Modelling the Environmental Fate of Polybrominated Diphenyl Ethers Using Partitioning Space Maps

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The Chemical Partitioning Space

The environmental fate or organic chemicals is strongly influenced by their distribution between different phases[1]. The three equilibrium partitioning coefficients between the pure phases gas, water and n-octanol (K_{AW}, K_{OA}, K_{OW}) are often used to characterize environmental distribution behaviour[1]. Environmentally relevant partition coefficients, e.g. between water and organic carbon K_{OC}, and between atmospheric particles and the gas phase K_{PA}, are estimated from K_{OW} and K_{OA} using simple linear free energy relationships[1]. A two dimensional "chemical partitioning space" can be defined as a function of log K_{OA} (x-axis) and log K_{AW} (y-axis) (Fig. 1). Each point in this space corresponds to a hypothetical chemical with a specific combination of partitioning properties. If the effect of the mutual solubility of water and octanol on the chemical's

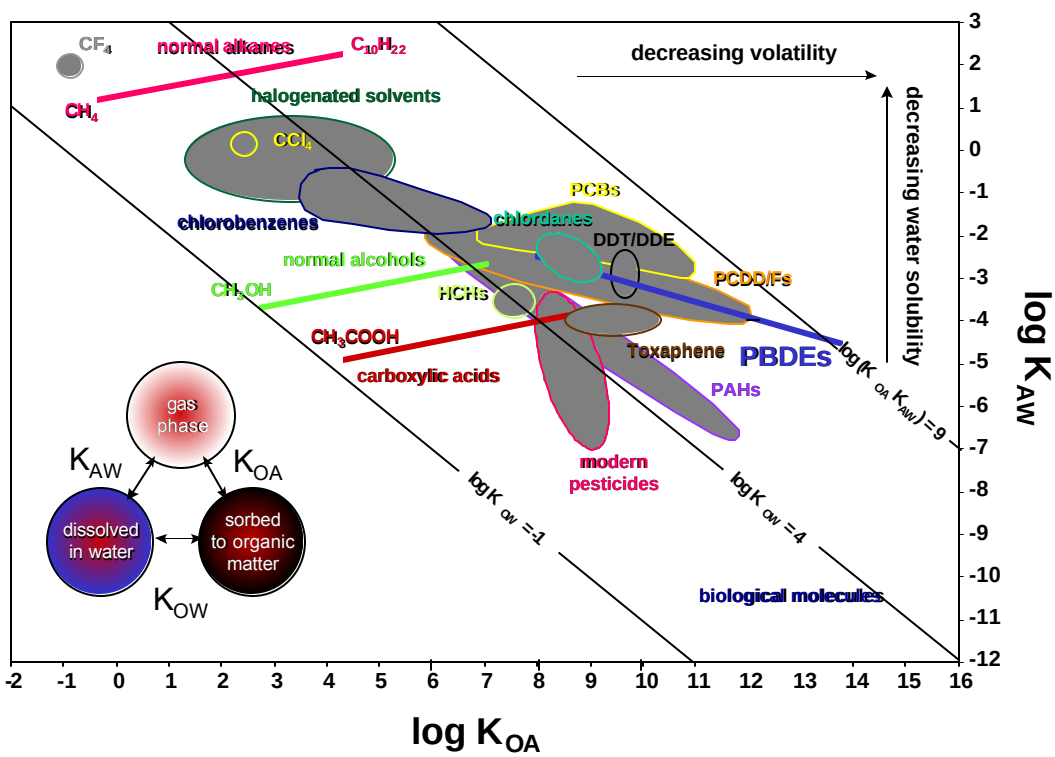

Fig. 1 The chemical partitioning space for organic chemicals as defined by the octanol-air and the water-air partition coefficients K_{OA} and K_{AW}.

solvation in water and octanol is neglected, $\log K_{OW}$ equals $\log K_{OA}+\log K_{AW}$, and diagonal lines from the upper left to the lower right of this space correspond to chemicals of equal $\log K_{OW}$. Real chemicals can also be placed within this space, if their partitioning properties are known. Figure 1 shows the approximate position of some chemical classes within this chemical space. Most known chemicals fall within the space $-2 < \log K_{OA} < 16$, $-12 < \log K_{AW} < 3$, $-1 < \log K_{OW} < 9$. The partition coefficients K_{OA} and K_{AW} are highly dependent on temperature, which implies that a chemical will shift its location on the partitioning space to the lower right in response to decreasing temperatures.

