

Summary of Session „Physical-chemical properties, distribution and modelling”

The title of the session combines three topics, which contribute to the description and assessment of environmental behaviour and fate. The three themes cover a broad spectrum of subtopics ranging from laboratory experiments to environmental process studies and georeferenced transport modelling. A total of 21 papers have been submitted of which 8 belong to physical-chemical properties, 8 to environmental distribution and 5 to environmental modelling. The number of oral presentations has been restricted to 8; thus 13 papers remain for poster presentation. Two papers have to be shifted from oral to poster presentations. All others have been indicated as poster or no preference. Papers are generally well written and present interesting results. However, some of them require major corrections. Three of the oral presentations have been rated “accepted”, two “accepted with minor changes” and three “accepted with moderate changes.” Five of the posters were “accepted”, the rest “accepted with changes”.

(1) Physical-chemical properties

Short papers deal mostly with PCB and PCDD/F, but properties of other compound classes (PBDE, polychlorinated dibenzothiophenes (PCDT), chloronaphthalenes and trans-polychlorinated azobenzenes) are also reported. Experimental as well as computational methods have been applied. Partition coefficients K_{oc} , K_{ow} , K_{aw} as well as vapor pressure and water solubility are reported.

(2) Environmental distribution

Transformation, fate and bioaccumulation in aquatic systems (lakes, sediments, fish, mussel) are the main environmental processes investigated. Three papers present results on terrestrial systems (different soil types, garden allotments, pasture-cow-milk pathway). PCB and PCDD/F dominate the investigations with two interesting exceptions (chloroboranes and chlorophenols).

(3) Environmental modelling

Five papers present developments and applications of multimedia fate models. They are used to elucidate the sources of PCBs in the Lake Baikal region, to identify the influence of

partition coefficients on the fate of important substance classes, and to screen chemicals on the potential for cold condensation in remote areas. One paper shows the transport of several persistent chemicals in a georeferenced model system of Japan. One paper reports on a dynamic model of the Tokyo Bay. Again PCBs, PCDD/F and general POPs are the focus of the papers.

***** Oral presentations *****

537 Evenset

Recommendation: oral presentation

Abstract: accepted

Specific Comments:

1. Results and Discussion: The statement "The results indicate that the food chain in Ellasjoen has been shifted upwards" is unclear and should be rephrased.
2. POPs results: The statement "The most persistent contaminants are less prone to long-range transport etc." is not supported by the findings. What are criteria for persistence and long-range transport by which the chemicals are characterized? The authors should refer as specifically as possible to the chemicals they want to mention and refrain from making too general and unspecific statements.
3. last page: "In Oyangen, the composition of POPs in the whole lake system seemed to reflect atmospheric deposition as a contaminant source." This statement brings up a new point since atmospheric deposition has not been discussed before (it is mentioned only very briefly in the introduction). Atmospheric deposition should be introduced earlier as an important alternative pathway.

114 Sofiev

Recommendation: oral presentation

Abstract: accepted

Specific Comments:

1. Units of concentrations for water, land total and air are missing in Fig 3
2. Delete section Summary (repetition). Instead present further options to explain the observed PCB levels.
3. The list of the source types should be sorted according to the analysis in the text, i.e. in the order of 1,3,2,4. Options 2 and 4 should be addressed by some more comments in the summary section. What are the next steps and how will the hypothesis be tested? What can one expect? As it is now, the end of the abstract is somewhat "disappointing".
4. Analysis of the second option: "After some 20 years, the trend is well inside the measurement uncertainty." This is not shown in the figure; it is necessary to give some evidence for this statement.

