

POP Candidates 2007: Model Results on Overall Persistence and Long-range Transport Potential obtained with the OECD Pov & LRTP Screening Tool

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Corrected version: in the first version of this document, there was a unit error in the half-life in air for β -HCH (days instead of hours).

Summary

We present overall persistence and long-range transport potential calculations from the OECD Pov and LRTP Screening Tool (“The Tool”) for the five 2007 POP candidate substances. The Pov and LRTP calculations for pentachlorobenzene, α - and β -HCH, octabromodiphenylether and short-chain chlorinated paraffins are based on input properties from the POPRC proposal documents. Our analysis includes a Monte Carlo-type uncertainty analysis to quantify the uncertainty in the calculated Pov and LRTP from uncertainty ranges for the input properties. The five new POP candidates have Pov and LRTP properties similar to those of identified POPs such as PCBs and organochlorine pesticides.

1 Introduction

During the evaluation of candidate substances for inclusion in the Stockholm Convention, a number of criteria are investigated (Annex D, see <http://www.pops.int>). The OECD Pov & LRTP Screening Tool (“The Tool”) is a software instrument specifically designed to serve regulators in the hazard assessment of potential persistent organic pollutants (POPs) by calculating indicators of overall environmental persistence (Pov) and potential for long-range transport (LRTP).

The Tool is based on the work of an OECD expert group that was tasked to make recommendations for applying multimedia environmental fate models to screen chemicals for overall persistence and potential for long-range transport. Scientific findings of this expert group were published in two papers (Fenner et al. 2005, Klasmeier et al. 2006). The Tool is a *consensus* model of environmental fate and transport of organic chemicals and has been used previously to investigate the Pov and LRTP of the four POP candidates evaluated in 2006 (Scheringer *et al.*, 2006). The Tool can be freely downloaded from the OECD website at <http://www.oecd.org/env/riskassessment> or is available from the authors.

The substances investigated here are the 2007 POP candidates that were submitted to the POP Review Committee (POPRC): α -hexachlorocyclohexane (α -HCH), β -hexachlorocyclohexane (β -HCH), the commercial octabromodiphenyl ether mixture (c-octaBDE), pentachlorobenzene (PeCB or 5-CB), and short-chain chlorinated paraffins (SCCP).

2 Model input and results

The Tool requires degradation half-lives for soil, ocean water and air as well as two partition coefficients, the octanol-water partition coefficient and the Henry's law constant, as substance-specific inputs. We compiled these data from the proposal documents provided to the POPRC during the meeting in November 2006 (see <http://www.pops.int/documents/meetings/poprc/chemreview.htm>). Based on the ranges of reported property values, we selected point estimate values for the five candidates, see Table 1. We have selected 1 yr as a 'high' half-life in cases where no numerical values were given in the POPRC proposal documents. It is important to note that these chemical property data are uncertain and that this uncertainty influences the results obtained with the Tool (see Section 5 below).

Table 1: Selected input properties for The Tool software.

Substance	$\log_{10} K_{AW}$ [-]	$\log_{10} K_{OW}$ [-]	degradation half-life in air	degradation half-life in water	degradation half-life in soil
α -HCH	-3.55	3.8	115 d (1)	1 yr (2)	82.5 d
β -HCH	-2.74	3.78	152 h (6)	5 yr (3)	129 d
c-octaBDE	-2.37	6.29	76 d	1 yr (4)	1 yr (4)
PeCB	-0.4	4.99	277 d (1)	492 d (5)	259 d
SCCP	-2.42	6.2	3.7 d	1 yr (4)	1 yr (4)

(1) The value reported as 'average' was taken. (2) Selected representative value. (3) Estimated based on the report of no hydrolysis in the POPRC documents (4) 1 year was assumed to represent 'high' half-life. (5) Geometric mean of the range limits 194 d and 1250 d. (6) Value is disputed, see text.

Two of the five POP candidates, c-octaBDE and SCCP, are complex mixtures of many individual chemicals. For these substances the property values shown in Table 1 are considered to be representative of the bulk of the mixture. Specific compounds from the mixture may have rather different chemical properties. The range of $\log K_{OW}$ for SCCP reported in the POPRC documents is very wide, and probably represents the variability in this property within the mixture. We have addressed this variability in our Monte Carlo uncertainty analysis described below.

