Analysis of Four Current POP Candidates with the OECD P_{ov} and LRTP Screening Tool

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Summary
The OECD Screening Tool for overall persistence (Pov) and long-range transport potential (LRTP) is applied to four POP candidates, γ-HCH, pentabromodiphenyl ether (BDE-99), hexabromobiphenyl (HBB), and chlordecone. Chemical properties required as input parameters for the Tool are compiled and Pov and two LRTP metrics, characteristic travel distance and transfer efficiency, are calculated for the four chemicals. Comparison of the Pov and LRTP estimates of the four POP candidates with results for several identified POPs shows that the four POP candidates have Pov and LRTP properties similar to those of several known POPs (PCBs, organochlorine pesticides). An uncertainty analysis indicates that this result is valid although there are considerable uncertainties in the chemical properties of the four POP candidates.

1 Introduction
Under the Stockholm Convention on Persistent Pollutants, the Persistent Organic Pollutants Review Committee (POPRC) has identified five substances as "POP candidates" and prepared draft risk profiles (http://www.pops.int/documents/meetings/poprc/tech_comments/default.htm). To support the process of compiling risk profiles, we have estimated chemical properties for four of the five candidate substances and modeled their overall persistence and potential for long range transport using the OECD Pov and LRTP Screening Tool ("the Tool"). The substances considered are γ-HCH, pentabromodiphenyl ether (BDE-99), hexabromobiphenyl (HBB), and chlordecone; perfluorooctane sulfonic acid (PFOS) was not evaluated because its chemical properties and environmental partitioning are not sufficiently well characterized.

The Tool is the end product of five years of work by 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).

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. For the four compounds considered here, these data are listed in Table 1. The Henry's law constant is given as the dimensionless air-water partition coefficient. 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: Chemical properties used as input for calculations with the Tool.

chemical	degradation half-life in soil (days)	degradation half-life in water (days)	degradation half-life in air (days)	log K_{aw} (–)	log K_{ow} (–)
γ-HCH	156	22	96	–3.96	3.76
BDE-99	833	833	19	–3.67	6.76
chlordecone	730	730	> 1000	–6.69	5
HBB	316	316	38	–4.62	6.39

Sources: see section 5 below.

From these input parameters 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).

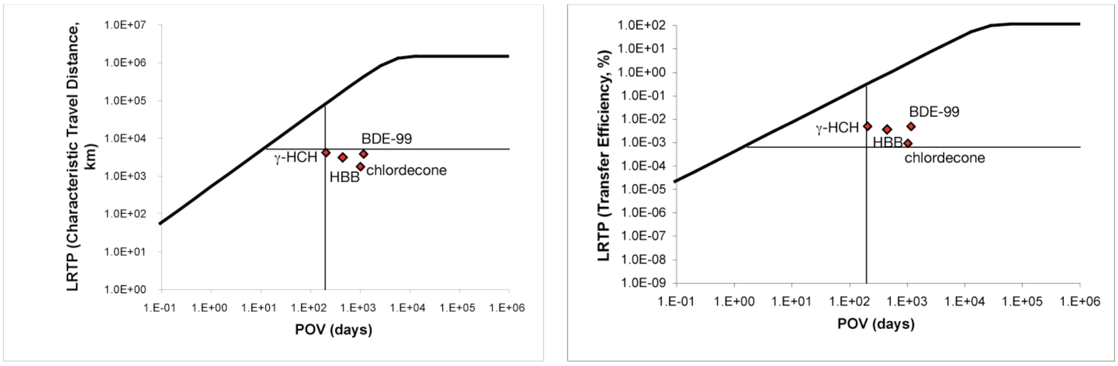


Figure 1: Pov, CTD and TE values calculated with the Tool for the four POP candidates. Left: CTD vs. Pov, right: TE vs. Pov.

3 Pov and LRTP 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. The relative importance of degradation and transfer is shown in Table 2 for the four POP candidates.

