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Predicting bioavailability of PAHs in field-contaminated soils by passive sampling with triolein embedded cellulose acetate membranes

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Triolein embedded cellulose acetate membranes can be a useful tool to predict bioavailability of PAHs in field-contaminated soils.

ABSTRACT

Triolein embedded cellulose acetate membrane (TECAM) was used for passive sampling of the fraction of naphthalene, phenanthrene, pyrene and benzo[a]pyrene in 18 field-contaminated soils. The sampling process of PAHs by TECAM fitted well with a first-order kinetics model and PAHs reached 95% of equilibrium in TECAM within 20 h. Concentrations of PAHs in TECAM (C_{TECAM}) correlated well with the concentrations in soils ($r^2 = 0.693$–0.962, $p < 0.001$). Furthermore, concentrations of PAHs determined in the soil solution were very close to the values estimated by C_{TECAM} and the partition coefficient between TECAM and water ($K_{TECAM-w}$). After lipid normalization nearly 1:1 relationships were observed between PAH concentrations in TECAMs and earthworms exposed to the soils ($r^2 = 0.591$–0.824, $n = 18$, $p < 0.01$). These results suggest that TECAM can be a useful tool to predict bioavailability of PAHs in field-contaminated soils.

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1. Introduction

Sampling the bioavailable fraction of hydrophobic organic contaminants (HOCs) in soils is the most important step in predicting their bioavailability and assessing their risk to living organisms. It is generally accepted that organisms can take up HOCs that are present in the aqueous phase and some of the potential bioavailable fractions such as the ones associated with dissolved organic matter and colloids (Ehlers and Loibner, 2006). Therefore, only a small fraction of HOCs in soils is considered to be available to living organisms (Jager, 1998; Jager et al., 2003; Van Der Wal et al., 2004). Chemical extraction methods are usually applied to sample HOCs in soils. However, vigorous extraction procedures may remove a larger proportion of the contaminants, resulting in an overestimation of their bioavailability (Tang et al., 2002). As a result, gentle and selective extractants have been proposed to predict bioavailability of HOCs in soils (Kelsey et al., 1997; Reid et al., 2000; Liste and Alexander, 2002). However, different extractants and extraction conditions or different ratios of extractant to soil may result in different results and the methods are difficult to compare.

An example of progress in sampling of HOCs is the development of passive sampling techniques. Passive sampling devices (PSDs)

such as solid-phase microextraction (SPME) (Conder et al., 2003; Van Der Wal et al., 2004), semipermeable membrane devices (SPMD) (Huckins et al., 1990, 1999) and C_{18} sampling bags (Awata et al., 2000; Zhang et al., 2006) or disks (Krauss and Wilcke, 2001) offer several advantages over the traditional methods, including simplifying and speeding up analysis procedures, using small volumes of solvent or even no solvent at all, and saving costs and labor (Górecki and Namiesnik, 2002). Although SPME has been slightly more widely used to sample the bioavailable fraction of HOCs in soils than other PSDs, sampling by SPME is mainly achieved by immersing the fiber in an aqueous suspension of soil with agitation or shaking (Boyd-Boland and Pawliszyn, 1995), and shortcomings have been noted related to fiber stability (physical or chemical) and sensitivity (Hernandez et al., 2000). C_{18} sampling bags (Awata et al., 2000; Zhang et al., 2006) or disks (Krauss and Wilcke, 2001) have been reported to sample the bioavailable fraction of HOCs in soils, but since the volume of the bag or disk and the corresponding volume of the hydrophobic C_{18}-material are much larger than that of SPMD or SPME fiber, a much higher water content than field soil water-holding capacity is required to avoid depletion. The triolein-containing SPMDs developed by Huckins et al. (1990) are widely used to sample HOCs in water (Petty et al., 2000), air (Söderström et al., 2005) and sediments (Rantalainen et al., 2000). However, their application in terrestrial environments (especially in field-contaminated soils) is relatively new and very limited applications of SPMDs have been reported for sampling or

monitoring HOCs in soils (Zabic et al., 1992; Rantalainen et al., 1998; Ahn et al., 2005).

