Seasonality of the Characteristic Travel Distance

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Abstract

The seasonality of the Characteristic Travel Distance (L_A) for various chemicals has been studied, using a non-steady state multimedia fate and transport model resembling the environmental conditions of the Baltic Sea drainage basin.

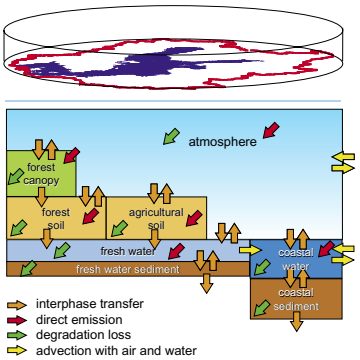

Figure 1. Projection of the Baltic Sea drainage basin (upper part) and environmental compartments and bulk processes considered in the model predictions (lower part). Advective inflow of chemical into the model domain is assumed to be zero in these model simulations.

Introduction

Multimedia fate and transport models are useful tools to describe the concerted action of organic chemical behavior in the atmosphere as well as interaction processes of the chemical between the atmosphere and underlying terrestrial and aquatic surface compartments. This makes them suitable for use in the assessment of the potential for long-range atmospheric transport (LRTP) (*1-3*). 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 have been:

1) to evaluate the seasonality of the Characteristic Travel Distance (L_A)
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 over which the initial concentration of a chemical is reduced to 1/e (~37%) in a plug-flow system (*1-3*). 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 (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 of interest 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 the CoZMo-POP1 model (Fig. 1), which was originally developed with the aim to describe the long-term fate of persistent organic pollutants (POPs) in a coastal area (*4*). CoZMo-POP1 is a non-spatially resolved dynamic non-equilibrium model with 8 well-mixed compartments, representing the atmosphere (A), the terrestrial environment (forest canopy, forest soil, agricultural soil) as well as the aquatic environment (fresh water, sea water), each with a sediment compartment below. Chemical fate processes in CoZMo-POP1 include: equilibrium phase partitioning between sub-compartments, advective and diffusive transport between compartments, first order degradation in each compartment (*second order in atmosphere between vapor phase chemical and OH radical*), and sediment burial. CoZMo-POP1 has recently been modified to take into account snow scavenging, a seasonal snow pack (N) and a dynamic water balance (*5*) (Fig. 2). For this particular work, this modified 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) in the model. Different seasonal trends in temperatures are individually described for the atmosphere, the terrestrial environment and the marine environment. CoZMo-POP1 also considers seasonal trends in wind speed over the surface, which are used to calculate mass transfer coefficients for air-water exchange. For a complete description of CoZMo-POP1 we refer to Wania et al. (*4*) and Daly and Wania (*5*). The seasonal fluctuation in atmospheric hydroxyl radical concentrations (C_{OH}) over the model domain was derived, based on information originally presented by Rodriguez et al (*6*). A long-term averaged atmospheric advection rate for the Baltic region as a whole of 42 hours was derived from an atmospheric transport model (*7*), and the wind speed, u, used to estimate L_A was calculated assuming a cylindrically shaped region (Fig. 1). We should note that certain persistent and volatile chemicals may exhibit a significant propensity for re-volatilization. Therefore, L_A was only 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 a test set of 14 different chemical compounds, including five polychlorinated biphenyls (PCBs), one polybrominated diphenyl ether (PBDE-47), five polyaromatic hydrocarbons (PAHs), two hexchlorocyclohexanes (α- and γ-HCH) as well as Atrazine. Common to the physical-chemical properties selected in this study, is that the original references report thermodynamically consistent properties for the compounds considered.

Results and Discussion

Seasonal variation and process controlling L_A

The default model scenario assumes a typical 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 3A.

- Maximum annual average L_A is estimated for PCB-101 (1.6*10^{7}m) while minimum annual average L_A is estimated for anthracene (1.1*10^5).
- L_A is mainly limited by atmospheric reaction for the lighter PAHs (anthracene, phenanthrene, pyrene), and the seasonal variability of L_A mirrors the seasonal variability of OH-radical concentrations for such compounds.
- L_A is mainly controlled by net atmospheric deposition for PCB-153, PCB-180, PBDE-47, atrazine, HCHs) throughout the year and not atmospheric reaction.
- For other chemicals, the relative importance of atmospheric reaction and net atmospheric deposition is dependent on the time of year.
- Chemicals that are significantly sorbed to atmospheric particles at lower temperatures (benzo[*a*]pyrene, PBDE-47) may be strongly affected by snow scavenging during winter, causing a notable reduction in L_A.
- More polar and water soluble-chemicals, such as atrazine, may experience enhanced L_A during winter, because rain may be a more efficient scavenger than snow for such substances.

