Model Results for Overall Persistence and Potential for Long Range Transport for the UNECE Convention on Long-range Transboundary Air Pollution Protocol on Persistent Organic Substances Candidate Substances

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Summary

We present overall persistence and long-range transport potential calculations from the OECD Pov and LRTP Screening Tool ("The Tool") for five of the 2007 POP candidate substances under the UNECE Convention on Long-range Transboundary Air Pollution Protocol on Persistent Organic Substances. The Pov and LRTP calculations for pentachlorobenzene, short-chain chlorinated paraffins, commercial octabromodiphenyl ether, hexachlorobutadiene and tetrachloronaphthalene are based on physical chemical properties gathered from the literature. This report includes results of a Monte Carlo uncertainty analysis to quantify the uncertainty in the calculated Pov and LRTP from uncertainty ranges for the input properties. We find that the five POP candidates have Pov and LRTP properties similar to those of identified POPs such as PCBs, α-hexachlorocyclohexane and hexachlorobenzene. This case study for the current POP candidates demonstrates the usefulness of The Tool as an instrument for hazard identification of possible future POP candidates under the UNECE LRTAP protocol.

Introduction

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 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). 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 POP candidates evaluated under the Stockholm convention in 2006 and 2007 (Scheringer *et al.*, 2006, Wegmann *et al.*, 2007). 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 five of the 2007 POP candidates that are under consideration by the UNECE Convention on Long-range Transboundary Air Pollution Protocol on Persistent Organic Substances. These are: pentachlorobenzene (PeCB), short-chain chlorinated paraffins (SCCP), commercial octabromodiphenyl ether (cOBDE), hexachlorobutadiene (HxBD) and tetrachloronaphthalene (TeCN), which has been selected to represent the homologous series of polychlorinated naphthalenes.

Model input and results

The Tool requires estimated degradation half-lives for soil, ocean water and air as well as two partition coefficients, the octanol-water partition coefficient (K_{OW}) and the Henry's law constant (K_{AW}), as substance-specific inputs. We compiled these data from handbooks of property data (Mackay *et al.*, 2006) and from a previous report on POP candidates (Wegmann *et al.*, 2007). Median selected property values for the five candidates are shown in Table 1. It is important to note that these chemical property data are uncertain and that this uncertainty influences the results obtained with the Tool (see below).

Table 1: Selected input properties for The Tool software.

Substance	Log K_{AW}	Log K_{OW}	Half-life in air (hours)	Half-life in water (hours)	Half-life in soil (hours)
PeCB	-0.4	5.0	6600	11800	6200
SCCP	-2.4	6.2	89	8800	8800
cOBDE	-2.4	6.3	1800	8800	8800
HxBD	-0.1	4.8	9100	1700	1700
TeCN	-1.3	6.0	5100	6200	6200

Three of the five POP candidates, SCCP, cOBDE and polychlorinated naphthalenes are complex mixtures of many individual chemicals. For cODBE and SCCP 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 reported range of log K_{OW} for SCCP 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. For polychlorinated naphthalenes we have selected property data for one homologue, tetrachlornaphthalene (TeCN) to represent the properties of the mixture.

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).

