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Can polyethylene passive samplers predict polychlorinated biphenyls (PCBs) uptake by earthworms and turnips in a biochar amended soil?

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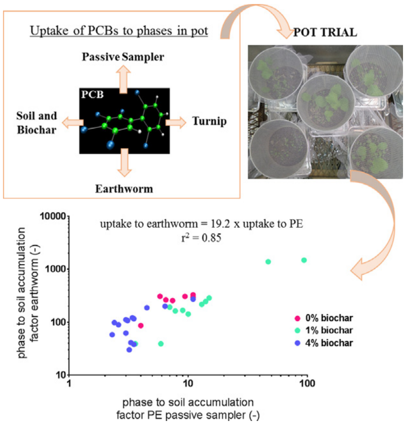
HIGHLIGHTS

- Two different biochars amended to PCB contaminated soil at 1% and 4% doses.
- Pot experiment carried out with polyethylene passive samplers, earthworms and turnips.
- A difference in the reduction of uptake of PCBs was seen with biochar type, but not dose.
- Earthworms accumulated 19 times more PCBs than polyethylene and uptake was well correlated.
- Lack of correlation between uptake of PCBs polyethylene and turnip

GRAPHICAL ABSTRACT



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ABSTRACT

A pot experiment was carried out in which aged polychlorinated biphenyls (PCBs) contaminated soil was amended with biochar, and three phases: earthworms, turnips and polyethylene (PE) passive samplers, were added simultaneously in order to investigate changes in bioavailability of PCB following biochar amendment. Two biochars were used: one made from rice husk in Indonesia using local techniques and the other made from mixed wood shavings using more advanced technology. The biochars were amended at 1 and 4% doses. The overall accumulation of PCBs to the phases followed the order: earthworm lipid > PE > turnip. The rice husk biochar reduced PCB accumulation to a greater degree than the mixed wood biochar for all phases, however there was no effect of dose for either biochar. Earthworm uptake was reduced between 52% and 91% for rice husk biochar and by 19% to 63% for mix wood biochar. Turnip uptake was not significantly reduced by biochar amendment. Phase to soil accumulation factors (PSAF) were around 0.5 for turnips, approximately 5 for PE and exceeded 100 for earthworms. This study demonstrates that both biochars can be a sustainable alternative for in situ soil remediation and that PE can be used as tool to simulate the uptake in earthworms and thus remediation effectiveness.

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1. Introduction

Polychlorinated biphenyls (PCBs) are known to be persistent, bioaccumulative and toxic and are heavily regulated and restricted, for example through the Stockholm Convention (Vijgen et al., 2011). PCB contaminated soils pose an environmental and human health hazard (Travis and Hester, 1991). Soils polluted by PCBs must be remediated and several methods exist in order to meet strict clean up guidelines. Disposal at landfills, the amendment of a strong carbonaceous sorbent material and various chemical and physical treatments that require severe reaction conditions (e.g. ultrasonication, photochemical degradation, reductive dechlorination using metals, base-catalyzed decomposition, hydrogen-transfer hydrodechlorination and fungous and bacterial treatments), can all provide solutions (Perelo, 2010; Slack et al., 2007; Denyes et al., 2013). When a strongly sorbing carbonaceous material is added to contaminated soil, repartitioning of pollutants occurs from the soil to the material itself, rendering the pollutants less available (Ghosh et al., 2011). Activated carbon (AC) has been most extensively tested and has been shown to remediate PAH (Hale and Werner, 2010; Hale et al., 2012; Brennan et al., 2014), PCB (Denyes et al., 2013; Wang et al., 2016), DDT (Denyes et al., 2016) and PCDD/F (Fagervold et al., 2010) impacted soils. More recently, the addition of biochar to contaminated soils has attracted attention (Ahmad et al., 2014; Beesley et al., 2011). Despite the efficacy of the current materials commonly used to remediate contaminated soils, there is a demand for new cost-effective and environmentally sustainable sorbents.

Biochar is the carbon-rich product obtained when biomass is pyrolysed in a limited oxygen environment. Unlike charcoal and other carbon based materials, biochar is primarily produced as a soil ameliorator or in a broader environmental management perspective (Lehmann and Joseph, 2015). Biochar (and AC) has an abundance of surface functional groups (carboxyl, carbonyl, hydroxyl and phenolic hydroxyl) and, usually, a high specific surface area that provides a large number of sorption sites for organic compounds; the mechanism of binding of organic compounds to biochar is extensively described in literature (Ahmad et al., 2014). An increasing number of studies have shown that biochar can serve as a more cost effective and more environmentally sustainable carbonaceous sorbent material than AC (Sparrevik et al., 2011). In addition, unlike AC, biochar can contribute positively to the mitigation of climate change (Yanai et al., 2007) and improve soil fertility (Sparrevik et al., 2011). Biochar has been added to remediate PAH (Hale et al., 2013), PCB (Denyes et al., 2012) and DDT (Bielská et al., 2018) contaminated soils. Once biochar has been added to soils with the goal of remediation, it is paramount to ascertain whether clean up targets have been met and this can be achieved by looking at specific endpoints. Commonly used end points include the reduction in total pollutant soil concentrations as well as the reduction in biological uptake. It is well known that total concentration based assessment can result in over estimations of risk, while bioavailable concentrations are more suited endpoints for risk assessment (Denyes et al., 2016; Beesley et al., 2011; Lehmann and Joseph, 2015; Alexander, 2000; Gomez-Eyles et al., 2011a).