Displaying Model Results in the Chemical Partitioning Space

Many numerical environmental fate models also characterise the distribution properties of organic chemicals with the help of K_{AW}, K_{OA} and K_{OW}. If degradation is of negligible importance, such a model can not only calculate environmental fate for one specific persistent chemical, but for the entire partititioning space. Results of model calculations can then be displayed as maps in the $\log K_{OA}$-$\log K_{AW}$ coordinate system. This allows for easy visualisation of the dependence of the model result on chemical partitioning properties. This approach has for example been used to investigate:

- the importance of forests in reducing the air concentrations of persistent semi-volatile organic chemicals [2,3],
- the importance of solid phase transport in soil on air-soil exchange of persistent organic pollutants[4],
- the potential of persistent organic chemicals to accumulate in arctic ecosystems[5] or in the human food chain[6], and
- the rate of atmospheric deposition[7], and the relative importance of various atmospheric deposition routes[8].

The approach can also be used for comprehensive sensitivity and uncertainty analyses of environmental fate models[9].

One of the advantages of displaying model results in partitioning space maps is that it becomes possible to evaluate the fate of individual, or groups of, persistent organic chemicals quickly without actually performing model calculations. The only required chemical information are the partitioning properties K_{OA} and K_{AW}. The results of even fairly complex model calculations can be obtained by simply locating the chemicals on the partitioning space maps. The polybrominated diphenyl ether are likely quite resistant to environmental degradation processes, and their physical-chemical partititioning properties have been measured and compiled[10]. They can thus serve as an example for this type of simplified chemical fate assessment.

Arctic Contamination and Human Bioaccumulation Potential of PBDEs

The graphical approach is particularly suitable for highly aggregated results of dynamic models, which may be quite complex and time consuming to obtain. Two pertinent examples are the Arctic Contamination Potential ACP calculated with the zonally averaged global transport model Globo-POP[5] and the environmental bioaccumulation potential EBAP calculated with ACC-HUMAN, a model of organic chemical bioaccumulation through the agricultural and aquatic food chains to humans[11].

The ACP is the quotient of the chemical quantity in Arctic surface media divided by the quantity of chemical in the total global environment (calculated after ten years of continuous emissions with the zonal distribution of the human population)[5]. The EBAP is defined as the quotient of the chemical quantity in a human divided by the quantity of

