LONG-RANGE TRANSPORT POTENTIAL OF PCB AND PCDD/F AND THEIR CLASSIFICATION

Michael Matthies, Andreas Beyer and Donald Mackay*

Institute of Environmental Systems Research, University of Osnabrück, D-49069 Osnabrück, Germany
* Environmental Modelling Centre, Trent University, Peterborough, Ontario, Canada

Introduction

Polychlorinated-p-dibenzodioxins and -furans (PCDD/Fs) and polychlorinated biphenyls (PCBs) are among the substances which were identified as Persistent Organic Pollutants (POP) and are the subject of internationally harmonized regulation. POPs have a combination of physico- and bio-chemical properties which favor the long-range transport (LRT) from the point or area of emission to remote areas, e.g. the marine environment or the Arctic. The UNEP Criteria Expert Group (UNEP, 1999) stated that the potential for long-range transport should be used as a criterion for identifying additional POPs as candidates for future international action. However, the long-range transport potential (LRTP) of a substance is not easy to assess, which is mainly due to complex interactions and transformations during their transport in air and water. It is widely accepted that – except for local assessments – a multimedia mass balance approach is the best available method to evaluate the fate, transport, persistence and exposure of most organic chemicals (Cowan et al., 1995; Trapp and Matthies, 1998). European chemical legislation recommends the use of a standard multimedia environment to calculate the regional background concentrations in air, soil, fresh water and sediment (EC 1996A).
Bennett et al. (1998) introduced the concept of the characteristic travel distance (CTD), which is defined as the distance within which the initial mass of an airborne chemical is reduced to 37% (=1/e) in a multimedia environment under steady-state conditions. Beyer et al. (1999) generalized the approach and proposed distances by which a substance is classified by its potential (susceptibility) to be transported out of its emission region. This paper applies the approach to the two classes of PCBs and PCDD/Fs in order to classify them according to their LRT potential.

Material and Methods: Model and Data

The EQC model was modified to account for the advective flow in air and water (Beyer et al., 1999). The EQC model is a generic multimedia fugacity model with a standard environmental default data set representing moderate climate zones (Mackay et al., 1996). In an open system with air as the moving phase and soil and water as the stagnant but reactive phases, the decrease of an initial concentration in air with the distance x from the source under steady state conditions is

$$C_A(x) = C_A(0) \exp(x/L_A)$$

The characteristic travel distance L_A in air can be deduced as (Beyer et al., 1999)

$$L_A = u \frac{M_A}{N_{AR} + N_{AE} \cdot F_E},$$

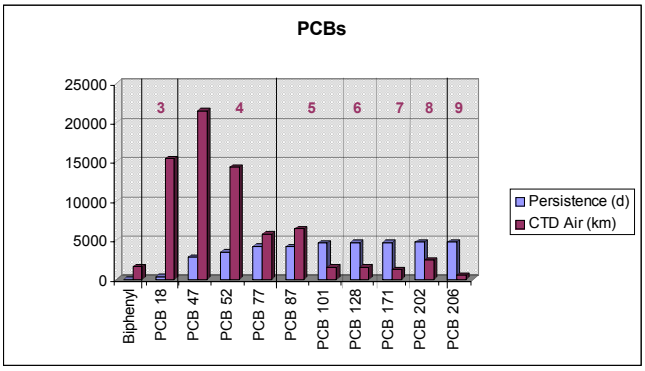
where
- u = wind velocity [m/s]
- M_A = steady-state mass in air [mol]
- N_{AR} = reactive loss flow in air [mol/s]
- N_{AE} = net mass exchange flow from air to soil and water [mol/s]
- F_E = effective degradation in air and soil ("stickiness")

L_A has the same meaning in terms of distance as the overall residence time in terms of time. Webster et al. (1998) used the overall residence time τ_{ov} calculated with the EQC model (Mackay et al., 1996) as a measure for persistence in a closed multimedia environmental system. With the modified EQC model both L_A and τ_{ov} can simultaneously be determined. All substance data required to run the model were taken from (Mackay et al., 1991-1997). The atmospheric mixing height is 1000 m and the wind velocity is 4 m/s. All other environmental data are defaults of the EQC model. Input was assumed to be into air, since transport in air is assumed to be the major process for long-range transport.

Results and Discussion

PCBs: Fig. 1 shows the characteristic travel distance L_A for biphenyl and PCB isomers, together with the overall residence time τ_{ov}. Obviously, there is no simple relationship between τ_{ov} and L_A. Persistence increases with the degree of chlorination with only minor differences within isomer classes, e.g. the penta-PCBs. However, the maximum characteristic travel distance occurs with the tetra-PCBs. Biphenyl and the higher chlorinated isomers have similar short distances L_A, which is

Fig. 1 Characteristic Travel Distance (CTD) L_A in air and overall residence time τ_{ov} of biphenyl and PCB isomers calculated with the modified EQC model; digits indicatedegreeofchlorination



due to the fast degradation of biphenyl and the deposition of the particle-bound hexa- to nona-PCBs. The low chlorinated tri- and tetra-PCBs are the most mobile isomers because they have long half-lives in all media, relative high air-water partition coefficients and are mainly in the gaseous state in air. PCB 47 has the longest travel distances of up to more than 20 000 km. Such long travel distances are artificial (half of the circumference of the earth). They only indicate the tendency (potential) of a substance to travel over such a distance if all parameters and boundary conditions are kept constant. They must never be taken as real distances, and should only be used for comparison and classification purposes. It is quite interesting that various monitoring studies conform with this ranking and classification. Ockenden et al. (1998) measured concentrations of various PCBs across a latitudinal transect from 50 N to 70 N. They found that concentrations of tetra-CBs were fairly constant over the study area, whereas those of higher chlorinated homologues (penta-, hexa-, hepta-) decreased with higher latitude. On the other hand, the relative proportion of tetra-CB of the total PCBs increased with latitude, while the proportions of hexa- and hepta-chlorinated PCBs decreased. These findings are supported by the model results.

