Processes Affecting the Long-Range Transport Potential of Selected Brominated Flame Retardants

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Introduction

Multimedia fate and transport models are useful tools to describe organic chemical behavior in the environment, in particular the exchange between the atmosphere and the underlying terrestrial and aquatic surfaces. This makes them suitable for use in the assessment of the potential for long-range atmospheric transport (LRTP)[1]. Most existing model-based approaches to LRTP assessment assume environmental conditions to be constant in time, even though many factors impacting on the atmospheric residence time of organic chemicals (e.g. temperature, precipitation, OH radical concentrations) are known to vary considerably over a variety of time scales (e.g. diurnal, seasonal, interannual).

The key objectives of this ongoing study are:

1) to evaluate the seasonality of the Characteristic Travel Distance (L_A) for selected brominated flame retardants (PBDE-28, PBDE-47 and PBDE-99)
2) to assess the controlling processes affecting L_A
3) to evaluate the impact of intermittent precipitation on L_A

Materials and methods

A useful and relatively simple measure of chemical mobility in the environment is the Characteristic Travel Distance (L_A), which is defined as the distance for which the initial concentration of a chemical is reduced to 1/e (~37%) in a plug-flow system1. In this study, L_A after ten years of steady emissions was calculated as:

$$L_A = u \cdot M_A / [N_{RA} + \Sigma(N_{ASnet})]$$

where u is the wind speed of air (m h^{-1}), M_A is the amount of chemical in the atmosphere (mol), N_{RA} is the rate of atmospheric reaction (mol h^{-1}) and $\Sigma(N_{ASnet})$ is the net atmospheric deposition to various environmental surface compartments in contact with the atmosphere (mol h^{-1}). The equation highlights that it is the relative importance of the competing processes of atmospheric reaction and net deposition that controls L_A at any point of time. Because some chemicals may have a significant potential for reversible atmospheric deposition, situations of net volatilization may occur [$N_{ASnet} < 0$]. Under such circumstances, we propose that the expression for L_A should be reduced to $L_A = u \cdot M_A / N_{RA}$.

We used a non-steady state multimedia fate and transport model (CoZMo-POP1)[2] which has recently been modified to take into account snow scavenging, a seasonal snow pack and a dynamic water balance[3-4]. Additionally, the model includes eight different environmental compartments (atmosphere, forest, forest soil, agricultural soil, fresh water and underlying sediment, sea water and marine sediment). For this particular work, the model was parameterized for the Baltic Sea drainage basin as a whole in order to evaluate L_A for a spatially explicit area. The impact of seasonally changing temperatures on partitioning and degradation is accounted for through the use of activation energies (reaction) and internal energies of phase transfer (partitioning). Different seasonal trends in temperatures are individually described for the atmosphere, the terrestrial environment and the marine environment. The model also considers seasonal trends in OH-radical concentrations as well as wind speed over the surface that is used to calculate mass transfer coefficients for air-water exchange. A long-term averaged atmospheric advection rate for the Baltic region as a whole of 42 hours was derived from an atmospheric transport model[5], and the wind speed, u, used to estimate L_A was calculated assuming a cylindrically shaped region. L_A was furthermore calculated after ten years of prolonged continuous emissions to avoid the unrealistic assumption of a "clean" environment with zero fugacities. The simulations were carried out for three polybrominated diphenyl ethers (BDE-28, BDE-47 and BDE-99). Data on physical-chemical properties were taken from the literature[6], Abraham solute descriptors were calculated using QSAR Builder, whereas environmental half-lives were estimated using the EPIWIN software.

Results and Discussion

Default scenario

The default model scenario assumes a constant drizzle or flurries throughout the year (1.56 mm day^{-1}), adding up to the measured long-term annual average precipitation rate of 570 mm year^{-1}. The overall results are shown in *Figure 1* for PBDE-28 and PBDE-99.

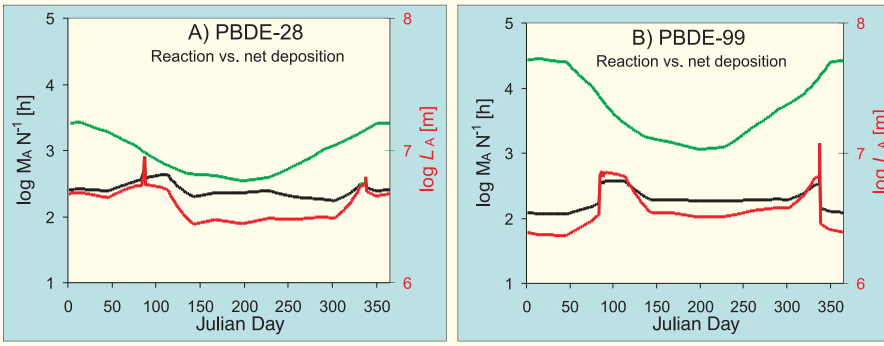

Fig. 1 *Estimated L_A (red line, 2nd y-axis) for BDE-28 (A) and BDE-99 (B) under the assumption of constant drizzle/flurries. The figures also illustrate the relative significance of atmospheric reaction (green line, 1st y-axis) versus net atmospheric deposition (black line, 1st y-axis). The results on the 1st y-axis are expressed as amount in air (M_A in mol), divided by the process rate (N in mol h^{-1}). A low value thus expresses a fast and significant process in reducing L_A.*

