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An Integrated Criterion for the Persistence of Organic Chemicals Based on Model Calculations

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Some Introductory Thoughts on Chemical Persistence

It may be pertinent to start the development and discussion of a criterion on chemical persistence with the question of whether persistence is always an undesirable property of a chemical. Often, durability is something we strive for. In very general terms, the aim of durability has been defined as “the lowest possible employment of resources and energy to achieve the highest possible use during the longest possible time.” (translated from Dahl, 1992).

What does that mean for man-made chemicals? We wish chemicals to be durable, or persistent, as long as we have a use for them, but we wish them to disappear quickly after we have no longer use for them. E.g. we wish that PCBs are durable as long as they are used in electrical installations, in heat exchangers, or as hydraulic fluids. If they weren't they would have to be replaced or replenished after a while or they lose their usefulness - may be even cause a hazard. This is why at first the extraordinary persistence of PCBs could be conceived as an advantageous rather than a hazardous characteristic of these chemicals. However, man-made chemicals dispersed in the environment, as a result of incidental and accidental release (e.g. spills) or release in the waste stream (e.g. sewage, land fills, exhaust, stack release, etc.), usually have lost their usefulness to society and we wish them to disappear quickly, i.e. be non-persistent. Pesticides and other chemicals used in agriculture or forestry constitute a special case because their use often involves deliberate release into the environment. We wish them to be just persistent enough to perform their given task, and then disappear.

The next question is whether society should mind a (man-made) chemical's persistence in the environment, even if no obvious risk associated with its presence in the environment can be identified. I suggest, that no matter whether a man-made chemical has detrimental effects or not, we should be concerned about it if it accumulates in the environment, because we can not foresee what hazards it may create in the future. An example are the chlorofluorocarbons or CFCs. In the 1970s, one may have argued that there is no need to worry about the build-up of CFC concentrations in the atmosphere, since these chemicals are not toxic to any organism. By then neither the role of CFCs in the depletion of the ozone layer, nor their role as a green house gas was anticipated. Scheringer and Berg (1994) come to the same conclusion when arguing that the “specification of environmental threat only requires the necessary conditions for effects to be known”, rather than a “detailed recording and evaluation of manifest effects”. They identify exposure, or the presence of an anthropogenic agent, as the necessary condition for the appearance of effects, and go on to identify spatial and temporal range as proxy measures of environmental threat. For chemical agents temporal range is obviously equivalent to persistence.

The final introductory question we may want to address is whether there are situations where a chemical could be not persistent enough in the environment? Obviously, we wish chemicals which are no longer useful to disappear without creating new hazards. In general terms, a toxic effect can only result from the interaction of a chemical toxicant with a biomolecule, i.e. from a chemical reaction. Toxicity is thus inherently related to reactivity and a chemical which does not react at all is unlikely to show any biological effects.

Examples where hazards are created during the disappearance of a chemical:

- a degradation product may be more toxic than the parent compound
- very reactive chemicals are responsible for photochemical smog
- the reactions leading to the degradation of the CFCs are responsible for ozone depletion

Persistence therefore has to be evaluated in conjunction with the implications of decay.

Suggested Persistence Criteria and Their Limitations

Various national and international bodies are presently developing regulatory policies for persistent organic pollutants (POPs). These activities generated the need to define in a scientifically sound and legally defensible fashion the chemical characteristics that constitute a POP. Whereas there seems to be agreement on a limited number of substances (see also Appendix 6), a process and criteria need to be developed that allow the identification of additional substances as POPs. Persistence in the environment is obviously one of the defining characteristics of a POP. Several jurisdictions have proposed persistence criteria which take the form of threshold half-lives in various environmental media. A substance is considered persistent if its half-life in any of the media exceeds the threshold for that medium. Persistence in one environmental compartment is thus sufficient to classify a chemical as persistent in general. Various jurisdictions have adopted or are suggesting different threshold values. The Toxic Substances Management Policy in Canada e.g. specifies the following thresholds: air two days, surface water and soil six months, sediment one year. The respective thresholds specified by the UN-ECE Protocol on the Long Range Transport of Air Pollutants (LRTAP) are two days in air, two months in water, and six months in soil and sediment.

Webster et al. (1998) have identified and discussed two major problems of that approach. The first is the difficulty of estimating these half-lives in the light of the large ranges reported in the literature. These large ranges are not merely caused by non-standardised test conditions, but reflect the real environmental variability that characterises these processes. The second problem is that “the effects of partitioning to other media and mode of entry are ignored in developing criteria half-lives”. Because the overall persistence of a chemical in the environment is influenced by its dynamic multimedia distribution, the approach based on individual compartment half-lives is conservative for a chemical not partitioning significantly into a compartment where it is very persistent, while being easily degraded in other compartments. Obviously the amount lost by degradation in a particular medium is determined both by the medium-specific degradation rate constant and the amount present in that medium. It follows, that for persistence in the overall environment, those degradation rate constants matter most, which refer to the compartments where most of the chemical resides. An integrated persistence criterion should weigh the persistence in the various environmental media according to where a chemical is likely to reside. This in turn is influenced by its physical-chemical properties and the environmental medium receiving the emissions.

Previous Work

Overall Persistence at Equilibrium Partitioning - Müller-Herold et al.

Müller-Herold (1996) derived an aggregated persistence value for organic compounds in the global environment by weighting the degradation rates in individual environmental compartments according to the amounts in the various compartments at equilibrium (calculated from K_{ow} , Henry's law constant H , and assumed relative compartment volumes). This is essentially equivalent to calculating the overall half-life in a three compartment (air-water-soil) level II model without advection terms. For chemicals, for which degradation occurs much slower than transport, this weighted-average decay rate constitutes an upper limit of persistence.

Müller-Herold et al. (1997) maintain to have "validated" this approach for such chemicals by a comparison of this upper limit with the persistence calculated in a simple level III unit world. However, there are some clear misclassifications that are simply ignored in their paper. Namely, benzene and chlorobenzene are among a group of six substances, that according to the authors "have a geographical range of 10,000 km and more [...] and they represent the type of pollutants with global pollution potential the limiting law was designed for". On the other hand, chemicals such as chlordane and dieldrin are described as having a geographical range of less than 2000 km, as being neither persistent nor having long range pollution potential. Whereas I never heard of benzene being considered a persistent pollutant subject to long range transport, chlordane and dieldrin are consistently found in the arctic environment despite never having been used there.

The limitation of this approach is that it is only valid for chemicals, for which degradation occurs much slower than transport. Due to the very efficient reaction with OH radicals, most organic chemicals have atmospheric degradation half-lives which are shorter than relevant atmospheric transport processes (Kwok et al. 1995). As Müller-Herold concedes, the rate limiting law does not apply for these chemicals, and it is obviously no longer possible to "avoid the touchy involvement into the intricacies of environmental distribution kinetics" in order to derive meaningful aggregate persistence value for such chemicals.

Overall Persistence in a Level III Multi-Media Environment – Webster et al.

A logical extension of the approach by Müller-Herold is to take into account the effect of the kinetic exchange of chemical between the compartments, i.e. using a non-equilibrium model to derive the weights (i.e. amounts in the various compartments), with which to average the compartmental degradation rates. The "overall reaction time", calculated with the generic level III fugacity model in the handbooks by Mackay et al. (1992-1997) could be considered a measure of overall persistence which is derived from persistence in four individual compartments and which takes into account the dynamic mass exchange between these compartments. It does not claim to approximate an "effective global decay rate" (or an upper limit of that), but could potentially be used as an integrated criterion of persistence.

Webster et al. (1998) modified this generic level III model by eliminating advective transport processes that only contribute to a redistribution of chemical within the global environment and investigated the impact of physical-chemical properties and discharge medium on persistence. The calculated overall reaction time was clearly dependent on

the selected emission scenario, i.e. it is important into which media discharge is assumed to occur. If generic emission scenarios are employed - like the ones in Mackay et al. (1992-1997) - the calculated fate will in many cases still not reflect the real dynamic picture of intermedia mass exchange of a particular chemical. The question is whether a screening criterion could be so complex as to require the specification of the media receiving emission.

Description of the Persistence Criterion Model

Building on the effort by Webster et al. (1998) a very simple model has been developed that estimates an "effective global decay rates" of an organic chemical from its degradation half-lives in the individual compartments and its likely average global intermedia distribution. This steady-state, non-equilibrium distribution is calculated from information on as few physical-chemical properties as possible, a knowledge of the receiving environmental media, and a number of environmental default parameters. These environmental properties are selected to reflect global totals (e.g. compartment dimensions, etc.) or globally averaged conditions.

The description of the global environment in such a model should be as simple as possible yet has to include the major bio-accessible storage and degradation compartments of a chemical. These include the global atmosphere, namely the troposphere, the world surface waters including the surface ocean, and the world's terrestrial interface (soils/vegetation). Only three compartments - air, water and soil - are included in the presented model and these could be considered to represent these three major reservoirs. Not part of the model system are sediments (freshwater and marine), deeper ocean layer, the stratosphere and deeper soil layers and bedrock.

In deviation from the approach taken by Webster et al. (1998), the model allows for loss processes other than degradation, namely loss processes that lead to a permanent and irreversible removal from the biosphere. Examples are the loss to the stratosphere, loss and retention in the Earth's interior, loss to the deep oceans, and net loss to sediments. These processes are only of importance for chemicals which are degraded very slowly and are included to avoid unrealistically high overall persistence values for such chemicals. To make obvious to what extent the overall persistence value is influenced by these processes, the fraction of loss which is due to degradation is calculated:

$$\Phi_R = \frac{\sum_i f_i \cdot D_{Ri}}{\sum_i f_i \cdot (D_{Ri} + D_{Li})}$$

The model systems thus is a three phase system with three emission and loss pathways, and five intercompartmental transfer rates (Fig. 1). A detailed description of the model equations can be found in Appendix 1. The environmental default parameters are listed in Appendix 2.

