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A Terrestrial Food-Chain Bioaccumulation Model for POPs

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Mechanistic bioaccumulation models for fish and piscivorous food-webs are widely used to assess the environmental hazard and risk of commercial chemicals, develop water quality criteria and remediation objectives, and conduct exposure assessment of pesticides in aquatic systems. Similar models for mammals and terrestrial food-webs are largely absent. As a result, the hazards and risks of bioaccumulative substances in mammals, birds, and humans remain unrecognized by regulators, and current globally used criteria for identifying bioaccumulative substances only apply to water-breathing organisms and are inadequate for protecting air-breathing organisms including mammals, birds, and human beings. In this paper, we develop and test a modeling framework that can be used to estimate the biomagnification potential and the organism-soil bioaccumulation factor of organic commercial chemicals in terrestrial food-chains. We test the model for the soil−earthworm−shrew food-chain and apply the model to illustrate that (i) chemicals with an octanol−air partition coefficient (K_{OA}) < $10^{5.25}$ do not biomagnify even if the K_{OW} is high and optimal for biomagnification in fish; (ii) chemicals with a $K_{OA} \geq 10^{5.25}$ and a K_{OW} between $10^{1.75}$ and 10^{12} have a biomagnification potential unless they are metabolized at a sufficiently rapid rate (e.g., in excess of 0.3 d^{-1} or a half-life time of 2.5 d for shrews).

Introduction

Current regulatory initiatives, including the UNEP Stockholm Convention on Persistent Organic Pollutants, the U.S. Toxic Substances Control Act, the recently adopted European Unions' REACh program, and the Canadian Environmental Protection Act include a set of criteria to assess the bioaccumulative potential of man-made substances in an effort to manage the production, use, and release of commercial chemicals into the environment. The criteria used to identify bioaccumulative chemicals include the bioconcentration factor (BCF), which is defined as the ratio of the chemical concentration in biota (mg kg^{-1} wet weight) and the surrounding water (mg L^{-1}) as measured in laboratory tests involving chemical exposure via the water, and in absence of such data, the octanol−water partition coefficient (K_{OW}) (*1*−*4*). In Canada, the bioaccumulation factor (BAF), i.e. the ratio of the chemical concentration in biota (mg kg^{-1} wet weight) and the surrounding water (mg L^{-1}) measured under field conditions is also a legal criterion for identifying bioaccumulative substances. Because empirical BCFs do not exist for the great majority of commercial substances in use (*5*), Environment Canada has applied an aquatic bioaccumulation food-web model to derive the BAF of commercial chemicals on their Domestic Substances List. While this approach is appropriate for identifying bioaccumulative substances in piscivorous food-chains, recent studies demonstrate that several widely used chemical products with (i) a K_{OW} far below 10^5, (ii) measured BCFs generally below 5000 L kg^{-1} ww, and (iii) with trophic magnification factors (TMF) < 1.0 (i.e.not bioaccumulative) in piscivorous aquatic food-webs, can biomagnify to a high degree in terrestrial and marine mammalian food-webs. This indicates that the application of an aquatic food-web BAF model is insufficient to identify bioaccumulative substances in terrestrial and agricultural food-webs that involve birds, mammals, and humans (*6*−*9*). Therefore, there is a need to develop terrestrial-based food-web bioaccumulation models that can be applied to assess the bioaccumulative potential of commercial chemicals. In addition to their application for hazard assessment, bioaccumulation models for aquatic food-webs are well-established methods used in the derivation of water quality criteria, cleanup and remediation of contaminated sediments, exposure assessment of pesticides and other commercial chemicals, ecotoxicological risk assessment, and bioaccumulation categorization. However, mechanistic bioaccumulation models for terrestrial systems are rare despite the occurrence of many contaminated terrestrial sites that are subject to risk assessment. To advance the science and regulations of bioaccumulative substances, we develop, evaluate, and apply a contaminant bioaccumulation model for terrestrial organisms that relates the concentration of chemicals in soil to the concentrations in soil-dwelling invertebrates and organisms that occupy higher trophic positions in terrestrial systems. The main focus of this study is to assess whether or not current bioaccumulation criteria for describing the bioaccumulative potential of organic substances are appropriate for terrestrial organisms. The soil−earthworm−shrew system was selected because of the availability of good quality concentration data for soil, shrews, and earthworms (*10*) that could be used for model performance analysis and the fact that earthworms often make up more than 80% of invertebrate biomass in floodplain soils and provide an important link of contaminant transfer in terrestrial food-webs (*10*, *11*).