Triolein embedded cellulose acetate membrane (TECAM), a type of passive sampling device (PSD), has been developed in which triolein drops are embedded in a matrix of cellulose acetate polymer (Xu et al., 2005), and this has been used successfully in aqueous systems (Xu et al., 2005; Ke et al., 2006). TECAM provides a sampling technique based on passive diffusion of the chemical compounds from the aqueous phase into thin cellulose acetate membranes impregnated with triolein. This design has several advantages. First, the membrane material is cellulose acetate, which can mix uniformly with triolein by dissolving in a strong organic solvent. An integrative semipermeable membrane can be easily obtained after solvent volatilization. Second, 1 mL triolein can be uniformly distributed on approximately 15,000 cm^2 of surface area of cellulose acetate, a much larger area than 1 mL triolein on 450 cm^2 surface of the low-density polyethylene of SPMD (Huckins et al., 1999), resulting in a larger contact area between the triolein and HOCs. Third, the preparation of TECAM is easily established in the laboratory and is inexpensive and readily available. These advantages provide TECAM with some potential applications in sampling of HOCs from complex environmental matrices such as soils. Our previous study (Tao et al., 2008) has indicated that TECAM can be applied successfully to accumulate naphthalene, phenanthrene, pyrene and benzo[a]pyrene from spiked soils and the uptake of PAHs by TECAM was correlated with soil properties and was sensitive to aging of PAHs in soils.

In this paper we report further research in which we tested the feasibility of using TECAM to predict bioavailability of PAHs in field-contaminated soils at low contamination levels. Sampling kinetics and the relationship between concentrations of PAHs in TECAMs (C_{TECAM}) and soils were investigated. Concentrations of PAHs in soil solutions were measured and compared with the estimated values from C_{TECAM} and partition coefficients between TECAM and water ($K_{TECAM-w}$). Furthermore, the relationship between the uptake of PAHs by TECAMs and uptake by earthworms (*Eisenia andrei*) was explored.

2. Materials and methods

2.1. Chemicals, reagents, TECAMs and earthworms

Naphthalene (Nap), phenanthrene (Phe), pyrene (Pyr) and benzo[a]pyrene (BaP) of >99% purity were purchased from Acros Organics (New Jersey, USA) and used for identification and quantification. All solvents used, i.e. *n*-hexane, dichloromethane, acetone and methanol, were of HPLC grade.

TECAMs were prepared according to Xu et al. (2005). They were made of cellulose acetate (17.5 wt%, Sigma, USA), acetone (69 wt%), 1,4-dioxane (10 wt%), anhydrous magnesium perchlorate (2 wt%) and triolein (1.5 wt%, Sigma, USA). All the membranes were kept in distilled water before use.

The earthworm species used was *Eisenia andrei* which was obtained from China Agricultural University. They were allowed to acclimatize to laboratory conditions in soil with relatively low PAH concentrations for 3 weeks and were analyzed for PAH residues before use. The individuals were of similar weight (fresh weight 0.15–0.20 g) and size (4–5 cm) with a moisture content of 79 ± 6.1 wt% and a lipid content of 3.08 ± 0.61 wt% (dry weight, $n = 15$).

2.2. Soil preparation and TECAM sampling

Eighteen field-contaminated soils were employed for the steady-state sampling. The soils were collected from the 5–20 cm depth zone of agricultural fields near Tianjin city in northern China where PAHs occur in many places as a result of coal, petroleum and biomass combustion and wastewater irrigation over several years or decades. Each soil sample was air-dried, passed through a 2-mm sieve, sterilized by γ-irradiation from a ^{60}Co source and stored in a brown glass container at room temperature. Concentrations of PAHs in the soils were analyzed before use. Sampling locations are given in Fig. 1.

Because of the relatively low concentrations of PAHs in the field-contaminated soils, a portion of the soil collected from site 6 with the lowest PAH concentrations was spiked with 5.0 μg g^{-1} of Nap, Phe, Pyr and BaP for the sampling kinetic study. The spiked soil was mixed thoroughly to distribute the contaminants uniformly and allow the solvent to evaporate and then stored in brown glass containers at room

Fig. 1. Sampling locations in Tianjin city.

temperature for 90 days. Previous studies (Tao et al., 2008) has indicated that the extractable fraction of PAHs in the spiked soil approaches a constant level after such incubation.

Ten grams of the spiked soil or each of the 18 field soils was placed in a 100 mL beaker. A piece of TECAM (2 cm × 3 cm × 0.1 mm, triolein 4.84 wt%, 2.5 mg cm^{-2} after evaporation of acetone) was buried in the soil and 3 mL distilled water added dropwise to the beaker. The beaker was covered with aluminum foil to prevent moisture loss and then kept in the dark at 20–22 °C. The moisture content of the soil was kept constant by regular weighing. Four replicates of each soil were set up. For the sampling kinetic study, TECAMs were collected from the spiked soil at intervals of 1, 2, 4, 8 h and 1, 2, 4, 7, 14 days. For the steady-state study, TECAMs were collected from the beakers after 7 days. At the same time soils after TECAM exposure were further analyzed for PAHs.