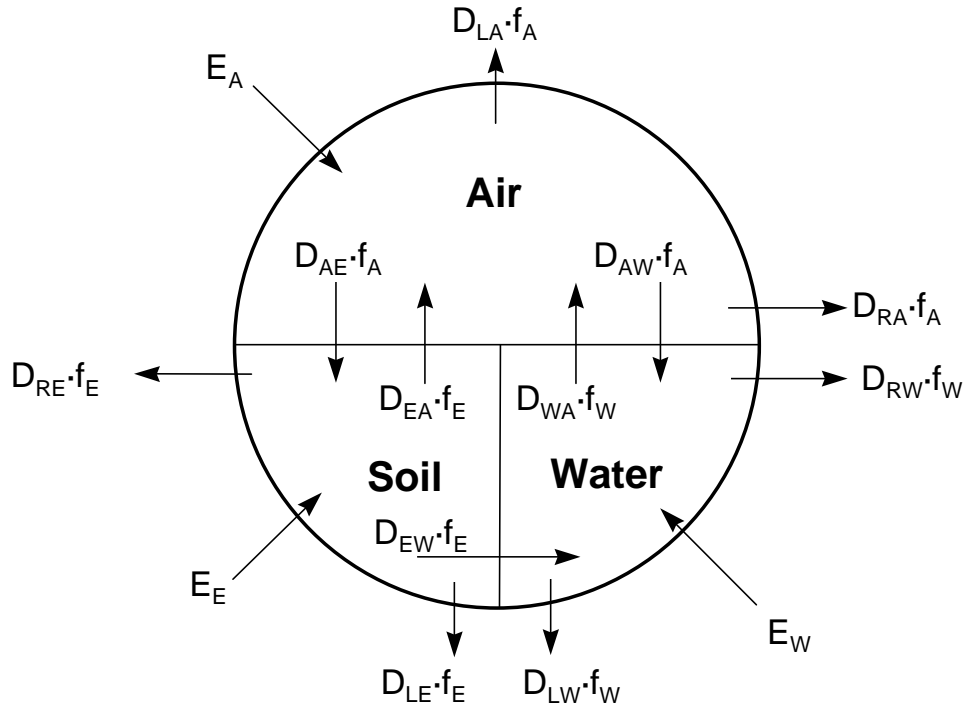


Fig. 1 The three compartment level III model used to estimate an overall persistence of an organic chemical in the global environment.

The Overall Persistence

The overall persistence is calculated from:

$$\text{Overall persistence } T = \frac{\sum_i f_i \cdot V_i \cdot Z_{Bi}}{\sum_i f_i \cdot (D_{Ri} + D_{Li})}$$

For comparison the computer program also calculates the overall persistence for the case of equilibrium distribution between the three compartments (level II):

$$\text{Overall persistence } T = \frac{\sum_i V_i \cdot Z_{Bi}}{\sum_i (D_{Ri} + D_{Li})}$$

The Impact of Long-Range Transport on Global Persistence

It may be argued that it is not possible to estimate a “effective global decay rate” using a model with only one well-mixed compartment for each major environmental medium, and that there is a need to account for long-range transport. For example, a chemical may be readily degraded in the soils of the source region, but persistent in the soils of remote regions. Then the overall global persistence depends on whether the chemical is

long range transported and deposited to remote soils or not. One compartment per primary environmental storage medium should be sufficient, as long as:

- the persistence of a chemical is independent from the distance from the source. If persistence is higher or lower at higher distance from the source, the degree to which the chemical gets there has implications for its overall global persistence.
- the intermedia transport rates are independent from the distance from the source. If this not the case, the media distribution changes and thus the relative importance of the various media degradation half-lives.

Intermedia transport rates and degradation half-lives, however do change with location on the globe because of their dependence on climate and other environmental characteristics. A model comparison conducted to evaluate the possible error from this simplification for one chemical indicated that the error may not be very large (for details see Appendix 3).

Testing and Evaluation of the Model

The sensitivity of the calculated overall persistence in the developed steady-state model on physical chemical properties, individual compartmental degradation rates, and medium of emission is assessed and interpreted in the following sections.

The Influence of Physical-Chemical Properties on the Calculated Persistence

Physical chemical properties have an influence on persistence because they control:

- the equilibrium partitioning among media
- the rate of some intermedia transfer processes.

We used the simple persistence criterion model to study this influence in more detail.

The partitioning properties of a chemical are characterized sufficiently with only two out of three partitioning properties:

- the air water partitioning coefficient K_{AW} or Henry's Law constant H ,
- the octanol-water partitioning coefficient K_{OW} , and
- the octanol air partitioning coefficient K_{OA} .

If two are known, the third of these parameters can be deduced from $K_{OW} = K_{OA} \cdot K_{AW}$. There is no need for a aqueous solubility or vapour pressure value because in the model:

- partitioning into air (air and soil air) and water (water, rain drops and soil water) is described using K_{AW} ,
- partitioning into suspended solids in water and soil solids is described using K_{OW} , and
- partitioning into aerosols is described using K_{OA} .

For details, see Appendix 1.

We varied these chemical properties to account for all possible organic chemicals. Based on a search for extreme cases, these are the ranges of K_{AW} and K_{OW} (see also Appendix 4) used in the calculations:

$$-15 < \log K_{AW} < 5$$

$$-2 < \log K_{OW} < 10$$

(Not enough measurements exist to assess the potential range of K_{OA} values, but the range of $0 < \log K_{OA} < 20$ was thought realistic.) Of course, not all combinations are realistic. A compound with a very low K_{AW} can not have an extremely high K_{OW} . Neither can a compound with a high K_{AW} have a very high K_{OW} . Using steps of 1 log unit we calculated all possible combinations of these properties and calculated the overall persistence with the model.

For this investigation we assumed that the chemicals have the individual compartmental half-lives specified as threshold values by the planned UNECE/ LRTAP protocol:

$$t_{1/2}(\text{air}) = 2 \text{ days}$$

$$t_{1/2}(\text{water}) = 2 \text{ month}$$

$$t_{1/2}(\text{soil}) = 6 \text{ month}$$

At this stage, it is assumed that the discharge occurs in equal proportions into all three media, i.e. 33.33% of the emissions occurs into air, water and soil, respectively. Figure 2 shows the calculated overall persistence as a function of $\log K_{AW}$ and $\log K_{OW}$ in a three-dimensional plot. The same results are presented in two two-dimensional plots in Figure 4 for better readability. Appendix 5 contains similar plots for combinations of $\log K_{AW}$ and $\log K_{OA}$ and combinations of $\log K_{OA}$ and $\log K_{OW}$.

For comparison, Figures 3 and 5 show the same type of plots assuming equilibrium partitioning between the three phases.

When interpreting all these figures it is obvious that if more chemical partitions into air (the compartment with the by far lowest degradation half-life) the overall persistence will be shorter, and if more chemical partitions into soil (and to some degree water) the persistence will be longer. Persistence thus tends to increase with increasing partitioning from air to octanol and air to water, because it reduces the amount in air. Persistence decreases with increasing $\log K_{AW}$, because more chemical is in the air phase. However, this decrease is very dependent on the $\log K_{OW}$, especially for chemicals with $\log K_{AW}$ between -2 and 3.

The interpretation of the level II results is simpler and three types of chemical can be identified clearly in Figures 3 and 5. Chemicals with $\log K_{AW} > -1$ and $\log K_{OW} < 4$ (Region A in the Figures) partition essentially completely into air and therefore the overall persistence is governed by the degradation half life in air ($T = 48 \text{ h} / \ln 2 = 69$ hours). Chemicals with $\log K_{AW} < -6$ and $\log K_{OW} < 4$ (region B) partition primarily into water and thus the overall persistence is governed by degradation half-life in water ($T = 1460 \text{ h} / \ln 2 = 2106 \text{ h}$). Finally, chemicals with $\log K_{OW} > 7$ and $\log K_{AW} < -4$ (region C) partition completely into organic matter-like material and their distribution is governed by the distribution of organic carbon among water and soil, and the amount of aerosols in air. With the default environmental parameters there is 66 % of the organic carbon, and thus of these chemicals, in soil and 33 % in water and a minor fraction in air. The overall persistence of the chemicals with these properties is thus influenced by all three individual phase degradation half-lives. The figures 3 and 5 also show that the equilibrium partitioning can shift dramatically with rather minor changes in partition properties.

Figure 2 and 4 are more complicated because the chemical properties can influence the rate of the intermedia transfer processes, in addition to the equilibrium partitioning between the media. On first inspection, Figures 2 and 4 do not look extremely different from Figures 3 and 5. The same three plateaus (Regions A, B and C) can be identified but they are smaller now, i.e. the range of chemical properties where more than one individual degradation half-life becomes important is larger. Also, these plateaus are not exactly at the same level as in the equilibrium partitioning case. Namely, the persistence in region A is higher and in region C it is lower for the level III case (Fig. 2) than for the level II case (Fig. 3). This is because there are now resistances of intermedia transfer that prevent that equilibrium partitioning is established. Let us take a more detailed look at some of these plateaus or limits of persistence:

Lower limit at $\log K_{AW} > -1$ and $\log K_{OW} < 6$ (Region A in Fig. 2 and 4): These chemicals are so volatile that virtually all of the chemical emitted to soil and water is evaporating. At higher $\log K_{OW}$ (>6) evaporation from water is reduced because of significant sorption to suspended solids. Persistence is controlled by the degradation half-life in air.

Intermediate limit $\log K_{AW} < -8$ and $\log K_{OW} < 0$ (Region B in Fig. 2 and 4). With this combination of properties, almost all of the chemical partitions into the water phase, and the water degradation half-life thus controls the overall persistence. If K_{AW} increases the amount in air increases and the persistence drops. If K_{OW} increases the amount in soil and thus the persistence increases.

Upper limit for K_{AW} smaller than -1 (depending on $\log K_{OW}$) (Region C in Fig. 2 and 4). At this limit, particle-mediated deposition processes from air are maximized because essentially 100 percent of the chemical in air is particle sorbed. For chemicals with $\log K_{OW}$ around 4 and 5 and $\log K_{AW}$ smaller than -6 this limit may be exceeded (Region C*), because for these chemicals wet vapour scavenging becomes an even more efficient atmospheric deposition process. However, such a combination of partition coefficients may not exist because chemicals with $\log K_{AW} < -6$ are too soluble in water to have a $\log K_{OW}$ of 4 or 5.

Intermediate upper limit for $\log K_{OW} > 6$ and $\log K_{AW} > -1$ (Region D). For chemicals with these properties the emission scenario of 1/3 in each compartment leads to a situation where in each compartments a third of the degradation takes place.

Areas of particularly strong sensitivity to partition properties are indicated by steep curves or large distance between curves in the figures. This is obviously where major shifts in partitioning from one phase to the other occur, e.g. from air to soil. This is the case for a $\log K_{OA}$ around 6 and $\log K_{AW} > -5$ or a $\log K_{OA}$ around 6 and $\log K_{OW} > 3$ (see figures in Appendix 5).

