

Including Sorption to Black Carbon in Modeling Bioaccumulation of Polycyclic Aromatic Hydrocarbons: Uncertainty Analysis and Comparison to Field Data

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Model estimations of bioaccumulation of polycyclic aromatic hydrocarbons (PAHs) have been higher than field or laboratory data. This has been explained by strong sorption to black carbon (BC). In this paper, eight previously published bioaccumulation datasets were reinterpreted in terms of additional BC sorption. Biota–Solids Accumulation Factors (BSAFs) of PAHs typically decreased by 1–2 orders of magnitude and were better in line with field data in marine, fresh water, and terrestrial ecosystems. Probabilistic BC-inclusive modeling showed that if BC content is not accurately known, uncertainty in BSAFs is 2–3 orders of magnitude (90 percentile confidence interval) due to uncertainty in the BC sorption term. When BC contents are measured, the deviation between model estimations and field measurements reduces to about a factor of 3. This implies that including routine measurements of BC contents is crucial in improving risk estimations of PAHs.

Introduction

Ecological risk assessment involves use of reliable models to estimate accumulation of hazardous substances in organisms. Concentrations of polycyclic aromatic hydrocarbons (PAHs) in biota derived from field-contaminated solids, however, are often substantially lower than estimations by bioaccumulation models using standard solids–water equilibrium partitioning (1, 2). Their low accumulation levels

have been attributed to strong sorption of PAHs to black carbon (BC; i.e. soot and chars), kerogen, and coal in the solids. This sorption to BC reduces availability of hydrophobic organic compounds as PAHs for partitioning to water (1, 3, 4). Reduced uptake from solids containing BC has been shown in experiments with marine invertebrates (5–8) and fresh water invertebrates (9). Field measurements on marine and fresh water invertebrates confirmed the experimental observations (9, 10). Including sorption to BC into equilibrium partitioning, as suggested by Gustafsson et al. (11) and Accardi-Dey & Gschwend (12) results in lower predicted concentrations in biota (6, 9, 13, 14). However, BC-inclusive models do not predict all field data very accurately yet (9, 14). It can be hypothesized that especially uncertainties in sedimentary BC contents and in the PAH–BC association parameters may limit the accuracy of model predictions. Accordingly, it is crucial to quantify the relative importance of these two sources of uncertainty. This will increase our understanding of which parameters contribute dominantly to variation in PAH concentration in biota.

The model OMEGA estimates bioaccumulation for species from four trophic levels and aquatic as well as terrestrial food chains (15, 16). It uses a one-compartment first-order kinetic approach similar to earlier bioaccumulation models (17–20). These models predict accumulation levels on the basis of modeling of uptake and elimination kinetics determined by advective flow, diffusion through water, and penetration through lipid membrane, each with its own resistance or delay.

The aim of this study is twofold: (i) to improve model estimations of PAH accumulation by incorporating BC in current state-of-the-art food chain models like OMEGA and to compare these estimations with field measurements; and (ii) to determine the range of variation in modeled bioaccumulation as a result of the newly included sorption term.

Methods

Model Equations. The accumulation of neutral organic compounds in biota can be expressed as the ratio between the concentration in the organism (C_i) and the concentration in the abiotic compartment. As most empirical data refer to total concentrations in sediment, suspended solids, or soil (C_s) this ratio is calculated as the Biota-Solids Accumulation Factor:

$$BSAF = \frac{C_i/f_{lipid}}{C_s/f_{OC}} \quad (1)$$

OMEGA calculates steady-state chemical residues in biota as the sum of influx via water (absorption) and uptake of food (assimilation) divided by the sum of elimination processes (eq 2) (17–20). Symbols are explained in Table 1 and a more thorough description of OMEGA is given in the Supporting Information.

$$C_i = \frac{k_{w,in}C_{0,w} + k_{n,in}C_{i-1}}{k_{w,ex} + k_{n,ex} + k_p + k_m} \quad (2)$$

The concentration in the organism is determined by a species-specific combination of all routes of uptake and elimination described in eq 2. The dissolved chemical fraction in water is available for uptake by biota. The concentration in water for a given concentration in solids depends on the solids–water partition coefficient (K_{sw}). In the traditional approach,