2.3. PAH uptake by earthworms

Three active earthworms were transferred to a 500 mL glass beaker containing 300 g spiked or field-contaminated soil. 90 mL distilled water were added dropwise to moisten the soil. The beakers were covered with moist filter paper and kept in the dark at 20–22 °C. Soil moisture was kept constant by regular weighing. Earthworms were collected from the spiked soil after 3, 6, 15, 21 and 31 days for study of uptake kinetics. For the steady-state study the earthworms were removed from the field-contaminated soils after 31 days.

2.4. Measurement of PAHs in soil solution

Ten grams of each air-dried field soil and 10 mL distilled water were added to a 50 mL centrifuge bottle with the soil-to-water ratio according to Ter Laak et al. (2006). The centrifuge bottles were placed in the dark at 20–22 °C for 7 days without agitation. They were then centrifuged at 10,000 × g for 30 min and the supernatants were collected and filtered through a 0.45-μm filter. A total of 5 mL of the filtrates were extracted with *n*-hexane (5 mL × 3). The extracts were dehydrated with 3–5 g anhydrous sodium sulfate, evaporated, purged to about 1–2 mL under a gentle nitrogen stream, and then cleaned with a silica (2 g, 6% water)/anhydrous sodium sulfate composite column and eluted with 20 mL *n*-hexane/dichloromethane (4:1 v/v). The eluates were evaporated, solvent-exchanged into methanol (0.1 mL) and stored prior to analysis.

2.5. Estimating concentration of PAHs in soil solution with TECAM

A good linear relationship exists between log $K_{TECAM-w}$ (partition coefficient between TECAM and water) and log K_{ow} of Nap, Phe, Pyr and BaP (Tao et al., 2008) in the aqueous system, and their relationship has been found to be:

$$\log K_{TECAM-w} = 0.98 \log K_{ow} - 0.28, \quad r^2 = 0.998 \tag{1}$$

When steady-state is reached,

$$K_{TECAM-w} = C_{TECAM}/C_{water} \tag{2}$$

In sampling of TECAM, there is a three-compartment equilibrium among TECAM, soil solution and soil. Ignoring the minimum influences by matrixes in soil solution such as dissolved organic matter and colloids, the concentration of PAH in soil solution (C_w) can be approximately expressed as:

$$C_w = C_{TECAM}/K_{TECAM-w} \qquad (3)$$

$K_{TECAM-w}$ in Eq. (3) is substituted with Eq. (1), then Eq. (3) is expressed as:

$$C_w = C_{TECAM}10^{0.28}K_{ow}^{-0.98} \qquad (4)$$

Eq. (4) is used to calculate the concentration of PAH estimated from TECAM, where C_{TECAM} is the concentration of PAH in TECAM sampled from soil.

2.6. Chemical analysis

After sampling, TECAMs were rinsed with distilled water, wiped with clean filter paper, and dialyzed in 20 mL *n*-hexane for 24 h and rinsed with *n*-hexane (1 mL × 3). The *n*-hexane solutions were combined, evaporated under a gentle nitrogen stream, solvent-exchanged into methanol (0.1 mL), and stored prior to analysis. TECAMs were stable in *n*-hexane, with negligible weight loss of triolein or cellulose acetate during dialysis.

Earthworms were collected from the soils and allowed to depurate for 24 h to purge the gut contents on wet filter paper. They were then cleaned with distilled water to remove external soil particles, freeze dried, weighed, cut into small pieces and ground with a mortar and pestle to obtain homogeneous samples.

A sub-sample of earthworm (0.1 g) or soil (2 g) after thorough mixing with 3–5 g anhydrous sodium sulfate was loaded into a Soxhlet thimble and extracted with 100 mL *n*-hexane/dichloromethane (1:1 v/v) at 60 °C for 24 h. The extract was reduced to about 5 mL with a rotary evaporator, purged to about 1–2 mL under a gentle nitrogen stream, and then cleaned with a silica (2 g, 6% water)/anhydrous sodium sulfate composite column and eluted with 20 mL *n*-hexane/dichloro-methane (4:1 v/v). The eluates were evaporated, solvent-exchanged into methanol (1.00 mL) and stored prior to analysis.

PAHs in samples were analyzed by HPLC-FLD (Agilent 1200 Series). Chromatographic separation and resolution were best achieved by using a LiChrospher (Merck, Darmstadt, Germany) reverse-phase C_{18} column (4.6 × 150 mm, 5 μm particle size) specific for PAH analysis.