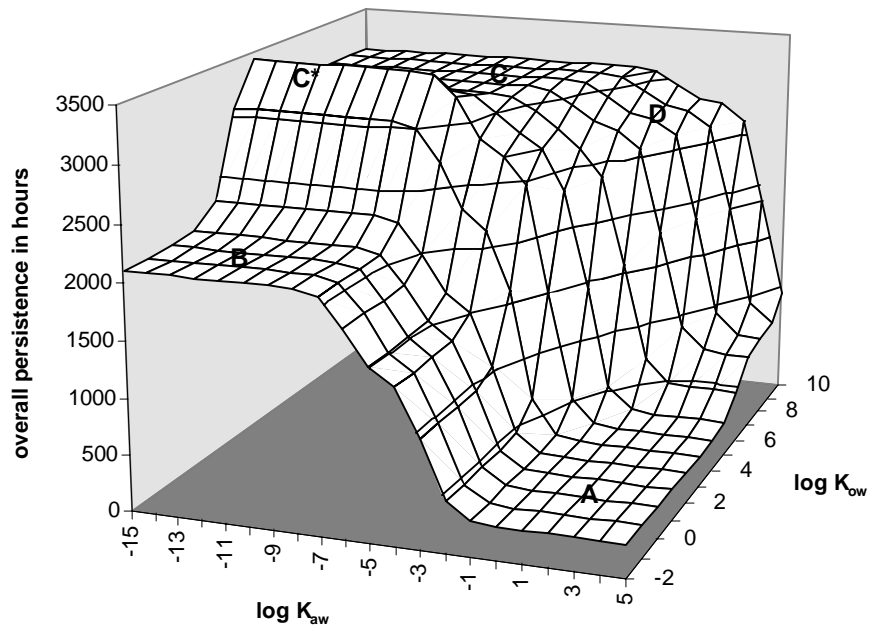


Fig. 2 Dependence of overall persistence on physical chemical properties as expressed by $\log K_{AW}$ and $\log K_{OW}$. Assumptions: Equal fraction of emissions into air, water and soil. Half-lives 48 h in air, 1460 h in water and 4380 in soil. Level III.

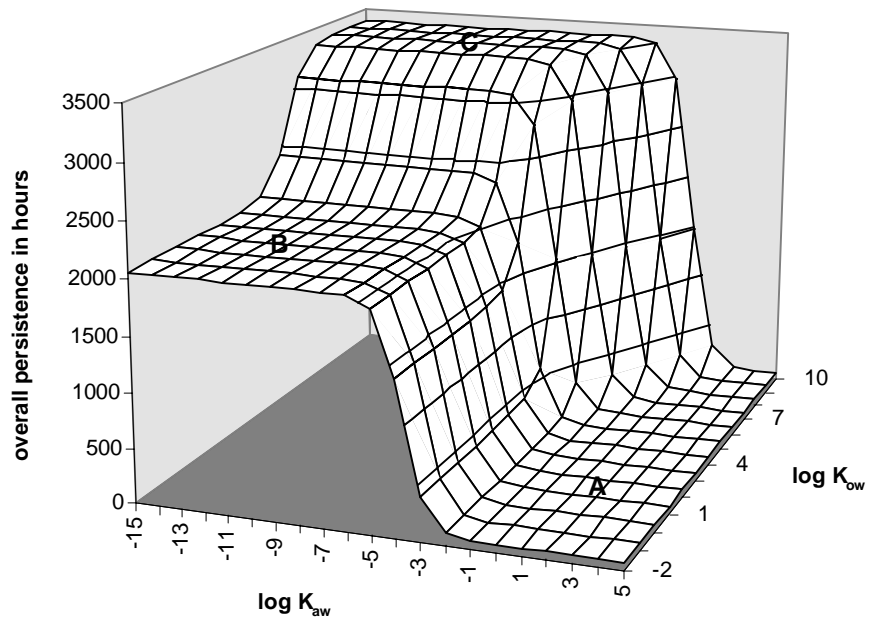


Fig. 3 As Figure 2, except assumption of equilibrium partitioning between the three phases (Level II).

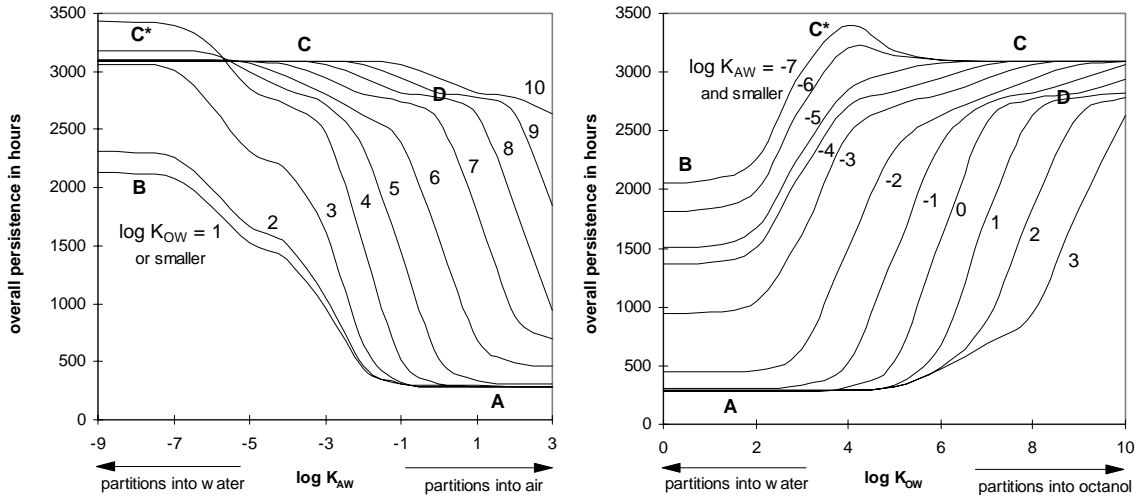


Fig. 4 2-dimensional version of Figure 2. Dependence of overall persistence on physical chemical properties as expressed by log K_{AW} and log K_{OW}. Assumptions: Equal fraction of emissions into air, water and soil. Half-lives 48 h in air, 1460 h in water and 4380 in soil. Level III.

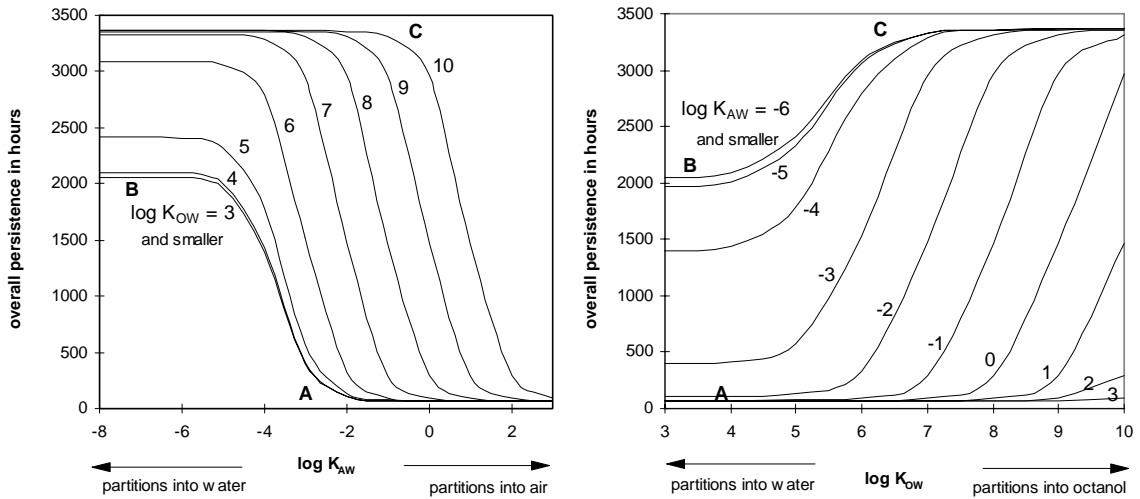


Fig. 5 As Figure 4, except assumption of equilibrium partitioning between the three phases (Level II).

The Influence of Individual Compartmental Half-lives on the Calculated Persistence

It is self-evident that the half-lives in the individual compartments have a significant impact on the calculated overall persistence. Figure 6 show plots equivalent to Figure 2 for different combinations of individual compartmental half-lives. Emission was assumed to occur in equal fractions to air, water and soil. Again, Figure 7 provides the same information for the case assuming equilibrium partitioning.

Not surprisingly, in Figure 7 the same three region A, B and C can be identified as in Figure 3, but now they have completely different levels reflecting the changed individual compartmental degradation half-lives. More surprisingly, also the sizes of the plateaus are different. E.g. the plateau indicating partitioning into air (region A) is reduced in size when the degradation half-life in water is very low. Obviously, a small fraction of chemicals with $\log K_{AW}$ between -1 and 2 partitions into water at equilibrium and that small fraction is sufficient to reduce the overall persistence noticeably.

Figure 6 also shows the three regions, but the overall persistence of the chemicals with intermediate properties is again more complicated than in the equilibrium partitioning case. A comparison of Figures 6 and 7 also reveals that there can be large deviations between level II and level III overall persistence. A notable example is region C in case 3 (fast reaction in water, slow reaction in soil). Whereas these chemicals show a low overall persistence with the equilibrium partitioning assumption, accounting for intermedia resistances increases the overall persistence even beyond the level of plateau A. Whereas in a level II calculation almost all of the chemical reacts in water, the soil to water transport resistance limits the amount of chemical that can react with the fast water degradation rate in the level III calculation raising the overall persistence to a much higher level. In case 4 (slow reaction in water, fast reaction in soil) this resistance to transport from soil to water results in a decrease of the overall persistence of chemicals in the B region. The effect of intermedia transport can thus be a higher or a lower overall persistence.

Case 4 (fast degradation in soil, slow degradation in water) in Figure 6 reveals a peculiar minimum of persistence for $\log K_{AW}$ around 0 and $\log K_{OW}$ around 5. A closer look indicates that for these chemical properties volatilisation is high from water but low from soil, thus maximizing the amount of chemical in the compartments with lower degradation half-lives.