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TABLE 1. Explanation of Symbols

symbol	description	unit	source
BSAF	biota-solids accumulation factor	$\mu\text{g}\cdot\text{kg}^{-1}$ lipid weight/ $\mu\text{g}\cdot\text{kg}^{-1}$ organic carbon	eq 1
C_i^a	concentration in biota of trophic level i	$\mu\text{g}\cdot\text{kg}^{-1}$ wet weight	eq 2, refs 28–34 (see Supporting Information)
f_{lipid}	lipid fraction in organism	kg lipid weight/kg wet weight	refs 28–34 (see Supporting Information)
C_s	concentration in solids	$\mu\text{g}\cdot\text{kg}^{-1}$ total dry weight	refs 28–34 (see Supporting Information)
f_{OC}	black carbon exclusive organic carbon fraction of solids	kg organic carbon/kg total dry weight	reference 15 ^e = $f_{\text{TOC}} - f_{\text{BC}}$
$C_{0,w}$	concentration dissolved in water	$\mu\text{g}\cdot\text{L}^{-1}$	fitted according to eq 4, see Supporting Information
$k_{w,\text{in}}$	rate constant for absorption	$\text{L}\cdot\text{kg}^{-1}$ wet weight d^{-1}	ref 15
$k_{n,\text{in}}$	rate constant for assimilation	kg food/kg wet weight d^{-1}	ref 15
C_{i-1}	concentration in food ^b	$\mu\text{g}\cdot\text{kg}^{-1}$	ref 15; eq 2
$k_{w,\text{ex}}$	rate constant for excretion via water	$\text{kg}\cdot\text{kg}^{-1}\cdot\text{d}^{-1}$	ref 15
$k_{n,\text{ex}}$	rate constant for egestion with faeces	$\text{kg}\cdot\text{kg}^{-1}\cdot\text{d}^{-1}$	ref 15
k_p	rate constant for dilution of biomass	$\text{kg}\cdot\text{kg}^{-1}\cdot\text{d}^{-1}$	ref 15
k_m	rate constant for metabolic transformation	$\text{kg}\cdot\text{kg}^{-1}\cdot\text{d}^{-1}$	ref 15 ^c
K_{sw}	solids–water partition coefficient	$\text{L}\cdot\text{kg}^{-1}$ total dry weight	eq 3; eq 4
K_{OC}	coefficient for partitioning to organic carbon	$\text{L}\cdot\text{kg}^{-1}$ organic carbon	= $f_{\text{iso}}\cdot K_{\text{ow}}$
f_{iso}	octanol-equivalent fraction in organic carbon	kg octanol equivalent/kg organic carbon	ref 15 ^d
K_{ow}	octanol–water partition coefficient	[-]	refs 21, 22
f_{om}	organic matter fraction	kg organic matter/kg total dry weight	= $2\cdot f_{\text{TOC}}$ for aquatic ecosystems (23); = $1.7\cdot f_{\text{TOC}}$ for terrestrial ecosystems (24); ref 15; refs 28–34 (see Supporting Information)
f_{TOC}	black carbon inclusive organic carbon fraction of solids	kg organic carbon/kg total dry weight	ref 15; refs 28–34 (see Supporting Information)
f_{BC}	black carbon fraction of solids	kg BC/kg total dry weight	refs 28–34 (see Supporting Information); Table 2
$K_{f,\text{BC}}$	Freundlich constant for sorption to black carbon	$\mu\text{g}\cdot\text{kg}^{-1}$ BC/ $(\mu\text{g}\cdot\text{L}^{-1})^n$	Table 2
$n_{f,\text{BC}}$	Freundlich coefficient for sorption to black carbon	[-]	Table 2

^a For invertebrates $i = 2$ in OMEGA. ^b The food of invertebrates is assumed to be detritus/algae. ^c k_m is not explicitly modeled in this study. ^d In OMEGA a default value of 36% is included. ^e In OMEGA a default value of 6% for soil and of 8% for suspended solids and sediments is included. These defaults agree reasonably with the datasets.

partitioning between solids and (pore) water is assumed to be at equilibrium (25). As organic chemicals have a strong affinity for organic matter, sorption to solids is determined by sorption to the organic carbon fraction (f_{OC}). The K_{sw} can be expressed by using the octanol–water partition coefficient (K_{ow}) of a substance and an octanol equivalent fraction in the organic solids (f_{iso}) (26):

$$K_{sw} = f_{\text{OC}}K_{\text{OC}} = f_{\text{OC}}f_{\text{iso}}K_{\text{ow}} \quad (3)$$

This partition coefficient describes the linear sorption of organic compounds to “amorphous” organic carbon. The release of these compounds from this organic carbon type is considered to occur with typical half-lives of hours to days (fast desorbing PAH fraction related to BC-exclusive organic carbon). Besides this fraction, a “slow desorbing” PAH fraction related to BC has release half-lives of years to decades (13, 14).