Solvent, TECAM and earthworm controls were included. Extraction recoveries of Nap, Phe, Pyr and BaP in TECAM were determined by adding the standard solution of these PAHs at seven different concentrations into the solvent mixture of acetone (69 wt%) and 1, 4-dioxane (10 wt%) before TECAM preparation, and the recoveries were 85.2 ± 2.1%, 88.7 ± 1.9%, 89.4 ± 2.7% and 93.5 ± 2.8%, respectively. A linearity of higher than 0.990 and detection limits (S/N = 3) as low as 7 μg kg^{-1} in soil and 1.6 ng L^{-1} in soil solution for all the four PAHs were found for sampling with TECAMs. Extraction recoveries of Nap, Phe, Pyr and BaP in field soils were 87.3 ± 2.7%, 94.3 ± 1.9%, 90.5 ± 2.2% and 87.3 ± 1.8% (n = 18).

2.7. Data analysis

Results were obtained from four replicates in the case of TECAMs, soil and soil solution, and from five replicates in the case of earthworms. Statistical analysis of the results was performed with SPSS 10.0 for Windows (SPSS Inc.) using analysis of variance. A first-order kinetic model for PAHs in soil sampled by TECAM and earthworms was fitted with Origin 7.0 (OriginLab Corporation).

3. Results and discussion

3.1. TECAM sampling kinetics

The amounts of Nap, Phe, Pyr and BaP sampled by TECAM from soil increased rapidly at the beginning, achieved the maximum concentration, and were maintained throughout the rest of the sampling process after about 1 day (Fig. 2a). The relationship between the concentrations of PAHs in TECAM ($C_{TECAM, t}$) and the exposure time (t) can be fitted with the first-order kinetic model:

$$C_{TECAM,t} = C_e(1 - \exp(-kt)) \qquad (5)$$

where $C_{TECAM, t}$ is the concentration of PAH in TECAM (μg g^{-1} TECAM); C_e is the concentration of PAH in TECAM at apparent equilibrium; and k is the exchange rate constant (h^{-1}). Sampling by TECAM resulted in only a negligible reduction in PAH concentrations in soil solution and the concentrations of PAHs in soil were virtually unchanged after sampling by TECAM by comparing their concentrations before and after TECAM exposure. The k, C_e and the related coefficients (r^2) for Nap, Phe, Pyr and BaP are shown in
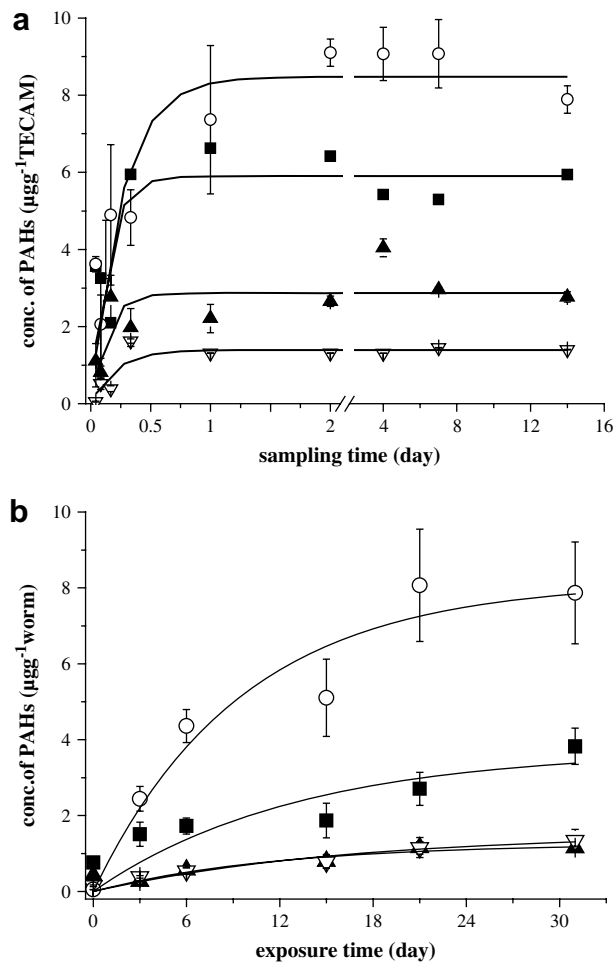

Fig. 2. Sampling kinetics of PAHs by TECAM (a) and earthworms (b). Nap (○), Phe (■), Pyr (▲) and BaP (▽). Values are means ± standard deviation, n = 4.