256 Lundgren

Recommendation: oral presentation

Abstract: accepted

Specific Comments:

1. Data in Table 3 are inconsistent. From my understanding BMF₃ is the product of BMF₁ and BMF₂, which is not fulfilled for all numbers given (e.g. PCB 118).
2. The term TEQ should be defined.
3. Text after tables 1 and 2: "depending on the low TEF values that have been assigned to these congeners" is confusing because it is not clear which congeners are referred to by "which" (mono-ortho?). The TEFs of the individual congeners should be given in a table.
4. The congeners should be ordered according to congener numbers in tables 1 and 2.
5. The reference to the maximum level in consumer fish is confusing because it interrupts the analysis of the experimental findings. As a further interpretation, it should be given at the end of this subsection.

6. "PCB pattern became dominated by higher chlorinated PCB congeners. For example, PCB 77 etc." This statement is confusing because PCB 77 is not an example of the higher chlorinated congeners. The point is correct but the presentation is awkward.

426 Adriaens

Recommendation: oral presentation

Abstract: acceptable with minor changes

Specific Comments:

1. Figure 3 is included twice with different scales on the y-axis. I'd prefer the logarithmic version.
2. I do not agree with the (sparse) conclusions given in the paper. As for me there is no clear significant trend in any of the homologue concentrations over the time period experiment. With the exception of very few single data points (e.g. Di-CDF after 1 month, OCDF after 12 months) no significant change in the relative homologue contribution occurs. Variabilities might well be due to the inhomogeneity of the sediment contamination of the collected samples.
3. In summary, I think the data are more indicative for rejection of the dechlorination hypothesis!
4. In Fig. 1, the O atoms are missing.

54 Toshiba

Recommendation: oral presentation

Abstract: acceptable with moderate changes

Specific Comments:

1. Central equation (1) is not sufficiently explained in particular with respect to the effect of effusion time t . Explain Δm and t . What time t did you use in your experiments?
2. As there is no calculation of vaporization enthalpy and entropy done in the paper, there is no need to show equation (2).
3. It is mentioned that "there is no clear tendency of the Kanechlor vapour pressures to vary with the size of the orifices". This is not surprising, as the vapour pressure at a given temperature is a constant. Thus, I do not understand the explanation that "any actual difference(s) among the measured vapour pressures is masked by experimental error".
4. Fig 2 cannot be interpreted without knowing the time of vaporization in the respective experiment. As a consequence of the different vapour pressures mass loss by vaporization is larger for the more volatile congeners leading to a relative change in congener composition. Thus, it would be more instructive to show relative mass fractions of selected congeners representing groups of low/medium/high vapour pressure. This should more clearly demonstrate the enrichment of the lower chlorinated congeners in gaseous PCB emissions at ambient temperature. Legend of Fig. 2: Relative composition of the major PCB congeners remaining in KC300 after vaporization at various temperatures; left bar: composition of starting material at room temperature.
5. Table 1: Delete first two rows with melting points. Instead insert your measured values of vapor pressure at room temperature, either as solid or supercooled liquid. Alternatively: Provide a second table with the results
6. Table 3 does not contain actual vapour pressure data. There is also no calculation of vaporization enthalpy and entropy (see comment 2). These data should be given and compared to recently published property data from Li et al. (J. Phys. Chem. Ref. Data, Vol. 32 (4), 1545-1590, 2003). Reference 8 (not cited) can be replaced by this paper.

649 Kerst

Recommendation: oral presentation

Abstract: acceptable with moderate changes

Specific Comments:

1. The last-before-last sentence in the introduction is hard to understand. There is no causal link between the transfer efficiency of POPs from ambient air to grass and the carry-over rates to the body fat of farm animals. However, the overall uptake rate of POPs from ambient air into body fat is the product of both. Thus, if the latter rate is similar for PCBs and PCDD/Fs higher efficiencies from air to grass must be compensated by lower carry-over rates and vice versa. This statement has to be made clearer and belongs into the results section.
2. In the tables the order of PCB sorting is irritating. I would prefer sorting by numbers.
3. For comparison of PCDD/F carry-over rates the paper of McLachlan (Chemosphere 34, 1263-1276, 1997) provides a summary of data from different other studies. All data are well below the here mentioned average rate of 0.50 (on WHO-TEQ basis). Reference 6 should be replaced.
4. "...while the lowest transfer rates (values below 0.1) were obtained for the tetrachlorinated congeners 77 and 81, indicating their comparatively fast metabolism." . Please give reference for this statement.
5. Tab.2 Are the carry-over rates correlated to physico-chemical properties, e.g. log Kow?
6. The carry-over rate should be explicitly defined on p. 3.
7. The discussion of the transfer factors (p. 3 bottom), which refers back to table 1, should be moved before the calculation of the carry-over rates. In the present version, it is confusing that after table 2 the results shown in table 1 are discussed.

219 Krauss

Recommendation: oral presentation

Abstract: acceptable with moderate changes

Specific Comments:

1. Exposing PUF plugs in a polyethylene jar for a certain amount of time is not a suitable method for determination of gaseous deposition rates. Gaseous deposition is driven by (i) the atmospheric concentration in the gas phase and (ii) the diffusive resistance at the surface of the target (apple wax layer and peel). Passive samplers exposed over an extended period of time must not reach equilibrium with the gas phase to represent average air concentration. This has to be controlled for any experimental setup.
2. Another necessary prerequisite for passive sampling is completely diffusion-controlled uptake of the compounds without any effect of air turbulence. This is highly questionable with PE jars 12 cm in diameter.
3. For these reasons it cannot be stated that "gaseous deposition of the Σ 32PCBs was highest at 25 cm ...", but only that the amounts sampled in the PUF plugs at different heights showed a vertical gradient.
4. It is conceivable that air concentration above a contaminated surface (in 25 cm) is elevated compared to an uncontaminated site if volatilization or resuspension is sufficiently high. Resuspension of wind or rain eroded particles have not been measured. Results given in Table 1 do not show a clear relationship between soil concentration and "gaseous deposition at 25 cm" for all allotments most likely due to mutual interactions. Thus, the effect of enhanced volatilisation from contaminated soil cannot be concluded from the results.
5. I also heavily doubt that "locally raised soil dust" significantly contributes to a particulate PCB deposition onto apples in 160 cm.

6. In summary I think the results given in this study have been over-interpreted by the authors and should be thoroughly re-evaluated. There are too many contradicting observations, which do not allow drawing any conclusion on the governing processes. Only a few examples: What is the inflow of particle-bound and gaseous compounds from outside the study area? What is the background concentration? Are the deposited particles from outside or inside (resuspended soil)? Is the soil uncovered or covered with grass? Do PCBs volatilize from soil?

513 Klasmeier

Recommendation: oral presentation

Abstract: accepted with minor changes

Specific Comments:

1. In the discussion of figure 1, it is said that for volatile compounds enhanced deposition is not sufficiently efficient. This is somewhat misleading because exactly for volatile compounds such as carbon tetrachloride or HCB the most pronounced cold condensation is observed. This is because these compounds have relatively uniform concentrations in air and the effect of the temperature-dependent Henry's law constant is fully reflected by the concentrations in water and soil. So the pronounced cold condensation of such compounds should be mentioned and "sufficient" in the statement mentioned should be explained in more detail (sufficient for what?).

***** Oral to Poster *****

481 Suzuki

Recommendation: poster presentation

Abstract: major changes required

Specific Comments:

1. There is no information given as to what the selected sites 1 – 5 are representative for.
2. Results given in Figure 3 are not clearly discussed. What does it mean that "...different proportion of the levels can be expected from the simulation, ..." ?
3. In the first sentence of the discussion TeBDE occurs twice (remove one time) and reference to figures is wrong.
4. Figures 4 - 6 are not interpretable in the black and white quality.
5. Discussion of Fig 7 is unclear and insufficient. What is a "fate in loss fluxes"? As far as I understood, the figure shows the relative contribution of processes to the loss of compound from the atmosphere. If so, this should be stated more clearly. Furthermore, a discussion of the identified major processes in the light of substance properties is missing.
6. In summary, results of the modelling study have to be more clearly discussed. In the actual version I cannot see any valuable output from the study.
7. A thorough grammar check is necessary.
8. p. 2: PCB 118 should not be mentioned here.
9. Is the model a steady-state model? What are "pseudo-steady-state conditions"?
10. The area included by line B should be 800 km x 1000 km, not 80 km x 1000 km.
11. The statement "output for air at the line-B boundary can be used in the discussion" is very unclear.
12. The last paragraph in the section on "Simulated outward fluxes from the region": This paragraph is difficult to read and needs rewriting. What is the point to be made here? A general comment on the mass fluxes shown here is that many of these observation could have been made with a much simpler model as well or, in other words, the results presented do not require the high resolution of the model.

58 Larsen

Recommendation: poster presentation

Abstract: major changes required

Specific Comments:

1. Description of used soil type in first sentence of Materials and Methods section is unclear. What does USDA series name and USDA textural designation mean?
2. Sorption studies were carried out at initial solution concentrations of 58 µg/L to 5.79 mg/L. Reported water solubilities for tetra-chlorinated dibenzo-p-dioxins are in the range of 8 – 730 µg/L indicating that at least the two highest concentrations used were above the water solubility. What is the water solubility of 1,4,7,8-TCDD? As K_d values for the sorption experiments were calculated from the highest initial concentrations results are extremely questionable.
3. Time-series data from batch experiments have been fitted to a linear sorption isotherm and a Freundlich isotherm as well. It is quite irritating to me that the goodness of fit represented by r^2 -values of 0.99 and 1.0 should be the same for both hypothesis given the significant difference in the shape of calculated isotherms with $n=1$ (linear) and $n=0.81-0.91$ (Freundlich). There is also no discussion as to which isotherm is better describing the sorption behaviour.
4. It is very optimistic to talk about significant (weak) correlations between organic matter and sorption with a correlation coefficient of $r=-0.18$ for 7 different soils. A one-sided t -test on the 5% significance level with 5 degrees of freedom ($df = n-2$) results in a required r -value of $|r| > 0.669$. This is definitely not given at 48 hours and even at 96 hours this value is not exceeded. Given the fact that kaolin and bentonite soils could possibly not included in this correlation analysis, the required r -value (for $df=3$) increases to $|r| > 0.805$ on the 5% significance level. For this reason the hypothesis of a significant correlation is **not** supported by the data.
5. Soil column experiments were carried out with solution concentrations of 125 µg/L, which is in the range of reported water solubilities. From the high K_d values it is not surprising that the compound strongly sorbs to the soil in the top three centimeters of the column.
6. Improve citations in section References according to instructions.
7. In the Results and Discussion section, it is stated that sorption affinity is related to the soil surface area. An influence of organic matter is only specified for 1478-TCDD. The following statement (“These batch experiments indicate that 1) etc.”) is not at all supported by the specific findings mentioned so far. This is highly confusing and the presentation of the results needs to be re-written.

***** Poster *****

#55 Li

p. 2, equ. (1): Explain t . What time t did you use in your experiments?

Some units are not displayed.

Avoid repetition in chapter Conclusions. Delete this chapter.

#199 Meyer

Section Methods: Give name and reference of the generic model used.

Level III model requires degradation rate constants or half-lives as input parameters. What about their sensitivity and influence on the model output?

Introduction: The statement that sensitivity and uncertainty can be investigated for all neutral organic chemicals is not supported by the scope of the analysis, because environmental half-lives are not considered at all. This means that an important source of uncertainty and a highly influential set of substance properties is not covered.

The same problem occurs in the last paragraph of the paper. Again, the important influence of half-lives is not mentioned and the relevance of the results is overstated.

