiments (410.76), indicating that apart from lipid fractions, other components in earthworms, such as protein fractions, might also play an important role in the adsorption of HOCs by earthworm. Besides, the difference between the mechanistic model for earthworm and partition-limited model used for plants are few, indicating that uptake and accumulation mechanisms of HOCs by earthworms and plants are highly consistent internally and are, essentially actually identical. It is also suggested that environmental fate of HOCs in soil-soil biota systems is dominated by their high hydrophobicity. Based on these conclusions, an improved mechanistic model for predicting the uptake of organic contaminants by earthworms has been proposed, which needs to be further evaluated. Furthermore, the feasibility of using vermiaccumulation in vermiremediation of soil contaminated by HOCs was discussed.

The adsorption of PHE by earthworm sub-organism fractions (pre-clitellum, clitellum and post-clitellum) and tissue fractions (body wall and gut) were also investigated to interpret the distribution pattern of HOCs in earthworms. At the sub-organism level, the adsorption capacity of PHE by different regions of the earthworm followed the order: post-clitellum > clitellum > pre-clitellum, meaning the distribution of PHE along the earthworm contributes not only to their chemical composition but also to the life activity of earthworms such as circular system. At the tissue level, the gut showed greater affinity with PHE than that of the body wall indicating that the distribution of PHE is mainly due to chemical components at the tissue levels. These results might provide additional understanding of the fate of HOCs in soil-earthworm systems.

1. Introduction

Earthworms are one of the most important soil fauna and play a key role in terrestrial ecosystems (Peijnenburg and Vijver, 2009). The accumulation of hydrophobic organic contaminants (HOCs) in earthworms leads to the transfer of contaminants into the terrestrial food chain/web, followed by the possible preying by moles, badgers, thrushes and other predators (Jager, 1998). Vermiremediation of organic polluted soils, which refers to the use of earthworms for the removal of contaminants from soil or when earthworms help to degrade non-recyclables, has recently drawn attention as a possible innovative technology (Dendooven et al., 2011; Gupta and Garg, 2009; Rodriguez-Campos et al., 2014). Further, earthworms are important model organisms used to indicate the status of soil health by investigating their responses to various external stressors such as soil contaminants (Lankadurai et al., 2015; Shi et al., 2013). Therefore, understanding the behaviour of uptake, accumulation, translocation and distribution of HOCs by earthworm is fundamental for soil pollution ecological risk

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assessment and provide guidance for the practice application of vermiremediation.

HOCs may enter earthworms via epidermal uptake and dietary uptake and then disperse within the earthworms. Epidermal uptake is usually predominant over dietary uptake for hydrophobic chemicals that have a $\log K_{ow} < 5$ (K_{ow} is the octanol-water partition coefficient) (Belfroid et al., 1995; Jager et al., 2003). The uptake of HOCs by earthworms is thought to depend on the properties of the contaminants, earthworm species, and soil types (Lanno et al., 2004). The relationships between earthworm uptake and the physical-chemical properties of contaminants have been established and have been described as linear between the logarithms of earthworm bioconcentration factors (*BCFs*) and the logarithm of the K_{ow} of contaminants. However, these relationships were formulated empirically (Jager, 1998; Raber et al., 1998). Afterwards, a mechanistic model was developed for estimating the bioconcentration of organic chemicals in earthworms, based on the contaminant passive uptake by earthworms in a series of partitioning processes among soil solids, soil water, and the resident organism's tissue (Hodson et al., 2011; Jager, 1998; Khan et al., 2011; Reiss et al., 2009).

The mechanistic model assumes that an earthworm is an inanimate container seeking to reach thermodynamic equilibrium with its medium. Therefore, studying the adsorption of organic contaminants by earthworm tissues is the key to understanding the uptake process. However, until now, it seems that there has been a lack of the quantitative evaluation of the partitioning coefficient between earthworms and water in equilibrium ($K_{w\text{-}w}$). Consequently, the assumption of the mechanistic model that the earthworm's lipid fractions are the main storage pool of HOCs and that other components, such as protein and carbohydrates, can be neglected, need further validation. If it is true, then $K_{w\text{-}w}$ derived from the sorption experiment should be consistent with that of the mechanistic model.