Several methods have been proposed to determine bioavailable pollutant concentrations. The most common ones include the use of earthworms, plants or passive samplers. The advantage of using earthworms is that they naturally reside in the soil matrix, have a tolerance for different types of soil, have a large epidermal surface and ingest more soil than many other soil dwelling organisms (Lanno et al., 2004) which results in efficient pollutant exposure. Hydrophobic organic contaminants are taken up by earthworms via a passive diffusion from the soil pore water through the cuticle and via an internal sorption of the compounds from soil passing through the gut and intestine (Lord et al., 1980; Belfroid et al., 1995). Plants offer the advantage of being native to the soil environment and the uptake of organic pollutants occurs via a diffusion from soil particles to soil pore water and subsequent uptake by plant roots as well as via assimilation from the aerial parts following volatilization from soil. Disadvantages or confounding factors introduced by both earthworms and plants are: occurrence of mortality, mobility (in case of earthworms), growth and possible biotransformation (for some hydrophobic organic compounds). These factors can complicate the assessment of clean-up efficacy. In order to circumvent this, passive samplers can be used. Passive samplers are plastic membranes that accumulate pollutants via a passive diffusion process reaching equilibrium with multiple soil compartments when they are exposed for a sufficient amount of time. Using pre-determined passive sampler-water partitioning coefficients, bioavailable (also referred to as aqueous) concentrations can be calculated (Mayer et al., 2003).

Several studies have shown that methods to determine bioavailable concentrations can be used to predict the uptake of organic pollutants from a contaminated soil to earthworms (Denyes et al., 2016; Gomez-Eyles et al., 2011a; Vinturella et al., 2004; Paul and Ghosh, 2011; Guo et al., 2017; Wang et al., 2018). In many cases the methods underestimate contaminant concentration accumulated in earthworms (Denyes et al., 2016; Vinturella et al., 2004; Guo et al., 2017; Wang et al., 2018). In comparison, very few studies exist in which uptake of pollutants to passive samplers, earthworms and plants have been compared, especially in the same system and in cases where biochar has been used as a soil amendment. Gomez-Eyles et al. (2011b) reported that passive samplers could be used to predict the accumulation of PAHs in earthworms and ryegrass roots from a biochar/amended contaminated soils. Denyes et al. (2016) used polyoxymethylene (POM) passive samplers to investigate whether the reduction in uptake of DDTs following amendment of biochar and AC to a contaminated soil mimicked the reduction in uptake to earthworms and squash. Their results showed that reductions were well correlated for passive samplers and earthworms, but not for passive samplers and plants.

This paper describes a pot experiment, where polyethylene passive sampler, earthworms (*Eisenia fetida*), and turnips (*Brassica rapa*) were co-exposed to an aged PCB contaminated soil amended with two biochars at different doses (rice husk and mixed wood based biochars at 0%, 1%, and 4%). The correlation between the reduction in bioavailability, assessed by concentrations accumulated in the phases, was investigated. The study tested two separate hypotheses. The first one was that a relationship exists between the uptake of contaminants in three phases (earthworms, turnips and passive samplers). If verified then the uptake in passive samplers could be used as a proxy for the uptake in earthworms and plants. To the best of our knowledge this is the first time a pot trial has been carried out in which all three phases have been exposed simultaneously. The second hypothesis was that both biochars would reduce uptake of PCBs in earthworms and turnips and thus biochar could be used for soil remediation. This study is the first to compare the remediation performance of a biochar produced using a low-technology method (rice husk biochar) with a biochar produced using a more sophisticated technology (mixed wood biochar).

The goal of this work is three fold: (i) to investigate if the tested biochars can be used as sorbent materials for the remediation of PCB contaminated soil, (ii) to investigate whether different end points can be used to assess the success of the remediation and (iii) to investigate whether a correlation exists between PCB accumulation in earthworms, turnips and passive samplers following biochar amendment.

2. Materials and methods

2.1. Materials and chemicals

Seven PCBs (28, 52, 101, 118, 138, 153 and 180) were used in the experiment. Information about all the chemicals used can be found in the supporting information (SI). Perlite (No. 2 extra pull, 0.6–3.0 mm) was purchased from Horticoop and added to the soil (4.4 dry weight %) in order to improve its structure and increase aeration. Perlite is an inert, and thus non-sorbing material and has been used in a similar way in previous studies (Jeffery et al., 2015).

Two biochars: one made from rice husk and the other from mixed wood shavings were used in the experiment. The rice (*Oryza sativa* L.) husk biochar was produced in a locally constructed pyrolysis unit (kiln) in Lampung, Indonesia at 250–350 °C with a pyrolysis time of 3.5 h (Martinsen et al., 2015). The mixed wood biochar was made from mixed wood shavings (mainly tree type *Miscantus*) in a Pyreg 500 W unit at 700 °C with a residence time of 20 min at Swiss Biochar, Switzerland (Kupryianchyk et al., 2016). These sorbents were chosen in order to compare a biochar produced using an uncontrolled, low technology method (rice husk) and a biochar produced using a controlled, high technology method (mixed wood). The biochars were sieved before use (size <2 mm). Information on biochars' properties can be found in Table 1.

