What Environmental Fate Processes Have the Strongest Influence on a Persistent Organic Chemical's Accumulation in the Arctic?

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Introduction

Environmental fate and transport models find increasing use in the assessment of the impact of organic pollutants. Sensitivity analyses of such models allow the identification of those input parameters which are of highest influence on the model result of interest. This makes it possible to decide which input parameters and environmental fate processes need to be known with high accuracy and precision, and for which parameters and processes approximate knowledge can be tolerated. We recently introduced a graphical method that facilitates the comprehensive investigation of model sensitivity for all persistent organic non-electrolytes at the same time[1]. This is achieved by defining a two-dimensional hypothetical "chemical partitioning space" as a function of the equilibrium partition coefficients between air, water, and octanol (K_{OW}, K_{AW}, K_{OA}), and plotting sensitivity of a specific model result to each environmental input parameter as function of this chemical space. Whereas this method can be used for investigating the sensitivity of any prediction obtained with any linear fate model that characterizes the partitioning behavior of organic chemicals with K_{AW}, K_{OW} and K_{OA}, it is most useful when a highly aggregated model result is calculated for a large number of diverse chemicals using a fixed environmental scenario.

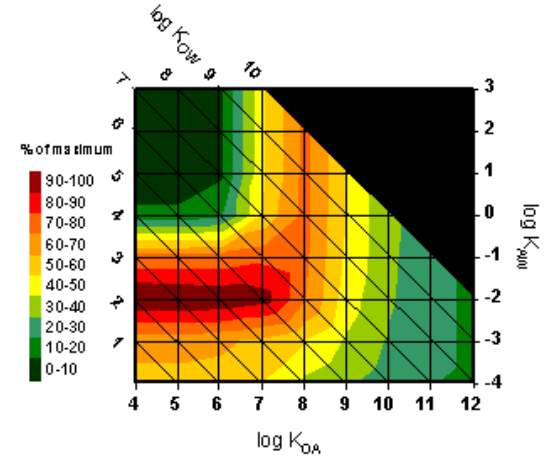

Fig. 1: ACP_{10air} for perfectly persistent organic chemicals as a function of the chemical partitioning space defined by log K_{AW} and log K_{OA}.

One such model result is the Arctic Contamination Potential[2] (ACP) calculated with the zonally averaged global transport model Globo-POP[3].A numerical indicator of a chemical's potential to be transported to polar latitudes and to accumulate in the Arctic ecosystem, the $eACP_{10}^{air}$is defined as the fraction of the globally emitted amount of a substance that is present within Arctic surface media after 10 years of steady emissions to the atmosphere[4]. The emissions are assumed to be spatially distributed according to human population. To identify which partitioning properties favour the accumulation of an organic substance in polar regions, Wania[2] calculated the ACP_{10}^{air} for perfectly persistent hypothetical chemicals of variable K_{OA} and K_{AW} and plotted the results as a function of the chemical partitioning space (Fig. 1). Regions of elevated ACP (red) within the space can be clearly distinguished from regions of low ACP (green). The sensitivity of the ACP_{10} value for five hypothetical chemicals to changes in environmental input parameters was found to be very dependent on their partitioning properties[2]. Here we use the graphical method by Meyer et al.[1] to further explore how the environmental input parameters of the Globo-POP model influence the ACP value calculated for all perfectly persistent chemicals within the relevant range of the partitioning space. In particular, we aim to identify the environmental fate processes of greatest significance for chemicals with a high potential for Arctic accumulation.

Methods

Globo-POP[3] was used to calculate the local sensitivity of ACP_{10}^{air}, defined as the relative change of the output value

ACP_{10}^{air} divided by the relative change of input parameter X[5]:

$S(X) = \partial ACP_{10} / ACP_{10} \cdot X / \partial X$.

Table 1: Model input parameters and acronyms.