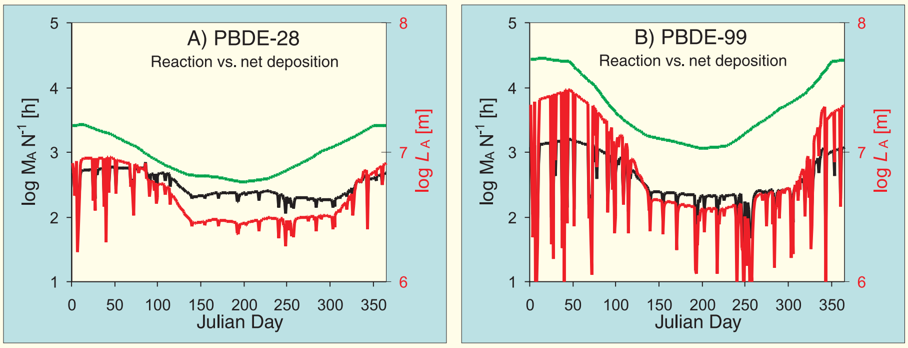

Fig. 2 *Estimated L_A (red line, 2nd y-axis) for PBDE-28 (A) and PBDE-99 (B) under the scenario of intermittent precipitation and snow.*

- The annual average L_A was estimated to be fairly similar: 3900 km (BDE-28), 3100 km (BDE-47) and 3800 km (BDE-99). Similarities in atmospheric transport efficiencies have been suggested for the lighter to the intermediate PBDE congeners based on soil data along a U.K. – Norwegian transect[7].
- L_A is primarily controlled by net atmospheric deposition (and not atmospheric reaction) throughout the year for all congeners studied (*Fig. 1*).
- Congeners that are significantly sorbed to atmospheric particles at lower temperatures (BDE-47 and 99) may be strongly affected by snow scavenging during winter, causing a notable reduction in L_A.
- BDE-28 may volatilize from the melting snowpack during spring, causing a short term peak in L_A.
- Enhanced deposition velocities to the forest compartment tend to reduce L_A for the selected PBDEs during summer.

Intermittent precipitation

In the model scenario above, precipitation occurs continuously rather than intermittently. Although this is a typical assumption in most multimedia fate models, its validity has been questioned[8]. The effect of intermittent precipitation on L_A is therefore explored in more detail in the following, using daily observations from a meteorological station in the model region which were scaled to yield an annual average precipitation rate identical to the default scenario. The overall results are shown in *Figure 2*.

- The annual average L_A increases when comparing the intermittent precipitation scenario with the default scenario (PBDE-28 120%, PBDE-47 171%, PBDE-99 255%).
- The increase in annual average L_A under the intermittent scenario from PBDE-28 to PBDE-99 reflects the increasing affinity for atmospheric particles.
- The assumption of constant flurries may significantly underestimate periods of elevated long-range transport that may occur under dry atmospheric conditions during wintertime (*Fig. 1B, 2B*).

Conclusions

Temporally variable environmental conditions may significantly affect estimates of L_A for PBDEs. In particular, dry atmospheric conditions may cause episodes of elevated atmospheric long-range transport, which may not be recognized under the typical assumption of steady-state environmental conditions. Future work may include additional brominated flame retardants, as well as further studies on the impact of temporal variability of other environmental variables (e.g. wind speed, temperature, snow cover).

Acknowledgements

Financial support from the Long-Range Research Initiative of the European Chemical Industry Association (CEFIC) as well as the Norwegian Research Council (NewPoll initiative) is highly appreciated. We are grateful to Dr. Eldbjørg Heimstad for estimating the Abraham descriptors used in this study.

References

(1) Beyer, A.; Mackay, D.; Matthies, M.; Wania, F.; Webster, E. Environ. Sci. Technol. **2000**, 34, 699-703.
(2) Wania, F.; Persson, J.; Di Guardo, A.; McLachlan, M.S. CoZMo-POP. A fugacity-based multi-compartmental mass balance model of the fate of persistent organic pollutants in the coastal zone. WECC Report 1/**2000**; Toronto, Canada; 26pp; *www.utsc.utoronto.ca/~wania*
(3) Daly, G.L.; Wania, F.; Simulating the Influence of Snow on the Fate of Organic Compounds. Environ. Sci. Technol. Accepted.
(4) Daly, G.L.; Gouin, T.; Lei, Y.D.; Wania, F.; Harner, T.; Mackay, D.; The role of snow in the environmental fate of PBDEs. Poster BFR **2004**.
(5) Jesper Christensen, National Environmental Research Institute, Roskilde, Denmark.
(6) Wania, F.; Dugani, C.B.; Environ. Toxicol. Chem. **2003**, 22, 1252-1261.
(7) Hassanin, A.; Breivik, K.; Meijer, S.N.; Steinnes, E.; Thomas, G.O.; Jones, K.C.; Environ. Sci. Technol. **2004**, 38, 738-745.
(8) Hertwich, E.G. Environ. Sci. Technol. **2001**, 35, 936-940.