The substance property values for commercial c-octaBDE reported in the proposal documents are not in good agreement with property data reported by Wania and Dugani (2003). We believe the Wania and Dugani data are more accurate than the values in the POPRC documents. However, for consistency with the other candidate chemicals, we have calculated Pov and LRTP values based on the POPRC proposal values, but still included a scenario using values in better agreement with Wania and Dugani in our Monte Carlo uncertainty analysis (see below).

For the same reason, we calculated results for β -HCH with the half-life in air of 152 hours, although we think this value is too low. In Figure 5, containing the Monte-Carlo results for β -HCH, we have included a yellow dot for β -HCH based on the EPI Suite point estimate of 56 d for the half-life in air. This value seems more realistic. In our opinion, the value of 152 h, which is given in the photolysis paragraph

of the POPRC proposal document, should not have been included in the document. From the original source (ATSDR, 2005), it is clear that the value of 152 h is not a photolysis half-life but may represent a more general removal half-life which may include revolatilisation.

From the input parameters in Table 1 the Tool calculates overall persistence (Pov), characteristic travel distance (CTD), and transfer efficiency (TE) for each chemical. These results are shown in Figure 1 in plots of CTD vs. Pov (left) and TE vs. Pov (right).

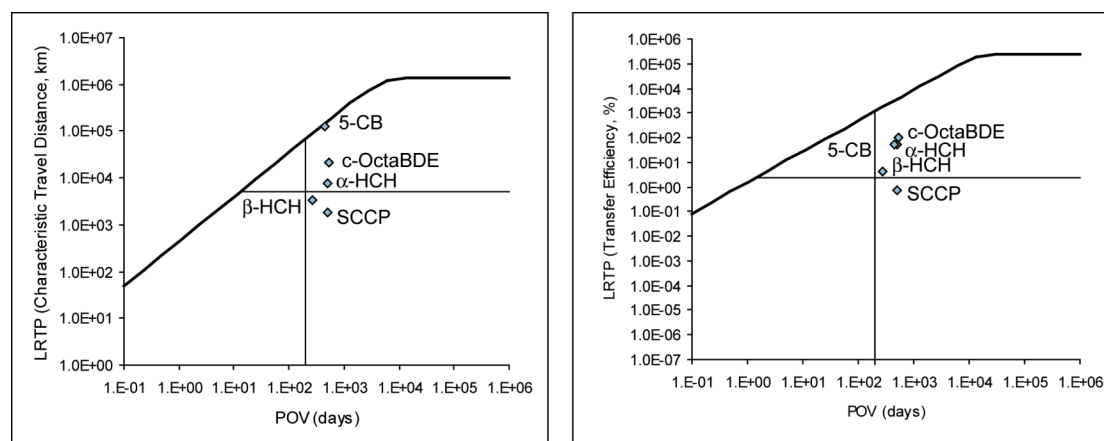


Figure 1: Pov, CTD and TE values calculated with the Tool for the five POP candidates. Left: CTD vs. Pov, right: TE vs. Pov.

3 Pov and L RTP metrics

Pov (unit: days) is derived from the degradation rate constants in soil, water and air weighted by the chemical's mass fractions present in the three media. In other words, Pov reflects the contribution that degradation in every medium makes to the overall degradation rate of the chemical in the whole environment. This combination of the media-specific contributions to the overall degradation distinguishes Pov from single-media half-lives.

In the Tool, Pov is calculated for three emission scenarios: emission to soil, water and air. The highest Pov value obtained with these three scenarios is displayed as the Pov result. This Pov value reflects the characteristic time for disappearance of a chemical after releases have been stopped and the overall degradation rate is determined by the slowest responding medium. In this “temporal remote state” (Stroebe et al. 2004) the overall persistence is determined by (i) the rate of degradation in the medium in which the chemical is most slowly degraded, and (ii) the rate of evasion from that medium and subsequent degradation.