Adding a term for calculating the concentration of organic compounds adsorbed to BC in solids under equilibrium conditions (11, 13, 14, 27) results in a new K_{sw} in OMEGA:

$$K_{sw} = \frac{C_s}{C_{0,w}} = f_{\text{OC}}K_{\text{OC}} + f_{\text{BC}}K_{f,\text{BC}}C_{0,w}^{n_{f,\text{BC}}-1} \quad (4)$$

By adding this second term, the concentration dissolved in water ($C_{0,w}$) is no longer linearly related to the concentration in solids (C_s).

Data Sources. Sampling locations, dates, and variables measured are summarized in the Supporting information. More detailed descriptions of sampling locations and analytical methods can be found in the references cited there. For comparison with model results, concentrations measured in biota and solids were converted to $\mu\text{g}\cdot\text{kg}^{-1}$ lipid weight and to $\mu\text{g}\cdot\text{kg}^{-1}$ organic carbon respectively.

Data on marine semi-field experiments were obtained from Vethaak et al. (28). They measured the concentration of 13 PAHs in sediment, suspended solids, and two herbivores (the lugworm *Arenicola marina* and the blue mussel *Mytilus edulis*) in large scale mesocosms using a relatively clean, an indirectly polluted, and a directly polluted system. Field measurements on marine ecosystems were obtained from research programs in the Western Scheldt estuary carried out by National Institute for Coastal and Marine Management (RWS-RIKZ) (29, 30). They cover measurements in sediment as well as in suspended solids and in *Arenicola marina*, *Cerastoderma edule*, and *Nereis diversicolor*. Chemical analyses were performed using validated and accredited (ISO 17025) methods. Field measurements on fresh water systems were obtained from monitoring

TABLE 2. Characteristics of the Probability Distributions Used for the BC Sorption Term in Eq 4

name	unit	distribution	aquatic ecosystems	terrestrial ecosystems	origin	reference
C_s	$\mu\text{g}\cdot\text{kg}^{-1}$ total dry weight	lognormal	median: 229; coefficient of variation: 2.5	median: 122; coefficient of variation: 1.4	variable	Table 2
f_{BC}	kg BC/kg total dry weight	lognormal	median: 0.002; coefficient of variation: 2.5	median: 0.007; coefficient of variation: 6.3	variable	refs in 13
$n_{f,\text{BC}}$	[-]	triangular	most likely: 0.7; minimum: 0.5; maximum: 0.9	most likely: 0.7; minimum: 0.5; maximum: 0.9	uncertain	9, 12, 13, 14, 37
$K_{f,\text{BC}}$	$\mu\text{g kg}^{-1}\text{BC}/(\mu\text{g L}^{-1})^n$	noncentral t distribution	degrees of freedom: 11; standard error = 0.07 – 0.16; mean: $\log K_{\text{BC}} = 0.7 \cdot \log K_{\text{ow}} + 2.8$	degrees of freedom: 11; standard error = 0.07 – 0.16; mean: $\log K_{\text{BC}} = 0.7 \cdot \log K_{\text{ow}} + 2.8$	uncertain	13

programs carried out by the Institute for Inland Water Management and Waste Water Treatment (RIZA) covering measurements in the mussel *Dreissena polymorpha* and suspended solids and in juvenile chironomids and sediment (31–33). Terrestrial data were taken from Van Brummelen (34), who measured concentrations of 8 PAHs in forest soil and in earthworms.