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

chemical	degradation	transfer
γ-HCH[a]	8.4	91.6
BDE-99[a]	31.7	68.3
chlordecone[b]	93.0	7.0
HBB[a]	8.5	91.5

a: maximum CTD obtained for emission to air; "transfer" is net dry and wet deposition from air to surface media.
b: maximum CTD obtained for emission to water; "transfer" is export to the deep ocean.

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 is bounded only by slow removal processes; transfer to the stratosphere for airborne substances and transport to deep oceans for waterborne substances. 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). High TE values from the Tool are around 5% and are obtained for chemicals with an "optimal" combination of transfer out of the source region and deposition from 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.

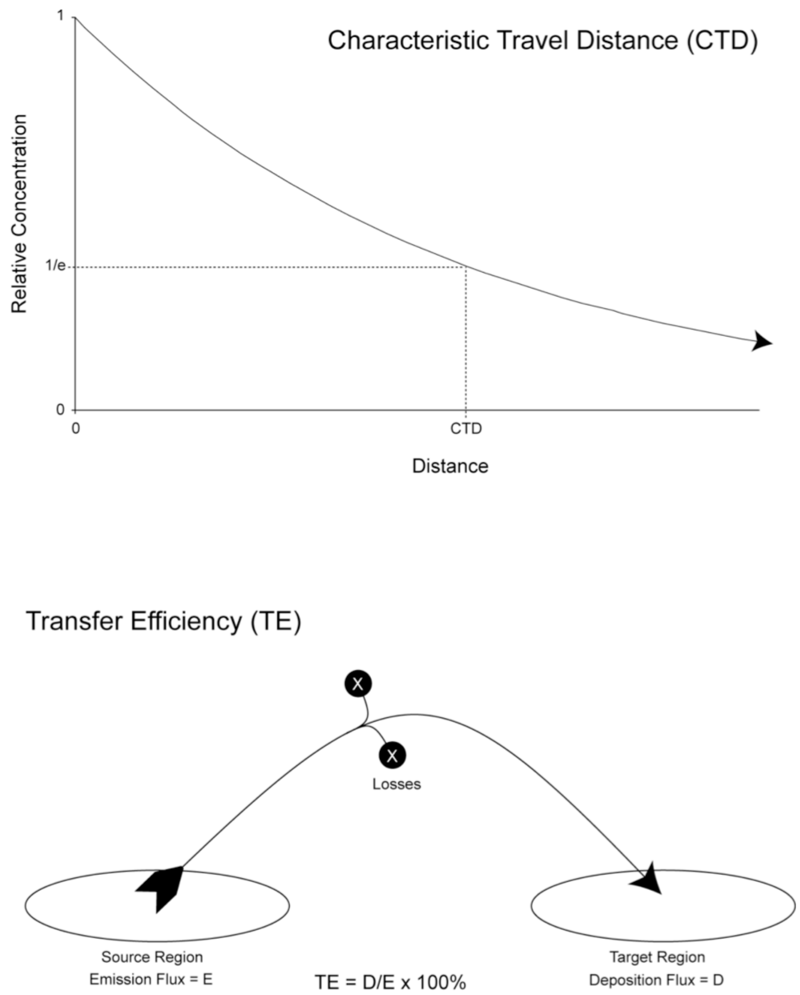


Figure 2: Conceptual illustration of the LRTP metrics CTD and TE.

4 Interpretation of results

In the graphs showing the model results (Figure 1), there are vertical and horizontal reference lines. These lines were derived from Pov, CTD and TE results calculated with the Tool for a set of chemicals with high Pov and LRTP that were used as reference chemicals (Klasmeier et al. 2006). The reference chemicals are α-HCH, hexachlorobenzene (HCB), carbon tetrachloride, and PCB congeners 28, 101, and 180. The lines represent the lowest Pov, CTD and TE values found in the set of these six reference chemicals, see Figure 3. 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.