Table 1. Direct comparison of exchange rate constants among different types of PSDs is difficult since very limited experiments have been carried out for the uptake of HOCs in soils by PSDs and information on exchange rate constants was unavailable. Therefore the times of 95% equilibration ($t_{95\%}$) for PAH uptake by TECAM were estimated using the following equation:

$$t_{95\%} = \ln20/k \qquad (6)$$

and they were 9.3, 9.7, 14.6 and 18.5 h for Nap, Phe, Pyr and BaP, respectively, much shorter than the 60 days required for 90% equilibration ($t_{90\%}$) found for PAH uptake by polyethylene semi-permeable membrane devices (Vinturella et al., 2004). C_{18} disks used to extract PAHs and PCBs from soils at 40 °C by Krauss and Wilcke (2001) reached apparent equilibrium after 15 days. Zhang et al. (2006) reported that C_{18} sampling bags required about 30 days to sample hexahydro-1-nitroso-3,5-dinitro-1,3,5-triazine (MNX) and hexahydro-1,3,5-trinitroso-1,3,5-triazine (TNX) from

Table 1
Parameters of the first-order kinetic model for PAHs in soil sampled by TECAM (n = 9), fitted with Origin 7.0 at the significance level of 0.05

Compound	k (h^{-1})	$t_{95\%}$ (h)	C_e (μg g^{-1} TECAM)	r^2
Nap	0.32 ± 0.03	9.3	8.48 ± 0.56	0.814
Phe	0.31 ± 0.02	9.7	5.90 ± 0.33	0.489
Pyr	0.21 ± 0.006	14.6	2.87 ± 0.19	0.587
BaP	0.16 ± 0.003	18.5	1.39 ± 0.12	0.812

soils. Rantalainen et al. (1998) spent 28 days deploying SPMD to sample chlorohydrocarbons from soil. Short equilibrium times for PAH uptake by TECAMs have also been demonstrated by Ke et al. (2006) in their work to compare the uptake rates of PAHs by TECAMs and triolein-containing semipermeable membrane devices (SPMDs). They found that the uptake rate constants for Nap, Phe, BbF and BaP in water by TECAM were about 1.4–6.7 times higher than by SPMD.

There may be several factors accounting for the shorter apparent equilibrium time for PAH uptake by TECAM. Characteristics of the PSD membrane play a key role in controlling the uptake rate of HOCs (Booij et al., 2003; Kot-Wasik et al., 2007). In contrast to the 'sandwich' structure of SPMD and C_{18} sampling bags in which the sorbent i.e., lipid or C_{18} material is separate from the outer membrane, TECAM is an integrated membrane in which the triolein is uniformly mixed with the cellulose acetate membrane material. Thus the resistance to mass transfer from the outer membrane to the lipid was decreased and hence the resistance to mass transfer through the membrane layer of the PSD. Furthermore, 1 mL (0.915 g) of triolein can be distributed on approximately 15,000 cm^2 surface of cellulose acetate of TECAM, which is much higher than 1 mL of triolein on 450 cm^2 surface of low-density polyethylene of SPMD (Huckins et al., 1999) or 1 g of C_{18} sorbent on 77 cm^2 surface of polyethylene of C_{18} sampling bags (Awata et al., 2000). This feature results in a larger contact area between triolein and PAHs in soil permitting rapid exchange kinetics. Moreover, the membrane material of TECAM is cellulose acetate which is more hydrophilic than the polyethylene of SPMD and C_{18} sampling bags due to the hydroxyl groups. This can decrease the surface tension between TECAM and the soil solution, resulting in a closer contact between triolein and PAHs in the soil solution. In addition, the exchange rate constant (k) of HOCs in the log K_{ow} range 3–7 was assumed to be proportionally correlated with the surface area-to-volume ratio (A/V) of a passive sampler deployed in stagnant water (Mayer et al., 2003). The A/V of TECAM is approximate 2×10^4 m^2/m^3, which is

higher than that of SPMD (Mayer et al., 2003), C_{18} disks (Freidig et al., 1998; Mayer et al., 2003) or C_{18} sampling bags (Awata et al., 2000).