Theory

General Approach. The model consists of a series of mechanistic equations that represent the dominant pathways for uptake and elimination of chemicals in the organisms of interest. Contaminant uptake from air, pore water, soil, and ingested food items are included. Elimination pathways include respiratory exchange (organism to environment), fecal elimination, urinary elimination, reproduction (transfer of chemical to offspring), and metabolic transformation. Growth, which results in the dilution of chemical concentrations, is also included as a pseudo-elimination pathway for both organisms. Biliary excretion and lactation are also considered as potential elimination pathways in shrews. Uptake of chemicals from air, water, and ingested material is represented by clearance rate constants (m^3 m^{-3} d^{-1}) multiplied by the concentration in each exposure media (ug m^{-3}) while elimination pathways are represented by the sum of first-order elimination rate constants and the concentration in the organism (C_B, ug m^{-3}). The change in

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chemical concentration in a soil invertebrate over time is represented as follows:

$$\frac{dC_B}{dt} = k_{UA}C_A + k_{UW}C_W + k_{UD}C_D - (k_{EA} + k_{EW} + k_{EF} + k_{EU} + k_{GD} + k_{MT} + k_{RD})C_B \quad (1)$$

where C_A, C_W, and C_D are the concentrations (ug m^{-3}) of chemical in air, soil pore water, and ingested matter, respectively, k_{UA} is the clearance rate constant describing uptake from air (d^{-1}), k_{UW} is the clearance rate constant describing uptake from soil pore-water (d^{-1}), k_{UD} is the clearance rate constant describing uptake from ingested items (d^{-1}) and k_{EA}, k_{EW}, k_{EF}, k_{EU}, k_{GD}, k_{MT}, and k_{RD} are the rate constants (d^{-1}) characterizing elimination to air, soil pore-water, fecal elimination, urinary elimination, growth dilution, metabolic transformation, and reproduction respectively. Earthworms are assumed to feed exclusively on soil, meaning C_D is equivalent to measured concentrations in the soil. The corresponding expression for shrews is as follows:

$$\frac{dC_B}{dt} = k_{UA}C_A + k_{UD}C_D + k_{US}C_S - (k_{EA} + k_{EU} + k_{EF} + k_{EB} + k_{LA} + k_{MT} + k_{GD} + k_{RD})C_B \quad (2)$$

where k_{EB} and k_{LA} are the additional elimination rate constants for biliary excretion and lactation respectively. Dietary uptake from prey items (i.e., earthworms) and incidental consumption of soil were considered separately and are represented by C_D and C_S respectively, multiplied by the respective clearance rate constants k_{UD} and k_{US}. Methods for calculating all uptake clearance and elimination rate constants are reported in the Supporting Information. Concentrations in soil, air, and pore water are required as inputs to both bioaccumulation models. At the site considered for the model evaluation, only measured soil concentrations were available. Observed soil concentrations (C_S) were used to estimate air (C_A) as $C_A = K_{AS}C_S$ assuming equilibrium partitioning where K_{AS} is the unitless air−soil partition coefficient, which is estimated as

$$K_{AS} = \frac{C_A}{C_S} = \frac{1}{\rho_S f_{OC} \chi_{OC} K_{OA}} \quad (3)$$

where ρ_S is the density of the soil (kg soil·L^{-1}), f_{OC} is the fraction of organic carbon in the soil (kg OC kg^{-1} soil), and χ_{OC} is the proportionality constant (L kg^{-1} OC) relating the sorptive capacity of organic carbon to that of octanol. Concentrations in soil pore water (C_W) were calculated from observed concentrations in soil (C_S) as $C_W = C_S/K_{SW}$ where K_{SW} is the unitless soil−water partition coefficient, which is estimated as

$$K_{SW} = \frac{C_S}{C_W} = \rho_S f_{OC} \chi_{OC} K_{OW} \quad (4)$$

Biota-soil accumulation factors (BSAFs) were calculated as C_B/C_S.

Model Parametrization and Application

Physicochemical Properties. Values for K_{OW} and K_{OA} were taken from refs *12*−*15* and were adjusted to the relevant environmental temperatures following (*15*). The bioaccumulation model for shrews used values of K_{OA} and K_{OW} adjusted to 37 °C while the soil−invertebrate model used values of K_{OA} and K_{OW} at 10 °C (see Table S1 in the Supporting Information). The dimensionless air−water coefficient (K_{AW}) was then calculated from the ratio of K_{OW} and K_{OA} (i.e. $K_{AW} = K_{OW}/K_{OA}$).