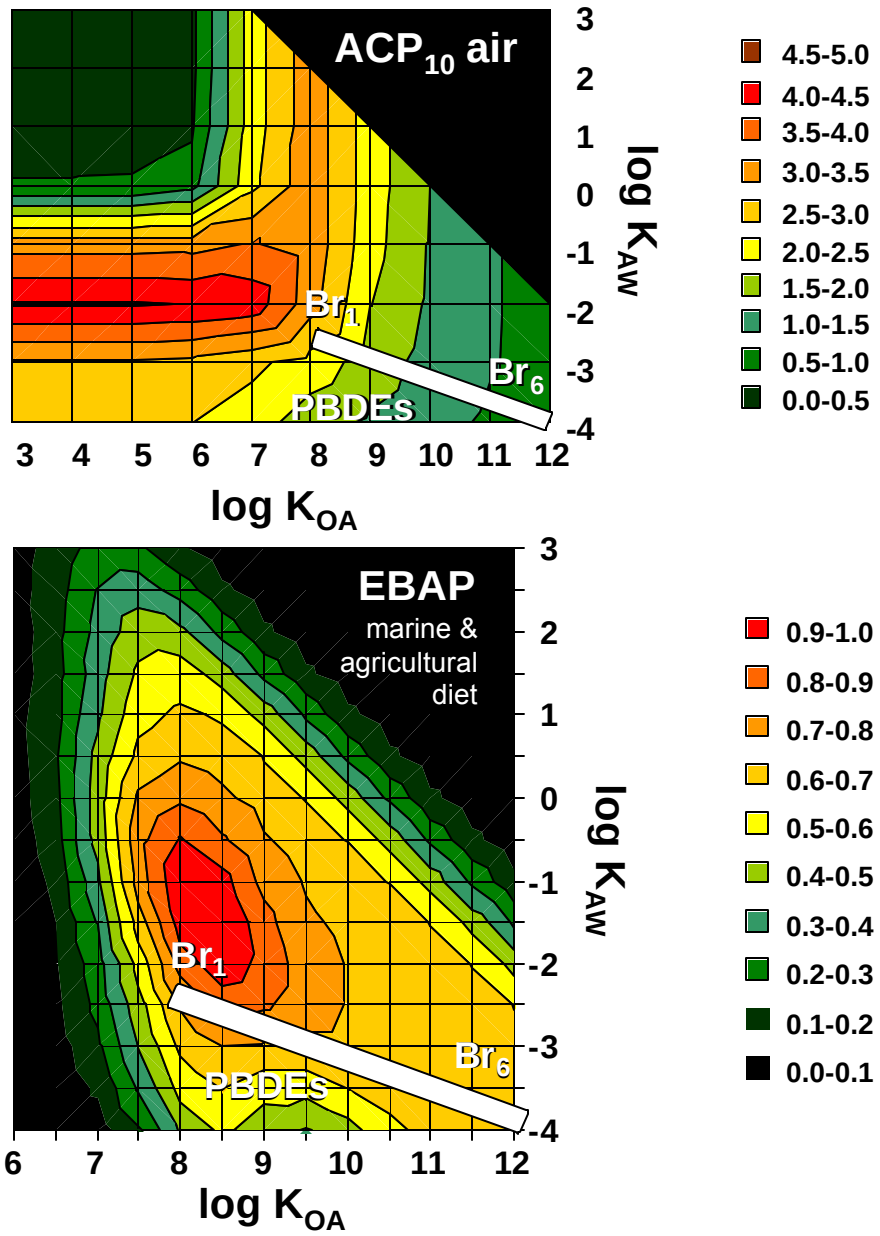

Fig. 2 Location of the mono- to hexabrominated diphenyl ethers on the partitioning space maps displaying the the Arctic Contamination Potential[5] (top) and the Environmental Bioaccumulation Potential[6] (bottom) of persistent organic chemicals.

chemical in the whole environment (calculated using a level I environmental fate model parametrized for conditions in Southern Sweden)[5]. Figure 2 shows the two partitioning space maps for these two model results with the superimposed partitioning properties of the mono- to hexabrominated diphenylethers. The PBDEs with more than six bromine substitutions have log K_{OA} above 12 and thus fall outside of the space defined by the plots. Several conclusions can be drawn from these diagrams.

PBDEs are a group of compounds with a wide range of partitioning properties, which therefore display differences in their environmental fate. For example, the white bar representing the PBDEs in the ACP diagram intersects segments coloured from yellow to green, suggesting that the light PBDEs with very few bromine substitutions have partitioning properties that favour accumulation in the Arctic, whereas the more heavily substituted congeners have a much smaller potential for transport to the Arctic. For the very light BDEs however, the assumption of persistence is least applicable and degradation will likely prevent most of them to undergo efficient long range transport. The calculations underlying the top graph in Fig. 2 assumed that a chemical is emitted into air. When superimposing the properties of the PBDEs on similar plots which are based on different emission assumptions[5], it transpires that their potential for Arctic accumulation will be smaller if emitted into soil and water.

The placement of the PBDEs on the EBAP diagram suggests that the PBDEs have partitioning properties favouring bioaccumulation in humans, with highest potential for diphenylethers with one or more than five bromine substitutions. The mono-brominated diphenyl ether is likely metabolised quite easily, and thus will not be able to bioaccumulate. Comparison with additional diagrams presented by Czub and McLachlan[6] suggest that it is the marine, and not the agricultural branch of the human food chain, that is responsible for the high EBAP of the highly brominated BDEs. Whether they will accumulate in humans or not, will thus depend on the capability of fish and humans to metabolise a particular PBDE congeners.

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