Probabilistic Modeling. A Monte Carlo simulation was carried out to assess the variation in BSAF estimations related to the BC sorption term (eq 4). Each simulation consisted of 10,000 iterations. The model OMEGA was adapted to include the Monte Carlo simulation using Crystal Ball 7.1.2 (35). According to Cornelissen et al. (13) and Koelmans et al. (14) the BC term in eq 4 is dominant under typical environmental conditions and PAH concentrations of interest for risk assessment. A preliminary sensitivity analyses confirmed dominance of the BC term in the K_{sw} in BSAF estimation. Two sources of variation are distinguished: (i) variability and (ii) uncertainty (36). Variable parameters can be measured, but vary inherently in the environment, such as PAH concentrations, organic carbon fractions, and BC fractions in solids. Uncertainty refers to the fact that parameter values are not perfectly known, for instance due to the lack of data or uncertain measurements. In our analysis this refers to the Freundlich parameter $n_{f,\text{BC}}$ and the $K_{f,\text{BC}}$ estimates from linear regression. Uncertainties due to measurement techniques are not taken into account.

Variability and uncertainty both contribute to the variation in modeled BSAFs. The total variation was quantified in a generic assessment to give a range of variation as comprehensive as possible. Table 2 summarizes the probability distributions for the input variables and the uncertain parameters for this generic assessment. For the concentrations in solids (C_s), probability distributions were fitted to the measured field data (references 28–34). These field data cover various Dutch environmental conditions. Values for the black carbon fraction (f_{BC}) were taken from the literature reviewed by Cornelissen et al. (13), where values for the BC fraction were explicitly reported or could be calculated (Supporting Information). Following Moermond et al. (9), Accardi-Dey et al. (12), Cornelissen et al. (13), Koelmans et al. (14) and Lohman et al. (37) the Freundlich parameter $n_{f,\text{BC}}$ was approximated by a triangular distribution with extremes reported in the literature of about 0.5–0.9 and an average of 0.7. The $K_{f,\text{BC}}-K_{\text{ow}}$ relation based on an empirical linear regression was taken from Koelmans et al. (14). The uncertainty in the regression equation was included in the Monte Carlo simulation using statistics for linear regression analysis (38; Supporting Information).

To assess uncertainty only, a second Monte Carlo simulation was conducted for the dataset that included location specific BC values (30). In this simulation location specific data were used for the variables black carbon fraction (f_{BC}), concentration in sediments (C_s), and lipid fraction and

the distributions from Table 2 were used for the Freundlich parameters for sorption to BC ($K_{f,\text{BC}}$, $n_{f,\text{BC}}$).

In addition, an uncertainty importance analysis was performed to identify the parameters or variables that contribute most to variation in BSAF. This analysis consisted of a Monte Carlo simulation in combination with a Rank correlation (expressed as percentage of total variance).

Results and Discussion

Reduction in Modeled BSAFs. The 5th-, 50th-, and 95th-percentiles of estimated BSAFs corrected with BC sorption are shown in Figure 1. For comparison, the BSAF calculated without BC correction is included as well. Typically, BSAF estimations for PAHs with BC are reduced by 1 order of magnitude compared to estimations without BC (Figure 1). However, the reduction of BSAFs ranges from half an order of magnitude for aquatic invertebrates up to 4 orders of magnitude for terrestrial invertebrates due to uncertainty in the BC sorption term (90% confidence interval). This difference in uncertainty between aquatic and terrestrial data can be explained by a larger uncertainty in the black carbon fraction (f_{BC}) for terrestrial data (Table 2). The modeled typical BSAF reduction observed for the terrestrial data is larger than for the aquatic data, which can be explained by a systematically higher black carbon fraction (f_{BC}) employed in the Monte Carlo Simulation for soil compared to aquatic solids (Table 2). Koelmans et al. (13) and Cornelissen et al. (14) report reductions in BSAFs up to 3 orders of magnitude. These values are comparable to our modeled estimations. This range is comparable with the variation in measured organic carbon–water partition coefficients (K_{oc}) values reported by Hawthorne et al. (39) and ascribed to differences in sediment characteristics.

