

Illustrating Sensitivity in Environmental Fate Models Using Partitioning Maps - Application to Selected Contaminants.

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Introduction

Generic environmental multimedia fate models are important tools in the assessment of the impact of organic pollutants. Because of limited possibilities to evaluate generic models by comparison with measured data and the increasing regulatory use of such models, uncertainties of model input and output are of considerable concern. This led to a demand for sensitivity and uncertainty analyses for the outputs of environmental fate models. Usually, variations of model predictions of the environmental fate of organic contaminants are analyzed for only one or at most a few selected chemicals, even though parameter sensitivity and contribution to uncertainty are widely different for different chemicals. We recently presented a graphical method that allows for the comprehensive investigation of model sensitivity and uncertainty for all neutral organic chemicals simultaneously¹. This is achieved by defining a two-dimensional hypothetical "chemical space" as a function of the equilibrium partition coefficients between air, water, and octanol (K_{OW} , K_{AW} , K_{OA}), and plotting sensitivity and/or uncertainty of a specific model result to each input parameter as function of this chemical space¹. Here we show how such sensitivity maps can be used to quickly identify the variables with the highest influence on the environmental fate of selected, chlorobenzenes, polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), hexachlorocyclohexanes (HCHs) and brominated flame retardants (BFRs).

Method

Sensitivity S is defined as the relative deviation of the output value Y deriving from variation in an input value X_i :

$$S(x_i) = \partial Y / Y \cdot X_i / \partial X_i, \quad (1)$$

where ∂Y and ∂X_i are the absolute change of output value and input parameter, respectively². The concentrations in the four bulk compartments air, water, soil and sediment calculated with a generic level III fugacity model³ was chosen as output values. Every environmental input parameter was increased individually by 10 % and the sensitivity of the four concentrations to these changes was plotted as a function of $\log K_{OA}$ and $\log K_{AW}$ ¹. This results in numerous maps delineating partitioning regions of similar sensitivity to an input parameter¹. Based on these maps, the chemical partitioning space was divided into segments of common parameter sensitivities¹. Thereby, only sensitivities above 0.5, occurring for the concentration in water, soil, and sediment, and sensitivities above 0.1, occurring in the air compartment were included. Figure 1 shows the location of the

segments in the chemical space, while Table 1 lists the input parameters with high sensitivities associated with each segment. The acronyms for the input parameters are explained in Table 2. The partitioning properties of the polybrominated diphenyl ethers (PBDEs)⁴, hexabromocyclododecane (HBCD)⁴, tetrabromobisphenol A (TBBP A)⁴, chlorobenzenes⁵, PAHs⁶, PCBs⁷, and HCHs⁸ were placed on the maps (Fig. 1) and assigned to the various segments (Table 1).

In the calculations underlying the sensitivity maps, the degradation half-lives were set to a very high value implying perfect persistence of the hypothetical chemicals. Additional calculations with different combinations of degradation properties, presented in more detail in the associated paper¹, show however, that the influence of degradability on the sensitivity of the model results to most of the investigated environmental model input parameters is very small, and in particular does not change the segmentation of the partitioning space according to common parameter sensitivities (Fig. 1).

