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**PERSISTENCE AND TRANSPORT POTENTIAL OF CHEMICALS
IN A MULTIMEDIA ENVIRONMENT**

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5. PERSISTENCE AND TRANSPORT POTENTIAL OF CHEMICALS IN A MULTIMEDIA ENVIRONMENT

5.0 Introduction

Persistence in the environment and potential for long-range transport are related since time in the environment is required for transport. A persistent chemical will travel longer distances than a reactive chemical that shares similar chemical properties. Scheringer (1997) has demonstrated the correlation between persistence and transport distance for different organic chemicals. However, this correlation is not sufficiently robust to predict one property from the other (see Figure 5-9). Specific chemicals that are persistent may or may not exhibit long-range transport potential. Persistence and long-range transport also present different societal concerns. Persistence concerns relate to the undesired possibility that chemicals produced and used now may somehow negatively affect future generations. Long-range transport concerns relate to the undesired presence of chemicals in areas where these compounds have not been used.

Environmental policy decisions can be based on either or both considerations depending on the aim of the regulatory program. In this chapter, definitions and methods for quantifying persistence and transport potential of organic chemicals are proposed which will assist in the development of sound regulatory frameworks.

5.0.1 *Multimedia modeling tools*

The models proposed for calculating both persistence and transport potential are based on the standard unit-world fugacity modeling concept as developed by Mackay and co-workers. Mass balance models of this kind have been discussed since the late 70s (Mackay, 1991). Versions and extensions of Mackay's modeling concept have been produced and tested by various authors (McKone, 1993; ECETOC, 1994, Van de Meent, 1993, Brandes *et al.*, 1996; Wania and Mackay, 1995, Trapp and Matthies, 1998). It has been shown that different models in this family yield similar results for primary compartments (*i.e.* air, water, soil, sediment) if calibrated with the same dimensions and chemical inputs (Cowan *et al.*, 1995,

Tell and Parkerton, 1997). This model concept is now widely accepted as a useful tool for gaining an understanding of the fate of chemicals in multimedia environments. This concept has also found acceptance in regulatory practice in a number of countries. For example, the EU uses a level III model as a regional distribution model for the evaluation of new and existing chemicals (Vermeire *et al.*, 1997; Brandes *et al.*, 1996). The US EPA has also proposed to use a level III multimedia model for evaluating Persistent, Bioaccumulative and Toxic (PBT) chemicals (U.S. Federal Register, 1999) while California EPA uses a level III model as a framework for regulating hazardous waste sites (Cal-EPA, 1997).

Application of the above models requires parameterization of the following key chemical-specific inputs:

- Intermedia partition coefficients describing the equilibrium distribution of the chemical between air-water and soil/sediment-water phases
- Pseudo first-order transformation rate constants or reaction half lives of the chemical in air, water and soil/sediment
- Mode of entry into the environment (proportions emitted to air, water and soil)

Application of the model implicitly assumes an array of intermedia mass transfer coefficients¹.

5.1 Persistence in a Multimedia Environment

5.1.1 Definition of Persistence

Given a defined rate of chemical release into the environment, concentrations in air, water and soil are controlled by various chemical and landscape properties, including the persistence of

¹ Some of the senior scientists stress that the numerical values of the intermedia transfer coefficients used in the present level III models lack scientific justification. There is considerable uncertainty about the correctness of the assumed values. These assumptions need further testing, especially so with respect to gas-phase exchange between the atmosphere and soil, and with respect to sediment-water exchange. They plea for use of a level II model, in which fast intermedia transfer is assumed. While the concern about intermedia transport coefficients was shared by the modeling workgroup, it was argued that the implicit assumption of zero mass transfer resistance in level II suffers from the same drawbacks.

the chemical. Persistent chemicals last longer in the environment. Persistence affects the potential for environmental exposure since persistent chemicals:

- *exhibit higher concentrations per unit emission*
- *are eliminated more slowly in response to emission reductions*

If emissions are relatively constant over a sufficiently long period of time, concentrations will build up to a steady state, in which releases are balanced by losses. For ordinary chemicals (extremely persistent chemicals e.g. metals excluded), time scales of practical use (decades) are usually “sufficiently long” to reach a steady state. At steady state, the amounts present in the environment are inversely related to the overall transformation rate (proportional to the overall residence time and half-life) in the environment. The overall transformation rate in the environment is a composite of transformation rates for air, water, and soil, weighted by the relative amount of chemical in these media.