2.2. Phases: soil, earthworms turnip and polyethylene passive samplers

Loam soil was sampled from 20 cm depth from Norderås, an agricultural field near Ås, at the Norwegian University of Life Sciences, Norway (UTM 32-N6617041/E599609) in November 2014. The soil was homogenized, sieved and stored at room temperature prior to use. The soil was spiked with the PCB standard solution in toluene to obtain a final spiked concentration of 83.3 μg kg_{soil}^{-1} of individual congeners and aged for 13 months prior to beginning the pot experiment. The water content of the soil was kept between 10 and 20% during spiking. Soil is classified as a loam (40% sand, 44% silt and 17% clay), TOC content of 3.4%. Further details can be found in the SI.

The earthworms, *Eisenia fetida* (also called tiger worms or red wigglers) were purchased from Riverside Products, Norway. They were bedded in damp peat and fed on cellulose and sheep manure-pellets during breading. Turnip seeds (*Brassica rapa* ssp. *rapa*) were purchased from Plantasjen (Oslo, Norway). Seeds were used as received. Polyethylene (PE) was used as a passive sampler to assess and to accumulate the PCBs soil porewater contaminant. PE plastic sheets (26 μm thick, 0.10 ± 0.01 g) were purchased from VWR International Ltd. (Leicestershire, UK). PE was precleaned with hexane, methanol and pure water, as described by Hale et al. (2010). PE was not spiked with performance reference compounds (Hale and Werner, 2010; Hale et al., 2010) and the degree of equilibrium achieved was not investigated here. The aim of the experiment was to investigate whether PE could be used as a proxy for the other phases. Bioavailable concentrations were therefore not calculated and comparison was made between absolute concentrations accumulated by the phases with and without the addition of biochar.

2.3. Experimental design

A schematic of the pot trial can be found in Fig. 1 and in the graphical abstract. Tests were carried out using a pot (17 and 18 cm, height and inner diameter respectively) setup in order to assess the effect of the addition of biochar to spiked soil on the uptake of PCBs to earthworms, turnip and PE passive samplers (Fig. S1, in SI). Three different biochar doses (% wt), 0% (control), 1% and 4% of both rice husk and mixed wood (each in 5 replicates), were added to the soil as amendment doses following previous similar work (Denyes et al., 2013; Ghosh et al., 2011; Denyes et al., 2016) All three phases were added to each pot simultaneously (apart from control pots which are described in the SI).

Spiked soil (1 kg), perlite (4.4 wt%), biochar (0%, 1% or 4% of rice husk or mixed wood), PE (placed approximately 4 cm below the soil surface), three turnip seeds and 25 earthworms were put into each pot. The pot experiments were carried out in a growth room to simulate a Norwegian summer day and night cycle (14 h of light and 10 h of dark, 20 °C and 15 °C respectively). The water content was maintained at 60% of soil water holding capacity (WHC) throughout the pot experiment. Further details can be found in the SI.

2.4. Sample processing, extraction and PCB quantification

The pots were sampled after 24 (biochar amended pots) or 30 days (unamended pots). The soil (and perlite) or soil and biochar (and perlite) was mixed using a spoon and a 10 g subsample was transferred to a glass vial prior to extraction. Earthworms were removed from pots, rinsed with spring water and depurated in glass jars for 24 h. Extraction was carried out using 80 mL of acetone:hexane mixture (1:1) (Škulcová et al., 2016). Further information related to sample processing and extraction as well as GCMS quantification can be found in the SI.

2.5. Data processing

2.5.1. Accumulation factors

The PCB concentration accumulated by the earthworms, turnip and PE were assessed as phase (earthworm/turnip/PE) to soil accumulation factors (PSAF). The PSAFs were calculated using Eq. (1):

$$\mathrm{PSAF} = \frac{C_{\mathrm{PCB\ (earthworm\ or\ turnip\ or\ PE)}}}{C_{\mathrm{PCB\ (soil\ or\ soil+biochar)}}} \qquad (1)$$

where $C_{\mathrm{PCB\ (earthworm,\ or\ turnip\ or\ PE)}}$ is the concentration (μg $g^{-1}{}_{dry}$) of PCB in the different phases, respectively earthworm lipid, turnip or PE and the $C_{\mathrm{PCB\ (soil\ or\ soil+biochar)}}$ is the concentration (μg $g^{-1}{}_{dry}$) of PCB in the soil without and with the addition of biochar. The PCB earthworm concentration was calculated based on the worm lipid weight (lw), as described in the SI. The PSAF was not normalised to the organic carbon content of the soil as the soil was amended with biochar which introduced a different type of carbon (black carbon) which would make organic carbon normalization irrelevant (Zimmerman, 2010).

2.5.2. Statistical analysis

Data points that were suspected to be outliers were tested using Dixons Q-test and removed accordingly. All plots and statistical analysis was carried out using GraphPad Prism 7 scientific software. To compare the difference between pairs of means for the unamended and biochar amended samples, the Tukey multiple comparison test was used following a one way ANOVA at the 95% confidence interval.