Soil Properties. The model was parametrized to match the average organic matter (%) and moisture content (%) of the soils sampled by Hendriks et al. (*10*) at two sites in the Rhine-Meuse Delta (Ochten and Gelderse Poort). The bulk density of the soil was assumed to be 1500 kg m^{-3} while the density of OM was assumed to be 1000 kg m^{-3}. Laboratory experiments with spiked sediments indicate that χ_{OC} typically ranges between 0.14 and 0.89 L kg^{-1} OC with a mean value of approximately 0.35 L kg^{-1} OC (*16*, *17*), but much larger values up to 8.2 L kg^{-1} OC (*18*) have also been observed. Field studies involving native contaminants indicate that the apparent χ_{OC} can be greater than that reported in spiked sediments with reported values as high as 60 L kg^{-1} OC (*18*) and even higher values for some contaminants in particulate matter containing significant amounts of carbonaceous geosorbents such as black carbon (*19*). Differences in organic carbon composition, aging, organic carbon degradation, contaminant entrapment, and high black carbon sorption are among the processes causing the high variability in apparent χ_{OC} among soil and sediment types (*18*−*24*). These processes remain difficult to model in the absence of site-specific data. To investigate the possible influence of sorption to carbonaceous geosorbents, we compared the observed BSAFs in earthworms at both study sites for more strongly sorbing coplanar PCBs (PCB22, 28, 111, 118, 123/147) and less strongly sorbing noncoplanar PCBs and found no significant difference ($p > 0.1$). In absence of evidence of extensive sorption to carbonaceous geosorbents, we selected a value for χ_{OC} of 2 L kg^{-1} OC for all substances at both sites, representing OC in the field collected soils with an apparent sorptive capacity twice that of octanol. Parameter values for soil properties are summarized in Table S2 and S3 in the Supporting Information.

Soil-Invertebrate Bioaccumulation Model. As earthworm populations are often dominated by juveniles and subadults (*25*), model simulations were conducted for three age classes (i.e., hatchling, subadult, adult). The model was applied assuming steady-state (i.e., $dC_B/dt = 0$) based on the fact that the exposure period in the field far exceeds the expected time period required for the chemical to reach 95% of steady-state, calculated as $3/\Sigma k_{ELIM}$, which corresponds to approximately 2, 3, and 7 days for hatchling, subadult, and adults, respectively. Details on the parametrization are provided in the Supporting Information along with a table summarizing key parameter values (see Table S4).

Terrestrial Vertebrate Bioaccumulation Model. Simulations using the terrestrial vertebrate bioaccumulation model were also conducted assuming steady-state conditions because the expected time required to achieve ~95% of steady-state for the test chemicals was, at the most, 2 months and less than the animal's actual exposure period. The fast response time of the shrew make it a good organism for both modeling and biomonitoring in comparison to larger organisms in which steady-state may not be achieved. Details on the parametrization of the model for this organism are provided in the Supporting Information along with tables summarizing key parameter values and data used to derive these values (see Tables S5−8).

Model Performance. The performance of the bioaccumulation models was evaluated by comparing the geometric mean observed and model predicted concentrations. For earthworms, wet-weight-based concentrations (ug kg^{-1} ww) were used, hence converting volumetric based concentration (ug m^{-3} ww) to weight-based concentrations using an earth worm density of 1000 kg.m^{-3}. For shrews, lipid equivalent concentrations (ug kg^{-1} lipid EQ) were used, which were calculated as follows:

$$C_B(\text{lipidEQ}) = \frac{C_B(\text{ww})}{(f_L + f_{NLOM}\chi_{NLOM})} \quad (5)$$

where f_L is the lipid fraction of the organism, f_{NLOM} is the nonlipid organic matter (NLOM) fraction of the organism, and χ_{NLOM} is the proportionality constant relating the sorptive capacity of NLOM to that of octanol. To quantitatively express model performance, the model bias (MB) and its 95% confidence intervals (CI) were calculated for each model outcome:

$$\text{MB} = 10^{\frac{\sum_i^n \log \frac{\text{Predicted}}{\text{Observed}}}{n}} \quad (6)$$

where n is the number of PCB congeners included in the calculation.