The distribution of HOCs in earthworm is usually considered the result of partitioning between different chemical fractions, which is not well defined between organs or regions or parts along the earthworm. Since different regions of an organism possess different physiological functions, understanding the exact distribution of HOCs in earthworm is very important to better clarify the toxic response mechanism (Escher et al., 2011; Escher and Hermens, 2004). In previous studies, application of the earthworm accumulation experiment and earthworm fractionation strategy, confirmed that phenanthrene (PHE) in earthworm tissue level and sub-organism levels is heterogeneously distributed (Shi et al., 2014). However, it is difficult to explain this heterogeneous distribution. If entry of PHE into earthworm is mainly through the body wall as a function of the partitioning processes, the distribution of PHE in the earthworm should be homogenous across the different fractionation levels and be consistent with that of the adsorption pattern in the different sub-organism regions.

Based on these statements, the study the adsorption of HOCs by earthworm tissues is important for understanding the fate of HOCs in soil-earthworm systems. Specifically, the adsorption of PHE, a representative HOCs, to the whole earthworm, sub-organism fractions and tissue fractions was investigated to validate the assumption of the mechanistic model and to explain the internal distribution behaviour of PHE within earthworms.

2. Material and methods

2.1. Test earthworm and chemicals

The *Eisenia fetida* (Savigny 1826) earthworm used in this study were purchased from a commercial supplier. Prior to the experiment, earthworms were pre-incubated in mixtures of potting compost soil and cow dung in the dark at $22 \pm 1\,^{\circ}C$ for 2 weeks.

Phenanthrene (PHE, purity ≥97%) was purchased from the Fluka Company, Germany. All reagents used in the study were of analytical grade.

2.2. Preparation of dry earthworm, sub-organism fractions and tissue fractions

Adult earthworms (each 200–300 mg, wet weight) with well-developed clitellum were chosen randomly and placed on a moist filter for 24 h to depurate their gastrointestinal tract. Gut-voided earthworms were then rinsed with deionized water and softly dried with absorbent paper. Dry whole earthworm, sub-organism fractions (pre-clitellum, clitellum and post-clitellum) and tissue fractions (gut and body wall) powder were obtained according to the methods established in our previous study (Shi et al., 2014).

The dead earthworm or fractions were weighted and freeze-dried using a vacuum freeze dryer (Alpha 1–2 LD plus, Sigma, German) for 72 h to determine the water content. Dried earthworm or fractions were then ground into powder using an agate mortar.

2.3. Adsorption experiments

All sorption isotherms were obtained using a batch equilibration technique at $30 \pm 1\,^{\circ}C$. The adsorption of PHE by earthworms or their parts was determined using the following approach: 20.0 mg of dry earthworm powder, sub-organism fraction (pre-clitellum, clitellum, and post-clitellum regions) powder and tissue fraction (body wall and gut regions) powder were transferred into 40 mL brown glass centrifuge tubes and 25 mL of 0.01 mol/L KNO_3 solution containing a certain concentration of PHE (nominal initial aqueous concentrations of 0.1, 0.25, 0.5, 0.7 and 1 mg/L according to the aqueous solubility of HPE at 25 °C). Less than 0.1% methanol and 0.02% NaN_3 were also added to the tubes to avoid any cosolvent effects and prevent any possible biodegradation, respectively. Tubes were shaken at 150 rpm for 36 h according to the preliminary kinetic study. Samples were prepared in triplicate for each treatment. Control samples containing PHE but no sorbent were prepared to determine solute loss possibly occurring due to handling, volatilisation and degradation.

2.4. Determination of PHE in water

Tubes were centrifuged at 4000 rpm for 10 min and 0.5 mL of supernatants was diluted with 0.5 mL of HPLC grade methanol. The supernatant was then filtered using a 0.22 μm Teflon filter membrane. A Shimadzu HPLC (LC-20A, Japan) equipped with an UV–visible detector and a reverse-phase C_{18} chromatographic column (25 cm × 4.6 mm, 5 μm particle diameter) was used for PHE quantification (Ma et al., 2012; Zhang and Zhu, 2009).

2.5. Statistical analyses

The amount of sorped PHE was calculated based on the difference between the solution concentration and the total amounts of PHE added to the solution. Slopes of sorption isotherms ($K_{w\text{-}w}$) were calculated from the linear part of each isotherm.