Available online at www.sciencedirect.com
ScienceDirect
Environmental Pollution 145 (2007) 154–160
ENVIRONMENTAL POLLUTION
www.elsevier.com/locate/envpol

Comparison of techniques for estimating PAH bioavailability: Uptake in *Eisenia fetida*, passive samplers and leaching using various solvents and additives

Magnus Bergknut*, Emma Sehlin, Staffan Lundstedt, Patrik L. Andersson, Peter Haglund, Mats Tysklind

Department of Chemistry, Environmental Chemistry, Umeå University, SE-90187 Umeå, Sweden

Received 15 November 2005; received in revised form 13 March 2006; accepted 23 March 2006

The total and relative amounts of PAHs extracted by abiotic techniques for assessing the bioavailability of PAHs was found to differ from the amounts taken up by Eisenia fetida.

Abstract

The aim of this study was to evaluate different techniques for assessing the availability of polycyclic aromatic hydrocarbons (PAHs) in soil. This was done by comparing the amounts (total and relative) taken up by the earthworm *Eisenia fetida* with the amounts extracted by solid-phase microextraction (SPME), semi-permeable membrane devices (SPMDs), leaching with various solvent mixtures, leaching using additives, and sequential leaching. Bioconcentration factors of PAHs in the earthworms based on equilibrium partitioning theory resulted in poor correlations to observed values. This was most notable for PAHs with high concentrations in the studied soil. Evaluation by principal component analysis (PCA) showed distinct differences between the evaluated techniques and, generally, there were larger proportions of carcinogenic PAHs (4–6 fused rings) in the earthworms. These results suggest that it may be difficult to develop a chemical method that is capable of mimicking biological uptake, and thus estimating the bioavailability of PAHs.
© 2006 Elsevier Ltd. All rights reserved.

Keywords: Bioavailability; Polycyclic aromatic hydrocarbons; Earthworms; Leaching; Hydroxypropyl-β-cyclodextrin; Solid-phase microextraction; Semi-permeable membrane device

1. Introduction

Research into the bioavailability of pollutants in soil is rapidly intensifying, and the number of articles concerning the bioavailability of polycyclic aromatic hydrocarbons (PAHs) in soil is increasing every year. However, the concept of bioavailability lacks a formal definition and there is little agreement on what bioavailability means, how it should be measured, and how it should be calculated. Consequently, it is difficult to compare findings by different authors or proposed techniques for assessing the bioavailability of PAHs in soil, since different studies are often based on different concepts of bioavailability. The bioavailable fraction of persistent organic pollutants (POPs) in soil is envisaged as the fraction of POPs in the matrix that can be taken up by organisms. However, it should be noted that uptake rates differ between species and that the timescale considered will affect the amounts of accumulated POPs. The most widely accepted theory concerning the uptake of chemicals by organisms in the soil is the equilibrium partitioning (EP) theory, i.e. that the bioavailability of POPs is controlled by equilibrium partitioning between the soil, water and the organisms (Shea, 1988; Ditoro et al., 1991; Sijm et al., 2000). Some deviations from expected EP results have been observed, which are usually attributed to sequestration of pollutants in the soil, the effects of feeding and biotransformation.

* Corresponding author. Tel.: +46 90 786 9339; fax: +46 90 128133.
E-mail address: magnus.bergknut@chem.umu.se (M. Bergknut).

0269-7491/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.envpol.2006.03.052

Soil is a very complex matrix, as are the POP sorption/desorption mechanisms associated with it (Reid et al., 2000a). Thus, when comparing results obtained using different techniques for assessing bioavailability, it is important to bear in mind that bioavailability is governed by the three-way interactions between the pollutant, the matrix and the organism(s) in the matrix (Reid et al., 2000a; Madsen, 2003). For a strict comparison of different techniques used to assess bioavailability, these variables should not be changed. If they are changed, several factors need to be considered. The choice of matrix will be of great importance and, if possible, use of artificial soil or spiked samples should be avoided since extrapolation of the resulting data to aged contaminated soils is problematic. Instead, it is preferable to use aged, weathered soils (Madsen, 2003). For the same reasons, the samples should not be ground or subjected to other pre-treatments that may substantially change the physical characteristics of the matrix. The reason for estimating bioavailability also has to be considered, since most test systems are more suitable for some applications than others. For instance, degradation parameters of various substances by microorganisms are often used as indicators of the bioavailability of substances when assessing the limitations of bioremediation scenarios, while the earthworm is a good test system when trying to estimate the potential exposure of biota. Earthworms' extensive use in soil ecotoxicology, known importance in the terrestrial food chain, high degree of pollutant accumulation, and ease of handling make them suitable test organisms (Lanno et al., 2004; Jager et al., 2005). However, earthworms are affected by pH and other soil properties, and they can only be used with limited concentration ranges of some substances, and not at all for other substances. Furthermore, the accumulation of pollutants and sensitivity to soil conditions vary between different earthworm species (Jager et al., 2005).

