

## Screening for Cold Condensation Potential of Organic Chemicals

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### Introduction

In the last decade, many persistent organic chemicals have been detected in the arctic environment far from any sources. A major role in this context is attributed to the processes of atmospheric transport over long distances and subsequent deposition in colder regions (cold condensation)<sup>1</sup>. For a relative evaluation of the long-range transport potential (LRTP) of chemicals, multimedia models delivering simple measures (e.g. spatial range, characteristic travel distance) can be used<sup>2</sup>. Although the environmental fate of a chemical is known to be strongly affected by temperature, model simulations are often carried out at fixed standard temperatures (25°C). Recently, the temperature dependence of the characteristic travel distance in air ( $L_A$ ) was investigated in detail<sup>3</sup>. It has been shown that the difference in  $L_A$  values between 5°C and 30°C can be up to a factor of 6 and that relative ranking of chemicals according to their LRTP may significantly change at different temperatures.

The process of cold condensation cannot be assessed without consideration of various temperatures at all. It is assumed that enhanced deposition (“condensation”) to surface media (water, soil and biota) occurs as a direct effect of reduced temperature in the different climatic zones. To date, model approaches for evaluating the cold condensation potential involve the application of more or less complex global multimedia models considering different latitudinal zones. The GLOBO-POP model calculates an “Arctic Contamination Potential” (ACP) as the fraction of the total substance amount in the global environment that is present in Arctic surface media<sup>4</sup>. A similar approach is used with the CliMoChem model, where cold condensation is expressed as the ratio of a chemical’s exposure at the poles to the minimal exposure of both hemispheres<sup>5</sup>. In this paper we investigate a screening approach using the ratio of calculated travel distances in air at two different temperatures as a simple relative measure for the “cold condensation potential” (CCP) of chemicals.

### Methods and Materials

**Model description.** Model simulations were performed with ELPOS, which is a steady-state multimedia box model based on the regional EUSES SimpleBox model. ELPOS calculates characteristic travel distances in air ( $L_A$ ) for continuous emissions into the air compartment. Further details of model calculations as well as the general parameterization of the model have been described elsewhere<sup>6</sup>. Data for  $L_A$  were generated at different temperatures in the

environmentally relevant region (5°C – 30°C). As a screening measure for the cold condensation potential (CCP) the ratio of the travel distances  $L_A$  at 10°C and 5°C, respectively, was calculated.

$$CCP = L_A^{10^\circ C} / L_A^{5^\circ C}$$

The chosen temperatures are on average representative for the temperate and the southern boreal climatic zone, respectively. If the characteristic travel distance decreases from 10°C to 5°C, CCP values are larger than unity and cold condensation in cooler regions is likely. It is assumed that lower temperatures result in elevated deposition and a reduction of atmospheric degradation. A lower  $L_A$  at 5°C therefore originates from a more effective net-deposition at this temperature, which over-compensates the reduced degradation losses. Hence, such a chemical has a potential to accumulate in cooler regions.

**Substance properties and environmental data.** Calculations were performed for a set of 53 chemicals including poly-chlorinated biphenyls (PCB), polychlorinated dibenzo-*p*-dioxins (PCDD) and polyaromatic hydrocarbons (PAH). Temperature-dependent substance properties considered were the partition coefficients  $K_{AW}$ ,  $K_{OW}$  and  $K_{OA}$  as well as the degradation rates in the different compartments. For the temperature dependence of partitioning data a modified van't Hoff equation was used with the internal energy change  $\Delta U$  of the respective property as influencing parameter. The degradation rate constants were temperature adjusted for their activation energies using the general Arrhenius equation<sup>3</sup>. Degradation rates in air were additionally adjusted for varying OH radical concentrations. Atmospheric hydroxyl radical concentrations ( $C_{OH}$ ) were the only environmental data varied with temperature, as this parameter significantly affects the calculated travel distances.  $C_{OH}$  is indirectly related to temperature, which is considered in the model simulations by a simple correlation function yielding reasonable values for average OH radical concentrations in the lower troposphere of the Northern hemisphere<sup>3</sup>. All necessary input data were compiled from literature sources<sup>3, 6-9</sup>. Partitioning data were already adjusted to conform to thermodynamic constraints in the original papers.

## Results and Discussion

The CCP values of all 53 test chemicals calculated with the screening approach varied between 0.55 and 1.62. Selected results are presented in Table 1. The simulated long-range transport behaviour for carbon tetrachloride ( $CCl_4$ ) agrees with the observed homogeneous global concentration distribution in air<sup>5</sup>.  $CCl_4$  is highly persistent and the mass fraction in air accounts for more than 95% even at low temperatures. This results in large travel distances slightly increasing with decreasing temperature.