Environmental input parameter	*Acronym*
OC fraction in uncultivated soil	$f_{OrgSoil}$
Depth of uncultivated soil	$Ht_{U\text{-}Soil}$
Depth of surface ocean	Ht_{Ocean}
Fraction of water in soil pore space	v_W
Fraction of air in soil pore space	v_A
Rain rate over oceans and continents	U_{Rain}
Particle settling rate	$U_{DepOcean}$
Eddy diffusion in oceans	$D_{EddyOcean}$
Particle scavenging ratio	Q
MTC between air and water (air side)	MTC_{AW}
MTC between soil and air (air side)	MTC_E
Dry deposition velocity over oceans	$U_{P\text{-}Ocean}$
Atmospheric macro-diffusion coefficients	K_Y, K_Z
Atmospheric advection coefficients	v, w
Sea ice cover	SIC
Temperature	T

All environmental input parameters were individually increased by 10% and the responding change in ACP_{10}^{air} for all hypothetical, perfectly persistent chemicals with a log K_{OA} between 3 and 14 and log K_{AW} between -5 and 2 was calculated and plotted as function of the chemical partitioning space. Input parameters that adopt different values in the 10 climate zones of the model were changed simultaneously. The absolute values of temperatures both above and below 0 °C were increased, i.e. the sensitivity to an increase in the annual temperature amplitude was investigated. All input parameters are assumed to be independent and input parameter variation is assumed to be linearly related to output response[1]. Selected input parameters and their acronyms are listed in Table 1. This process yields a sensitivity map for each environmental input parameter, which displays regions of similar sensitivities to that specific parameter (Fig. 2). Only maps for the input parameters with most influence on $eACP_{10}^{air}$ are presented.Furthermore, the chemical space was segmented into areas of similar parameter sensitivities (Fig. 3) with a focus on patterns and not on absolute values of sensitivity. The areas of the chemical space relating to default ACP_{10}^{air} values larger than 1% and 2.5% respectively, were superimposed on the segmented map which enables identification of the sensitivities for hypothetical chemicals with a high default ACP_{10}.

Results and Discussion

The atmosphere and ocean are the main global transport media, and atmosphere, ocean, and uncultivated soil are the major model compartments. Accordingly, the majority of the input parameters with notable sensitivities describes the size and composition of these compartments and the dynamics of chemical transport in ocean and air (Fig. 2, 3). Parameters related to cultivated soil and the freshwater environment have negligible influence on the $eACP_{10}^{air}$ and are not presented here.

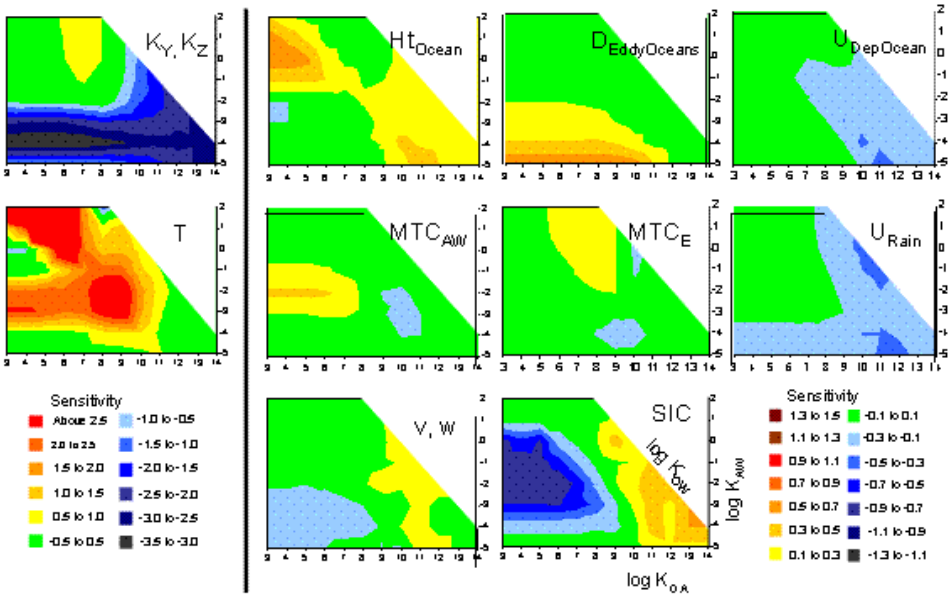

Fig. 2: Sensitivities of ACP_{10}^{air} to changes in selected environmental input parameters as a function of the equilibrium partitioning coefficients K_{OA} and K_{AW}.