#172 Olszek-Kadlak

Tab. 2: Explain AAE

The quality of the figures is very poor. Axes labels and legends in figure 1 are not legible. The gray background makes the figure even more difficult to read and must be removed. In figure 2, the symbols for the different compounds cannot be distinguished. The figure needs to be re-drawn with more different symbols.

#282 Maruya

1. Fig.1: Why is the concentration in fish so high on day 7? Authors wrote: Upon transfer to clean water, fish exposed to M1 eliminated the compound rapidly, with 42% on average remaining after 7 d, disregarding an anomalously high concentration at day 7. This is impossible. M1 is eliminated because the fugacity in fish is higher than that of clean water. How should fish uptake M1 again?
2. "Bioconcentration factors (BCFs), defined as the concentration in fish (ng/g wet) divided by the concentration in the aqueous phase (ng/ml), were estimated for M1 and P-50 from the time point where maximum tissue concentration was achieved". BCF is usually defined at the ratio of concentration in fish and water at *steady-state*, not at any arbitrarily chosen time. BCF values can thus not be transferred to other situations or related to K_{ow}.

#392 Kobayashi

1. Model: Why is volatilization neglected? Might be a sensitive fate process of PCDD/F in sea water. Model formulation is available from literature.
2. Fig. 3: Simulated peak concentrations in October and August would be much more informative for comparison with measured values. Are measured values not available?
3. Why is deposition from the atmosphere and air-water exchange excluded from the models? This seems to be a major shortcoming of the model and should be justified more extensively in the abstract.
4. The amounts, types and sources of the dioxins carried by the rivers should be explained. What are the industrial processes leading to the dioxin load of the rivers?
5. What is meant by "However, in this study only the sinking of the particulate matter was taken into account"? Is there no resuspension? The model should include a surface mixed sediment layer (SMSL) (Schwarzenbach et al., Environmental Organic Chemistry, second edition, Wiley, 2003).
6. The statement that dioxin concentrations compare well with field measurements is not really supported by the material shown. The resolution of the graphs in figure 3 is too low for a sound evaluation of how well measured and modeled data correspond. Moreover, the conclusion drawn from the assumed correspondence between measured and calculated data is not valid. The coincidence could be by chance and at least a model that takes into account atmospheric deposition and air-water exchange should be tested as an alternative. This part needs to be rewritten in a more careful manner.

458 Puzyn

Introduction: 1996, not 1986.

Fig. 1: x- and y-axis display Kow, not Koa.

The English needs improvement. There are too many spelling errors; “naphtalene” instead of “naphthalene” is particularly awkward.

It is not correct that Koa and vapor pressure are “the key” parameters in the theory of global distillation. There are many more parameters such as activation energies of degradation processes, phase transfer enthalpies for air-water and air-soil exchange that have high influence on the global distribution behavior of POPs. This statement in the introduction needs to be modified (at least: “... are among the key parameters etc.”)

#460 Rostkowski

The statement in the conclusions that transport of PCDTs in the environment can be predicted on the basis of the partition coefficients is not correct because it neglects the chemicals’ half-lives, the activation energies of their degradation processes and many more important parameters. The statement needs to be re-phrased in a less exaggerated manner. The same applies to the following sentence (“mobility of PCDTs is similar to other dioxin-like compounds”); this statement is not at all supported by the findings of the study and must be removed. Environmental mobility is not a subject dealt with in the study and there is no basis for such a conclusion.

#499 Kitamura

Delete title, authors’ names and affiliation.

#560 Kuramochi

Provide a table with all values, which you have determined. Figures give only rough numbers. A table with the exact values of the properties is necessary.

#588 Falandysz

The text of the paper is hard to read and the English needs improvement.

The statement (results and discussion) that energy of HOMO and polarity are probably responsible for diverse environmental and body transport, fate and toxicity of PCABs is not at all supported by the findings of the study and needs to be removed.

All other posters and no preferences accepted without changes.