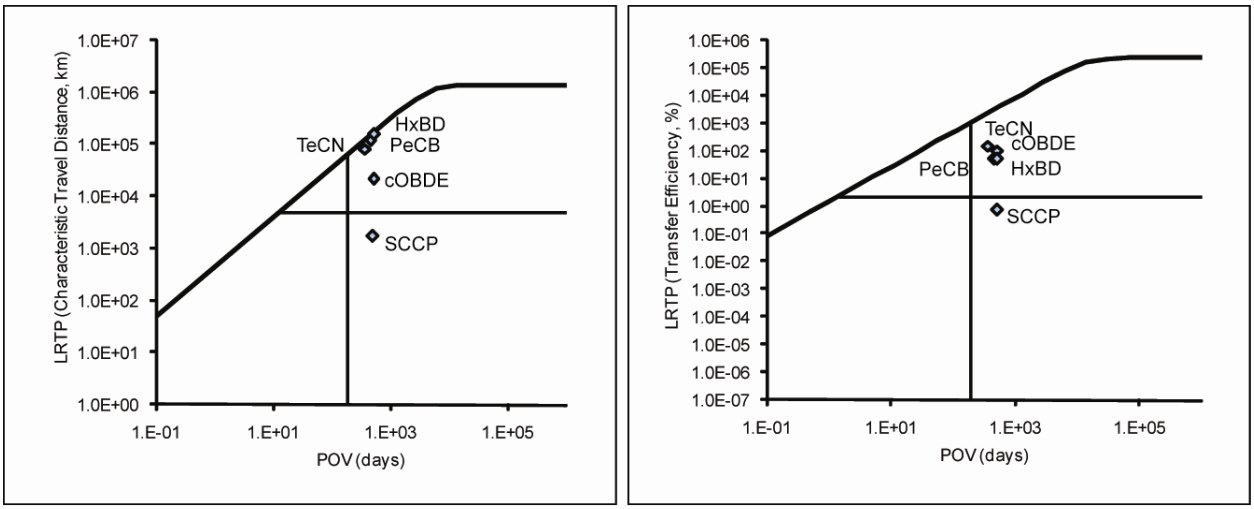

Figure 1: Pov, CTD and TE values calculated with the Tool for the five POP candidates. Left: CTD vs. Pov, right: TE vs. Pov.

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 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. This is also a significant loss process that limits CTD for HxBD and TeCN. 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 revolatilization 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.

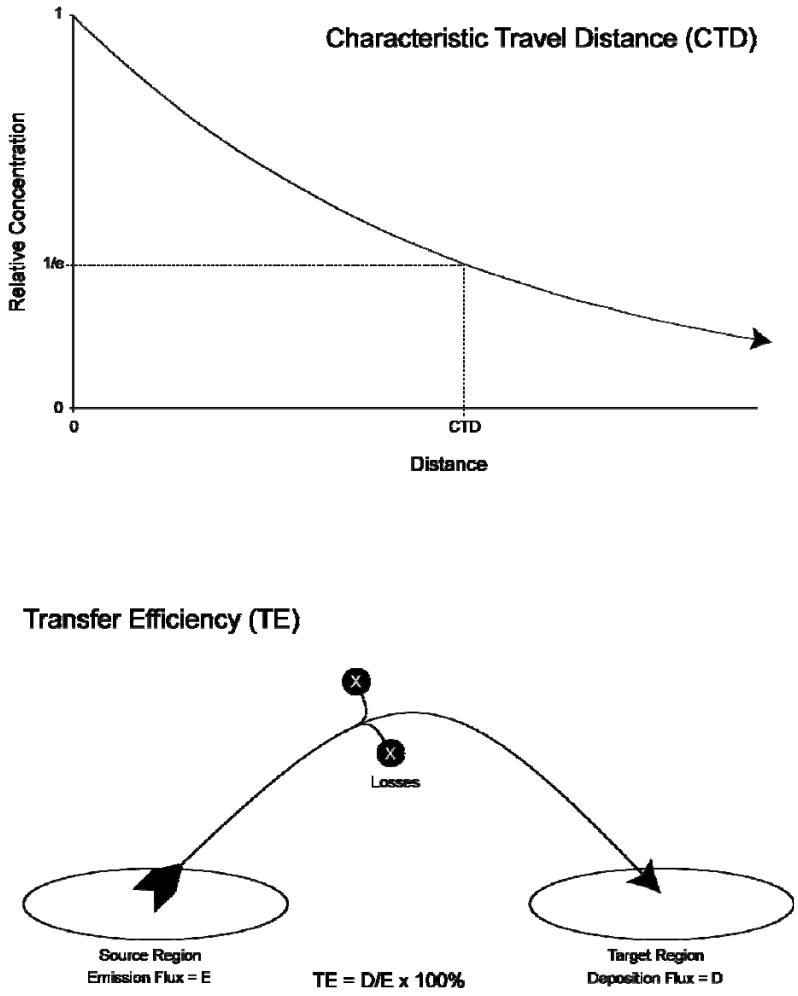

Figure 2: Conceptual illustration of the LRTP metrics CTD and TE.

Results in comparison to identified POPs

The reference lines in the graphs shown in Figure 1 are explained in Figure 3. The reference lines 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.

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.

It should not be concluded that chemicals that 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 bottom panels of Figure 3 (same as Figure 1 above).