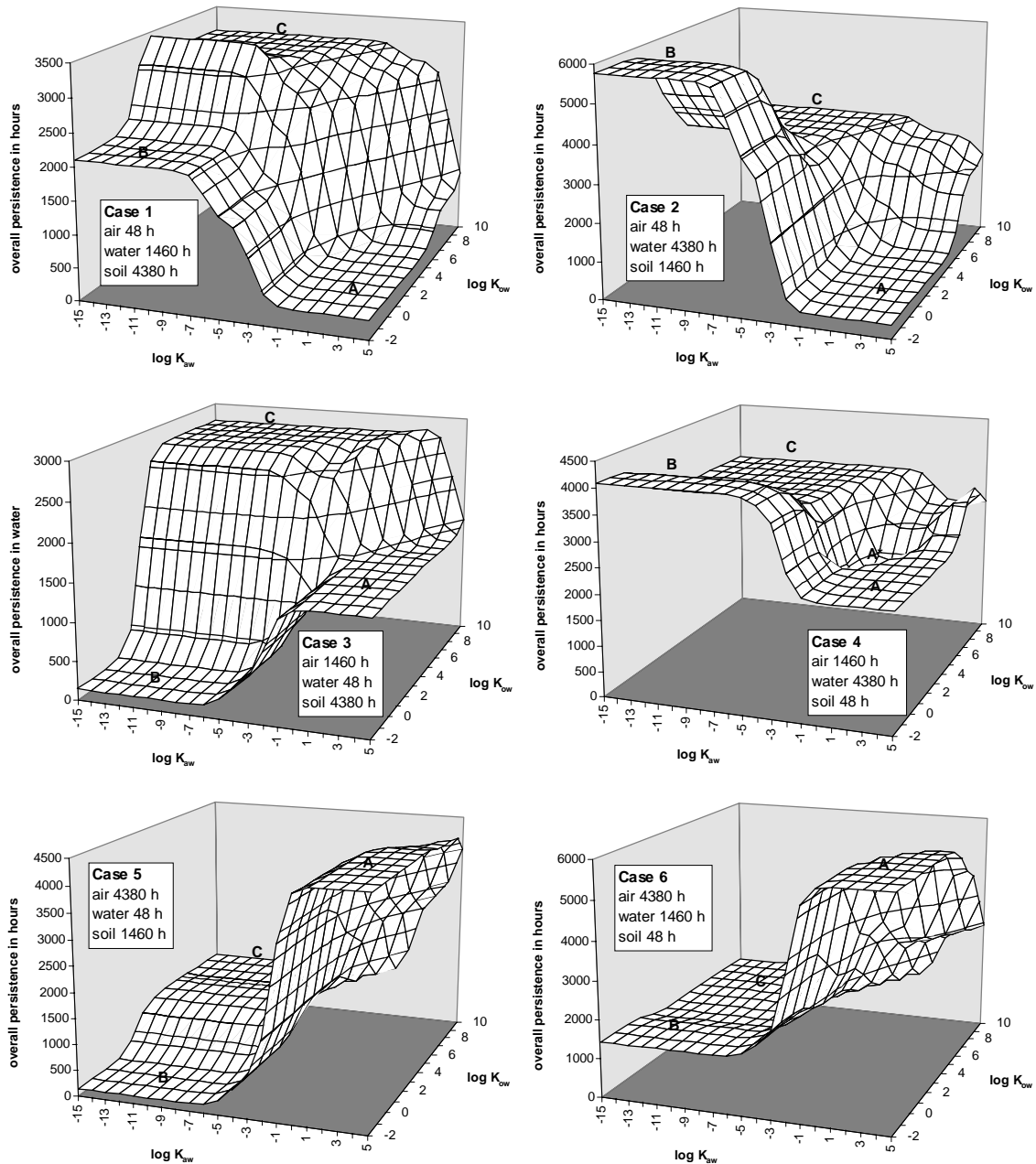


Fig. 6 Dependence of overall persistence on physical chemical properties (as expressed by $\log K_{AW}$ and $\log K_{OW}$) for six different combinations of degradation half-lives in the individual compartments. Assumptions: Equal fraction of emissions into air, water and soil. Level III. Case 1 is identical to Fig. 2.

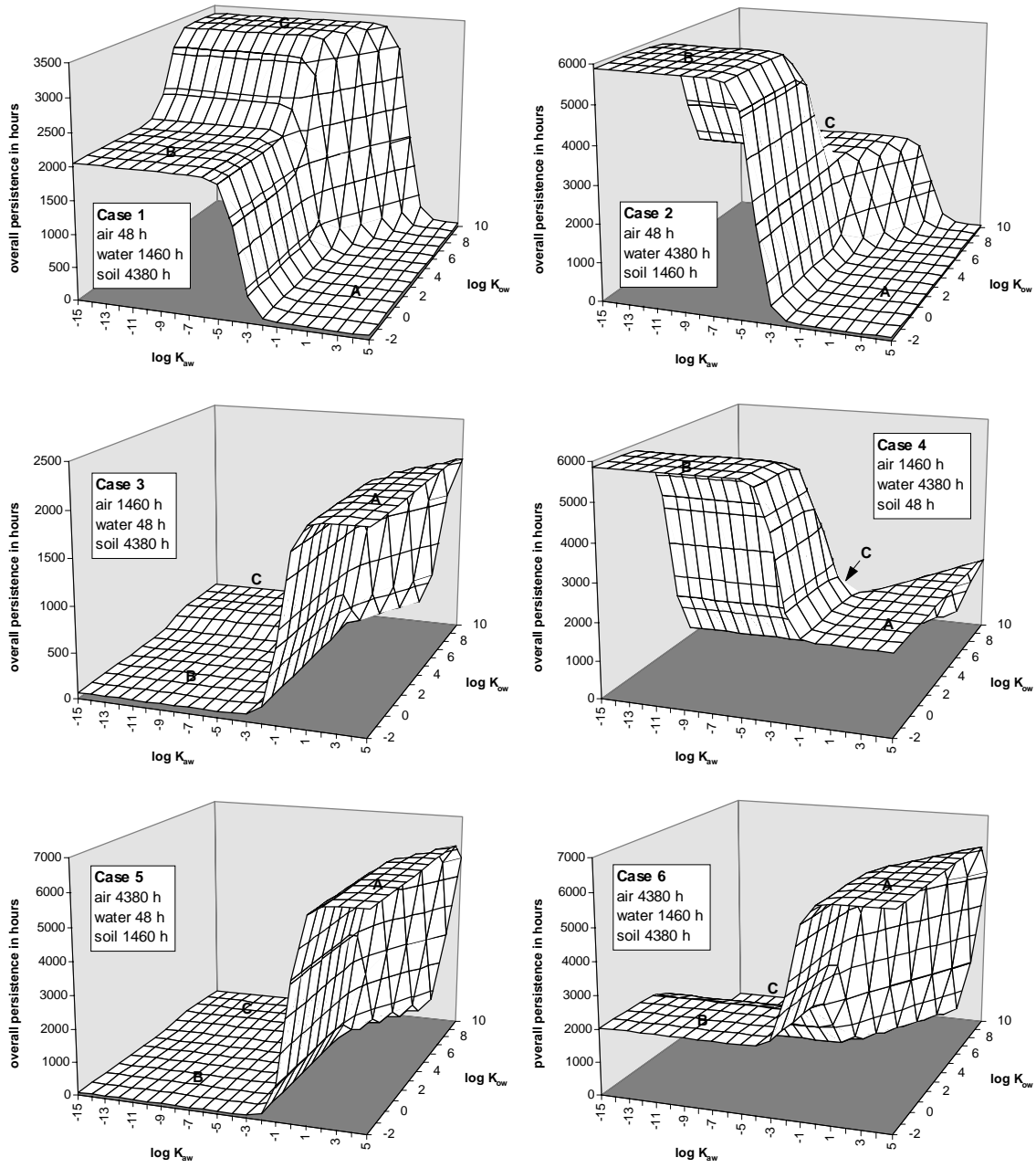


Fig. 7 As Figure 6, except assumption of equilibrium partitioning between the three phases (Level II).

The Influence of Medium of Emission on the Calculated Persistence

In a next step, the influence of the medium of discharge on the calculated overall persistence value was investigated. Degradation half-lives in the air, water and soil were again assumed to be 48, 1460, 4380 hours. For all combination of $\log K_{AW}$ and $\log K_{OW}$, three scenarios with discharge assumed to occur completely into one of the compartments were calculated in addition to the initial scenario which assumed that one third of the total emission is being emitted into each of the compartments. The results are shown in Figures 8 (three-dimensional plots) and 9 (two-dimensional plots).

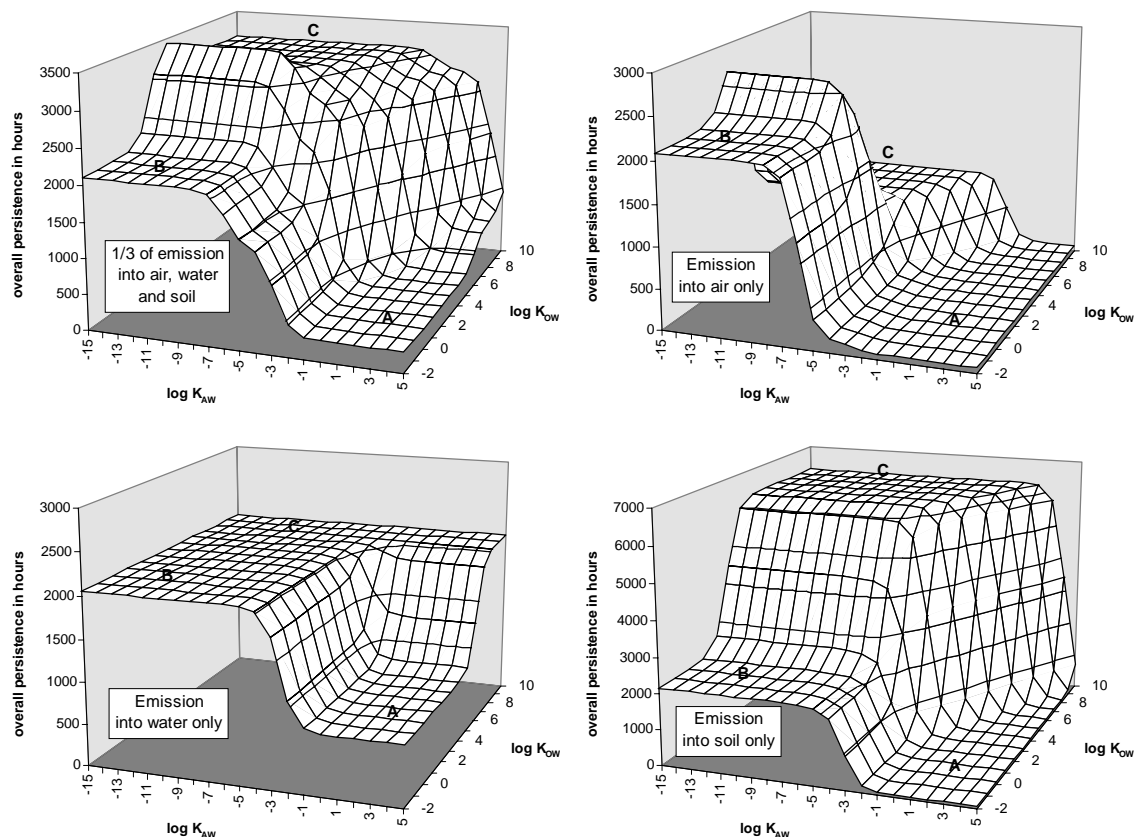


Fig. 8 Dependence of overall persistence on physical chemical properties (as expressed by $\log K_{AW}$ and $\log K_{OW}$) for four different emission distributions. Half-lives 48 h in air, 1460 h in water and 4380 in soil. The plot in the upper left corner is identical to Fig. 2.