PCDD/Fs: The long-range transport behavior of PCDD/Fs is less complex than that of PCBs, because they cover a smaller range of physico-chemical properties. 2,3,7,8 TCDF has the lowest persistence, i.e. the overall residence time is 1340 days, and the longest travel distance of about 900 km. The higher chlorinated congeners have a lower L_A because they are mostly sorbed to aerosols. The travel distance is dominated by the degree of sorption to particles, which determines the deposition as well as the atmospheric degradation rate constant. (The particle-bound fraction is not decomposed by OH radicals.) The small differences between the hexa-, hepta- and octachlorinated congeners neither influence their travel distance nor persistence.
Classification: The PCBs and PCDD/Fs are ranked according to their travel distances in air, L_A. Beyer et al. (1999) proposed three classes. Tab. 1 classifies the PCDD/F and PCBs into the proposed scheme.

Tab.1 Classification of PCBs and PCDD/Fs according to their characteristic travel distance in air

Substance	τ_{ov} (d)	L_A (km)
PCB 47	2808	21533
PCB 18	340	15406
PCB 52	3463	14308
PCB 87	4175	6456
PCB 77	4235	5801
PCB 202	4745	2441
Biphenyl	5	1605
PCB 101	4617	1585
PCB 128	4720	1569
PCB 171	4728	1275
2,3,7,8-TCDF	1340	932
2,3,7,8-TCDD	1374	754
PCB 206	4758	520
1,2,3,4,7-PeCDD	1573	479
1,2,3,4,7,8-HxCDD	4542	471
1,2,3,4,6,7,8 HpCDF	1683	468
1,2,3,4,6,7,8-HpCDD	4543	467
OCDD	4600	467
OCDF	4600	467

- *Class 1* contains chemicals which have L_A below 700 km, and which are of no global concern. They are typically „local“ compounds which do not tend to be distributed over large areas, e.g. most of the PCDD/F.
- *Class 2* chemicals are those with a regional range transport potential, which is of particular importance for Europe. These chemicals can reach marine environments like the North and the Baltic Sea, e.g. penta-PCB and tetra-PCDD/F, depending on the location and strength of the source.
- *Class 3* chemicals have a global range transport potential, i.e. they can be subject to interhemispheric and meridional transport, e.g. tri- to tetra-PCB.

It should be noted that a similar concept can be applied to long-range transport in water (Beyer et al., 1999). The concept of the characteristic travel distance has some advantages which favors its application for regulatory purposes:

- It relates the spatial range to the source region and is independent of the emitted quantity.
- It can be calculated using well established multimedia mass balance models, e.g. EQC (Beyer et al., 1999), EUSES (EC 1996B) or Caltox (Bennett et al., 1998), which simultaneously estimate persistence.
- It is a one-dimensional quantity, which ideally provides an ranking and classification scale.
- It reflects the observations made on the long-range transport of POPs with monitoring studies.

References

1. Bennett, D.H.; McKone, T.E.; Matthies, M.; Kastenberg, W.E. *Environ. Sci. Technol.* **1998**, 32, 4023-4030.
2. Beyer, A.; Mackay, D.; Matthies, M.,; Wania, F.; Webster, E. *Environ. Sci. Technol. (submitted)* **1999**.
3. Cowan; C.; Mackay, D.; Feijtel, T.; van de Meent, D.; di Guardo, A.; Davies, J.,; Mackay, N. *The Multi-Media Fate Model: A vital tool for predicting the fate of chemicals*. SETAC Press, Pensacola, **1995**.
4. EC 1996A: Technical Guidance Document in Support of the Commission Directive 93/67/EEC on Risk Assessment for New Notified Substances and the Commission Regulation (EC) 1488/94 on Risk Assessment for Existing Substances, Parts I-IV. Luxembourg, **1996**.
5. EC 1996B: EUSES - the European Union System for the Evaluation of Substances. Institute of Public Health and the Environment (RIVM), The Netherlands. European Chemicals Bureau, Ispra, **1996**.
6. Mackay, D.; Di Guardo, A.; Patterson, S.; Cowan, C.E. *Environ. Toxicol. Chem.* **1996**, 15, 1627-1637.
7. Mackay, D.; Shiu, W.Y.; Ma, K.C. *Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals – Vol. I to V*; Lewis Publ. **1991–1997**.
8. Ockenden, W.A.; Sweetman, A.J.; Prest, H.F.; Steinnes, E.; Jones, K.C. *Environ. Sci. Technol.* **1998**, 32, 2795-2803.
9. Trapp, S.; Matthies, M. *Chemodynamics and Environmental Modelling.* Springer, Heidelberg, **1998**.
10. UNEP *"Report of the First Session of the Criteria Expert Group for Persistent Organic Pollutants.* Bangkok 26-30 October **1998**. Document UNEP/POPS/INC/CEG/1/2.
11. Webster, E.; Mackay, D.; Wania, F. *Environ. Toxicol. Chem.* **1998**, 17, 2148-2158.