3.2. Concentration relationship of PAHs among soils, TECAMs and soil solutions

The kinetic study showed that a steady-state was reached for PAH uptake by TECAM after 7 day-exposure, and the concentrations of PAHs in TECAMs (C_{TECAM}) and the 18 field-contaminated soils (C_{soil}) followed significant linear relationships ($r^2 = 0.693$–0.962, $n = 18$, $p < 0.01$) (Fig. 3). This suggests that TECAM responded proportionally to the concentrations of PAHs in soils and TECAM could effectively sample PAHs from field-contaminated soils with concentrations of PAHs varying from approximately 0.007 to 0.545 μg g^{-1}. The slope of C_{TECAM} and C_{soil} can be referred as the membrane soil accumulation factor (MSAF) at steady-state. MSAFs for Nap, Phe, Pyr and BaP were 53.22 ± 3.97, 51.65 ± 3.73, 40.94 ± 1.97 and 8.06 ± 0.53, respectively, which showed a decreasing trend with increasing hydrophobicity and molecular volumes of these PAHs. This suggests that the sampling of PAHs in soils by TECAM depends on the physico-chemical properties of these PAHs. PAHs with higher hydrophobicity have higher affinity to soil organic matter, resulting in their strong sequestration in soil and resistance to desorption, and therefore a smaller available fraction in the soil solution. Furthermore, nano-pores or voids are abundant in the organic fraction of soils (Malekani et al., 1997). PAHs with higher hydrophobicity usually have larger molecular volumes. If the molecules were entrapped in such pores or voids they would not tend to escape and they would become unavailable to TECAM. In addition, sampling of PAHs with larger molecular volumes by TECAM may also be restricted owing to the pore size of TECAM.

It is generally accepted that HOCs in soil solution can be considered to be available to organisms (Jager, 1998; Jager et al., 2003; Van Der Wal et al., 2004) and a direct method to assess bioavailability of HOCs in soil is to determine the HOC
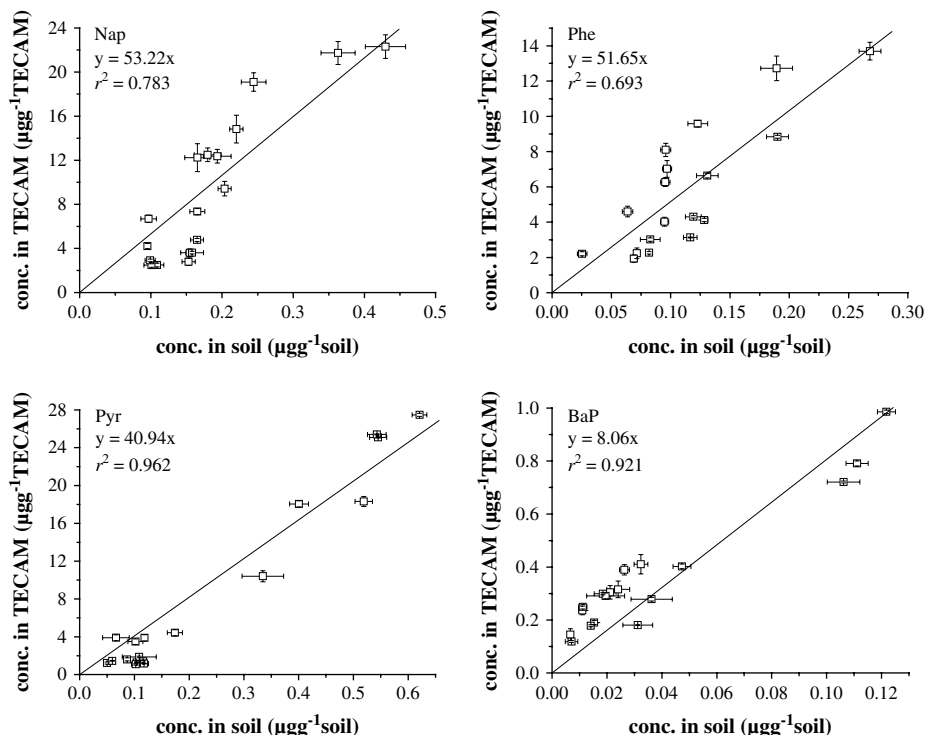