Sensitivity Analyses. The uncertainty importance analysis showed that the variation in the black carbon fraction (f_{BC}) contributes dominantly to the variation in BSAFs of PAHs for the whole range of octanol–water partition coefficients (K_{ow}). Table 3 shows a representative example for a K_{ow} of 3.5×10^5 . This implies that the variation in model estimations can be substantially reduced when measured f_{BC} values are used. Others (1, 3, 40) also observe an important influence of the BC content on bioaccumulation. Overestimation of solids–water partitioning might be attributed to competitive sorption by other organic compounds (8, 13, 14). The $K_{f,\text{BC}}$'s in the regression analysis were derived from in-situ partitioning data from different locations, which means that this attenuation effect is already accounted for in the BSAF estimations and will not lead to additional overestimation or uncertainty.

Field BSAFs. Accumulation ratios for *Dreissena polymorpha* in the Rhine–Meuse delta show levels similar to the data found for marine polychaetes and bivalves (Figure 1a–e). Accumulation levels for juvenile chironomids are lower

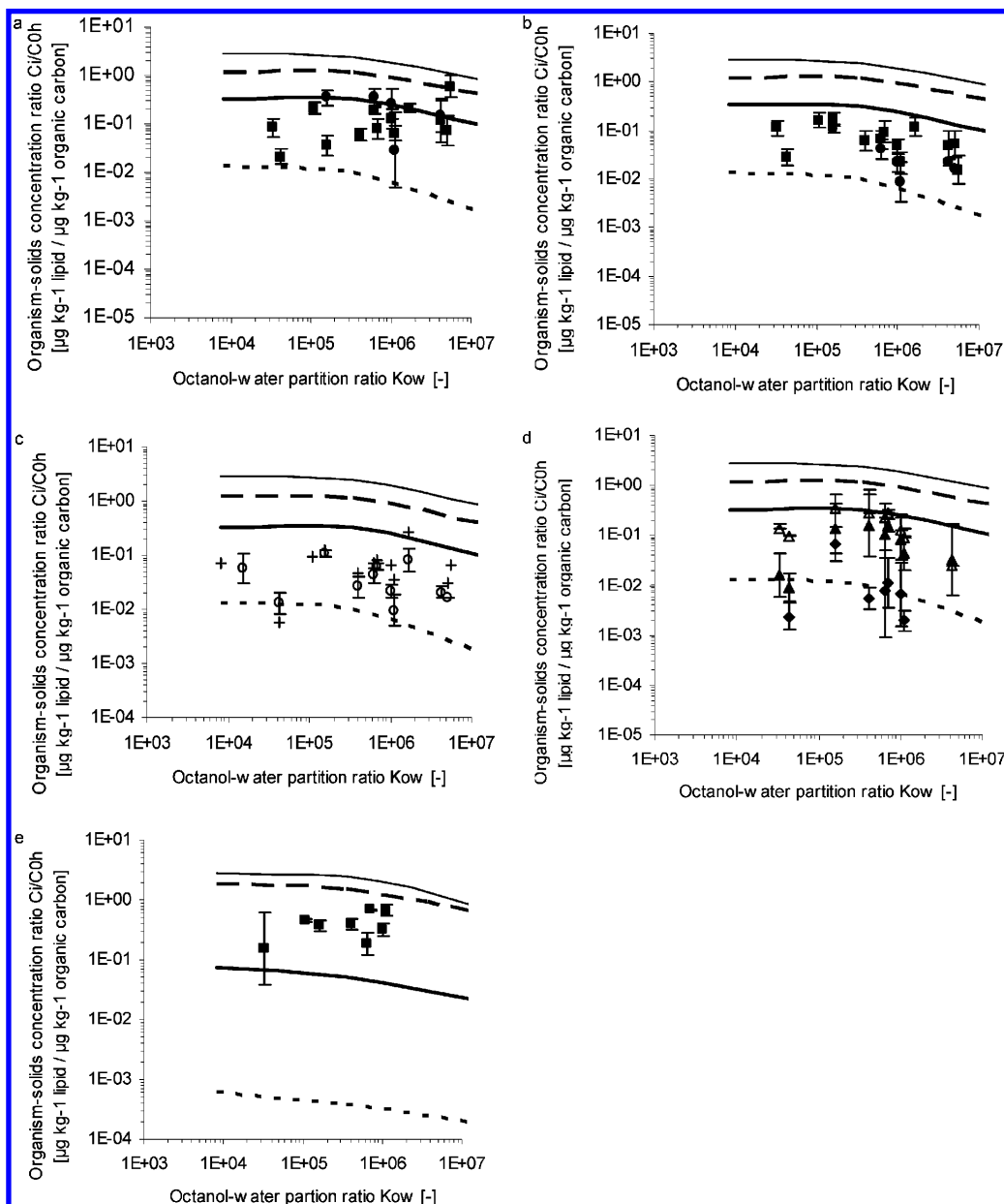


FIGURE 1. OMEGA estimation of Biota-Solids Accumulation Factors for PAHs — using eq 3 and — 50th (thick line), — — 95th, and ---- 5th percentile values using eq 4 versus K_{ow} , compared to (a) *Arenicola marina* to sediment concentration ratios (■ ref 28; ● ref 29); (b) *Mytilus edulis* to sediment concentration ratios (■ ref 28), and *Nereis diversicolor* to sediment concentration ratios (● ref 29); (c) *Cerastoderma edule* to suspended solids concentration ratios (+ ref 30) and *Nereis diversicolor* to suspended solids concentration ratios (○ ref 29); (d) *Dreissena polymorpha* to suspended solids concentration ratios (▲ ref 31; △ ref 32) and juvenile *Chironomidae* to sediment concentration ratios (◆ ref 33); (e) *Lumbricus rubellus* to soil concentration ratios, (ref 34) including standard deviations of the measurements where available. Panels a–c show marine species, panel d shows freshwater species and panel e shows terrestrial species.

TABLE 3. Contribution to Variance in BSAF Estimation for Parameters Included in the Soot Sorption Term for a K_{ow} of 3.5×10^5

	sediment/suspended solids	soil
black carbon fraction f_{bc}	82%	88%
Freundlich $n_{f,BC}$	8%	9%
concentration in solids C_s	8%	2%
Freundlich $K_{f,BC}$	2%	1%

(Figure 1e). This deviation is discussed by Reinhold et al. (33), but no general explanation is given. BSAFs for the earthworm *Lumbricus rubellus* are slightly higher (Figure 1f) than those for the aquatic data. Within the marine species the measured bioaccumulation in *Arenicola marina* (Figure