For chemical with properties in the regions A and B the results are very similar independent of the medium of discharge. The largest differences in overall persistence appear for chemicals with high $\log K_{OW}$ and low $\log K_{AW}$ (region C), i.e. the chemicals that sorbed mostly onto organic carbon. If such chemicals are discharged to soils they tend to stay in soils. If the soil has the highest individual degradation half-life - as in our example calculation - this results in very high overall persistence values. If such chemicals are emitted to water they tend to stay in the water and the water degradation half-life is decisive.

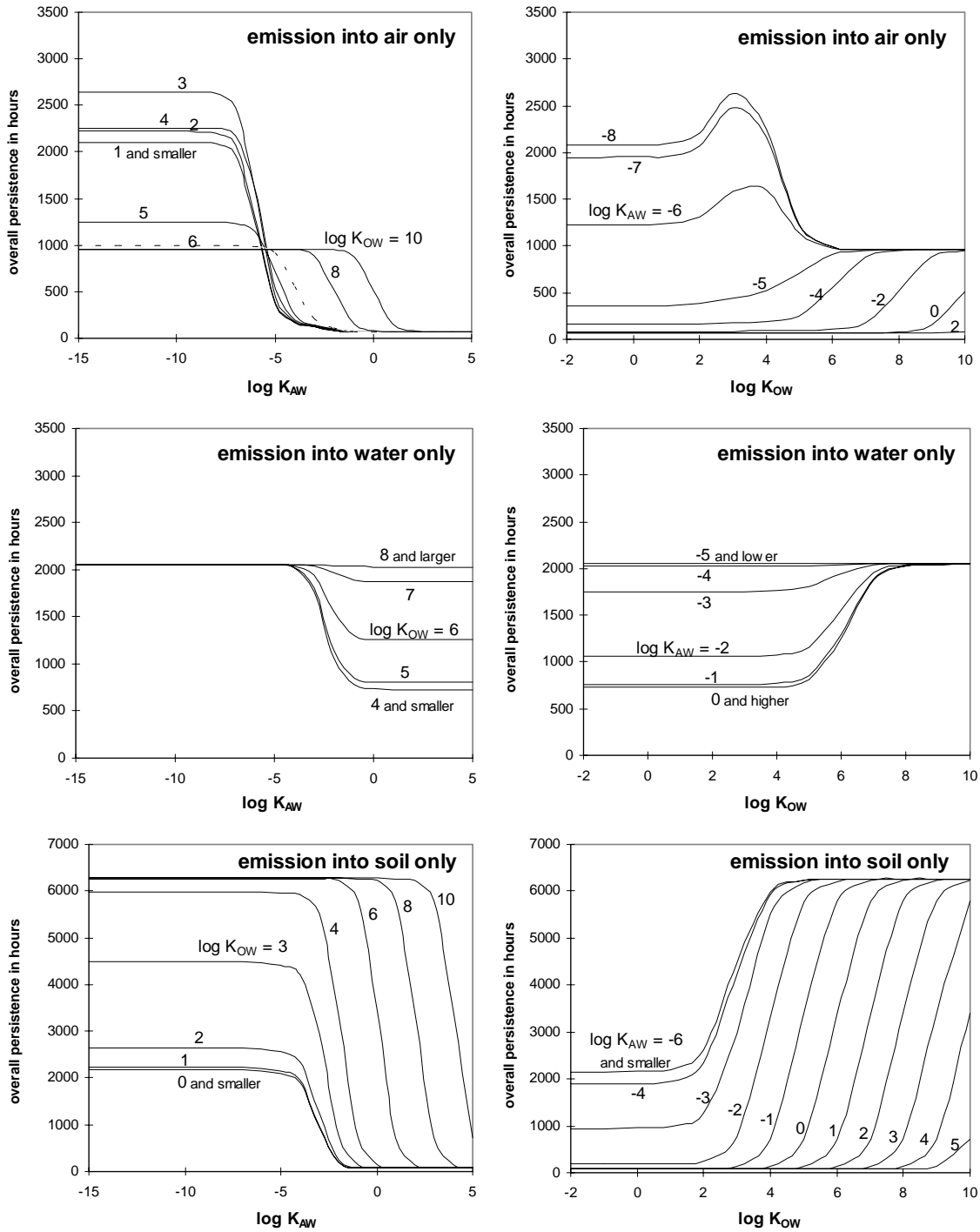


Fig. 9 2-dimensional version of Figure 8. Dependence of overall persistence on physical chemical properties (as expressed by log K_{AW} and log K_{OW}) for emission into air, water and soil only. Half-lives 48 h in air, 1460 h in water and 4380 in soil.

For all chemicals the half-life in soil turns out to be unimportant, if emission occurs to water only. This is because there is no direct intermedia transfer from water to soil in the model, and the transport pathway evaporation from water followed by deposition to soil is not sufficiently important for any chemical property combination to make an impact. A chemical that is discharged to water, survives sewage treatment, and is transferred with sewage sludge to the soil environment has a direct water-to soil transfer route that is not represented in the model. This could be accounted for by having a certain fraction of the emission occur into soils.

Because the model is completely linear, the results for the overall persistence for different emissions are additive. In a triangular diagram with the percent emission into the three compartments as the coordinates, the overall persistence is represented by a planar surface as shown in Figure 10. This implies that for any emission distribution scenario, the overall persistence can be determined by weighing the overall persistence determined for the scenarios with emission occurring into only one of the three compartments - the weights being the percentage emission occurring into a compartment.

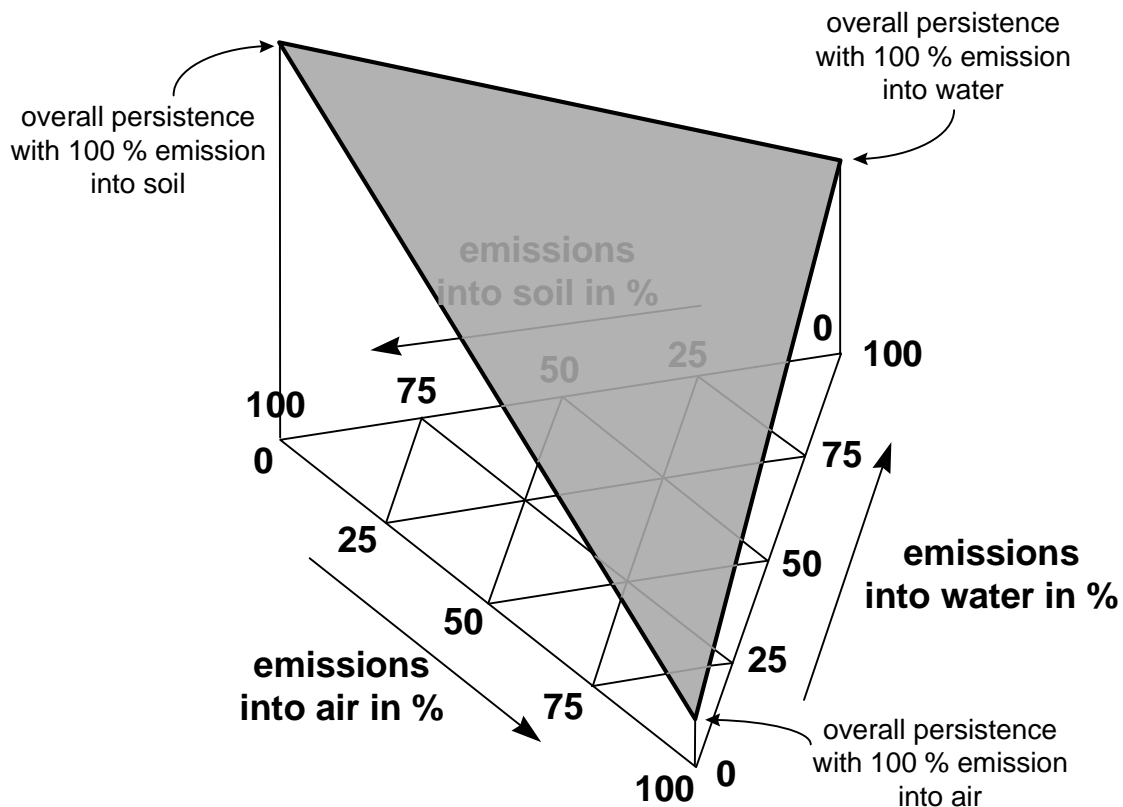


Fig. 10 Triangular diagram displaying the linear additivity of overall persistence.

Summary and Conclusions

A simple steady-state non-equilibrium model has been developed that estimates an overall persistence value for any organic chemical from:

- the chemical's air-water and octanol-water partition coefficient K_{AW} and K_{OW} ,
- the chemical's degradation rates into air, water and soil,
- the emission distribution (i.e. how much of the chemical is emitted into air, water and soil, respectively),
- and a set of default environmental parameters.

These factors have been shown to have a strong impact on the calculated overall persistence and to interact with each other in a complex manner. A chemical's overall persistence in the environment is limited only by the fastest and slowest degradation rate in an individual compartment and can adopt virtually every value in between these bounds depending on physical-chemical properties and emission scenario. An estimation of overall persistence based on equilibrium partitioning between environmental compartments can result in a significant over- and underprediction of a chemical's life time in the overall environment. Taking into account the resistances to chemical intermedia transfer therefore seems warranted when estimating an integrated persistence parameter. It is conceivable that a model as the one described here could serve to evaluate a chemical's overall persistence relative to a specified threshold of persistence. That approach is considered superior to an assessment of chemical persistence based on several thresholds for individual compartmental degradation half-lives.

This document is not venturing to suggest what the threshold for the overall persistence value should be that classifies a chemical as persistent. For chemicals which already have been classified as POPs within the framework of international negotiations the persistence criterion model calculates overall persistences in excess of one year (Annex 6). The actual threshold would obviously have to be considerably shorter than one year and is probably dependent on the specific question that a regulatory policy is aiming to address. The persistence threshold may for example serve to identify chemicals whose concentrations in the environment is likely to increase beyond a certain level for a given emission rate. Or a chemical should not be persistent enough to survive the transport over long distances in the atmosphere and ocean currents.