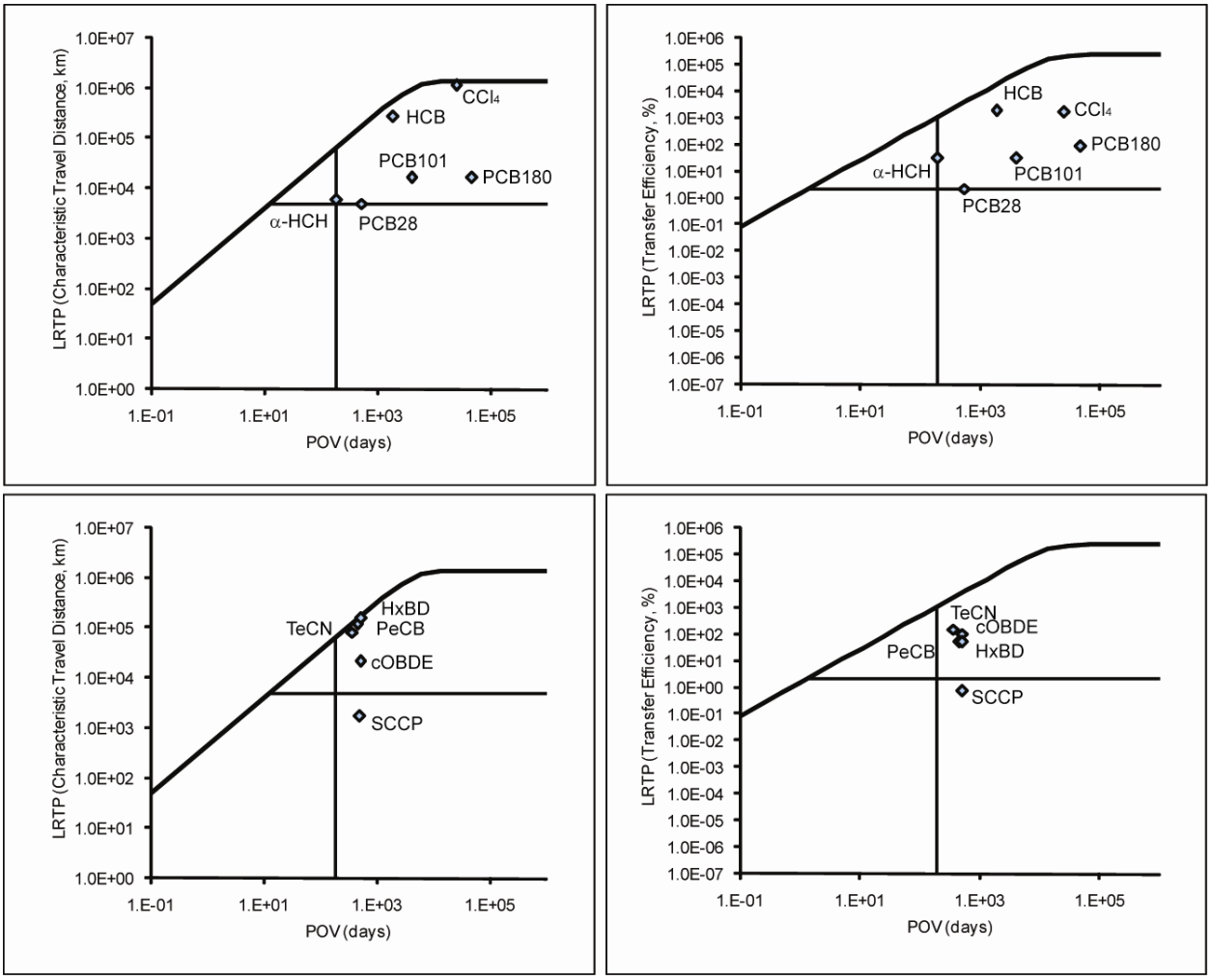

Figure 3 Top Panel: Results from the Tool for six reference compounds with evidence of POP-like behavior in the environment. These results are used to derive the reference lines in the plots. Bottom Panel: Pov and LRTP values of the POP candidate substances.

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". We applied the standard values for the dispersion factors in the evaluation of the POP candidates except for SCCP, where we applied a dispersion factor of 100 for the K_{OW} to account for the wide range of values found in

literature. By using ANOVA techniques, we mapped the observed variances of the results (Pov, CTD, TE) to contributions from the individual input properties. The Monte Carlo results provide information to prioritize efforts to reduce uncertainty in substance properties to achieve the maximum reduction in uncertainty in overall persistence and the long-range transport indicators.