1a and b) reaches higher levels than in *Cerastoderma edule*, *Mytilus edulis*, and *Nereis diversicolor* (Figure 1c and d). Penry et al. (41) mention feeding behavior and digestive physiology to affect PAH bioaccumulation, which might explain these higher levels in sediment feeders. Others, however, report no such differences in bioaccumulation (42).

Estimated BSAFs and Field Data. The majority (93%) of the BSAFs of PAHs in Figure 1 are between 0.002 and 0.7, whereas OMEGA without BC correction estimates a BSAF of PAHs of about 3. The measured BSAFs lie within the range calculated in the Monte Carlo simulation with BC. However, 95% of the field data lie below the 50th-percentile of estimations. Some substances are above the 50th-percentile line of model estimations for high K_{ow} values where model lines show a decline in BSAF that is not reflected in the field data. The variation in the field data, however, is high. No

clear pattern can be observed in the differences between substances, this may be overlain by the difference between individual biota in the measurements. Within the group of PAHs, partitioning to water is often observed to decrease with increasing molecular surface area and K_{ow} (3). Few substances in Figure 1, however, exceeded a K_{ow} of 10^6 and bioaccumulation is expected to be reduced above this value (18, 43).

The tendency for overestimation is in line with observations by Moermond et al. (9), who, with BC contents comparable to the median in Table 2, found that their BC-inclusive model perfectly fitted polychlorinated biphenyl data but still overestimated BSAFs for PAHs by a factor of 3–9. They mention that part of the deviation could be attributable to metabolic transformation. Other factors could also lead to additional reduction in BSAFs or represent an alternative explanation as discussed below.

Metabolic Transformation. Metabolic transformation of pyrene and benzo(a)pyrene has been reported for some invertebrates, including for example for *Nereis diversicolor* (44–47), but is considered to play a limited role in elimination kinetics of oligochaetes and bivalves (48–51). As metabolic transformation is not explicitly modeled in this study, it might still have a lowering effect on the BC-exclusive BSAFs. Metabolic transformation leads to lower BSAFs, particularly for higher molecular weight substances (52). Van der Linde et al. (53) estimate rates of metabolic transformation of PAHs by annelids around 1 d^{-1} . Such a transformation rate would lead to a reduction of BSAFs between a factor of 2 (lower weight PAHs) and a factor of 200 (higher weight PAHs) as modeled using OMEGA. This does not seem sufficient to explain the lower field data over the whole range of octanol–water partition coefficients ($K_{ow,s}$).