For the purpose of comparison, BSAFs in soil-invertebrates were also calculated using the more commonly applied equilibrium partitioning theory (EPT) model (*26*, *27*). According to EPT, BSAF (kg dry kg^{-1} wet weight) can be calculated as follows:

$$\text{BSAF} = \frac{C_{SI}}{C_S} \quad (7)$$

$$\text{BSAF} = \frac{\text{BCF}}{K_{SW}} \quad (8)$$

where C_{SI} (g kg^{-1} wet weight) is the concentration of contaminant in the soil-invertebrate, C_S is the concentration of contaminant in the soil (g kg^{-1} dry), BCF is the bioconcentration factor relating concentrations in the organism to that in the pore water, and K_{SW} is the soil−pore-water partition coefficient, in this case having units of L kg^{-1}. Substituting for BCF and K_{SW}, the calculation simplifies to the following expression:

$$\text{BSAF} = \frac{(f_L + f_{NLOM}\chi_{NLOM})}{f_{OC}\chi_{OC}} \quad (9)$$

This expression indicates that BSAF is a function of the relative sorptive capacities of the organism versus the surrounding soil.

Model Uncertainty. Multivariate Monte Carlo simulations of model outputs were conducted using Crystal Ball (Decisioneering) to identify which parameters have the greatest influence on model output as well as to generate a range of model outcomes reflective of the uncertainty associated with the input parameters. Details of the parameters included in the analysis and the distributions selected to describe the variability are given in the Supporting Information section (see Table S9).

Model Application. The relationship between bioaccumulative potential and physicochemical properties was investigated by estimating the BMF (kg lipid EQ. kg^{-1} lipid EQ), and BSAF (kg OC·kg^{-1} lipid EQ) for adult male shrews as a function of K_{OW} and K_{OA}, both ranging from 10^1 to 10^{15}. The original invertebrate model for the Ochten site was used. The chemical concentration in soil particles, soil pore-water (C_W, ug m^{-3}), and air (C_A, ug m^{-3}) were estimated according to eqs 3 and 4 for an ambient temperature of 10 °C. The output of this model was then used as the concentration in the diet of the shrew (C_D). Since the terrestrial vertebrate model requires values for K_{OW} and K_{OA} adjusted to a temperature of 37 °C, it was necessary to assume a uniform temperature-dependence of these partition coefficients since this relationship varies by compound and cannot be generalized in this broad application. To link the values of K_{OA} at 10 °C and 37 °C in the generic model, K_{OA} was assumed to decrease with temperature in all cases and was estimated as

$$K_{OA}{}^{10°C} = \phi\, K_{OA}{}^{37°C} \quad (10)$$

where ϕ represents the ratio of K_{OA} at 10 °C to K_{OA} at 37 °C. ϕ was initially set to 20 for the base scenario based on data for PCBs and then varied from 2 to 50 to investigate the sensitivity of the model outcome to ϕ. The predicted BMFs were then generated across the range of values for ϕ. K_{OW} was assumed to be independent of temperature for this model application due to the low sensitivity to temperature of K_{OW} in comparison to K_{OA}. The effect of metabolism on the BMF was also explored by incrementally increasing the rate constant for metabolic transformation (k_{MT}) until the lipid EQ-normalized BMF fell below 1 across the range of K_{OW} and K_{OA}.

Results and Discussion

Soil-Invertebrate Bioaccumulation Model. Figure 2 shows the comparison of the geometric means of observed and model predicted chemical concentrations in earthworm. The MB and its 95% CI for the predicted concentrations for adults using default parameter values was 1.0 (0.31−3.3) and 2.1 (0.63−6.7) for the Ochten and Gelderse sites, respectively, suggesting good agreement overall at the Ochten site and a 2-fold over-estimation at the Gelderse site. It is important to stress that the MB for the invertebrates is sensitive to the value of χ_{OC}, which is poorly known.

The mechanistic model produces BSAFs for PCBs in worms that are comparable to BSAFs calculated using equilibrium partitioning theory (i.e., MB of 0.92 and 1.9 for the Ochten and Gelderse Poort sites, respectively; Table S10 in the Supporting Information). This is due to the poor digestibility of the soil substrate, which causes an insignificant degree of chemical biomagnification and, hence, an insignificant elevation of the chemical concentration in the worm over that expected from equilibrium partitioning. Although the added complexity of the mechanistic model described in this paper does not result in an improvement of the estimation of the BSAF in worms over the simpler chemical equilibrium model, the current model is expected to be applicable to a much wider array of soil-dwelling invertebrates with different feeding strategies (e.g., insects, slugs, snails) and also provides mechanistic insight into the relative rates of uptake and elimination pathways.