The meaning of the reference lines is not that chemicals which do not fall in this quadrant do not have POP-type Pov or LRTP values. The reference chemicals were selected because there is sufficient 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.

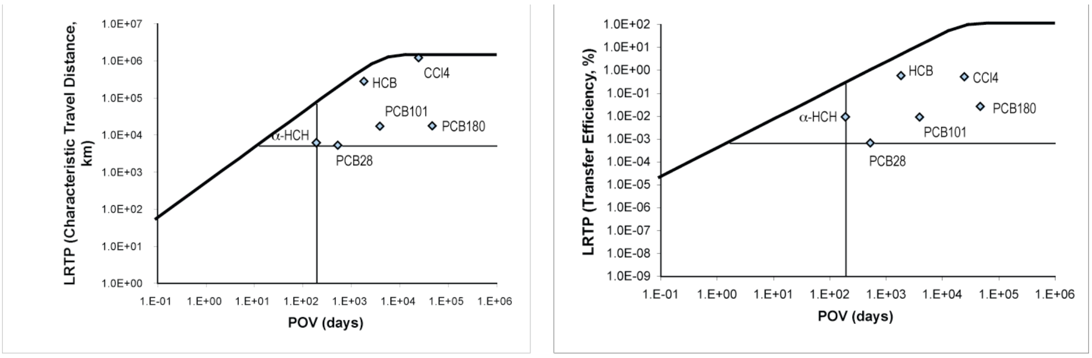


Figure 3: Results from the Tool for six compounds with high Pov and LRTP (reference chemicals).

In Figure 4, we show the results for the four POP candidates relative to 10 generic PCB homologues and in Figure 5 in comparison to five other identified POPs. First of all, the two Figures demonstrate that some identified POPs lie outside the domain defined by the reference chemicals. Again, the Pov and LRTP reference lines only indicate the lowest Pov and LRTP values obtained for the six reference chemicals (model results for α-HCH and PCB-28).

Second, Figures 4 and 5 show that the four POP candidates exhibit Pov and LRTP values similar to those of the identified POPs; there is no systematic discrepancy between the results for the POP candidates and the results for the set of identified POPs depicted in Figures 4 and 5.

Third, the results for the PCBs (Figure 4) show a general trend of increasing Pov and LRTP with increasing degree of chlorination. A key factor for this is that the half-lives of the PCBs in all media increase with increasing degree of chlorination. A second factor is that nona- and decachlorobiphenyl are strongly associated with aerosol particles and are removed more effectively from the atmosphere by dry and wet particle deposition, which reduces their LRTP compared to that of octachlorobiophenyl. In general, it is the balance of degradation in air and deposition from air to the surface media that determines the LRTP of semivolatile chemicals.

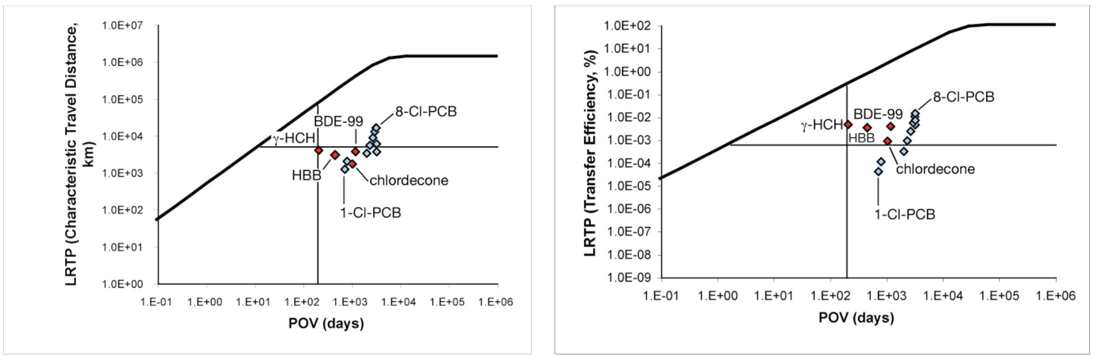
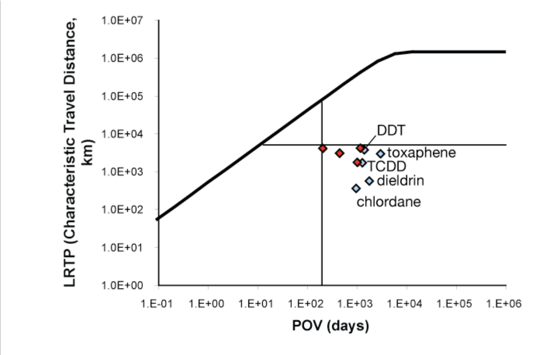