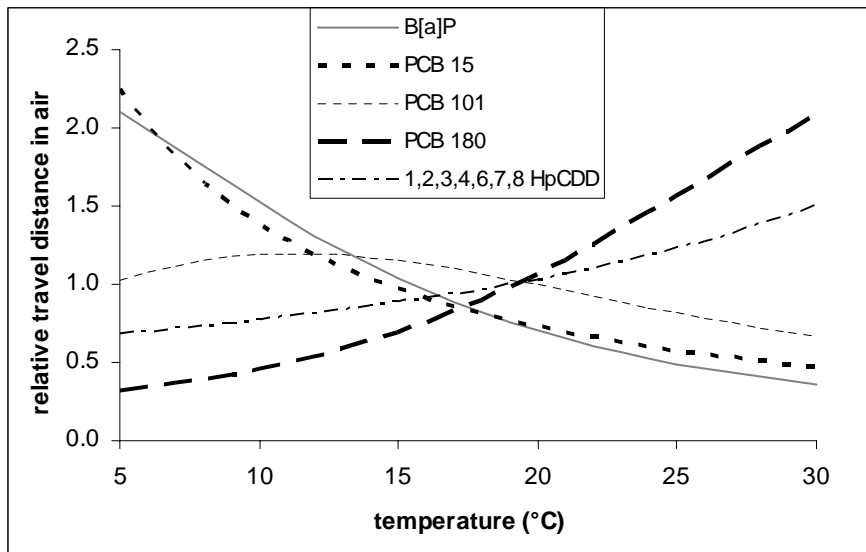
**Table 1:** Simulated Cold Condensation Potentials (CCP) and Characteristic Travel Distances in air ( $L_A$ ) at 5°C, 15°C and 25°C for selected substances

	CCP	$L_A$ (5°C)	$L_A$ (15°C)	$L_A$ (25°C)
carbon tetrachloride ( $CCl_4$ )	0.74	2.1E+07	1.2E+07	7.0E+06
phenanthrene	0.58	549	223	142
anthracene	0.56	83	32	20

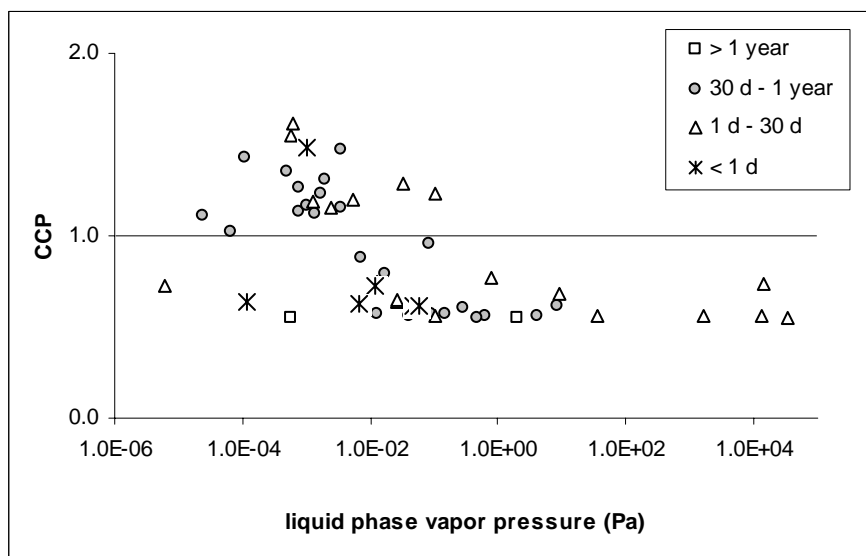
## PHYSICO-CHEMICAL PROPERTIES, DISTRIBUTION AND MODELLING

benzo[ <i>a</i> ]pyrene	0.73	578	286	135
$\alpha$ -HCH	<b>1.23</b>	4697	6888	8481
$\gamma$ -HCH	<b>1.29</b>	2641	4242	5719
2,3,7,8-TCDD	<b>1.30</b>	2197	3524	4171
1,2,3,4,6,7,8-HpCDD	<b>1.13</b>	956	1239	1723
PCB-3	0.55	4831	1826	1089
PCB-15	0.62	7298	3160	1890
PCB-31	0.64	11577	5214	3086
PCB-61	0.88	10861	7521	4550
PCB-101	<b>1.16</b>	12758	14313	10155
PCB-118	<b>1.46</b>	3880	7355	8104
PCB-155	<b>1.47</b>	9880	18337	17986
PCB-180	<b>1.43</b>	1570	3388	7619
PCB-194	<b>1.11</b>	869	1131	1883

Among the different investigated substance classes the 10 PAHs show relatively short travel distances due to their short half-lives in air and no apparent potential for cold condensation ( $CCP < 0.75$ ). In contrast, the five PCDDs and the two HCH-isomers are classified as prone to cold condensation ( $CCP > 1.1$ ) with intermediate travel distances in air. Within the group of the PCBs the relationship between  $L_A$  and temperature changes from the lower chlorinated (one to four Cl-atoms) to the higher chlorinated congeners (with more than four Cl-atoms). While the latter exhibit a cold condensation potential ( $CCP > 1.15$ ) in the screening approach, the lower chlorinated congeners do not ( $CCP < 0.9$ ). This can be explained by the overall temperature dependence of  $L_A$ , which is a combined effect of the changes of the degradation rate in air, the total deposition and the steady-state mass distribution between air and surface media and has been shown to have a global maximum<sup>3</sup>. Typical examples are depicted in Figure 1. Travel distances of Benzo[*a*]pyrene and PCB 15 are steadily decreasing with temperature, whereas PCB 180 and the HpCDD show the opposite behaviour. PCB 101 is an interesting example with a maximum  $L_A$  in the environmentally relevant temperature range at 12°C. CCP values above unity always occur, when the maximum  $L_A$  is calculated for temperatures above 10°C, which is the case for the PCDDs and the higher chlorinated PCB congeners. In other words, with this screening approach we classify chemicals as susceptible to cold condensation, if they exhibit the maximum  $L_A$  at temperatures above 10°C.