Adopting a suggestion by Webster et al. (1998), the presented persistence criterion model could be modified to accept media specific half-lives as log normal distributions with defined standard deviations rather than as fixed single values. The model result would then be a distribution of overall persistences instead of a single value, reflecting more realistically the large variability of degradation potential in the environment. A persistence criterion could then take the form "overall persistence should be less than 100 days, with a frequency of at least 50%, and 90 % less than 200 days" (Webster et al., 1998).

References

- Dahl, J. **1992**. Papiertaschentuch und Atomreaktor. Aspekte der Dauerhaftigkeit, auch im weiteren Sinne. *Scheidewege* **22**, 238-248.
- Kwok, E.S., Atkinson, R., and Arey, J. **1995**. Rate constants for the gas-phase reactions of the OH radical with dichlorobiphenyls, 1-chlorodibenzo-p-dioxin, 1,2-dimethoxybenzene, and 1,2-dimethoxybenzene, and diphenylether: Estimation of OH radical reaction rate constants for PCBs, PCDDs, and PCDFs. *Environ. Sci. Technol.* **29**: 1591-1598.
- Mackay, D., Shiu, W.Y., and Ma, K.C. **1992 to 1997**. *Illustrated handbook of physical-chemical properties and environmental fate for organic chemicals. Vol.I to V*. CRC Press, Lewis Publishers, New York.
- Müller-Herold, U. **1996**. A simple general limiting law for the overall decay of organic compounds with global pollution potential. *Environ. Sci. Technol.* **30**: 586-591.
- Müller-Herold, U., Caderas, D., and Funck, P. **1997**. Validity of global life-time estimates by a simple general limiting law for the decay of organic compounds with long-range pollution potential. *Environ. Sci. Technol.* **31**: 3511-3515.
- Scheringer, M., and Berg, M. **1994**. Spatial and temporal range as measures of environmental threat. *Fresenius Environ. Bull.* **3**: 493-498.
- Webster, E., Mackay, D. and Wania, F. **1998**. Evaluating Environmental Persistence. *Environmental Toxicology and Chemistry*, in press.

Appendix 1: Description of the Model Equations

Calculation of Z-values

From the equilibrium partition coefficients, pure phase Z-values in units of mol/(Pa·m³) are calculated as follows:

air	$Z_A = 1 / (R \cdot T)$	(Mackay, 1991)
water	$Z_W = 1 / (R \cdot T \cdot K_{AW})$	(Mackay, 1991)
aerosols	$Z_Q = 3.5 \cdot K_{OA} \cdot Z_A$	(Finizio et al., 1997)
organic carbon	$Z_{OC} = 0.41 \cdot Z_W \cdot K_{OW}$	(Karickhoff, 1981)

These pure phase Z-values are weighted with volume fractions to yield the three bulk phase Z-values (in units of mol/(Pa·m³)):

air	$Z_{BA} = Z_A + v_{SA} \cdot Z_Q$
water	$Z_{BW} = Z_W + v_{OW} \cdot Z_{OC}$
soil	$Z_{BE} = v_{AE} \cdot Z_A + v_{WE} \cdot Z_W + (1 - v_{WE} - v_{AE}) \cdot v_{OE} \cdot Z_{OC}$

v_{SA}	volume fraction of solids in air
v_{OW}	volume fraction of organic carbon in water
v_{AE}	volume fraction of air in soil
v_{WE}	volume fraction of water in soil
v_{OE}	volume fraction of organic carbon in soil solids

Calculation of D-values

There are three types of D-values: for degradation, for intermedia transport and for loss by means other than degradation.

Reaction D-values are calculated from first order rate constants ($k = \ln 2 / t_{1/2}$):

in air	$D_{RA} = V_A \cdot Z_{BA} \cdot k_{RA}$
in water	$D_{RW} = V_W \cdot Z_{BW} \cdot k_{RW}$
in soil	$D_{RE} = V_E \cdot Z_{BE} \cdot k_{RE}$
V_X	volume of phase X in m ³
k_{RX}	degradation rate constant in phase X in h ⁻¹

Intermedia Transport D-values

The description of intermedia transport processes is largely based on work by Mackay (1991).

water-air	$D_{WA} = \frac{A_W}{\frac{1}{U_1 Z_A} - \frac{1}{U_2 Z_W}}$
air-water	$D_{AW} = D_{WA} + A_W \cdot (v_D \cdot v_{SA} \cdot Z_Q + U_3 \cdot (Z_W + r_S \cdot v_{SA} \cdot Z_Q))$

$$\text{soil-air} \quad D_{EA} = \frac{A_E}{\frac{1}{U_7 Z_A} - \frac{1}{U_6 \cdot Z_W + U_5 \cdot Z_A}}$$

$$U_5 = 0.0179 \cdot \frac{v_{AE}^{10/3}}{(v_{WE} + v_{AE})^2} \cdot \frac{1}{0.390865 \cdot h_E}$$

$$U_6 = 0.00000179 \cdot \frac{v_{WE}^{10/3}}{(v_{WE} + v_{AE})^2} \cdot \frac{1}{0.390865 \cdot h_E}$$

$$\text{air-soil} \quad D_{AE} = D_{EA} + A_E \cdot (v_D \cdot v_{SA} \cdot Z_Q + U_3 \cdot (Z_W + r_S \cdot v_{SA} \cdot Z_Q))$$

$$\text{soil-water} \quad D_{EW} = wG_{EW} \cdot Z_W + oG_{EW} \cdot Z_{OC}$$

$$wG_{EW} = (1 - frU_E) \cdot U_3 \cdot A_E$$

$$oG_{EW} = wG_{EW} \cdot v_{SE} \cdot v_{OE}$$

A_X	surface area of compartment in m^2
U	mass transfer coefficient (MTC) in m/h
U_1	MTC for air-water exchange, air side
U_2	MTC for air water exchange, water side
U_3	precipitation rate
U_5	MTC for diffusion through soil air
U_6	MTC for diffusion through soil water
U_7	MTC for air-soil exchange, air side
h_E	soil depth in m
v_D	dry depositon velocity in m/h
r_S	particle scavenging ratio
wG_{EW}	flow of water from soil to water in m^3/h
oG_{EW}	flow of organic carbon from soil to water
frU_E	fraction of precipitation to soil evaporating from soil
v_{SE}	volume fraction of solids in soil run-off water

Loss D-values describing loss by mechanisms other than reaction

$$\text{from air} \quad D_{LA} = A_A \cdot U_{AdvA} \cdot Z_{BA}$$

$$\text{from water} \quad D_{LW} = A_W \cdot U_{AdvW} \cdot Z_{BW} + oG_{LW} \cdot Z_{OC}$$

$$\text{from soil} \quad D_{LE} = A_E \cdot U_{Sorb} \cdot Z_{OC}$$

U_{AdvA}	MTC for the exchange between troposphere and atmosphere
U_{AdvW}	MTC for the exchange between surface water and deeper water
oG_{LW}	net-loss of organic carbon from water in m^3/h
U_{Sorb}	MTC for the irreversible sorption of chemical to soil or the bedrock beneath

D_{LA} describes the exchange between troposphere and stratosphere. D_{LW} comprises net sedimentation of chemical sorbed to POC to sediments and deeper water layers, loss of chemical by water being advected to deeper water layers. The loss by net-diffusion of chemical to sediments is assumed to be negligible. D_{LE} describes the irreversible sorption in soil or in the ground below.

Mass Balance Equations

The steady state mass balance equations for the three model compartments read:

$$\text{Air} \quad E_A + D_{WA} \cdot f_W + D_{EA} \cdot f_E = (D_{RA} + D_{LA} + D_{AW} + D_{AE}) \cdot f_A$$

$$\text{Water} \quad E_W + D_{AW} \cdot f_A + D_{EW} \cdot f_E = (D_{RW} + D_{LW} + D_{WA}) \cdot f_W$$

$$\text{Soil} \quad E_E + D_{AE} \cdot f_A = (D_{RE} + D_{LE} + D_{EW} + D_{EA}) \cdot f_E$$

Which are solved for the three fugacity values f_A , f_W and f_E .

Calculation of Persistence

The overall persistence in the environment is calculated as:

$$T = (f_W \cdot Z_{BW} \cdot V_W + f_E \cdot Z_{BE} \cdot V_E + f_A \cdot Z_{BA} \cdot V_A) / ((D_{RA} + D_{LA}) \cdot f_A + (D_{RW} + D_{LW}) \cdot f_W + (D_{RE} + D_{LE}) \cdot f_E)$$

Finizio, A., Mackay D., Bidleman T., and Harner T. **1997**. Octanol-air partition coefficient as a predictor of partitioning of semivolatile organic chemicals to aerosols. *Atmospheric Environment* **31**, 2289-2296.

Karickhoff, S.M. **1981**. *Chemosphere* **10**, 833-849.

Mackay, D. **1991**. *Multimedia Environmental Models: The Fugacity Approach*. Chelsea, MI: Lewis. 257 pp.

Appendix 2: Environmental Default Parameters

TK	temperature	283.15 K
h_A	atmospheric height	6000 m
h_E	soil depth	0.05 m
h_W	depth of the water compartment	50 m
A_T	total global surface area	$5.1 \cdot 10^{14} \text{ m}^2$
FRTAW	fraction of the total area that is covered by water	$0.702 \text{ m}^2/\text{m}^2$
V_{SA}	volume fraction of aerosol in atmosphere	$2 \cdot 10^{-11} \text{ m}^3/\text{m}^3$
V_{WE}	volume fraction of water in soil	$0.2 \text{ m}^3/\text{m}^3$
V_{AE}	volume fraction of air in soil	$0.3 \text{ m}^3/\text{m}^3$
V_{SE}	volume fraction of suspended solids in soil run-off water	$0.00005 \text{ m}^3/\text{m}^3$
U_7	air side MTCs over soil	5 m/h
U_1	air side MTC over water	5 m/h
U_2	water side MTC for air-water exchange in m/h	0.05 m/h
V_D	dry particle deposition velocity in m/h	10 m/h
U_{AdvW}	MTC for exchange between surface and deep water	5 / 8760 m/h
U_{AdvA}	MTC for exchange between troposphere and stratosphere	0.01 m/h
U_{Sorb}	MTC describing irreversible sorption in soil and ground below	$1.338 \cdot 10^{-9} \text{ m/h}$
r_S	particle scavenging ratio	200000
U_3	rain rate	100 cm/a
frUE	fraction of the precipitation to soil, which evaporates from the soil	0.5
OC_E	organic carbon mass fraction of solids in soil	0.02 g/g
BP_W	biological production of organic carbon in water	$100 \text{ gC}/\text{m}^2\text{a}$
C_{pocW}	concentration of POC in water	$5 \text{ g}/\text{m}^3$
facOWmiw	fraction of POC input to water mineralised in the water	0.95

Environmental parameters should as much as possible reflect global average conditions, or global totals.