Terrestrial Vertebrate Bioaccumulation Model. Figure 3 shows a comparison of the geometric mean of the observed shrew concentrations against the model predictions (based on default parameter values) for recalcitrant PCB congeners using observed earthworm concentrations as input to the model. Observed and predicted concentrations are presented in the Supporting Information (Table S11). The MB and its 95% CI for the predicted concentrations using default parameter values was 1.1 (0.28−3.9) and 1.0 (0.12−9.1) for the Ochten and Gelderse sites respectively. Model sensitivity to χ_{OC} is substantially smaller than that for the invertebrate model as soil is only a minor part of the shrew's ingesta. Assimilation efficiencies for lipids (α_L) and nonlipid organic matter (α_{NLOM}) are also sensitive model parameters in the shrew model but uncertainty in these parameters is relatively small, resulting in a reasonable range of model calculated concentrations (e.g., 95% of the MBs generated by the Monte Carlo simulations using the range of input values were between 0.52−2.4 and 0.53−2.9 for the Ochten and Gelderse sites, respectively).

Model Application. Figure 4, which shows model calculated BMFs and BSAFs in shrews for chemicals as a function

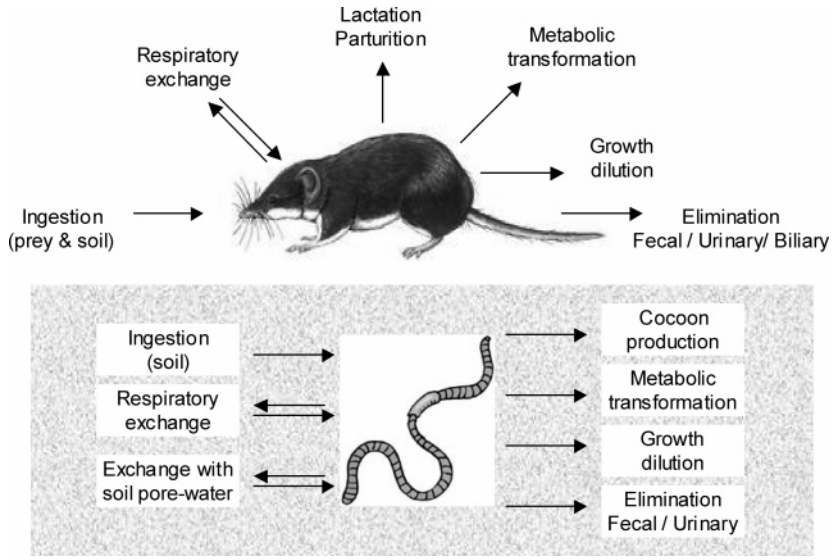

FIGURE 1. Conceptual diagram of routes of uptake and elimination of organic chemicals for earthworms and shrews.

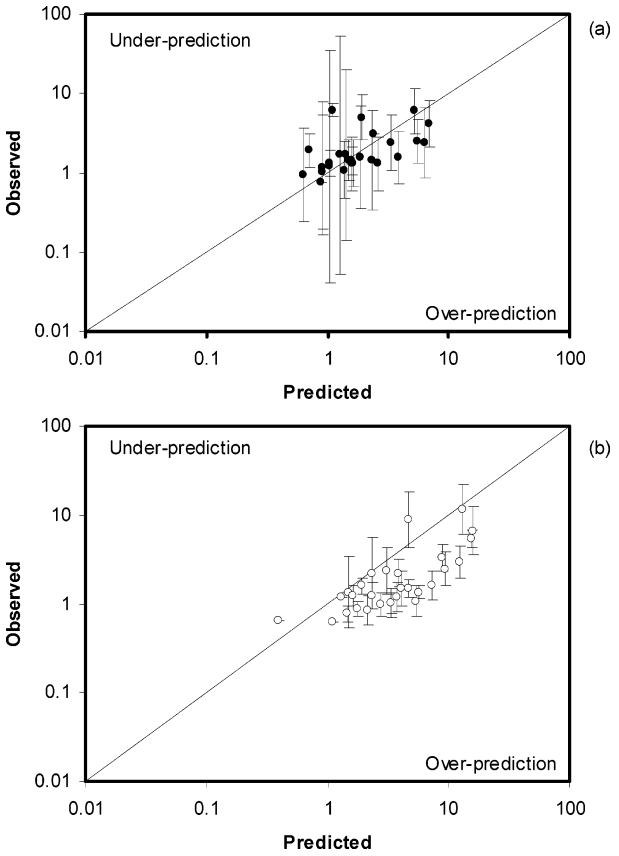

FIGURE 2. Model calculated concentrations of the test chemicals in adult earthworm (μg kg^{-1} ww) versus observed geometric mean concentrations for the (a) Ochten site and (b) Gelderse Poort sites, respectively. Vertical error bars represent the reported 95% CI of the observations (*10*) and the solid diagonal line represents equality of calculated and observed concentrations. See Table S10 for substances included.