3. Results and discussion

3.1. Absolute concentrations of PCBs in earthworms, PE and turnips

The concentrations of PCB 28 and PCB 101 in the earthworms, PE and turnips are reported in Fig. 2a–c (PCB 28) and Fig. 2d–f (PCB 101). These congeners were chosen as representative examples and the accumulation of all other PCBs can be found in the SI, Fig. S2a-e, Figs. S3a–e and

Table 1
Mixed wood and rice husk biochar property.

Biochar	$T_{pyrolysis}$ °C	C %	H %	N %	O %	H/C	O/C	Ash (550 °C)%	Surf.area $m^2\ g^{-1}$	pH ($CaCl_2$)
Mixed wood	700	74.5	2.13	0.68	4.5	0.34	0.05	18.2	404	8.3
Rice husk	400–500	49.0	2.02	0.93	6.8	0.49	0.10	41.2	51	7.3

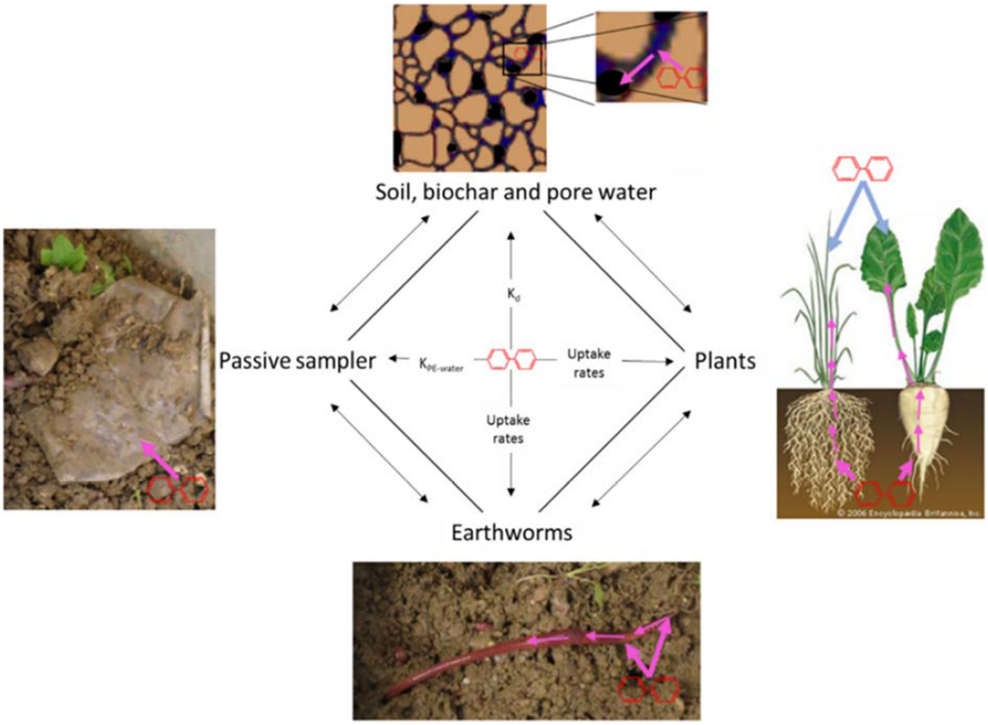

Fig. 1. The pathways (pink arrows) for a polychlorinated biphenyls (red in figure) contained in a polluted soil to be accumulated via the soil pore water to biochar particles (black in figure), plants, earthworms and passive samplers.

S4a–e. The figures compare the concentration in the unamended pot to those of 1% and 4% mixed wood and 1% and 4% rice husk amended pots. The overall accumulation of PCBs to the phases followed the order: earthworm lipid > PE > turnip (statistical analysis between phases can be found in Table S1 in SI). The absolute concentrations of PCB 28 in the unamended pots were 23.2, 0.86 and 0.05 μg g^{-1} for earthworm lipids, PE and turnips, respectively. For PCB 101, the concentrations were 28.2, 0.86 and 0.06 μg g^{-1} for earthworms, PE and turnips, respectively. The differences between the phases are related to the different uptake mechanism of the phases and the relative magnitude of the partitioning coefficients; earthworm lipid-water ($K_{lipid\text{-}water}$), polyethylene-water ($K_{PE\text{-}water}$) and turnip-water ($K_{turnip\text{-}water}$). Earthworms accumulate PCBs via internal sorption of the compounds from soil passing through the gut and intestine and via passive diffusion from the soil solution through the cuticle (Lord et al., 1980; Belfroid et al., 1995). Sun et al. (2009) investigated the bioaccumulation of PCBs by the benthic invertebrate (*Lumbriculus variegatus*) assessing the contaminants' dermal absorption, ingestion, and uptake efficiency. They concluded that biouptake was (i) related to soil/sediment desorption kinetics where biouptake was greatest for PCBs that were sorbed to the smallest degree, (ii) linearly related to the worm size, (iii) affected by compounds assimilation and post-digestive soluble excretion and (iv) was correlated with the PCBs hydrophobicity. The uptake of PCBs by the passive sampler occurs via passive diffusion from the soil porewater (Hale and Werner, 2010). The turnips accumulate PCBs via uptake by the roots following a diffusion of the PCBs to the soil pore water or via the aerial parts following volatilization from soil. The much larger concentration taken up by the earthworms compared to the PE and turnips could be thus explained by the inherent mobility of worms in soil, their different uptake processes and the expectation that earthworms are probably closer to pseudo-equilibrium than the passive samplers in this static system.