Characteristic travel distance (unit: km) is the distance at which the chemical's concentration at the point of release has decreased to 37% if it is assumed that the chemical is transported by a constant flow of air (wind speed of 4 m/s) or water (ocean water circulation speed of 0.02 m/s), see Figure 2, top. CTD is calculated for release to water and air and the higher of the two values is plotted in the left-hand panel of Figure 1. The decrease in concentration is caused by degradation of the chemical in the mobile medium and by irreversible transfer out of the mobile medium, for example by dry and wet deposition from the atmosphere.

Table 2: Relative contribution (%) of degradation and irreversible transfer to the overall removal of the five POP candidates from air.

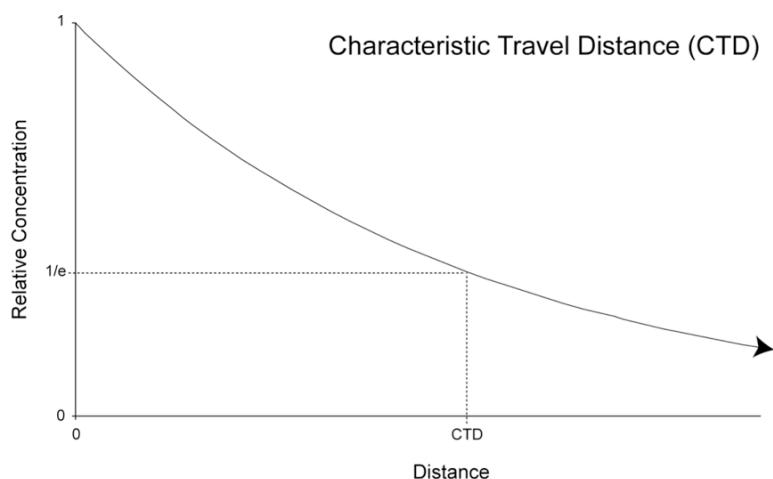
chemical	degradation	transfer
α -HCH	8.1%	91.9%
β -HCH	78.1%	21.9%
c-octaBDE	33.8%	66.2%
PeCB	82.9%	17.1%
SCCP	90.6%	9.4%

For all five candidate POPs, the maximum CTD is obtained for emission to air and transport in air; “transfer” in Table 2 is net dry and wet deposition from air to surface media and transfer to the stratosphere.

The scale of CTD is linear. Very high CTD values – equivalent to several times the circumference of the earth – are obtained for volatile chemicals that are persistent in the air, for example, carbon tetrachloride or chlorofluorocarbons. For such chemicals, the CTD in air is bounded by transfer to the stratosphere; a very slow process. In the case of PeCB, transfer to the stratosphere is calculated to contribute 8.5 % of the overall removal from air. For the other four POP candidates, this process is negligible (< 1% of total removal from air). The heavy diagonal line in plots of CTD vs. Pov represents the maximum CTD in air for volatile substances.

The CTD represents the potential of a chemical to be transported over long distances in air or water. For chemicals that are transported in air and ultimately degraded, transformation products formed in the troposphere will be deposited to the surface media in the domain indicated by the CTD of the parent compound.

TE (dimensionless or given in %) is a metric of potential for atmospheric transport and deposition of the parent compound to water and soil in a remote region. It is calculated as the ratio of two mass fluxes: the depositional flux to water and soil in a remote, target region (mol/day) divided by the emission flux in a source region (mol/day). TE values greater than 100% are possible because some chemicals may undergo several cycles of deposition and re-volatilization during their residence time in the environment. High TE values from the Tool are obtained for chemicals with an “optimal” combination of transfer out of the source region and cycling between air to surface media in the target region. TE is calculated for the three scenarios of emission to soil, water and air. The emission to air scenario always yields the highest TE, and that value is displayed in the plot.