of K_{OW} and K_{OA}, illustrates that chemicals with a $K_{OA} < 10^{5.25}$ do not biomagnify in the shrews irrespective of the chemical's K_{OW} and even if the K_{OW} is high and optimal for biomagnification in fish. These chemicals can also be expected to exhibit a BSAF less than 1. The lack of biomagnification is due to the relatively high rate of respiratory elimination that counteracts any magnification due to dietary uptake. Metabolic transformation, which was not included in the model calculations depicted in Figure 4, can be expected to further lower the BMF and BSAF of the parent substance, hence indicating no bioaccumulative potential of low K_{OA} chemicals in this terrestrial food-chain.

Substances with $K_{OW} < 10^{1.75}$ also appear to have no biomagnification potential. This is due to efficient elimination via urine excretion (for high K_{OA} chemicals) and respiratory elimination (for low K_{OA} chemicals). The calculated BMFs range between 1 and a maximum of 7. Substances with a K_{OW} between approximately 10^4 and 10^{10} and a $K_{OA} > 10^7$ exhibit the greatest BMFs, indicating that these chemicals have the highest potential to biomagnify in terrestrial organisms like the shrew. Further magnification may take place when shrews are consumed by predators such as raptors and other mammals.

Figure 4 illustrates that superlipophilic chemicals with K_{OW} between 10^8 and 10^{12}, which are absorbed from the diet less efficiently compared to lower K_{OW} substances and which show a small or no degree of biomagnification in piscivorous food-chains, show a BMF greater than 1 in this system. The BMF declines for substances with $K_{OW} > 10^{10}$ as the rate of uptake from the diet declines significantly relative to respiratory exchange and growth dilution and falls below 1 for substances with a $K_{OW} > 10^{12}$. For chemicals with $K_{OA} > 10^{10}$, this upper threshold is sensitive to the growth dilution rate constant, which exerts an influence even if it is low ($k_{GD} = 5.10^{-5}$ d^{-1}) when mimicking adult animals at their maximum size. For substances with a K_{OA} between 10^5 and 10^{10} and a K_{OW} between 10^8 and 10^{12}, model calculations show that unmetabolizable substances can be expected to biomagnify as long as K_{OA} is less than 3 orders of magnitude lower than K_{OW} (e.g., if $K_{OW} = 10^8$, BMF > 1 if $K_{OA} > 10^5$).

The results of this analysis are in agreement with the results reported by Czub and McLachlan (*9*) using a bioaccumulation model describing chemical transfer through aquatic and agricultural food chains to humans (ACC-HUMAN). They concluded that substances with K_{OW} less than 10^{11} and K_{OA} greater than 10^6 have an inherent potential to biomagnify in the human food web. The highest bioaccumulative potential was found for non-metabolized substances with K_{OW} values from 10^2 to 10^{11} and K_{OA} values from 10^6 to 10^{12}.

The predicted lipid equivalent BMFs were insensitive to the value of ϕ used to account for the temperature dependence of K_{OA} and K_{AW}. The most significant effect of the assumption regarding the temperature dependence of K_{OA} and K_{AW} concerned the K_{OA}-threshold above which the BMF exceeds 1. The baseline scenario ($\phi = 20$) predicts that