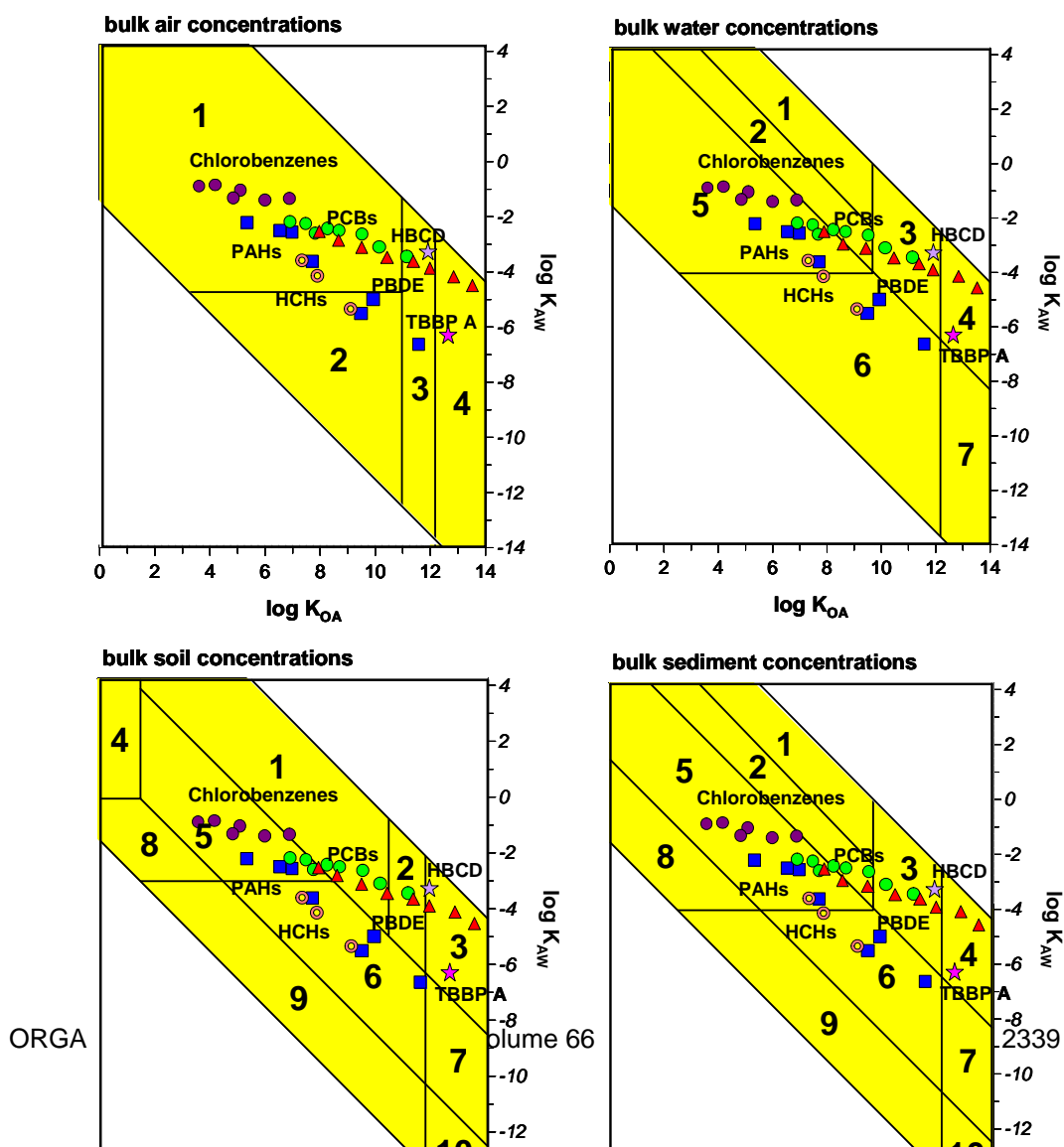


Fig. 1 Chemical space segments of identical input parameter sensitivities for the bulk phase concentrations in air, water, soil and sediment in a level III model calculation with emissions to air. Input parameters influential in the segments in which BFR, chlorobenzenes, PAHs, PCBs, and HCHs fall are listed in Table 1.

Tab. 1 Chemical space segments of identical input parameter sensitivities for the bulk phase concentrations in air, water, soil and sediment in a level III model calculation with emissions to air. Listed are all input parameter with sensitivities $S > 0.5$, except for the concentration in air, when $S > 0.1$. The segment numbers refer to the plots in Fig. 1. Segments are only listed if there are BFRs, chlorobenzenes, PAHs, PCBs, or HCHs with such partitioning properties.

Medium	Segment	Chemicals	Influential Input Parameter
Air	1	- chlorobenzenes, - all PCBs except PCB-194, - naphthalene, acenaphthene, fluorene, phenanthrene - α -HCH, γ -HCH - PBDEs with $n_{Br} < 5$	G_{air}
	2	- pyrene, chrysene - β -HCH	G_{air} , U_{rain}
	3	- PCB-194 - benzo(a)pyrene - Br ₅ DE, Br ₆ DE, HBCD	G_{air} , U_{rain} , v_Q , v_{OrgQ} , ρ_{OM} , Q , U_P
	4	- PBDEs with $n_{Br} > 6$, TBBP A	G_{air} , U_{rain} , Q , U_P
Water	2	- PCB-52, PCB-101, PCB-153 - Br ₃ DE	v_P , f_{OrgWat} , G_{air}
	3	- PCB-180, PCB-194 - Br ₄ DE, Br ₅ DE, Br ₆ DE, HBCD	A_{Wat} , v_P , U_{DX} , U_{RX} , U_{BX} , f_{OrgWat} , f_{OrgSed} , ρ_{OM} , G_{air}
	4	- PBDEs with $n_{Br} > 6$, TBBP A	A_{Wat} , v_P , U_{DX} , U_{RX} , U_{BX} , f_{OrgWat} , f_{OrgSed}
	5	- chlorobenzenes - PCB-3, PCB-8, PCB-15 - naphthalene, acenaphthene, fluorene, phenanthrene - α -HCH - Br ₁ DE, Br ₂ DE	G_{air}
	6	- pyrene, chrysene, benzo(a)pyrene - β -HCH, γ -HCH	G_{air} , G_{water}
Soil	1	- pentachlorobenzene - PCB-52, PCB-101, PCB-153, PCB-180 - Br ₂ DE, Br ₃ DE, Br ₄ DE	$f_{OrgSoil}$, G_{air}
	2	- PCB-194 - Br ₅ DE	U_{SW} , v_{OrgQ} , ρ_{OM} , G_{air}
	3	- PBDEs with $n_{Br} > 5$, TBBP A, HBCD	U_{SW}