PeCB

The Monte Carlo results for PeCB show a cloud of points that exhibit a very specific, diagonally stretched shape that follows the limiting line in the CTD/Pov plot. PeCB is quite volatile, 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.

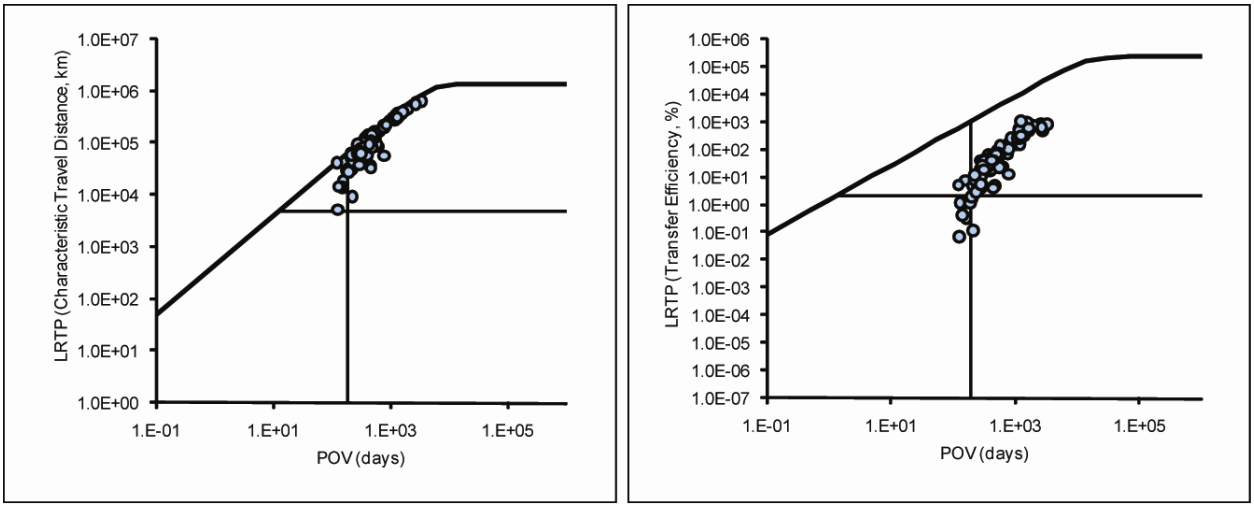

Figure 4: Results for the Monte Carlo analysis for PeCB.

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 literature. The cloud for SCCP has a circular shape. 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 LRTP line derived from the reference chemicals, but is still close to other, acknowledged POPs.

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.

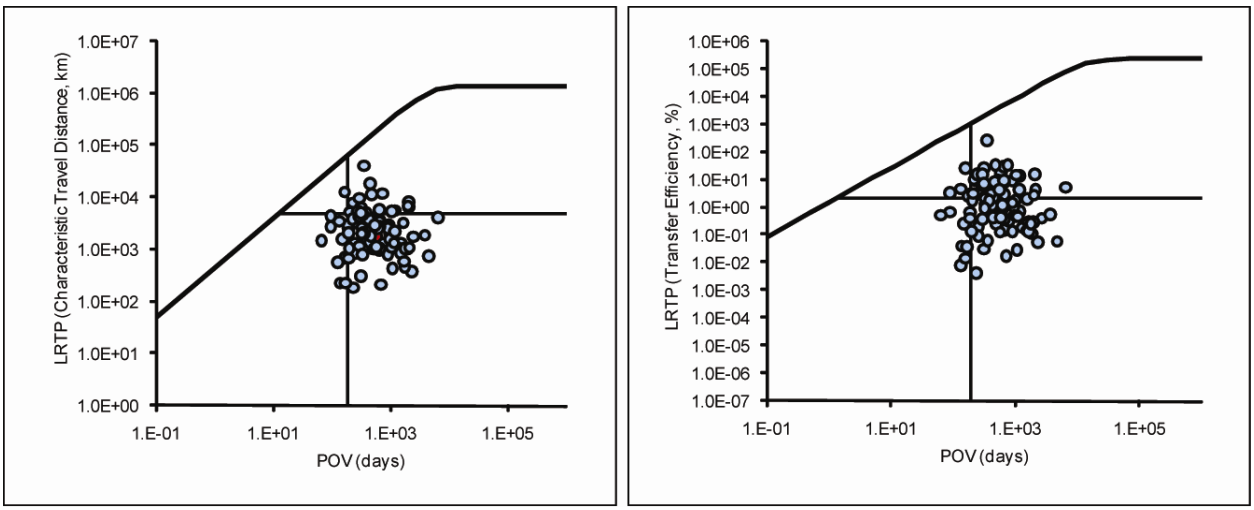

Figure 5: Results for the Monte Carlo analysis of SCCP.

cOBDE

The cloud of Monte Carlo results for commercial octabromodiphenyl ether exhibits a symmetrical shape. The center of the cloud is clearly located in the upper-right quadrant.