In an earlier study we investigated how pre-treatment and extraction conditions affected the availability of PAHs in aged soil collected from a former gasworks site (Bergknut et al., 2004). In the study presented here the aim was to compare different abiotic techniques for assessing the bioavailability of PAHs in the same soil, using *Eisenia fetida* as the reference system for bioavailability. The bioavailability of the 16 U.S. EPA PAHs was assessed by: leaching with various solvents or mixtures of solvents (methanol, water/methanol and water/*n*-butanol) (Kelsey and Alexander, 1997; Kelsey et al., 1997; Liste and Alexander, 2002); leaching with aqueous solutions of Tween-80 (Volkering et al., 1995), and hydroxypropyl-β-cyclodextrin (HPCD) (Reid et al., 2000b); solid-phase microextraction (SPME) (Mayer et al., 2000; van der Wal et al., 2004); and extraction with semi-permeable membrane devices (SPMDs) (Strandberg et al., 1997).

2. Experimental design

The study was divided into six parts: (i) exhaustive Soxhlet extraction to determine the total PAH concentration of the soil; (ii) sequential leaching using solvents of decreasing polarity (methanol, *n*-butanol, acetone, and *n*-hexane, followed by toluene, which has high affinity for planar compounds) to assess the relative sorption strength of various PAH pools; (iii) batch leaching experiments using mixtures of methanol/water, 50:50 (v/v), methanol/water 1:99 (v/v), and *n*-butanol/water (1:99 v/v); (iv) batch leaching experiments using aqueous solutions of two modifiers with different modes of action—a bioavailability-enhancing detergent (Tween-80, 3 mM; Volkering et al., 1995) and a complex-forming agent used in bioavailability assessments (HPCD, 50 mM; Reid et al., 2000b); (v) passive sampling using SPME and SPMDs; and (vi) uptake by earthworms (*Eisenia fetida*) to obtain a measure of the bioavailability of the PAHs (at least for a specific organism).

The selection of solvents used in (ii) and (iii) were based on previous studies in which solvents or mixtures of solvents and water have been used to assess bioavailability (Kelsey and Alexander, 1997; Kelsey et al., 1997; Liste and Alexander, 2002). The SPME and SPMD experiments were included since POP levels determined by SPMEs have recently been shown to correlate well with earthworm uptake levels (van der Wal et al., 2004), and SPMDs have potential value for estimating the bioavailable fraction in soil-inhibiting organisms such as earthworms according to Strandberg et al. (1997). It should be noted that pre-defined sampling rates or partitioning coefficients are normally used to calculate the POP concentrations in soils from SPMD and SPME data, respectively. However, in this study they were used as indicators of availability, and thus the relative amounts of the various PAHs were primarily considered. The proposed working principles of, and soil compartments sampled by, the different techniques are listed in Table 1. Variations in the relative amounts of the PAHs sampled by the different techniques were evaluated using Principal Component Analysis (PCA; Wold et al., 1984, 1987).

3. Materials and methods

3.1. Chemicals

Soxhlet cellulose extraction thimbles were purchased from Whatman International Ltd (Maidstone, Kent, UK). Silica gel 60 (0.063–0.200 mm) was

Table 1
Working principles and compartments sampled by each of the techniques included in the study

Technique	Compartment sampled	Extraction mode	Capacity
Soxhlet	Soil Suspended particles Colloids Dissolved analytes	Exhaustive	Total
Solvents (pure and mixtures)	Soil Suspended particles Colloids Dissolved analytes	Partial	Variable
SPMD[a]	Dissolved analytes	Linear uptake	High
HPCD[b]	Dissolved analytes	Steady state (equilibrium)	Low
SPME[c]	Dissolved analytes	Steady state (equilibrium)	Low

[a] SPMD: extraction using semi-permeable membrane devices.
[b] HPCD: extraction using hydroxypropyl-β-cyclodextrin.
[c] SPME: solid-phase microextraction.

Download English Version:

https://daneshyari.com/en/article/4427418

Download Persian Version:

https://daneshyari.com/article/4427418

Daneshyari.com