If, after a certain period of use, emissions drop to near zero, the amount of chemical in the environment will decrease. The rate of elimination is characterized by the overall transformation rate in the environment. Initially, this is the rate constant at steady state. However, as elimination proceeds, the relative amounts of chemical in air, water and soil will generally change. This will be more pronounced if the differences in transformation rates are great, inter-media mass transfers are slow, and significant amounts are present in a “slow” compartment. As a result, the effective transformation rate constant will decrease with time. Generally, the time necessary for half or near-complete (e.g. 50% or 95%) elimination will be longer than suggested by the steady state rate constant as illustrated in Figure 5-1. These principles have been used to develop operational definitions of persistence (Van de Meent *et al.*, 1992; Webster *et al.*, 1998).

To provide a consistent, pragmatic approach, we propose to operationally define “persistence in the environment” as the overall residence time at steady state in a multimedia environment. A simple level III multimedia mass balance model is used for this calculation in which only irreversible losses are considered. Irreversible losses consist primarily of chemical transformation of the parent compound, but also include unidirectional transport such as

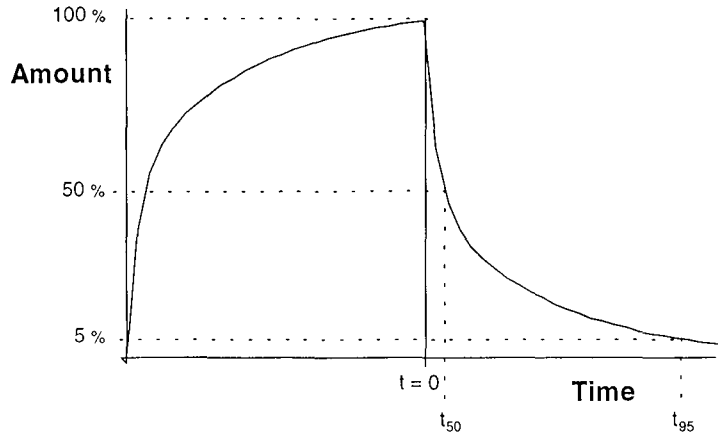


Figure 5-1 Persistence may be defined on the basis of half-life at steady state or time to eliminate $x\%$.

transport to deep ocean layers, burial in deep sediments and transport to groundwater as well as the upper atmosphere. The dimensions of the model are set to global proportions so as to mimic a closed system, from which no advective losses occur (via air or water flows) as shown in Figure 5-2.

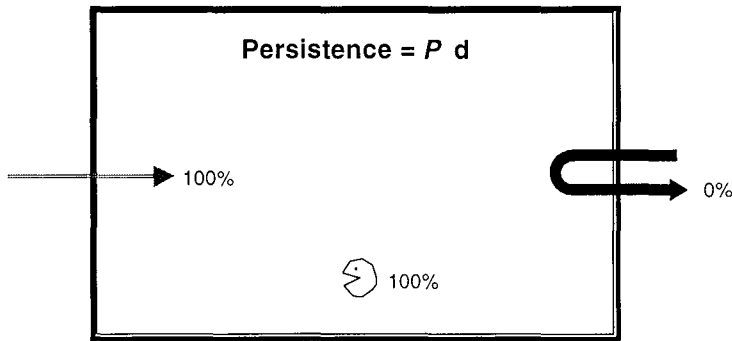


Figure 5-2 A closed-system model (no transport, transformation only) is proposed for calculating the overall residence time in the environment as a measure of persistence, P . An open system (with advective transport) is described in section 5.2.2 for defining characteristic scale, L , as a measure of transport potential.