Tables S2, S3 and S4 in the SI show the absolute concentrations accumulated for all PCBs and all phases. All PCB congeners were spiked to the soil at the same concentration and a clear trend for the uptake based on the molecular size or the stereochemistry of the PCB is not evident. This is most likely due to the interplay of many (often contrasting) mechanisms affecting uptake including diffusion kinetics in soil solids, porewater and the accumulating media, which are slower for the larger PCBs, as well as the magnitude of K_{lipid}, which is larger for the larger PCBs. It is unlikely that the compounds reached equilibrium among the phases during the experiment as previous work has shown that thermodynamic equilibrium between soil (or sediment) particles and PE samplers can take decades to be achieved in static systems (Hale and Werner, 2010). In previous studies, stronger sorption of planar PCBs, PCDD/Fs and PAHs than nonplanar ones to carbonaceous geosorbents (Jonker and Smedes, 2000; Cornelissen et al., 2005; Cornelissen et al., 2008) was seen, however this is not evident here. For example, Jonker and Smedes (2000) reported preferential sorption of planar contaminants in lake sediments, which was attributed to their higher affinity for soot-like materials found in the sediments.

3.2. Effect of the biochar amendment on uptake of PCBs to earthworms, PE and turnips

From Fig. 2a, b and c for PCB 28 for earthworms, PE and turnips, respectively, it is possible to calculate the effectiveness of the biochar amendments in reducing PCB uptake. For the earthworms, 91% and 87% reductions in PCB 28 uptake were observed following the amendment of 1% and 4% rice husk biochar and 55% and 63% reductions were seen after the amendment of 1% and 4% mixed wood biochar. Tables S5-S7 in the SI show the percent reductions for all congeners and phases following the amendment of both biochars. There was no significant effect of biochar dose for either of the biochars ($p = 1.0$ rice husk, $p = 0.93$ mixed wood biochar), showing that in this case a 1% biochar amendment to this PCB contaminated soil was enough to reduce earthworm uptake to a large degree when compared to the unamended pots. For the PE, a reduction of 73% after both 1% and 4% rice husk biochar were added to the soil and an 18% and 60% reduction after the amendment of 1% and 4% mixed wood biochar, were observed. The trends for turnips were quite different from those for earthworms and PE. The addition of rice husk and mixed wood biochar did not