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	5	- all chlorobenzenes except pentachlorobenzene - PCB-3, PCB-8, PCB-15 - naphthalene, acenaphthene, fluorene - Br ₁ DE	$f_{\text{OrgSoil}}, G_{\text{air}}$
	6	- phenanthrene, pyrene, chrysene, benzo(a)pyrene - HCHs	$U_{\text{WW}}, U_{\text{rain}}, f_{\text{OrgSoil}}, G_{\text{air}}$
Sediment	2	- PCB-52, PCB-101, PCB-153 - Br ₃ DE	$U_{\text{DX}}, f_{\text{OrgSed}}, G_{\text{air}}$
	3	- PCB-180, PCB-194 - Br ₄ DE, Br ₅ DE, Br ₆ DE, HBCD	$A_{\text{Wat}}, U_{\text{BX}}, G_{\text{air}}$
	4	- PBDEs with $n_{\text{Br}} > 6$, TBBP A	$A_{\text{Wat}}, U_{\text{BX}}$
	5	- chlorobenzenes - PCB-3, PCB-8, PCB-15 - naphthalene, acenaphthene, fluorene, phenanthrene - α -HCH - Br ₁ DE, Br ₂ DE	$f_{\text{OrgSed}}, G_{\text{air}}$
	6	- pyrene, chrysene, benzo(a)pyrene - β -HCH, γ -HCH	$f_{\text{OrgSed}}, G_{\text{air}}, G_{\text{water}}$

Tab. 2 Definition of the influential environmental model input parameters listed in Tab 1.

A_{Wat}	Area of water compartment
v_{Q}	Volume fraction of aerosols in air
v_{p}	Volume fraction of particles in water
U_{DX}	Sediment deposition rate
U_{RX}	Sediment resuspension rate
U_{BX}	Burial rate
U_{WW}	Soil water runoff
U_{SW}	Soil solids runoff
U_{rain}	Rain rate
Q	Scavenging rate
U_{p}	Dry particle deposition
v_{OrgQ}	Volume fraction of organic carbon on aerosols
f_{OrgWat}	Fraction of organic carbon on water particles
f_{OrgSoil}	Fraction of organic carbon on soil particles
f_{OrgSed}	Fraction of organic carbon on sediment particles
ρ_{OM}	Density of organic matter
G_{air}	Advective flow in air
G_{water}	Advective flow in water

Results and Discussion

The maps in Figure 1 have three types of thresholds, depending on the governing partition coefficient. The horizontal thresholds relate to K_{AW} , and indicate when the parameters describing water fluxes (U_{rain} , G_{water} , U_{WW}) become influential. Vertical thresholds relate to K_{OA} , and generally determine when various parameters related to atmospheric particles become influential. Diagonal thresholds show the importance of K_{OW} , and typically indicate when parameters related to particles in the aqueous phase start to exert influence on the calculated concentrations.