The chemical space is characterized by vertical, horizontal and diagonal thresholds that describe transitions related to different parameter dependencies and therefore different environmental behavior (Fig. 2, 3). E.g., the sensitivity map for the parameter $D_{EddyOceans}$ (Fig. 2) clearly identifies the chemicals which are sufficiently water soluble (log K_{AW} < -2, log K_{OW} < 6) for oceanic currents to play a role in transporting chemicals to the Arctic. Similarly, the map for MTC_{AW} highlights the chemicals for which diffusive air/water exchange plays a significant role (log K_{AW} between -1 and -3). The parameters causing the highest sensitivities are the coefficients describing macro-diffusive transport in the atmosphere (K_Y and K_Z), temperature amplitude (T), and the energies of phase transfer (Ent) describing the temperature dependence of the partition coefficients (sensitivity map not shown). In particular, the output of a wide range of "high-ACP_{10}^{air}" chemicals is very sensitive to the increase of the annual temperature amplitude (Fig. 3). Increasing the range of temperature variations presumably leads to reinforcement of temperature-driven air/surface exchange processes of those chemicals and thus an intensification of the "grass-hopper effect" and ultimately a higher ACP_{10}^{air}. It is noteworthy that many persistent organic contaminants known to accumulate in the Arctic marine food chain, such as the PCBs, have partitioning properties corresponding to segment 5 in Fig. 3. The temperature amplitude is one of the few highly influential input parameters for these substances, and hints at the importance of temperature-driven grass-hopping for their transport into the Arctic.

Maybe one of the most interesting findings of this study is that sea ice cover, temperature, and macro-diffusive atmospheric transport coefficients (and to a lesser extent precipitation rate) have the largest impact on an organic chemical's calculated potential for Arctic accumulation.

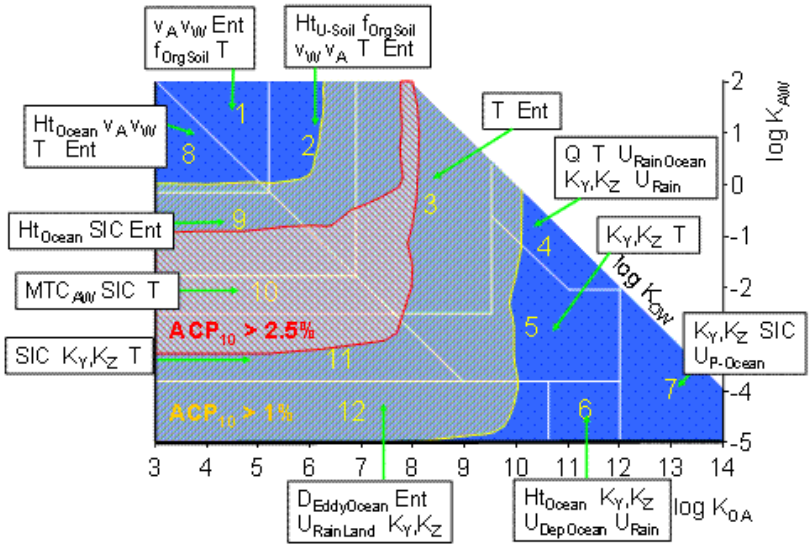

Fig. 3: Chemical space segments of identical input parameter sensitivities for the ACP_{10}^{air} and superimposed fields with default ACP_{10}^{air} > 1% and > 2.5%.

These are also environmental characteristics which are expected to be significantly impacted by global climate change processes. We may thus hypothesise that the global transport and distribution behaviour of many persistent organic chemicals, and in particular their accumulation in polar marine ecosystems, may be significantly impacted by global climate change.This has been previously stated by Macdonald et al.[6] and there is now also experimental evidence that climate fluctuations can impact on the atmospheric transport of persistent organic pollutants[7]. We suggest that global transport and distribution models such a Globo-POP may play a role in defining more clearly what the impact of global climate change on global POP behaviour might be.

Acknowledgments

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