Figure 4: Results from the Tool for the four POP candidates and 10 generic PCB homologues in comparison.



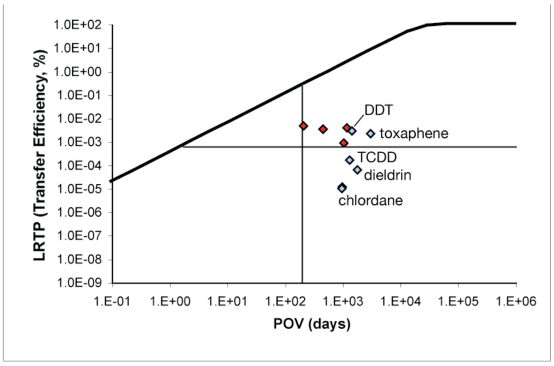


Figure 5: Results from the Tool for the four POP candidates and five identified POPs in comparison.

Finally, the results for the existing POPs are subject to considerable uncertainty (Scheringer 2002, chapter 9). For chlordane and dieldrin particularly short half-lives in air (around 1 day) have been estimated, which leads to relatively low LRTP for these compounds. Measured half-lives in air are not available for these compounds, and more research is needed to elucidate the atmospheric fate of semivolatile organic chemicals.

5 Discussion of uncertainty

To demonstrate the influence of uncertain chemical properties, we show results from a Monte Carlo calculation for each of the four chemicals in Figures 6 to 9 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.

γ-HCH

Partition coefficients for γ-HCH were taken from the compilation by Xiao et al. (2004) and were then adjusted for internal consistency with the procedure by Schenker et al. (2005). Half-lives for soil and water are from Howard et al. (1991) and Mackay et al. (1999); these are averages of various estimated and measured values. The half-life in air is an experimental value measured by Brubaker and Hites (1996) and relatively reliable; in this case, we used a dispersion factor of 5 instead of 10.

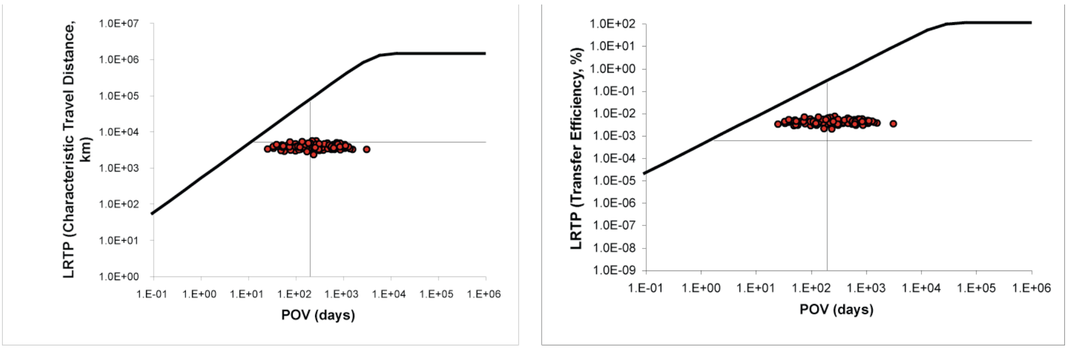


Figure 6: Results from a Monte Carlo calculation for γ-HCH.