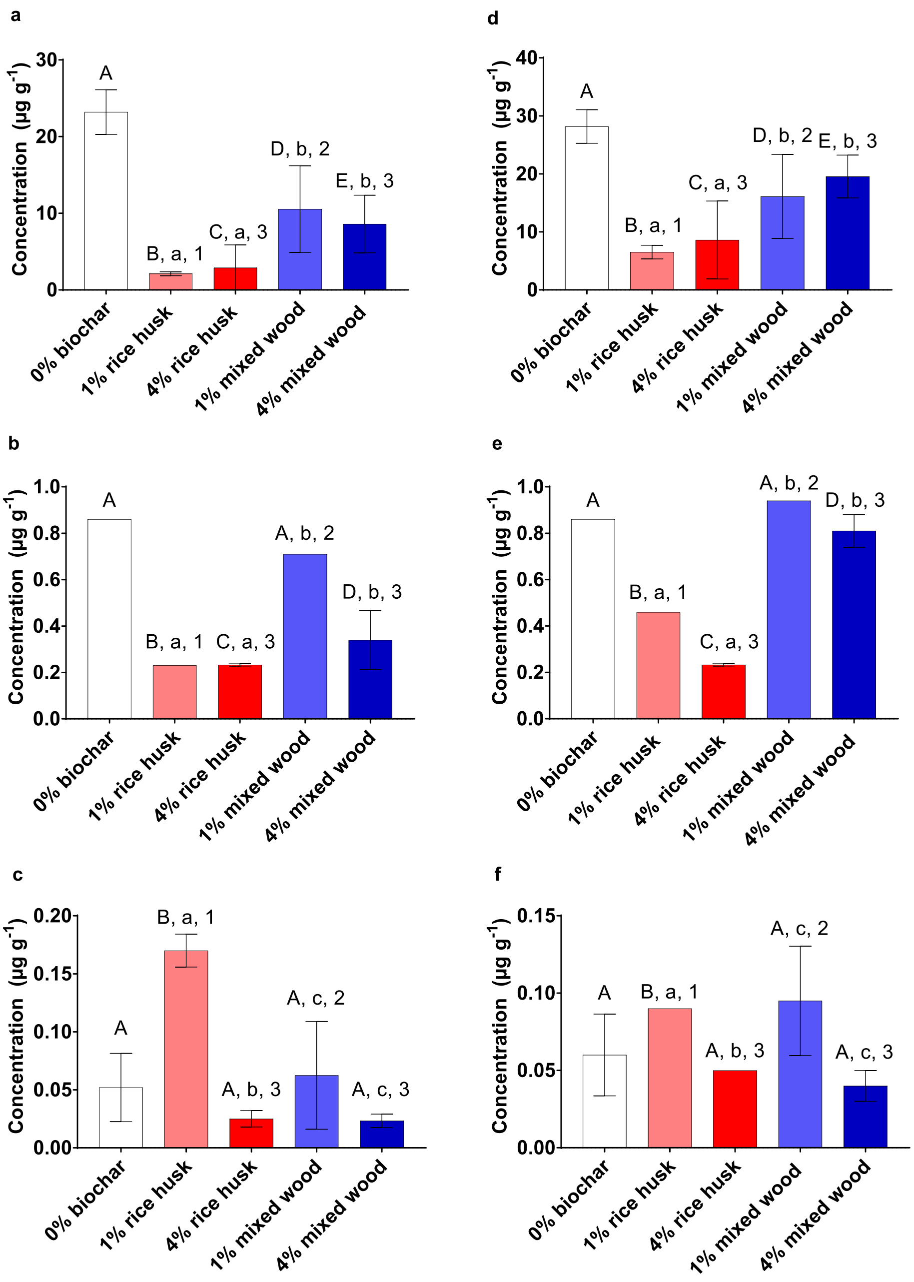

Fig. 2. a–f: Concentration (µg g^{-1}) of PCB 28 accumulated by the earthworm (a), the polyethylene passive sampler (b) and the turnip (c); and concentration of PCB 101 accumulated by the earthworm (d), the polyethylene passive sampler (e) and the turnip (f). Statistics are as follows: capital letters indicate a statistically significant difference in concentration when comparing the unamended pots to the biochar (both 1 and 4% amended) pots, lower case letters indicate a statistically significant difference between biochar dose for the same type of biochar amendment, numbers indicate a statistically significant difference between biochar type for the same biochar amendment dose.

significantly reduce the uptake of PCB 28 to turnips, indeed the addition of 1% rice husk biochar increased uptake 3-fold compared to the unamended pot. To the best of our knowledge, this is the first time a turnip-biochar trial has reported an increase in pollutant uptake following biochar amendment. Uptake by turnip roots might have been reduced due to the low permeability of these PCBs and accumulation may be airborne dominated. However in this test, we did not test this explicitly, but may explain the observed low accumulation of the aerial parts of the turnip compared to earthworms and PE. In addition, the result may be due to the difficulty in effectively separating the soil (and the biochar particles) from the turnip roots. The positive effect of biochar on turnips concentrations remains, however, unexplained.

For PCB 101 (Fig. 2d, e and f) a 77% and 69% reduction for 1% and 4% rice husk biochar and a 43% and 31% reduction for mixed wood biochar was seen in earthworm uptake. There were no significant differences between the effectiveness of biochar doses for either biochar ($p = 0.97$, $p = 0.85$). For PE the reductions were 46% and 73% after 1% and 4% rice husk biochar was amended, while mixed wood biochar did not reduce uptake, and in some cases appeared to increase it. This is likely caused by working with very low concentrations, near to the analytical limit of detection. As for earthworms, there were no statistically significant differences in the effect of the biochar dose. The amendment of both biochars did not significantly reduce PCB uptake to turnips.

The overall better efficacy of the rice husk biochar in reducing the uptake of PCBs to the phases tested supports the notion that the remediation efficiency of a biochar is dependent on the biochar physicochemical characteristics (Table 1). The rice husk biochar has a higher ash content (41.2% compared to 18.2%) than the mixed wood biochar, although it has a lower carbon content (49% compared to 74.5%) and a lower surface area (51 m^2 g^{-1} compared to 404 m^2 g^{-1}), than the mixed wood biochar. The higher effectiveness of the rice husk biochar in comparison with the mixed wood biochar can't be explained on the base of the physicochemical properties taken into account here; without further detailed investigation it is difficult to pinpoint the characteristics of the biochar that control sorption in this case.

3.3. Phase to soil accumulation (PSAF) factors

The PSAFs are shown in Table 2 for each phase (earthworm, PE and turnip) for both biochars and both amendment doses for PCB 28 and PCB 101. Data for all other PCBs can be found in the SI (Table S8). The PSAFs for both PCB 28 and PCB 101 for all phases are smaller in the biochar amended than unamended pots. As for the absolute concentrations, and reductions in PCB uptake, the PSAFs followed the order: $PSAF_{worm} > PSAF_{PE} > PSAF_{turnip}$ for all PCBs. Phase to soil accumulation factors (PSAF) were around 0.5 for turnips, were approximately 5 for PE and exceeded 100 for earthworms. The PSAFs were generally lower for the rice husk biochar than for the mixed wood biochar. PSAFs were also lower for the 4% biochar dose than for the 1% dose.

This study is the first accumulation experiment in which the three phases were added to the same system simultaneously, rather than to expose each phase separately. Results for individual phases can be tentatively compared with previous studies in which accumulation factors were calculated. Denyes et al. (2016) carried out trials in which biochar was amended to a DDT contaminated soil and then earthworms (*Eisenia fetida*), POM passive samplers and pumpkin (*Cucurbita pepo*) were exposed (but in two separate experiments). The results from their study showed that DDT had a higher sorption affinity for earthworm lipids and POM than for plants based on the magnitude of the accumulation factors, in agreement with the results from this study. Brennan et al. (2014) carried out a pot trial to investigate the effects of the amendment of 3 wt% biochar produced from pine wood and maize stubble on the availability of PAHs to maize. The results showed non-significant reductions in PAH biota to soil accumulation factors (BSAF) upon amendment with mixed wood biochar, but significant reductions for maize stubble biochar, compared to unamended controls. The maize stubble biochar reduced the BSAFs by 58%, 57% and 65% for 3 ring, 4 ring and 5 ring PAHs, respectively. Wang et al. (2014) calculated the BSAF of atrazine for two worm species that were exposed to pine wood biochar amended and unamended soil. They found clear differences between earthworm species and biochar amendment dose. The BSAF (calculated based on earthworm lipid concentration) was 5 times higher (0.42 versus 0.079) for *Metaphire guillelmi* than for *Eisenia fetida* in the unamended pots. Biochar amendment resulted in BSAF reductions for both earthworm species, but the reduction was much greater for *M. guillelmi* (factors of 3.5 and 12 for 0.5 and 2% biochar doses, respectively) than for *E. fetida* (factor of 2 for both dosages).