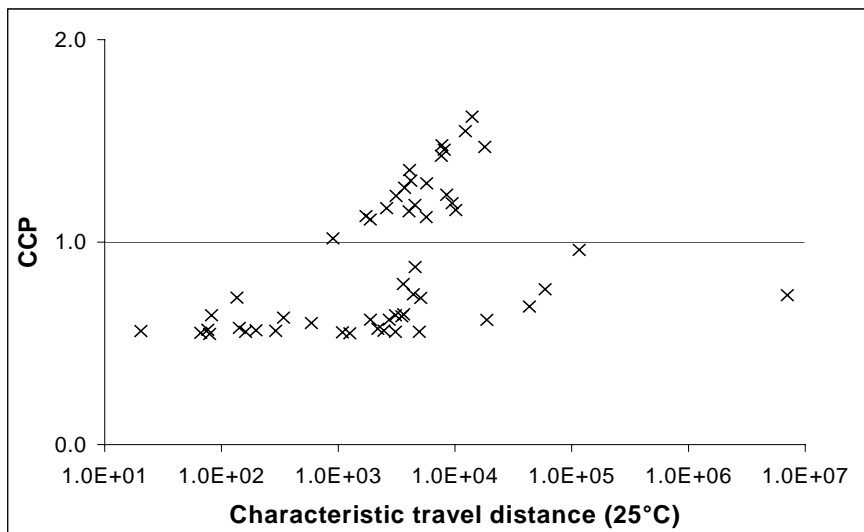
**Figure 1:** Temperature dependence of the calculated travel distance in air for selected substances. Relative travel distances are related to the average of travel distances of the respective substance over the whole temperature range (calculated in steps of 1°C).



**Figure 2:** Cold condensation potential (CCP) vs. liquid phase vapour pressure. Substances are additionally categorized according to their degradation half-life in air at 10°C.

In Figure 2 CCP values of all 53 chemicals are plotted against the sub-cooled liquid vapour pressure at 25°C. It can be seen that for volatile compounds with a liquid phase vapour pressure above 1 Pa cold condensation at 5°C is not suggested by the model. For such compounds, e.g. CCl<sub>4</sub>, mass fraction in air is high even at low temperatures and enhanced deposition in colder regions is not strong enough to compensate for reduced degradation in the environment. Thus, calculated steady-state concentrations in air are increasing with decreasing temperature resulting in larger travel distances. To further evaluate the effect of degradation in air, substances have been categorized according to their estimated half-lives in air at 10°C. However, from Figure 2 no simple relationship between the absolute values of half-lives in air and the CCP can be deduced. This is due to the fact that the CCP is affected by the relative change of the degradation rates driven by the varying OH radical concentrations and the activation energies rather than the absolute values.

In Figure 3 the CCP values are plotted against the characteristic travel distance calculated for standard conditions at 25°C. This parameter has been suggested as a measure for the long-range transport potential of a chemical and its temperature dependence has been already investigated<sup>2,3</sup>.



**Figure 3:** Cold condensation potential (CCP) vs. characteristic travel distance at 25°C.

It is obvious that a large  $L_A$  does not necessarily imply a high cold condensation potential. The highest CCP values are calculated for substances with an intermediate long-range transport potential. This again corroborates the need for consideration of temperature effects in modelling the environmental fate of chemicals especially with respect to their long-range transport behaviour. In this context, the suggested screening approach of a CCP value calculated with a standardized multimedia model (ELPOS) could help to identify those chemicals, for which a cold condensation effect is most likely. Despite being a relatively simple measure for cold condensation, the CCP takes into account the exchange with surface compartments in both directions. Thus, it has a broad range of potential applications including the comparison of different environmental scenarios with different surface characteristics, or comparing cold condensation in different temperature regimes

(e.g. cooling from 10° to 5°C versus cooling from 5° to 0°C). However, the applicability of the temperature relationships used in this investigation is restricted to the temperature range of 0°C – 30°C. At lower temperatures the effect of ice and snow has to be taken into account, which may lead to a more pronounced deposition than calculated in our scenarios. Further work is necessary to include the effects of ice and snow into multimedia models and to establish the necessary temperature relationships of the parameters. If in the future reliable simulation of deposition via snow and exchange with icy surfaces becomes possible,  $L_A$  and CCP can also be calculated for lower temperatures.

### Acknowledgements

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