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.

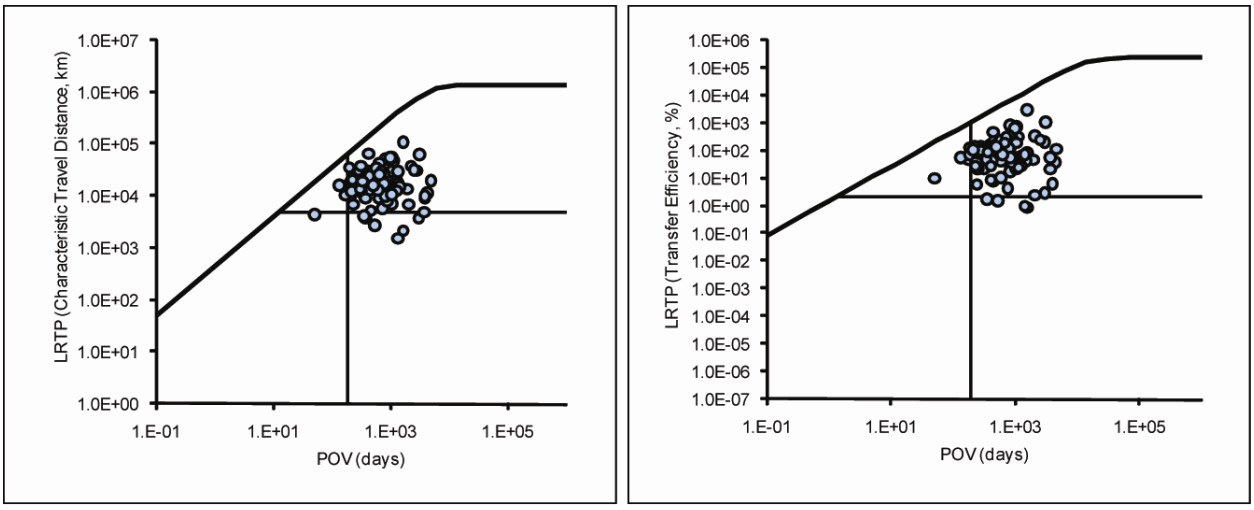

Figure 6: Results for the Monte Carlo analysis of cOBDE.

HxBD

The Monte Carlo results for HxBD show a clear diagonal pattern in both the CTD vs Pov and TE vs Pov plots. This shape arises because of the dominance of half-life in air in determining the overall uncertainty in the transport and persistence of HxBD. This chemical partitions nearly completely to air in the model calculation, and thus fate processes in air determine its behavior. The majority of Monte Carlo combinations result in points falling in the upper-right quadrant of the plots.