The chlorobenzenes have relatively high K_{AW} values and low K_{OA} values reflective of their high volatility. Their concentrations are influenced by very few model input parameters. Concentrations in all 4 bulk compartments are sensitive to the air advection rate G_{air} , whereas their concentrations in soil and sediments are also sensitive to the organic matter content of the phase solids ($f_{OrgSoil}$, f_{OrgSed}). Concentrations of chemicals which are rather insoluble and unlikely to sorb to atmospheric particles, such as the chlorobenzenes, are not influenced by parameters that describe deposition processes. The majority of polychlorinated biphenyl congeners (PCBs) can sorb to particles in air, but also shows volatile behaviour, reflecting their semi-volatility. Concentrations of most PCBs in air are only influenced by the air advection rate G_{air} while the concentration of the least volatile investigated congener (PCB-194) is sensitive to a number of parameters related to particle capacity and deposition (G_{air} , U_{rain} , v_Q , v_{OrgQ} , ρ_{OM} , Q , U_P). Those parameters are significant to concentrations of chemicals with intermediate partitioning properties which allows them to switch between the particulate and the gaseous phase depending on input parameter variations. In water, soil, and sediment, concentrations of more volatile PCBs are sensitive to G_{air} and in the latter two media also to the fraction of organic carbon on particles. With decreasing volatility and increasing hydrophobicity, PCB concentration becomes sensitive to more input parameters. Especially concentrations of chemicals in segment 3 of the air, water, and sediment map and segment 2 of the soil map are sensitive to numerous input parameters (Fig. 1, Tab. 1).

Polycyclic aromatic hydrocarbons (PAHs) comprise chemicals with a large range of partitioning properties. The concentration of volatile compounds in all bulk compartments is mainly sensitive to G_{air} . The number of influential input parameters increases with decreasing volatility. In particular, dynamic parameters (U_{rain} , U_{WW} , G_{water} , Q , U_P) are gaining in importance. HCHs have partitioning properties comparable to those of intermediate sized PAHs, i.e. have lower K_{AW} -values than halogenated aromatic compounds (hexachlorobenzene, small PCBs) of similar volatility. Their concentrations in most media are nevertheless influenced mostly by the same parameters. An exception is β -HCH, which has a K_{AW} approximately one order of magnitude lower than α - and γ -HCH. Its concentrations are additionally influenced by parameters related to the transport of water, such as U_{rain} , G_{water} . The lower K_{AW} of the HCHs also causes their soil concentrations to be sensitive to U_{WW} and U_{rain} , which was not the case for HCB or the light PCBs.

The PBDEs, HBCD and TBBP A fall in the upper right corner of the partitioning space. The air concentrations of these BFRs are influenced by the air advection rate G_{air} and input parameters describing the rate of particle deposition (Q , U_P , U_{rain}). Only for the intermediate PBDEs with 5 to 6 bromine substitutions and HBCD, are the parameters describing the capacity of the atmospheric particle phase (v_Q , v_{OrgQ} , ρ_{OM}) relevant, whereas for the less volatile PBDEs these parameters are no longer influential, because these BFRs can be expected to be associated with particles irrespective of the particle concentration and composition. All the mass transfer coefficients describing gas exchange with the Earth's surface are of no significance for the fate of these BFRs.

The water concentrations of the investigated BFRs are sensitive to the input parameters describing the capacity (v_P , f_{OrgWat} , f_{OrgSed}) and the dynamics (U_{DX} , U_{RX} , U_{BX}) of particles in the water column and the underlying sediments. The sediment concentrations are mainly influenced by the water surface area A_{wat} and the burial rate U_{BX} . The concentrations in soil are mostly controlled by the soil solids run-off rate U_{SW} , and – for the intermediate size PBDEs and HBCD – also by the capacity of atmospheric particles (v_{OrgQ} , ρ_{OM}). The organic matter content of soil $f_{OrgSoil}$ is only relevant for the lighter PBDEs with four and less bromines.

From the list of influential input parameter, a picture of the fate processes of relevance for a particular chemical emerges. In general, volatile chemicals are mostly controlled by the air advection rate. With decreasing volatility and in particular increasing hydrophobicity the chemicals are influenced by additional input parameter describing phase capacities and interphase dynamics. In all four environmental media concentrations of non-volatile, hydrophobic chemicals are controlled by particle-associated processes, i.e. by how quickly particles deposit from the atmosphere, how quickly particles are washed off from soils, and how particles are exchanged between water and sediment. This is a result of their very low volatility (high K_{OA} , location at the right side of the partitioning space) and generally low water solubility (high K_{AW} , location at the top of the space). Many input parameters (not listed in Tab. 2) are of no consequence for the model result, and would not need to be known with high accuracy or precision when making predictions of the fate of these chemicals.

A sensitivity analysis such as presented here can focus attention on those processes that should be studied in more detail when seeking to improve the understanding of the environmental fate of a contaminant. No new model calculations were required for this analysis. It was sufficient to know the major partitioning properties (K_{OA} and K_{AW}) of the contaminants of interest and to simply place them on previously created, segmented partitioning maps¹. The information obtained is however equivalent to what a full sensitivity analysis for each of the chemicals would have provided.

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