Transfer Efficiency (TE)

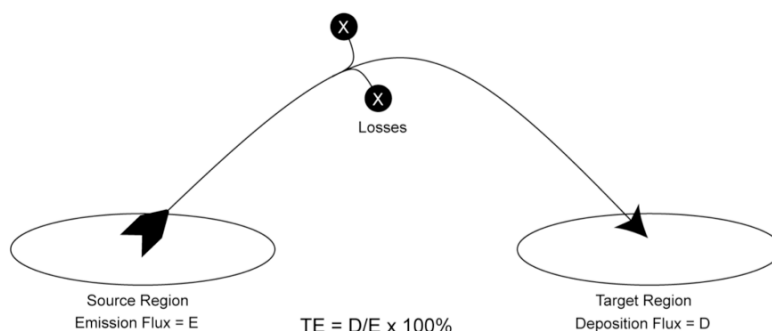


Figure 2: Conceptual illustration of the LRTP metrics CTD and TE.

4 Results in comparison to other POPs

The reference lines in the graphs shown in Figure 3 are derived from a set of reference chemicals as described by Klasmeier et al. (2006). The top panel of Figure 3 shows the reference chemicals used by Klasmeier et al. to derive the position of reference lines that could be used to identify behavior in the environment similar to acknowledged POPs. The reference chemicals are α -HCH, hexachlorobenzene (HCB), carbon tetrachloride, and PCB congeners 28, 101, and 180. Note that Klasmeier et al. (2006) used α -HCH as a reference chemical based on laboratory and field evidence that it had high persistence and long range transport potential. The physical-chemical properties used by Klasmeier et al. (2006) for α -HCH are somewhat different from the ones used in this study, which accounts for the different position of points representing this chemical.

The lines intersect the lowest Pov, CTD and TE values found in the set of these six reference chemicals. The only purpose of the lines is to provide a point of reference to which results for other chemicals can be compared. When the Tool is opened the first time, these lines are not shown; they can be switched on by the user as an option provided on the “preferences” page of the Tool. Chemicals which fall in the upper-right quadrant of the plots have Pov and LRTP that exceed the lowest values for the six reference chemicals.

The meaning of the reference lines is not that chemicals which do not fall in the upper-right quadrant do not have POP-type Pov or LRTP values. The reference chemicals were selected because there is empirical evidence (independent of model results) of their persistence and long-range transport (Klasmeier et al. 2006). With a larger set of reference chemicals, the top right quadrant in Figure 3 might look different; however, the OECD expert group did not include more of the identified POPs in the set of reference chemicals because for many of the identified POPs the empirical evidence of persistence and long-range transport is more uncertain than for the six reference chemicals.

From the inputs in Table 1, The Tool calculates overall persistence (Pov), characteristic travel distance (CTD), and transfer efficiency (TE) for each chemical. These results are shown in the middle panels of Figure 3 (same as Figure 1 above) and, for comparison with Pov and LRTP results for acknowledged POPs, in the bottom panels of Figure 3 in plots of CTD vs. Pov (left) and TE vs. Pov (right).