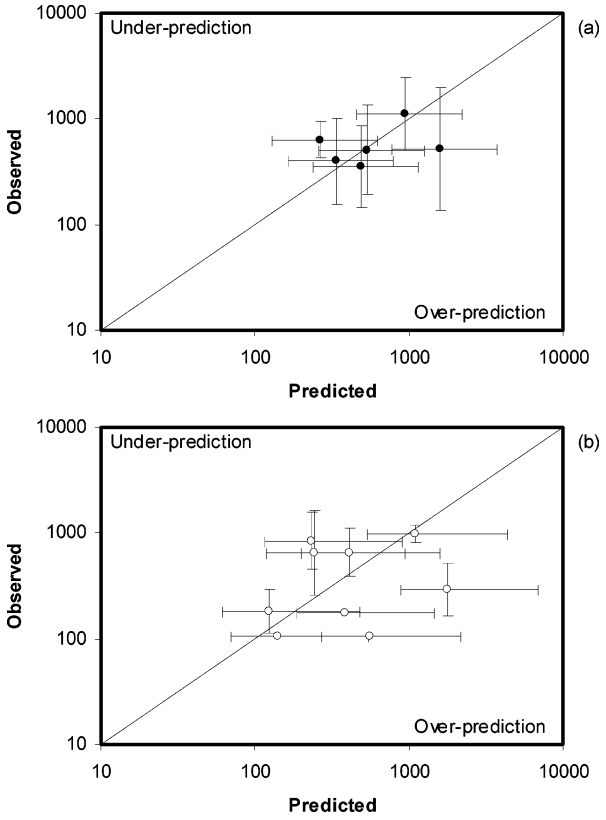

FIGURE 3. Model calculated concentrations of the test chemicals in adult male shrew (μg kg^{-1} lipid EQ ww) versus observed geometric mean concentrations for the (a) Ochten site and (b) Gelderse Poort sites, respectively. Vertical error bars represent the reported 95% CI of the observations (*10*), horizontal error bars represent the 95% CI of model predictions, and the solid diagonal line represents unity between predicted and observed values. See Table S11 for substances included.

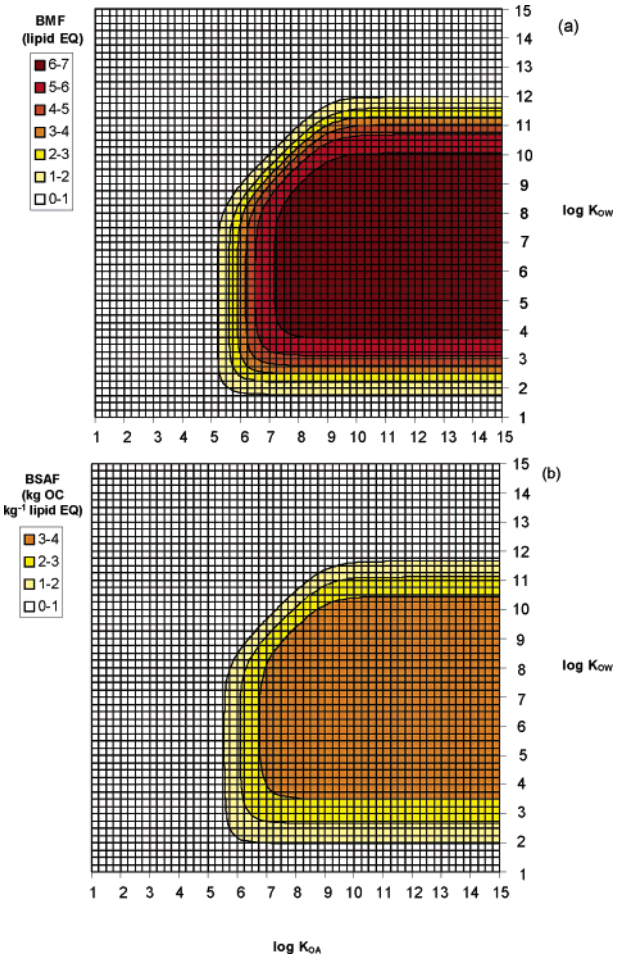

FIGURE 4. Predicted shrew (a) BMFs (lipid EQ) and (b) BSAFs (kg OC kg^{-1} lipid EQ) as a function of K_{OW} and K_{OA} using the generic model.

substances with K_{OA} values less than approximately $10^{5.25}$ will not biomagnify. This threshold value is not affected by changes in ϕ values between 20 and 50. However, as ϕ declines below 20, the K_{OA} threshold value at which the BMF exceeds 1 drops due to a lower rate of respiratory elimination in the shrew. For example, if $\phi = 2$, substances with K_{OA} values less than approximately 10^5 (rather than $10^{5.25}$) do not biomagnify.