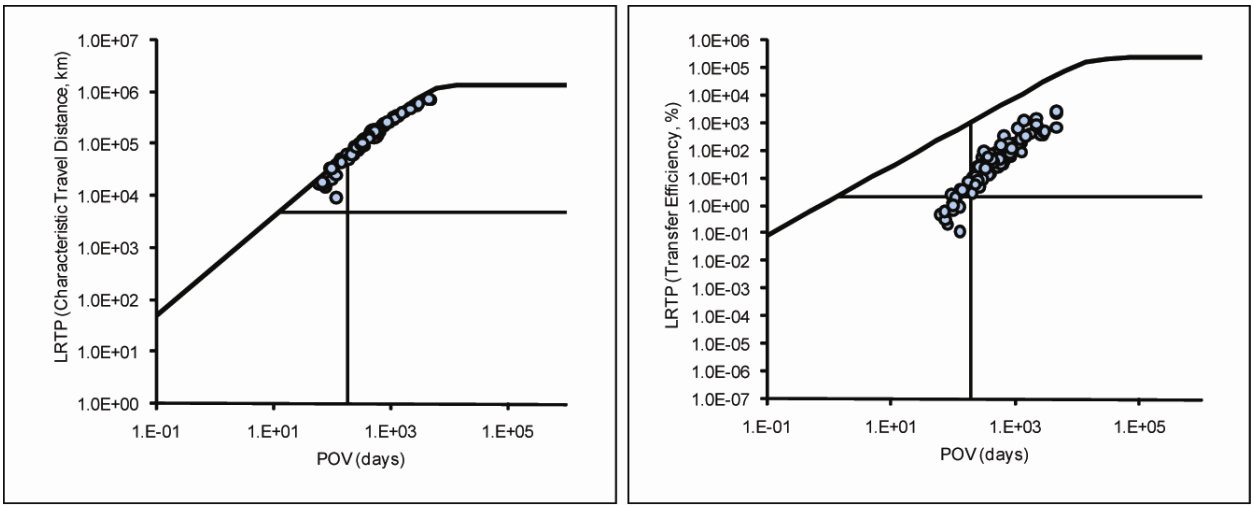

Figure 7: Results of the Monte Carlo analysis for HxBD.

TeCN

The Monte Carlo results for TeCN produce a near-symmetrical distribution of outcomes in both the plots. Uncertainty in half-lives in soil and air contribute approximately equally to output uncertainty in Pov. Uncertainty in CTD is dominated by uncertainty in half-life in air, while uncertainty in TE is 90% attributable to uncertainty in half-life in air and 10% attributable to Log K_{AW}. Virtually all of the Monte Carlo combinations result in points falling in the upper-right quadrant of the plots.

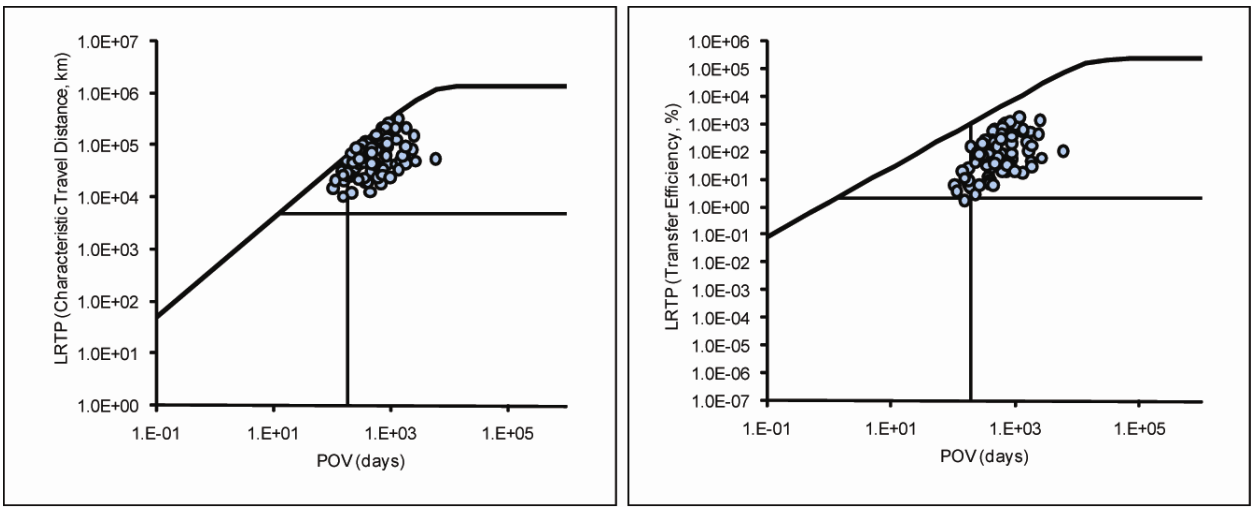

Figure 8: Results of the Monte Carlo analysis for TeCN.

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. Three of the five selected POP candidates have high volatilities and half-lives in air; this makes them excellent candidates for inclusion into the Aarhus long-range transboundary air pollution protocol.

Although there are considerable uncertainties in the chemical properties of the five chemicals under investigation, the results indicate that all of the POP candidates have Pov and LRTP properties similar to those of known POPs. We believe this case study for the current POP candidates demonstrates the usefulness of The Tool as an instrument for hazard identification of possible future POP candidates under the UNECE LRTAP protocol.

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