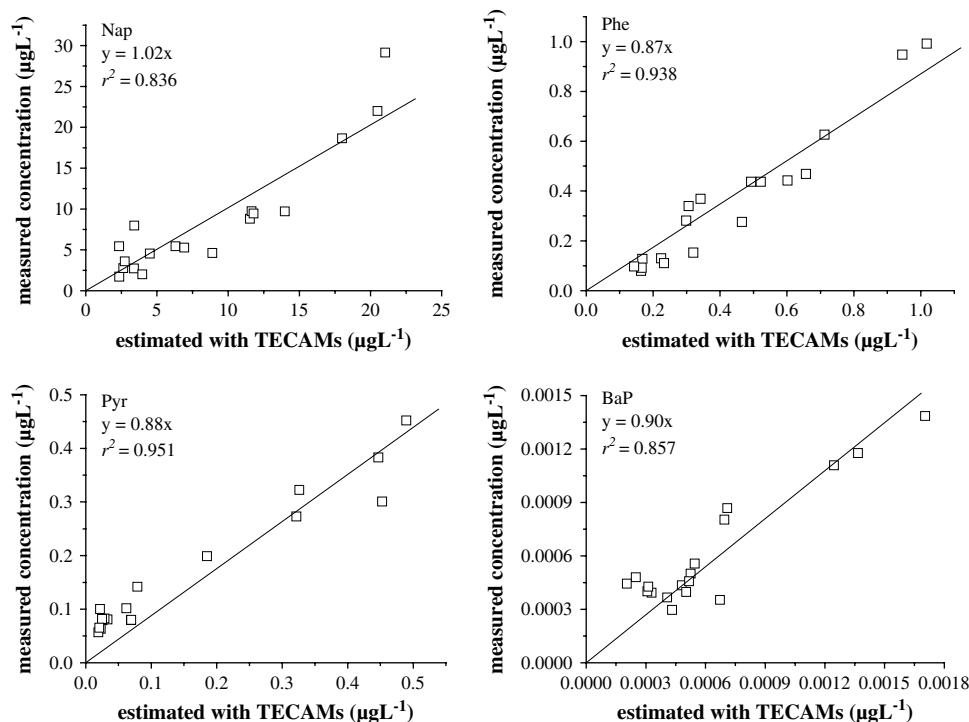**Fig. 3.** Relationships between concentrations of PAHs in TECAMs and soils, $n = 18$, $p < 0.01$.

Fig. 4. Relationships between PAH concentrations estimated from TECAM and measured in soil solution, n = 18, p < 0.01.

concentration in the soil solution (Krauss et al., 2000). In order to test the feasibility of using TECAM to sample the bioavailable PAHs in soils, concentrations of PAHs in the soil solutions were measured and compared with the data estimated from TECAM. Concentrations of PAHs measured in the soil solution and estimated from TECAM are compared in Fig. 4. Significant relationships were found between the measured and the estimated concentrations ($r^2 = 0.836$–0.951, $n = 18$, $p < 0.01$). The slopes (ratio of measured concentration to estimated value) for Nap, Phe, Pyr and BaP were 1.02 ± 0.06, 0.87 ± 0.03, 0.88 ± 0.05 and 0.90 ± 0.04, respectively, values which are very close to 1. Therefore the concentrations of PAHs estimated from TECAM are very close to the measured concentrations in the soil solution. Moreover, TECAM deployment is much easier than soil extraction methods. Therefore, TECAM can be a useful tool to sample PAHs in the soil solution. In the case of Phe, Pyr and BaP, the measured concentrations in solution were slightly higher than those estimated from TECAM. However, the discrepancies are acceptable considering the complexity of pollution sources and history as well as the relatively low PAH concentrations present in the 18 field-contaminated soils.

3.3. Relationship between PAH uptake by TECAMs and earthworms

Uptake kinetics of PAHs by earthworms are shown in Fig. 2b. The concentrations (C_t) of PAHs in earthworms and the exposure time (t) could be well fitted with the first-order kinetic model (Eq. (1)). k, $t_{95\%}$, C_e and the relation coefficient (r^2) for Nap, Phe, Pyr and BaP are shown in Table 2. The $t_{95\%}$ values for the uptake of these PAHs by earthworms were 27.2, 29.9, 30.0 and 33.3 days, respectively. Uptake of PAHs by TECAMs could therefore reach apparent equilibrium much more quickly than by earthworms. Compared with triolein, the fraction of PAHs sampled by cellulose acetate was very small due to its higher hydrophilicity. Jonker (2008) has found that the affinity of PAHs for cellulose is about 400 times lower than for octanol. The lipids in earthworms are also considered to play a key role in their accumulation of HOCs from soils (Jager, 1998). Therefore, the concentrations of PAHs in TECAMs and earthworms were