It is also interesting to note that uncertainty in the value of K_{OA} in the extreme ranges (e.g., $K_{OA} > 10^{12}$) has little or no influence on the model outcome. As Figure 4 illustrates, the exact value of K_{OA} is irrelevant above a K_{OA} of approximately 10^9 to 10^{10}, i.e., well below the range where empirical measurement of K_{OA} becomes suspect. Uncertainty in K_{OW} for high K_{OW} chemicals (e.g., $K_{OW} > 10^8$) is also of little consequence as long as $K_{OA} < 10^5$ because biomagnification is absent for substances with a high rate of respiratory elimination. Uncertainty in K_{OW} at high K_{OW} chemicals (e.g., $K_{OW} > 10^8$) can be expected to have a significant effect on the model outcome for chemicals with a $K_{OA} \geq 10^5$ because of the decline in dietary absorption efficiency with increasing K_{OW} that takes place for high K_{OW} substances (*28*).

Currently, regulatory initiatives only recognize substances with a K_{OW} larger than 10^5 to have the potential to biomagnify in absence of a significant rate of metabolic transformation. This threshold value for K_{OW} is a reasonable "rule of thumb" for substances in food-webs containing water-respiring organisms. However, the model calculations and empirical observations (*6*−*8*) demonstrate that this rule cannot be extended to simple terrestrial food-webs containing organisms that respire air. In terrestrial food-webs, organic chemicals have a biomagnification potential (i.e., BMF > 1) if they possess a K_{OW} larger than approximately 10^2 and a K_{OA} greater than approximately 10^5. The significance of the findings is that there are currently many commercial chemicals, which lack the capacity to biomagnify and bioconcentrate highly (i.e., BCF > 5000) in fish, but can biomagnify in terrestrial food-chains as long as they are not quickly metabolized. Approximately 36% of the approximately 12 000 commercial organic chemicals on the 1986 Canadian Domestic Substances List have a $K_{OA} > 10^5$ and a K_{OW} between 10^2 and 10^5 (*8*). The inherent biomagnification potential of these substances in terrestrial food-chains and air-breathing organisms is currently unrecognized in environmental regulations around the world. This is a major gap in the environmental safety net for commercial chemicals, which particularly affects air-breathing organisms including human beings. A revised "rule of thumb" for bioaccumulative potential in terrestrial organisms must, therefore, recognize the general principle that substances that are relatively involatile and possess a high affinity for biotic macromolecules (e.g., lipids, proteins) in comparison to water have the potential to biomagnify in terrestrial food-webs that contain air-breathing organisms. Such substances not only include highly lipid soluble substances but also contaminants (e.g., PFOS, PFCAs) that bind strongly to proteins and which indeed have been found to biomagnify in air-breathing organisms (*29*). Further testing and development of the model for such substances is important for correctly identifying bioaccumulative substances among the tens of thousands of commercial substances in use. For the correct assessment of the environmental behavior of new and existing chemicals

other than simple hydrophobic organic chemicals it will be particularly important to further test and calibrate the model.

It is important to stress that many of the commercial chemicals in the low-K_{OW}–high-K_{OA} class may never exert their maximum biomagnification potential if they are susceptible to biodegradation and the effect of metabolic transformation. As illustrated in Figure S1 in the Supporting Information, the model illustrates that a metabolic rate constant (k_{MT}) of 0.3 d^{-1} or greater effectively negates the bioaccumulative potential of contaminants regardless of their physicochemical properties. This metabolic rate constant translates into a half-life ($t_{1/2}$) of approximately 2.5 days but is sensitive to digestion parameters (i.e., α_L, α_{NLOM}) and is also related to the size of the organism and the corresponding magnitude of the uptake and elimination rate constants for other processes. Therefore, as the size of the organism increases, the metabolic rate constant required to negate the bioaccumulative potential of contaminants drops in accordance with the decline in the overall elimination rate constant (*30*). In this context, shrews, and other small mammals, may represent conservative indicators of the degree to which contaminants must be susceptible to metabolic transformation to void their inherent bioaccumulative potential. Empirical studies and the development and evaluation of bioaccumulation models for other species are recommended to further investigate the influence of metabolic transformation on bioaccumulative potential of organic chemicals. However, in those studies it is important to consider both water-breathing organisms like fish and air-breathing organisms such as the shrew.

Acknowledgments

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Supporting Information Available

Description of the equations used to calculate uptake and elimination rate constants, physical-chemical property values for the test chemicals, details on the parameter values for both bioaccumulation models, details on the parameters included in the Monte Carlo analysis, tables showing the predicted and observed BSAFs in earthworms and predicted and observed concentrations in shrews, a figure showing the influence of metabolic transformation on predicted BMF, and a listing of additional references used to develop and parametrize the models. This material is available free of charge via the Internet at http://pubs.acs.org.

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