Appendix 3: Evaluating The Influence of Long Range Transport on the Estimated Global Persistence of α -HCH

The overall persistence value derived from the simple persistence criterion model presented above was compared with the overall persistence of α -HCH calculated using a complex global distribution model. The highly complex global distribution model by Wania and Strand (1998) takes into account climatic differences in chemical degradation and intermedia transport rates. Degradation rates in that model are calculated as functions of environmental parameters such as temperature, OH radical concentration and pH.

A detailed description of the global model calculations for α -HCH for the time period 1947 to 1996 can be found in Wania et al. (1998) and Wania and Mackay (1998). The persistence of α -HCH in the global distribution model changed in time (Fig. A3), because the zonal and the compartmental distribution of this chemical changed in time - mostly as a result of changes in the location and amount of emission. Namely, the persistence increased in the 1990s because an increasing fraction of the total global inventory of this chemical is in high latitudes with low degradation potential. There is also a seasonal dependence with lower persistence during the northern hemispheric summer, because degradation rates are correlated with temperature and most of the α -HCH resides in the Northern hemisphere. The calculated persistence during the 50 years of α -HCH usage averages at 280 days and is almost entirely due to degradation, i.e. transfer to the deep sea and sediment burial are insignificant loss processes.

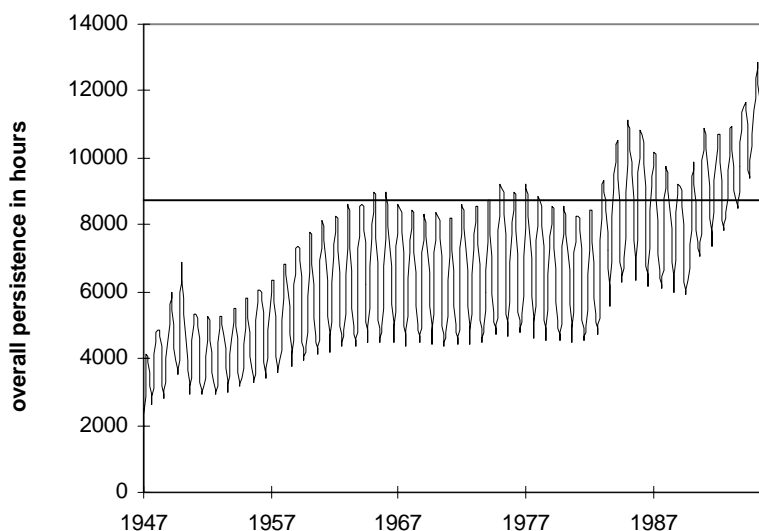


Fig. 3A Overall persistence of α -HCH as calculated by a global distribution model during the time period 1947-1996. Persistence is defined as the ratio between total amount of chemical in the global environment in kg divided by the total loss by degradation, loss to the deep sea and sediment burial in kg/h.

For the estimation of the overall persistence of α -HCH using the simple Persistence Criterion model we calculated degradation half-lives in air, water and soil of 187, 10443 and 5236 hours, respectively. These are derived from the functions used in the global

distribution model to calculate reaction rate constants assuming an average temperature of 10 °C, a pH of 8.1, and an OH radical concentration in air, that reflects the annual average conditions in mid-latitudes (subtropical zone of the global distribution model) at sea level.

With 92.5 % emissions into soil, 5 % into air and 2.5% into water, the calculated overall persistence is 321 days, which is rather close to the average value of 280 days obtained by the global distribution model.

Wania, F., Strand, A. **1998**. Introducing Atmospheric Layering in a Global Distribution Model for Persistent Organic Pollutants Based on the Fugacity Approach. Manuscript.

Wania, F., Mackay, D., Li, Y.-F., Bidleman, T.F. **1998**. Global Chemical Fate of α -Hexachlorocyclohexane. 1. Evaluation of a Global Distribution Model. Manuscript.

Wania, F., and Mackay, D. **1998**. Global Chemical Fate of α -Hexachlorocyclohexane. 2. Use of a Global Distribution Model for Mass Balancing, Source Apportionment, and Trend Predictions. Manuscript.

Appendix 4: Extreme Partition Coefficients

To decide on the range of partition coefficients used in the evaluation of the persistence criterion model, extreme values of K_{AW} and K_{OW} were identified using the series of handbooks on physical-chemical properties by Mackay et al. (1992-97) and Table 6.1 in Majewski and Capel (1995). The tables list the maximum and minimum K_{AW} and $\log K_{OW}$ values found.

Air water partition coefficient K_{AW} :

	H in Pam ³ /mol	log H	log K_{AW} (at 10 °C)	log K_{OW}
maximum				
2-Methylbutane	479118	5.68	2.31	≈ 3
n-Decane	478861	5.68	2.31	6.25
minimum				
Amitrole	1.65e-10	-9.78	-13.15	0.52
Metsulfuron-methyl	1.34e-11	-10.87	-14.24	?

Octanol-water partition coefficient log K_{OW} :

maximum	dioctyl phthalate	log K_{OW} = 9.87
	stearic acid	log K_{OW} = 8.23
	OCDD	log K_{OW} = 8.2
	DecaCB	log K_{OW} = 8.26
minimum	Diquat	log K_{OW} = -3.05
	Urea	log K_{OW} = -2.11

Mackay, D., Shiu, W.Y., and Ma, K.C. **1992 to 1997**. *Illustrated handbook of physical-chemical properties and environmental fate for organic chemicals. Vol. I to V*. CRC Press, Lewis Publishers, New York.

Majewski, M.S., and Capel P.D. **1995**. *Pesticides in the atmosphere: distribution, trends and governing factors*. Ann Arbor Press, Ann Arbor, MI.

Appendix 5: Overall Persistence for Different Combinations of Partition Coefficients

log K_{OA} and log K_{AW}

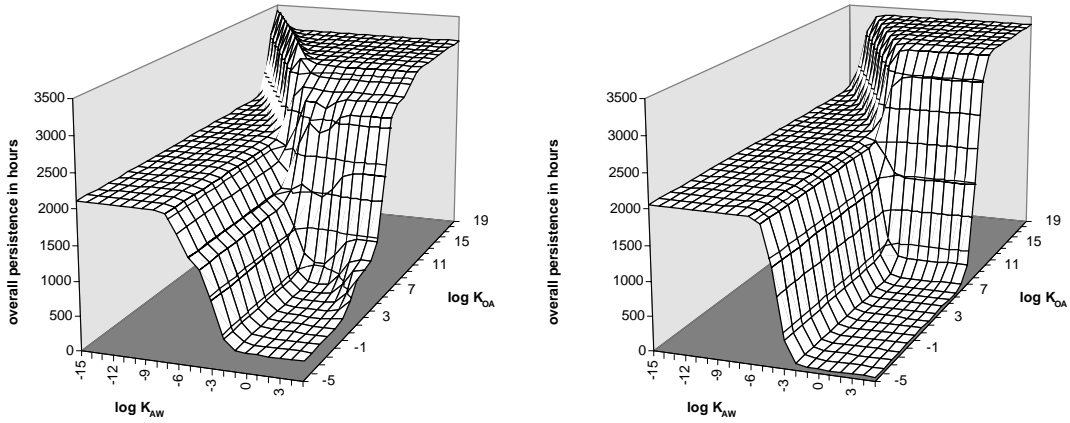


Fig. 5A Dependence of overall persistence on physical chemical properties as expressed by log K_{OA} and log K_{AW}. Assumptions: Equal fraction of emissions into air, water and soil. Half-lives 48 h in air, 1460 h in water and 4380 in soil. Level III on the left, level II on the right.

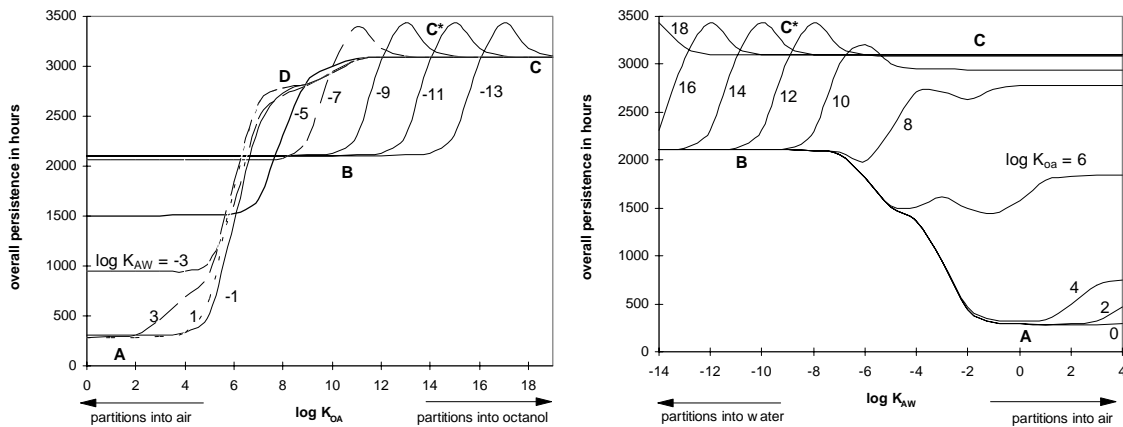


Fig. 5B Two-dimensional version of the left graph in Figure 5A.