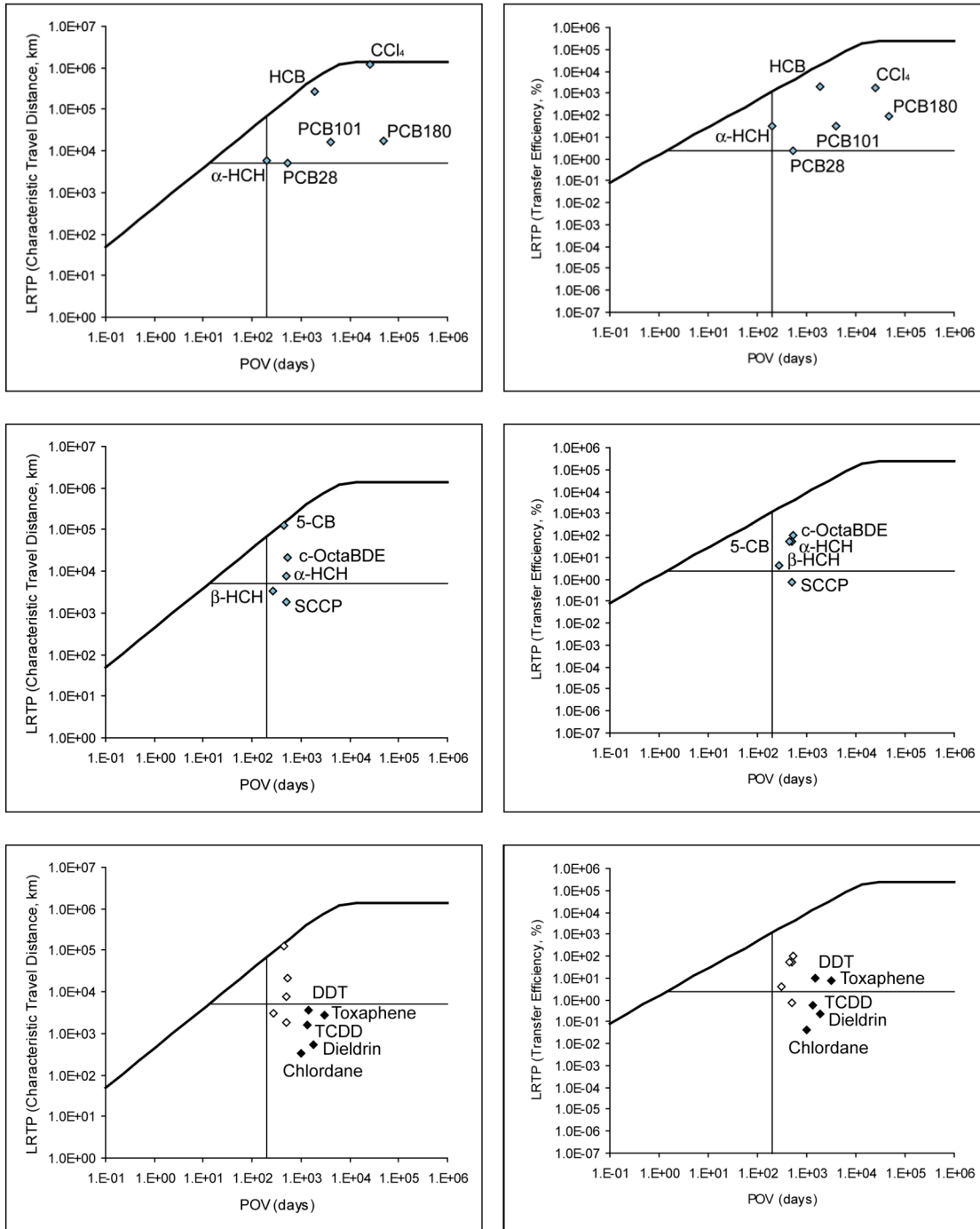


Figure 3 Top Panel: Results from the Tool for six reference compounds with evidence of POP-like behavior in the environment. These results are used to derive the reference lines in the plots.

Middle Panel: Pov and L RTP values of the POP candidates α -HCH, β -HCH, c-octaBDE, pentachlorobenzene (5-CB), and SCCP.

Lower Panel: Pov and L RTP values of the POP candidates in relation to the values of selected other POPs.

Figure 3 shows that the five new POP candidates have calculated Pov and L RTP similar to those of identified POPs. As a group, the five POP candidates have slightly lower Pov and higher L RTP than the identified POPs depicted in Figure 3.

5 Monte Carlo uncertainty analysis

To demonstrate the influence of uncertain chemical properties, we show results from a Monte Carlo calculation for each of the five chemicals in Figures 4 to 8 below. In the Monte Carlo calculations, we assume that the values of all chemical properties are distributed log-normally. The distributions of the property values are defined with the values in Table 1 as median and the 95th and 5th percentile estimated by multiplying or dividing the median by a factor of 5 for the partition coefficients and by a factor of 10 for the environmental half-lives. These factors are called “dispersion factors” and are given on the main page of the Tool if the option “Include Monte Carlo analysis for single chemical” is switched on; they can be changed by the user. We applied the standard values for the dispersion factors in the evaluation of the POP candidates except for the SCCP, where we applied a dispersion factor of 100 for the K_{OW} to account for the value range given in the POPRC documents. By using ANOVA techniques, we mapped the observed variances of the results (Pov, CTD, TE) to contributions from the individual input properties.

α -HCH

The cloud of Monte Carlo output for α -HCH has its center in the upper-right quadrant but points are found in the three other quadrants as well.