Table 2
Phase to soil accumulation factors (PSAF) for PCB 28 and 101 for pots with 0% biochar, 1% and 4% rice husk and mixed wood biochar. In cases where data is not given, the concentration in one of the phases was below the analytical limit of detection.

Phase	Treatment	PCB-28	PCB-101
Earthworms	0% biochar	296	306
	1% rice husk	–	–
	4% rice husk	41	111
	1% mixed wood	142	217
	4% mixed wood	58	272
PE	0% biochar	11	9.4
	1% rice husk	–	–
	4% rice husk	3.3	3.0
	1% mixed wood	10	13
	4% mixed wood	2.3	11
Turnip	0% biochar	0.7	0.5
	1% rice husk	–	–
	4% rice husk	0.4	0.6
	1% mixed wood	0.8	1.2
	4% mixed wood	0.2	0.5

3.4. Correlation of PCB uptake between earthworms, PE and turnips

The PSAFs for all PCBs in individual phases (for the unamended, 1% and 4% biochar doses) were plotted against each other in order to investigate whether there were correlations in uptake, and whether uptake in plants and worms could be predicted from uptake in passive samplers. In Fig. 3a–c each PCB congener is plotted as a separate point (using the average of measurements), for a) earthworms vs. PE passive samplers b) earthworms vs. turnips and c) turnips vs. PE passive samplers. PSAF for earthworms and PE passive samplers were well correlated ($r^2 = 0.85$, $p < 0.0001$), while the correlations for the other phases were poorer, but still significant: $r^2 = 0.68$ ($p < 0.0001$) for earthworms vs. turnips and $r^2 = 0.62$ ($p < 0.0001$) for PE vs. turnips. The relationship between phases was assessed forcing the line through (0,0). These results indicate that the uptake of PCBs by earthworms can be predicted by the uptake by PE. The regression analysis resulted in the following equation: $PSAF_{earthworm} = 19.19 \times PSAF_{PE,}$ indicating that the earthworms took up 19 times more PCBs than PE, during the time frame of this exposure experiment. This is likely due to the fact that the earthworms are closer to pseudo-equilibrium than the passive samplers in this static system. Previously passive samplers were reported to reach equilibrium with sediment particles only after decades in a static system (Hale and Werner, 2010). The poorer correlation between plants and the other phases may have resulted from (i) insufficient separation of soil and biochar particles from the turnip roots, similar to earlier reported insufficient separation of sediment and AC from folded skin of gastropods (Cornelissen et al., 2006) and (ii) a significant leaf-air exchange which was not taken into account in this experiment. However the PCB concentration in the soil was comparable with the PCB concentration in the turnip; thus suggesting that the artefact observed by Cornelissen et al. (2006) did not present a problem here.

Previous studies, carried out in the absence or presence of biochar (or AC), have shown that passive samplers can be used as proxies to predict the uptake of organic compounds by various organisms. In these previous studies, all phases and the amendment material were added to experimental setups at the same time (the beginning of the trial period). While this introduces a degree of uncertainty with regard to extend of equilibrium achieved, it is representative of initial amendment conditions (corresponding to the time in which the experiment is carried out for) if such a method is used in the field. Vinturella et al. (2004) reported that marine sediment worms (specifically benthic polychaetes) accumulated more PAHs per gram of lipid than PE, reporting the relationships $\log C_{worm} = 0.6 \log C_{PE} + 1.8$ ($r^2 = 0.65$; $p < 0.0001$) for individual PAHs and $\log C_{worm} = 0.6 \log C_{PE} + 2.4$ ($r^2 = 0.67$; $p < 0.002$) for $\sum$PAH in unamended tests. Denyes et al. (2016) reported a good correlation between the uptake of DDT to POM passive samplers and earthworms, also concluding that soil porewater concentrations can underestimate earthworm accumulation following biochar (and AC) amendment. Paul and Ghosh (2011) reported a linear 1:1 relationship ($y = 0.98x - 0.01$; $r^2 = 0.91$) between aqueous tetrachlorobiphenyl concentration (measured by POM) and earthworm (*Eisenia fetida*) concentrations, both before and following AC amendment. Gomez-Eyles et al. (2011a) reported that passive sampling methods (POM and solid phase micro extraction) could be used to assess PAH bioavailability to earthworms (*Eisenia fetida*) within a factor of 10, and were better correlated than solvent and cyclodextrin extractions.