The Monte Carlo results mainly show that both LRTP metrics are relatively insensitive to changes of the chemical properties; the results for Pov reflect the factor of 100 between the 5th and 95th percentile of the half-life distributions. Only with half-lives in soil and water that are lower than the values from Table 1 by a factor of 5 or more, γ-HCH would lose its high Pov.

BDE-99

Partition coefficients for BDE-99 were taken from Wania and Dugani (2003) and adjusted for internal consistency with the procedure by Schenker et al. (2005). Half-lives for soil, water, and air are from Gouin and Harner (2003); these values were estimated with the estimation programs BIOWIN (biodegradation) and AOPWIN (degradation by OH radicals in the troposphere), which belong to the Estimation Program Interface (EPI) Suite provided by the US EPA, see www.epa.gov/opptintr/exposure/docs/episuite.htm. BIOWIN estimates are typically uncertain by a factor of 5 to 10, which is well covered by our ratio of 100 between 95th and 5th percentile of the half-life distribution.

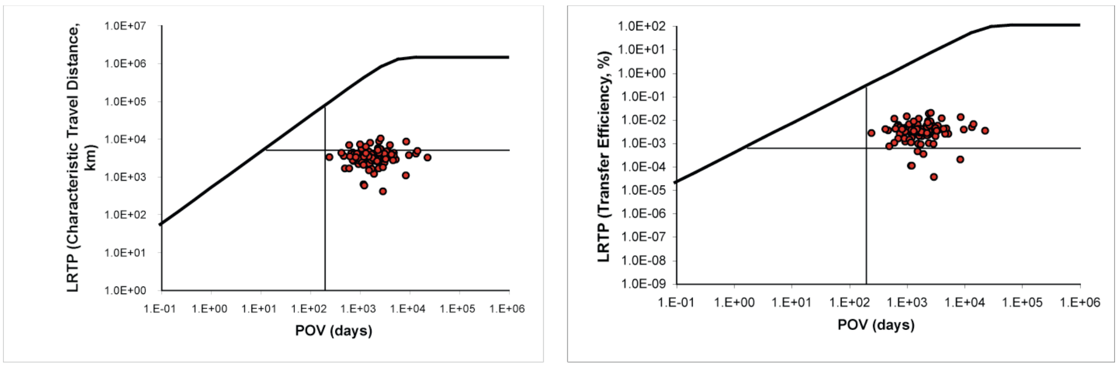


Figure 7: Results from a Monte Carlo calculation for BDE-99.

As for γ-HCH, the Monte Carlo results span a factor of 100 for Pov; CTD and TE are more sensitive to changes in chemical properties than for γ-HCH. However, all Monte-Carlo results for BDE-99 lie in the domain that is typical of POPs as seen in Figures 4 and 5. In other words, even with high uncertainty assumed for the chemical properties of BDE-99, the POP-like Pov and LRTP of BDE-99 remain.

Chlordecone

Measured values of water solubility, vapor pressure, Henry's law constant and octanol-water partition coefficient for chlordecone were obtained with EPI Suite and adjusted for internal consistency with the procedure by Schenker et al. (2005). Half-lives for soil and water were estimated with BioWin; these are generic estimates and are relatively uncertain. The half-life in air represents the very high chemical stability of chlordecone; for such a non-reactive chemical, the dominating atmospheric loss process in the model is transfer to the stratosphere.