The analysis of the contributions to variance for Pov reveals that the variance in the input property half-life in water clearly dominates the variance of the Pov values. No such dominance is found for the LRTP variance contributions; the variances of the three properties K_{AW} , half-life in water and half-life air contribute to the variance of the LRTP values.

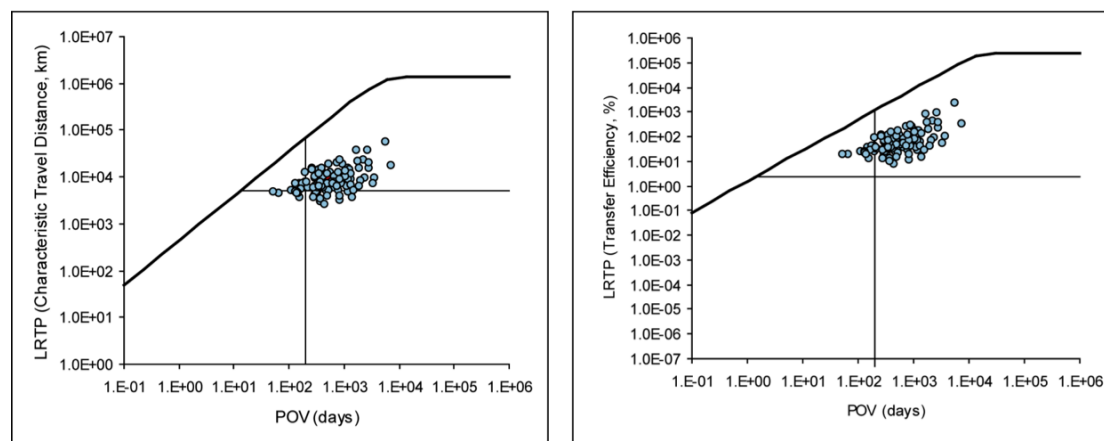


Figure 4: Results for the Monte Carlo calculation for α -HCH.

β -HCH

In general, β -HCH is more persistent and has a higher K_{AW} than α -HCH. However, for the sake of consistency, we have used the low photolysis half-life of 152 h as reported in the POPRC proposal document for the half-life in air (see also Section 2). Thus, Monte Carlo results are found in all four quadrants, but a majority of points are located right of the Pov criteria line, indicating POP-like overall persistence. A yellow dot indicates Pov/LRTP results derived with a half-life in air of 56 days (EPI suite estimate). The yellow dot is clearly in the upper-right quadrant, supporting the classification of β -HCH as a POP with respect to Pov and LRTP.

The analysis of the contributions to variance for Pov reveals, in contrast to α -HCH, no clear dominance. The variances in K_{AW} , half-life in soil and half-life in air contribute to the variance in Pov. On the other hand, variance in the half-life in air dominates uncertainty in the LRTP metrics. This demonstrates the importance of half-life in air for the evaluation of β -HCH.

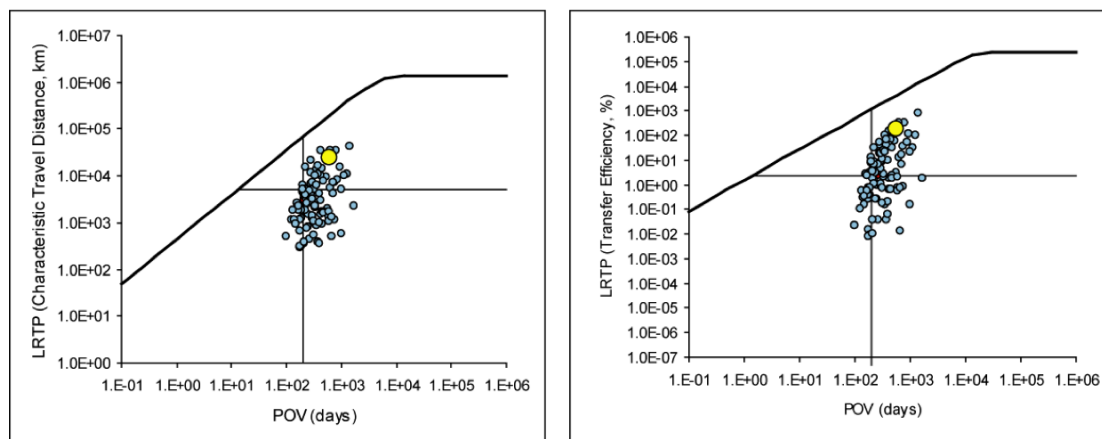


Figure 5: Results for the Monte Carlo calculation for β -HCH using the property values from the POPRC proposal documents. The yellow dot represents Pov and LRTP indicator values that are obtained if the EPI suite estimate of 56 days for the half-life in air is used instead of 152 h.