Model Assumptions. Concentrations in biota are calculated assuming steady state (eq 2). Non-steady-state situations might lead to an overestimation of BSAFs by the model as well. Steady state in aquatic invertebrates is reported to be reached after 4–20 days for compounds with K_{ow} around 10^5 – 10^6 by several studies (42, 45, 47, 54). It is expected that field exposure exceeds this period. Hendriks (31) and Reinhold (33) show that field conditions can be described by steady state. Results are therefore not affected by the steady state assumption.

Another assumption is that the influence of other carbonaceous geosorbents, such as coal and kerogen, were not included in the uncertainty analysis. Cornelissen et al. (55) showed that ignoring these sorbents in the Freundlich partitioning can lead to overestimations of the $K_{f,BC}$ up to a factor of 5. However, in this case this will not yield significant bias because (a) kerogen and coal levels will be minor in comparison to BC, and (b) any systematic underestimation due to ignoring kerogen or coal phases is counteracted by the overestimation in BC normalized $K_{f,BC}$ values from the sediments used in the regression analysis (14).

Remaining Uncertainty. Figure 2 compares BSAFs calculated with location-specific values for concentrations in solids (C_s), organic carbon fractions (f_{OC}), black carbon fractions (f_{BC}), and lipid content measured by Van den Heuvel-Greve et al. (30) to corresponding field BSAFs. These f_{BC} values were measured with the CTO375 method (11), which ascertains consistency with the BC sorption parameters provided by Koelmans et al. (14) and applied in the present study, which were also derived from CTO375 based BC measurements. The variation in predicted BC-inclusive BSAFs (5th-, 50th-, and 95th-percentile lines in Figure 2) is entirely caused by uncertainty in the Freundlich parameters $K_{f,BC}$ and $n_{f,BC}$, as variability has been excluded by using location-specific measurements. These uncertainties, as assessed in this paper, can only be reduced by an improved estimation of the parameters, particularly the Freundlich coefficient.

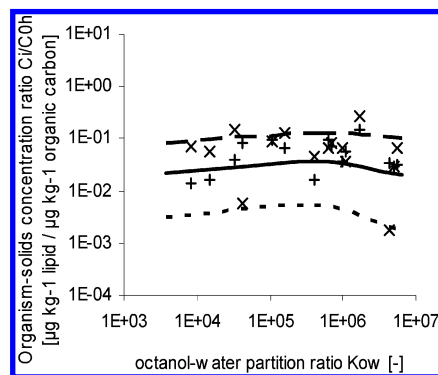


FIGURE 2. Field *A. marina* sediment concentration ratios (+) and field *C. edule* (x) suspended solids concentration ratios of PAHs versus K_{ow} (ref 30). Lines represent the — 50th, - - - 95th, and ···· 5th percentile values of estimated BSAFs including the uncertainty in the Freundlich parameters for the same data.

Figure 2 shows that the uncertainty is reduced to 2 orders of magnitude (the 90% confidence interval). The deviation between measured BSAFs and the 50th-percentile values of BC-inclusive modeled BSAFs is reduced to a factor 3 on average.

Implications. It was found that including sorption of PAHs to BC in the estimation of BSAFs results in model estimations that are better in line with field measurements. This indicates that BC sorption should be included in future risk assessments of PAHs. However, the uncertainty in the modeled BSAFs due to the uncertainty in sorption to BC spans 1.5 (for known BC contents) to 3 orders of magnitude (90% percentile confidence interval), which shows that further research is needed to better quantify reduced accumulation of PAHs. The BC fraction most strongly influences predicted BSAFs, implying that BC contents are particularly important in estimating bioaccumulation ratios and should be measured routinely, particularly as this does not involve substantial additional cost or difficulties.

Acknowledgments

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Supporting Information Available

Tables with overview of the data sources, concentrations in organic carbon of the solids and lipid of the biota (BSAF) from the original data, black carbon fractions compiled from literature, explanation of the fitting procedure for the concentration in water and the statistical procedure for including the uncertainty in the regression analyses, including the regression data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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