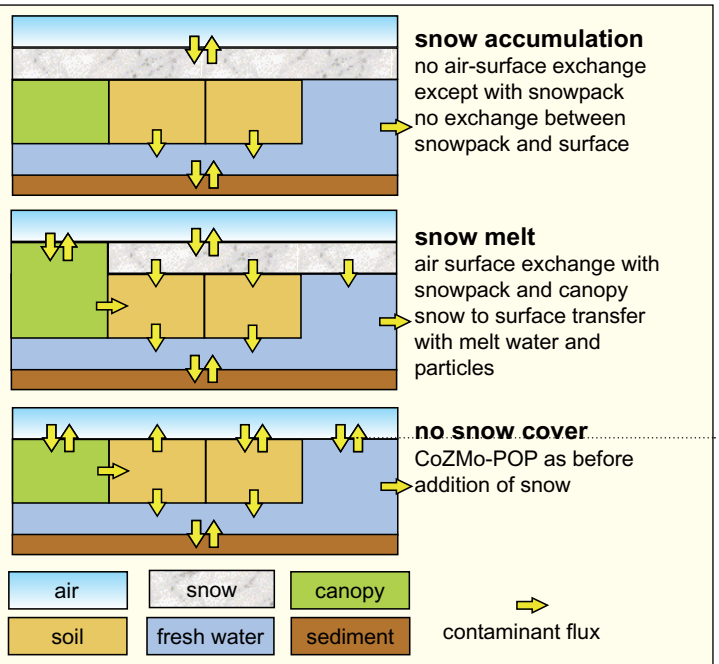

Figure 2. The revised CoZMo-POP model used herein includes a seasonally dependent description of contaminant transfer processes (from 5); snow accumulation season (T<0 ºC), snowmelt season (T>0 ºC) and summer season (T>0 ºC after snow has disappeared).

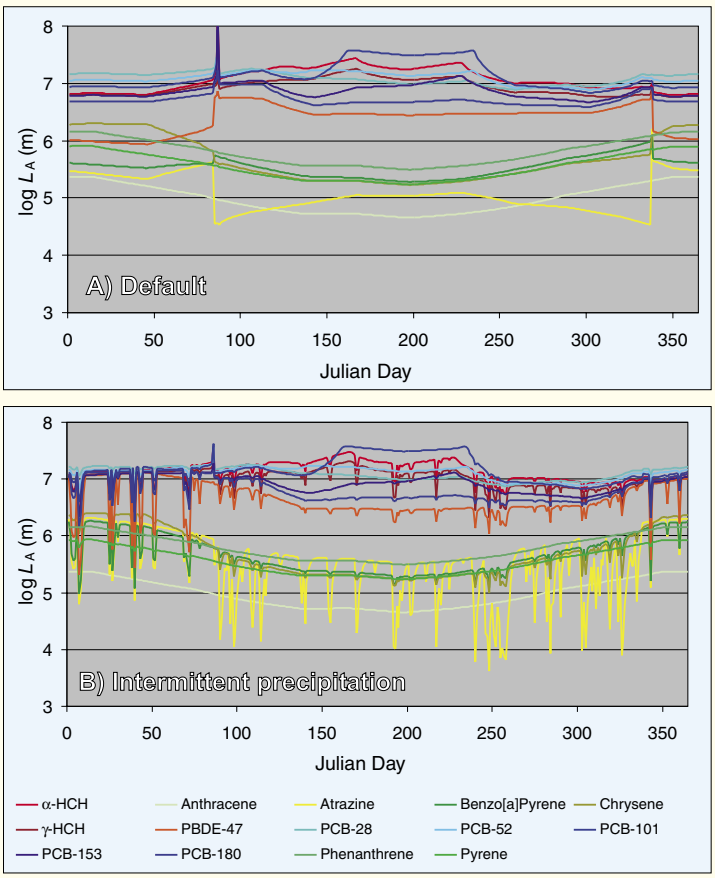

Figure 3. Calculated seasonal variation of L_A in air; log (L_A) in meters under default conditions (A) and intermittent precipitation (B).

- Certain chemicals may volatilize from the melting snowpack during spring, causing a peak in L_A (lighter PCBs, α-HCH).
- Enhanced deposition velocities to the forest compartment reduce L_A for heavier PCBs and PBDE-47 during summer.

Intermittent precipitation

In the model calculations above, a constant drizzle is assumed which is a typical assumption within most multimedia fate models that has been questioned (*8*). It has also more recently been pointed out that when evaluating the atmospheric long-range transport potential of fairly water-soluble substances (i.e. some currently used pesticides), it is imperative to account for periods of no precipitation (*9*). 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 3B.

- The annual average L_A is either virtually identical or increases when comparing the intermittent precipitation scenario with the default scenario.
- An increase in annual average L_A is suggested for water-soluble chemicals (Atrazine 410%, γ-HCH 118%) as dry atmospheric conditions may cause periods of elevated L_A.
- Chemicals that are significantly associated with atmospheric particles may also be more effectively transported when intermittent precipitation is taken into account (PBDE-47 187%, benzo[*a*]pyrene 169%, PCB-180 136%).
- Insignificant changes in annual average L_A are observed for the more volatile chemicals that are controlled by atmospheric reaction (anthracene, phenanthrene).

Conclusions

Temporally variable environmental conditions may significantly affect estimates of L_A for certain chemicals. In particular, dry atmospheric conditions may cause episodes of elevated L_A, which may not be recognized under the typical assumption of steady-state environmental conditions. Further work may include additional chemicals 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.

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