c-OctaBDE

The cloud of Monte Carlo results for commercial octaBDE exhibits a shape that is more symmetrical than the ones for the HCHs. The center of the cloud is clearly located in the upper-right quadrant. The large yellow circle is located at Pov and LRTP values that are obtained if property values suggested by Wania and Dugani (2003) are used instead of the values in the POPRC documents ($\log K_{AW}$ of -4 instead of -2.37 and $\log K_{OW}$ of 7 instead of 6.29). This modification lowers the long-range transport potential, as a smaller amount of octaBDE is in the mobile air compartment, and a larger fraction of the amount in air is sorbed to aerosols that are deposited more efficiently to the surface.

The variance of the Pov is clearly dominated by the variance in the half-life in soil. This is typical for compounds with high K_{OW} values. Both the CTD and the TE variances are dominated by the variance in the half-life in air. The K_{AW} only contributes marginally to the variances in Pov and TE, but around 15% for the CTD.

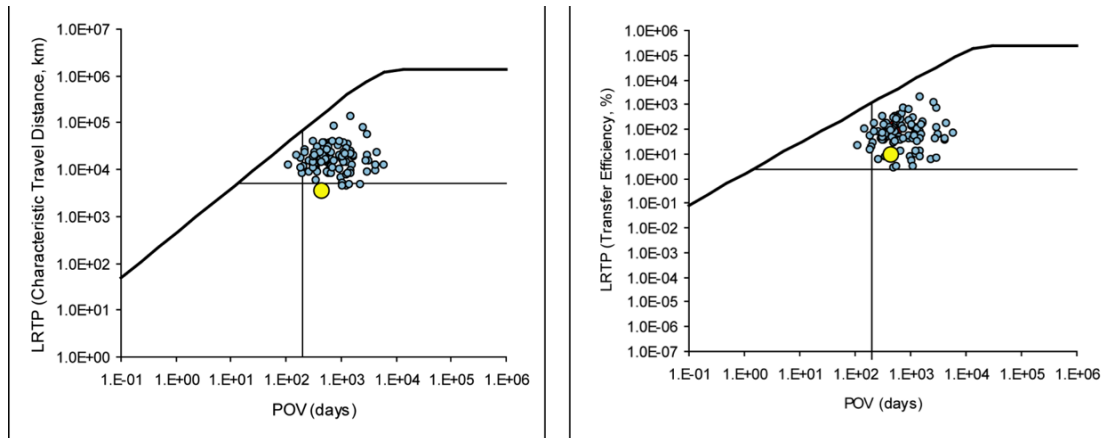


Figure 6: Results for the Monte Carlo calculation for c-octaBDE.

PeCB

The PeCB cloud exhibits a very specific, diagonally stretched shape that follows closely the limiting line in the CTD/Pov plot. PeCB is the most volatile of the POP candidates, as indicated by its K_{AW} value. A majority of points are located in the upper-right quadrant in both plots.

Given the high volatility of PeCB, the variance in the half-life in air is clearly dominating the variance in Pov, CTD, and TE, with contributions of the K_{AW} and the half-life in soil below 5%. Thus, it is important to have accurate values for the half-life in air for a hazard assessment of this compound.