further lipid normalized. After lipid normalization, nearly 1:1 relationships (1.22 ± 0.11, 0.84 ± 0.05, 1.01 ± 0.06 and 0.89 ± 0.06 for Nap, Phe, Pyr and Bap, respectively) were found between the concentrations of PAHs taken up by TECAMs and earthworms exposed to the 18 field-contaminated soils ($r^2 = 0.591$–0.824, $p < 0.01$) (Fig. 5). Although the exposure of earthworms to soil contaminants include several pathways (i.e. by food and the aqueous or gaseous phase), uptake into earthworms has been well described by their concentration in the soil solution (Jager, 1998; Jager et al., 2003; Van Der Wal et al., 2004). Furthermore, the main route of exposure of earthworms to organic contaminants such as PAHs in the soil solution is considered to be uptake from the soil solution through the outer skin (Belfroid et al., 1996). Jager et al. (2003) found that the uptake of tetrachlorobenzene, hexachlorobenzene and PCB153 through both the skin and gut was a passive diffusion process. Thus, the uptake of PAHs in soil by earthworms may also be a passive diffusion process. In the present study the concentrations of PAHs in earthworms and TECAMs showed good linear relationships with concentrations in soil solution of the 18 field-contaminated soils, indicating that PAHs in soil solution are the main source for the uptake of PAHs by earthworms and TECAMs, and passive diffusion via the soil solution is the main route. The nearly 1:1 relationships between the concentrations of PAHs uptake by TECAMs and earthworms suggest that TECAMs are able to predict the bioavailability of PAHs in field-contaminated soils.

Table 2
Parameters of the first-order kinetic model for PAHs in soil taken up by earthworms ($n = 6$), fitted with Origin 7.0 at the significance level of 0.05

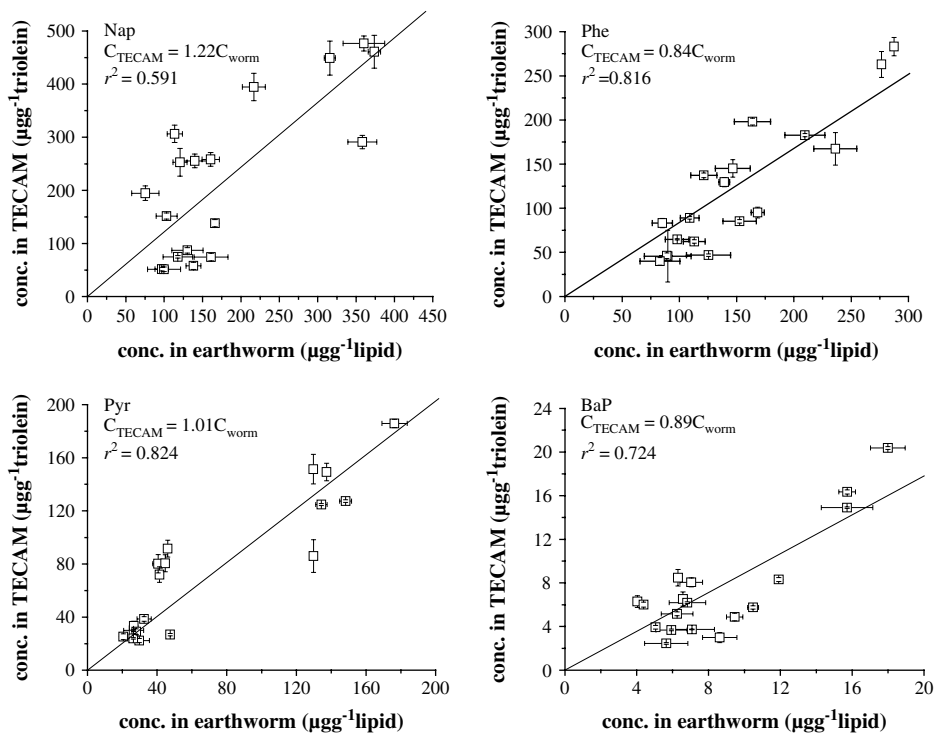| Compound	k (day^{-1})	$t_{95\%}$ (day)	C_e (µg g^{-1} worm)	r^2
Nap	0.11 ± 0.02	27.2	8.16 ± 0.35	0.941
Phe	0.10 ± 0.003	29.9	3.73 ± 0.27	0.649
Pyr	0.10 ± 0.002	30.0	1.54 ± 0.13	0.935
BaP	0.09 ± 0.001	33.3	1.27 ± 0.10	0.712

Fig. 5. Relationships between concentrations of PAHs taken up by TECAMs and earthworms. Values are means ± standard deviation, $n = 18$, $p < 0.01$.

4. Conclusions

Concentrations of PAHs in TECAMs correlated well with the concentrations in field-contaminated soils. Concentrations of PAHs measured in soil solutions were close to the corresponding values estimated from TECAM. Moreover, relationships close to 1:1 were observed between PAH concentrations in TECAMs and earthworms. These results demonstrate that TECAM can be a useful tool to predict the bioavailability of PAHs and perhaps other HOCs in field-contaminated soils.

Acknowledgements

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