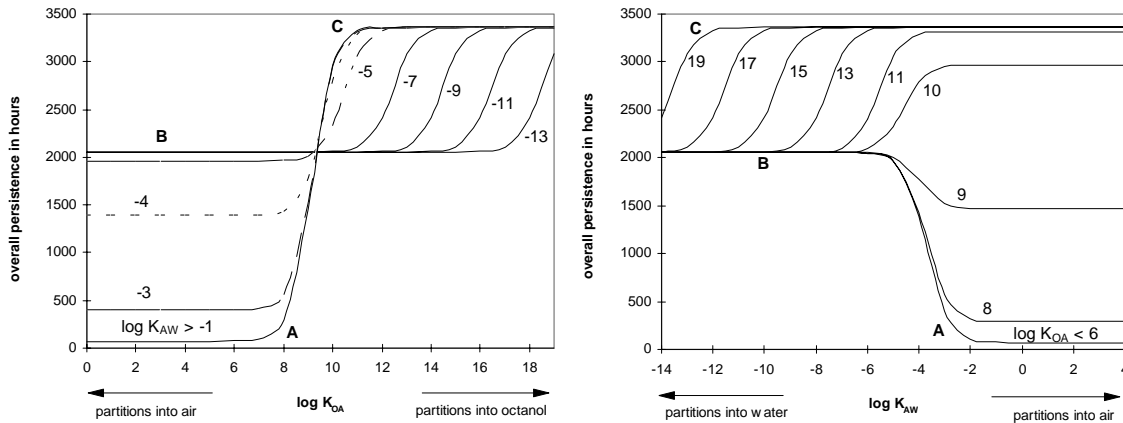


Fig. 5B Two-dimensional version of the right graph in Figure 5A.

log K_{OA} and log K_{OW}

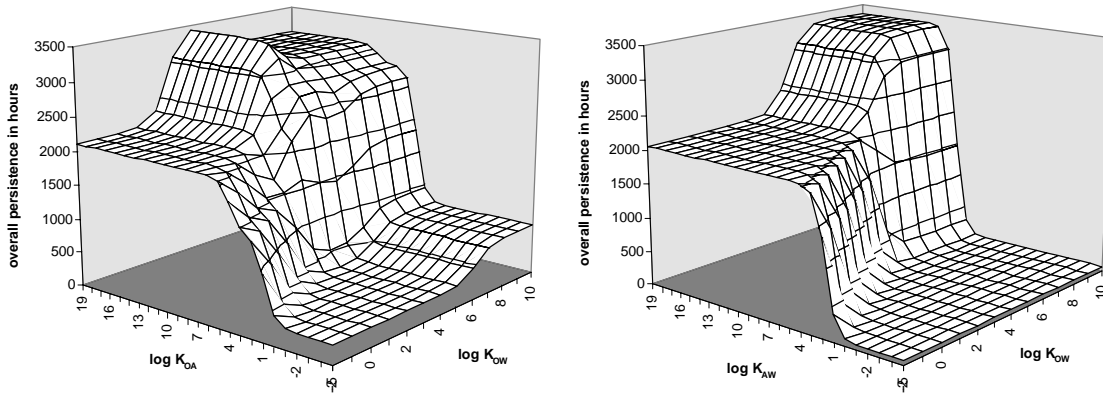


Fig. 5D Dependence of overall persistence on physical chemical properties as expressed by log K_{OA} and log K_{OW}. Assumptions: Equal fraction of emissions into air, water and soil. Half-lives 48 h in air, 1460 h in water and 4380 in soil. Level III on the left, level II on the right.

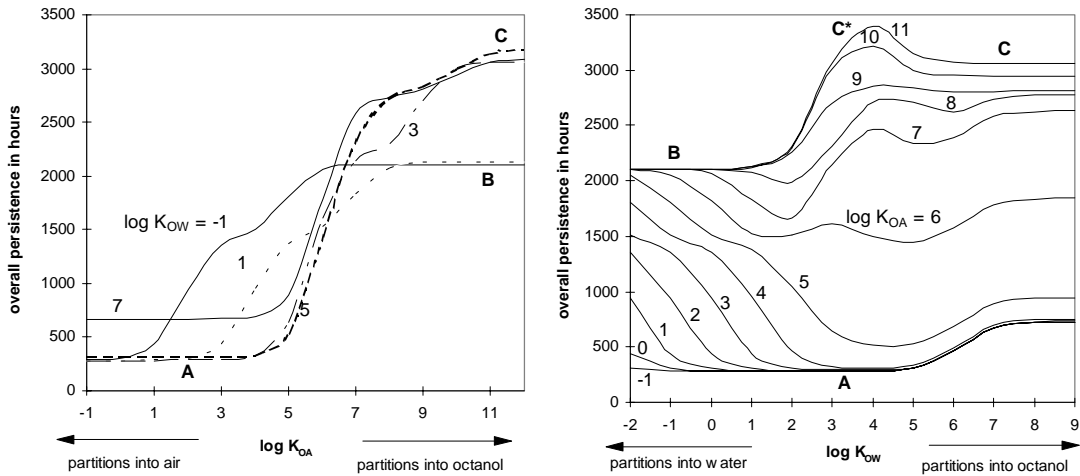


Fig. 5E Two-dimensional version of the left graph in Figure 5D.

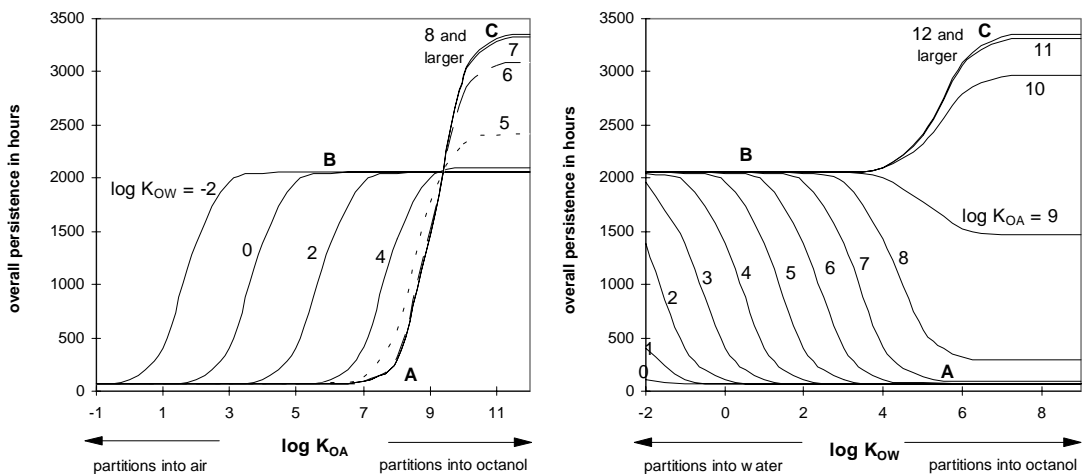


Fig. 5F Two-dimensional version of the right graph in Figure 5D.

Appendix 6: Calculating Overall Persistence for typical POPs

To assess the performance of the persistence criterion model, we calculated the overall persistence for the substances that are under consideration for global action by UNEP. These chemicals can be interpreted as being prototypes of the type of chemicals that the persistence criterion model is aiming to identify. It should thus be illuminating to compare and evaluate the overall persistence values calculated by the persistence criterion model for these chemicals

Table 6.1 lists the model input parameters. The physical-chemical properties and the estimated degradation half-lives are taken from the series of handbooks by Mackay et al. (1992 to 1997). Endrin was not included in this exercise, because no degradation half-lives for this pesticide are given in that reference. For PCBs, average chemical properties describing approximately the mixture of isomers that make up the technical PCB mixtures were used, whereas for the polychlorinated dioxins and -furans (PCDD/DFs) the physical-chemical properties and degradation half lives of a representative isomer were selected. The half-lives from the handbooks were convenient to use in this exercise as they provide a consistent and thus comparable data set. However, they should be regarded as only a first guess at the environmental persistence in various media.

For the pesticides among the chemicals, it was assumed that most is emitted into soils, with minor fractions into atmosphere and water. The PCBs were assumed to reach the environment predominantly through the atmosphere, whereas PCDD/DFs were assumed to reach the environment through a multitude of pathways (see Table 6.1).

Tab. 6.1 Input parameters for the persistence criterion model for 11 selected compounds.

name	physical chemical properties at 25°C			degradation half life in hours			medium of emission in %		
	log K _{ow}	H	log K _{AW}	in air	in water	in soil	air	soil	water
Aldrin	3.01	91.23	-1.43	5	17000	17000	5.0	92.5	2.5
Chlordane	6	0.302	-3.91	55	17000	17000	5.0	92.5	2.5
DDT	6.19	2.36	-3.02	170	5500	17000	5.0	92.5	2.5
Dieldrin	5.2	1.12	-3.35	55	17000	17000	5.0	92.5	2.5
Heptachlor	5.27	353.4	-0.85	55	550	1700	5.0	92.5	2.5
HCB	5.5	131	-1.28	17000	55000	55000	5.0	92.5	2.5
Mirex	6.9	839.4	-0.47	170	170	55000	5.0	92.5	2.5
Toxaphene	5.5	0.745	-3.52	170	55000	55000	5.0	92.5	2.5
"PCBs"	6.5	100	-1.39	1700	55000	55000	90.0	5.0	5.0
2,3,7,8-TCDD	6.8	3.337	-2.87	170	550	17000	33.3	33.3	33.3
2,3,7,8-TCDF	6.1	1.461	-3.23	170	550	17000	33.3	33.3	33.3

Table 6.2 lists the calculated overall persistence values calculated by the persistence criterion model. For comparison, also the overall persistences from a level II approach are presented.

Tab. 6.2 Overall persistence calculated by the persistence criterion model.

name	level III		level II	
	days	years	days	years
Aldrin	10	0.0	0.3	0.0
Chlordane	944	2.6	400	1.1
DDT	926	2.5	281	0.8
Dieldrin	916	2.5	79	0.2
Heptachlor	77	0.2	4	0.0
HCB	1775	4.9	1133	3.1
Mirex	1961	5.4	15	0.0
Toxaphene	2759	7.6	440	1.2
PCBs	399	1.1	353	1.0
2,3,7,8-TCDD	369	1.0	83	0.2
2,3,7,8-TCDF	359	1.0	70	0.2

These chemicals have overall persistence values of one year or more. Two notable exception, aldrin and heptachlor, have relatively short calculated persistences. This, however is misleading, because these chemicals are rather rapidly transformed into the more persistent degradation products photoaldrin and heptachlor epoxide. For such chemicals it is imperative to use degradation half-lives in the model that are indicative of the persistence of both the chemical and its degradation product(s).

The overall persistence value calculated for the OC pesticides tends to be very high (longer than 2 years) because they are (1) highly hydrophobic ($\log K_{ow} > 5$), (2) are emitted into soil and (3) have high persistence in the soil environment (usually assumed to be in the range of several years). These chemicals therefore are emitted into a medium in which they have high persistence and from which they are transferred only slowly to other media in which they may react faster.

A level II-based estimation which assumes equilibrium partitioning, may severely underestimate the real environmental half-life of such a chemical by assuming partitioning into a phase with high degradation half-life, which the chemical cannot reach because of significant intermedia transfer resistances. A good example is Mirex, which in the level III approach has a very long half-life of more than five years, reflecting its high persistence in soil. In contrast, a level II approach suggest a half-life of only 15 days due to relatively high degradation rates of mirex in water and air. Because of its extremely low water solubility and vapour pressure, Mirex is likely to be retained very effectively in the soil, and is unlikely to evaporate into the atmosphere or leach into water to an extent that would result in a significantly lower overall half-life.

Mackay, D., Shiu, W.Y., and Ma, K.C. **1992 to 1997**. *Illustrated handbook of physical-chemical properties and environmental fate for organic chemicals. Vol.I to V*. CRC Press, Lewis Publishers, New York.