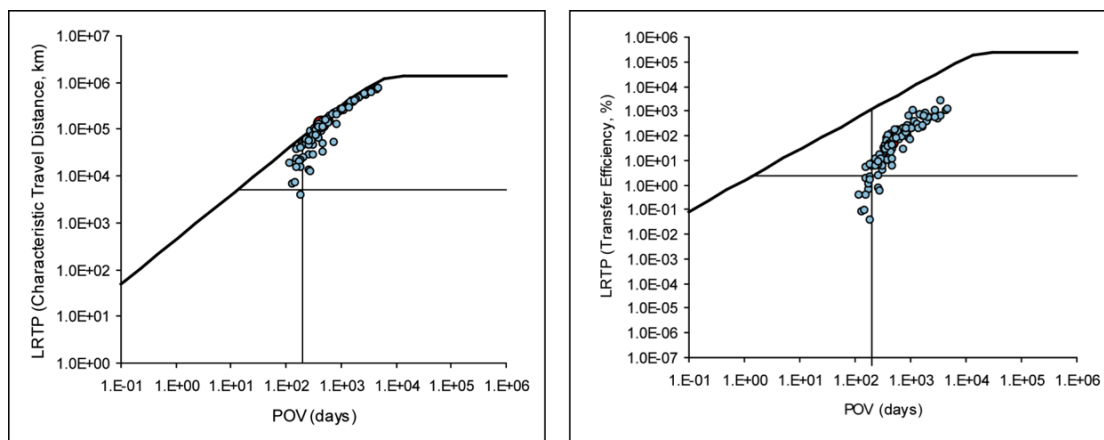


Figure 7: Results for the Monte Carlo calculation for PeCB.

SCCP

The dispersion factor for the K_{OW} of SCCP was increased from its standard value of 5 to 100, to account for the reported range of approximately 4 orders of magnitude in the POPRC documents. The cloud for SCCP has a circular shape, like the one for c-octaBDE. Points are found in all quadrants but most points are found in the two right quadrants with high Pov values. The center of the cloud lies below the L RTP line derived from the reference chemicals, but is still close to other, acknowledged POPs such as TCDD.

As is typical for compounds with high K_{ow} , the half-life in soil contributes most to the variance in Pov. The half-life in air variance is most dominant in the LRTP metrics.

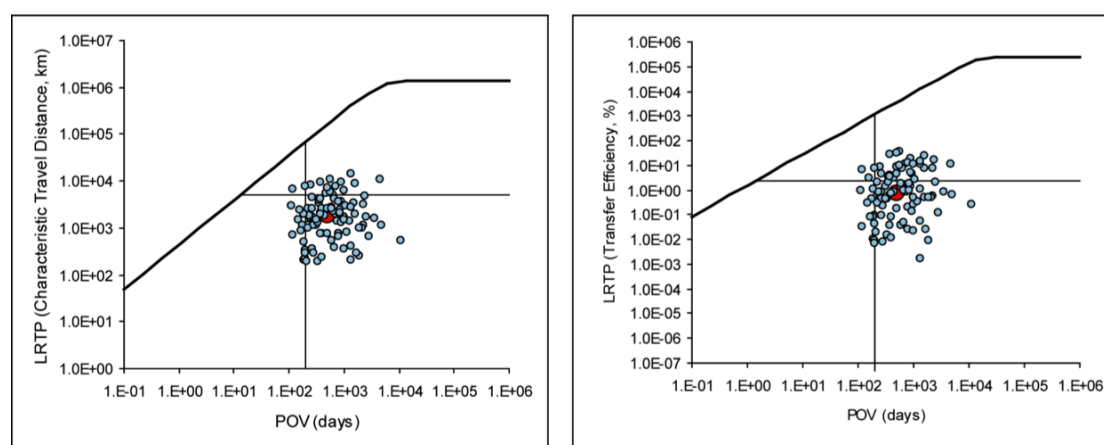


Figure 8: Results for the Monte Carlo calculations for SCCP.

Conclusions

Because no absolute scales have been established for Pov and LRTP, comparison to reference chemicals is the most informative way of evaluating results from the Tool. The only purpose of the Tool is to provide estimates of Pov and LRTP. Results from the Tool do not indicate absolute levels in the environment but help to compare possible POPs with identified POPs according to their environmental persistence and potential for long-range transport.

Although there are considerable uncertainties in the chemical properties of the five chemicals under investigation, the results indicate that the POP candidates have Pov and LRTP properties similar to those of several known POPs.

References

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