4. Conclusion

Using passive samplers as proxies for the uptake of pollutants to biota and plants has numerous advantages. In this study PE passive samplers were able to mimic the uptake of PCBs from biochar amended soil to earthworms lipids but not to turnips. Earthworms accumulated more PCBs than the PE passive samplers, and it is important therefore to be aware that there is not always a 1:1 correlation between the uptake of

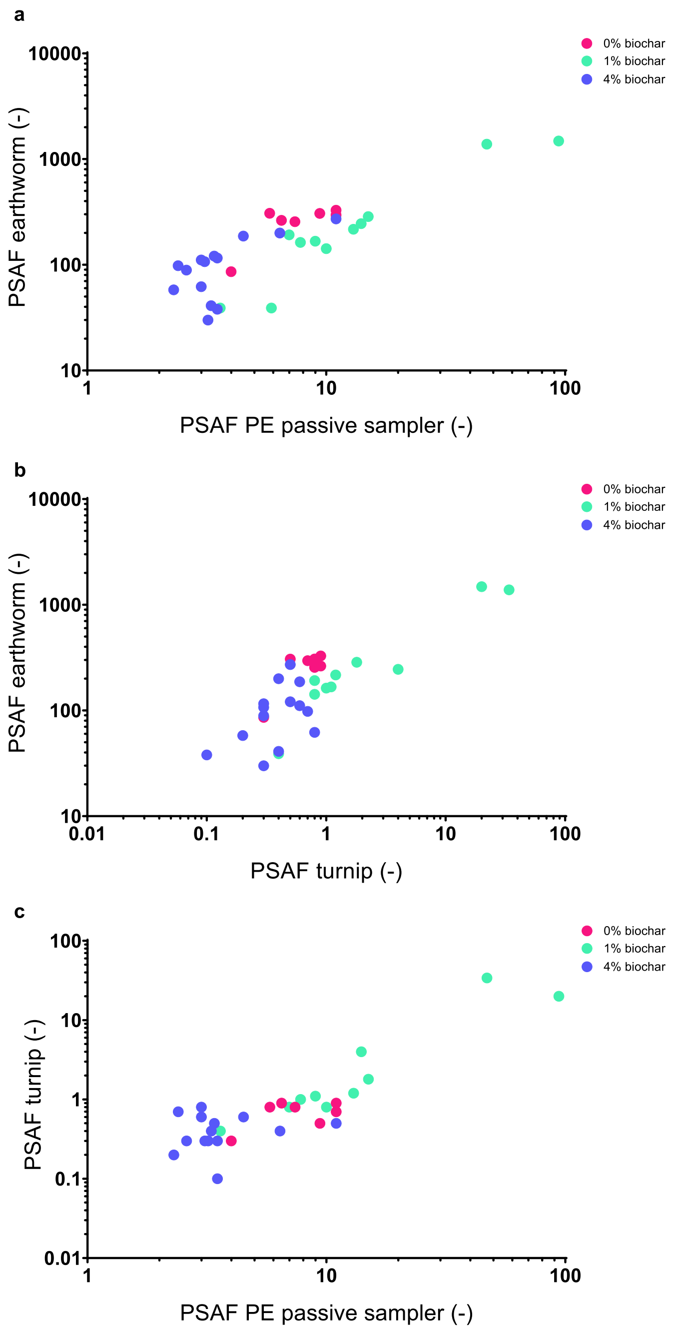

Fig. 3. a–c: Correlation between PSAF values for: (a) earthworms vs. PE passive samplers ($y = 19.19\times$, $r^2 = 0.85$) (b) earthworms vs. turnips ($y = 50.52x$, $r^2 = 0.68$) and (c) turnips vs. PE passive samplers ($y = 0.29$, $r^2 = 0.62$). The scale used on the y and x axis is automatically calculated by GraphPad Prism 7 scientific software.

pollutants by both phases, due to both uptake kinetics and differences in sorption strength (Heijden and Jonker, 2009). The exposure period used here (24 or 30 days) resulted in different extents of equilibrium being achieved for the different phases, and thus probably contributed to the much larger uptake of PCBs by the earthworms than the passive samplers. However, passive samplers can be considered as a useful tool to assess whether site remediation has been successful, without the need for monitoring campaigns with biota or plants, avoiding the number of confounding factors introduced by the use of these organisms as biomonitors. This confirms the initial hypothesis, thus the uptake in passive samplers could be suggested as a proxy for uptake in organisms.

This study also contributes to current evidence that biochar can be used as a sorbent material for the remediation of PCB contaminated soil, confirming the second hypothesis of the study. Biochar is more sustainable and often cheaper than AC, providing an additional benefit for its use (Sparrevik et al., 2011). This must however be weighed against its lower effectiveness in reducing contaminant uptake as compared to other carbonaceous geosorbent amendments (Denyes et al., 2012). In this study, the amendment of 1% biochar was sufficient to significantly reduce PCB concentrations in earthworms and passive samplers, which is also promising for large scale remediation efforts as relatively limited amounts of biochar would need to be produced. Variation in effectiveness between the biochars indicates that translating these results into a wider context should be done with care, as each biochar will perform differently and the dose required to reach acceptable remediation goals will vary. However, the observation is encouraging as the rice husk biochar was made using simple and cheap technology. It is important that small scale lab and possibly field trials are carried out prior to the onset of a large scale field remediation efforts in order to determine the appropriate biochar amendment dose.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2019.01.202.

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