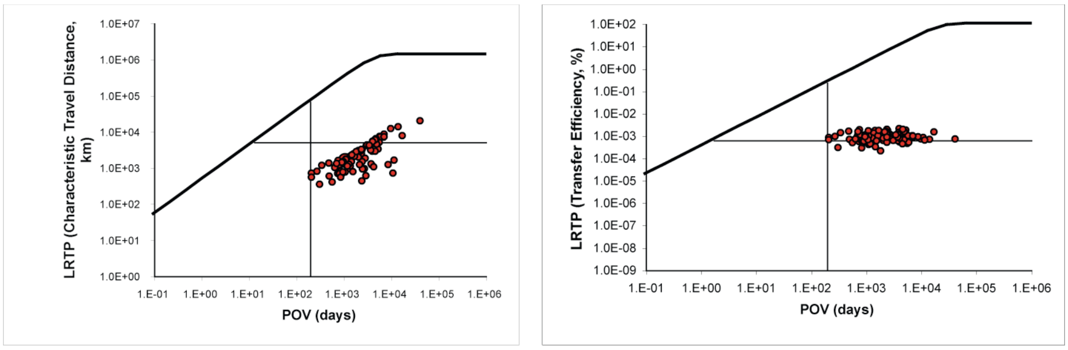


Figure 8: Results from a Monte Carlo calculation for chlordecone.

Chlordecone has a very low Henry's law constant and a high mass fraction is found in water. Accordingly, transport with ocean currents contributes to the long-range transport of chlordecone. This is indicated by the diagonal line that limits the domain in which the 100 Monte-Carlo realization lie in the plot on the left-hand side of Figure 8. This line represents the travel distances caused by transport in water; it shows up in the plot because the half-life in water of chlordecone is varied by a factor of 100 in the Monte-Carlo calculations so that different travel distances in water can be observed. TE does not show this sensitivity since it is a measure of atmospheric transport and deposition. The result that chlordecone has POP-like Pov and LRTP does not change in the light of the uncertainty analysis.

HBB

Measured values of water solubility, vapor pressure, Henry's law constant and octanol-water partition coefficient for HBB were obtained with EPI Suite and adjusted for internal consistency with the procedure by Schenker et al. (2005). Half-lives for soil and water were estimated with BIOWIN; the half-life in air was estimated with AOPWIN.

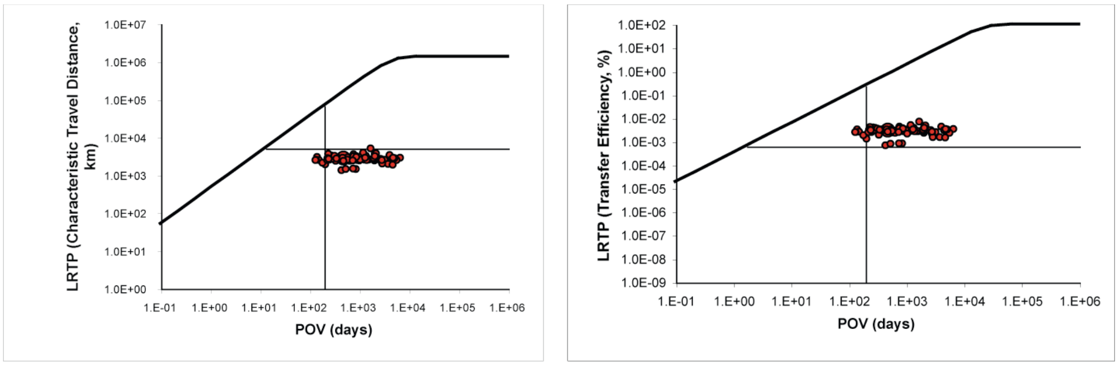


Figure 9: Results from a Monte Carlo calculation for HBB.

Similar to γ-HCH, HBB shows the factor 100 in the Pov results and only a weak sensitivity of the LRTP metrics to changes in chemical properties. Even with half-lives in water and soil clearly lower than the ones from Table 1, the Pov of HBB is not much below the reference line (Pov of α-HCH). The LRTP value remains high.

6 Conclusions

Although there are considerable uncertainties in the chemical properties of the four chemicals under investigation, the results indicate that the four chemicals have Pov and LRTP properties similar to those of several known POPs (PCBs as shown in Figure 4; organochlorine pesticides as shown in Figure 5; six reference chemicals defining the top-right domain limited by the reference lines in all Figures).

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.

Acknowledgement

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