5.1.2 Environmental Distribution Considerations in Persistence Assessment

The primary shortcoming of relying on single media degradation half-lives in assessing persistence is that each media is given equal importance in the decision process. Thus, there is a possibility that the importance of a half-life is severely over or underestimated. A half-life in a media in which the chemical does not partition is of little significance, whereas a half-life in a medium into which a chemical is emitted and from which it is only slowly transferred to other media is obviously of critical importance.

For chemicals which appear principally in only one environmental medium, the decay rates in the remaining media are of no significance, and should therefore not be used in persistence classification decisions. Therefore, a tiered screening procedure is suggested. First, classify chemicals as either single media chemicals or as multimedia chemicals. Then, for single-media chemicals, use the half-life in the applicable single media to identify non-persistent single media compounds that warrant low priority. For single media chemicals with half-lives in the relevant media that exceed prescribed half-life criteria, additional evaluative tiers are considered.

For multimedia chemicals, we propose an initial screening process based on a classification process discussed in section 5.5, followed by the use of multimedia models for possibly persistent chemicals.

Screening for Single-media Chemicals - This tiered process proceeds by first assigning chemicals to four classes based on partitioning properties:

A: gas phase chemicals: chemicals which partition into the gas phase, no matter what the mode of entry into the environment or the environmental characteristics.

B: aqueous phase chemicals: chemicals which partition into the aqueous phase, no matter what the mode of entry into the environment or the environmental characteristics.

C: solid phase chemicals: chemicals which partition into the solid phases (soils, sediments), no matter what the mode of entry into the environment or the environmental characteristics.

D: multimedia chemicals: chemicals which do not fall into one of the three other categories, i.e. chemicals which partition into more than one environmental medium at least under some circumstances (i.e. mode of entry).

Only two physical chemical-property parameters should be necessary for this classification, namely two out of the following three equilibrium partitioning coefficients:

octanol-water partition coefficient K_{OW}

air-water partition coefficient (Henry's law constant) K_{AW}

octanol-air partition coefficient K_{OA}

This categorization can be visualized on a coordinate system mapping chemicals according to partitioning properties (Figure 5-3). Class A chemicals are located in the corner of the diagram with high $\log K_{AW}$ and $\log K_{OW}$, class B chemicals are in the corner of low $\log K_{AW}$ and low $\log K_{OW}$, whereas class C chemicals are characterized by low $\log K_{OA}$ values. These boundaries are defined such that a classification can be made regardless of mode of entry, i.e. the partitioning is strong enough to overcome the resistance to transfer between phases. The decision on which combination of physical-chemical properties leads to a classification into one of these four groups is based on model calculations using the previously described global model.

It is suggested that the boundaries in Figure 5-3 used to identify single media chemicals versus multimedia chemicals be constructed as follows.

To define the limits for class A chemicals, a global scale multimedia model (Model A described in detail in section 5.1.4) is used and the half-lives in all compartments except air are set to infinity. The degradation half-life in air is set to the specified criteria value, T_{Acrit} . Class A compounds are then defined as chemicals with a combination of K_{AW} and K_{OW} values that yield a calculated persistence that is within a factor of X of T_{Acrit} , i.e. $T_{overall} < X \cdot T_{Acrit}$. X is determined such that $T_{overall}$ never exceeds the desired value for overall persistence. For example, $X = 2$ means that despite being infinite, the degradation half-lives in the other media can only double the overall persistence relative to the half-life in air. This implies that the other phases have such a minor influence that they can safely be neglected. The boundaries

must be confirmed for all three modes of entry. An identical procedure is then employed to define classes B and C.

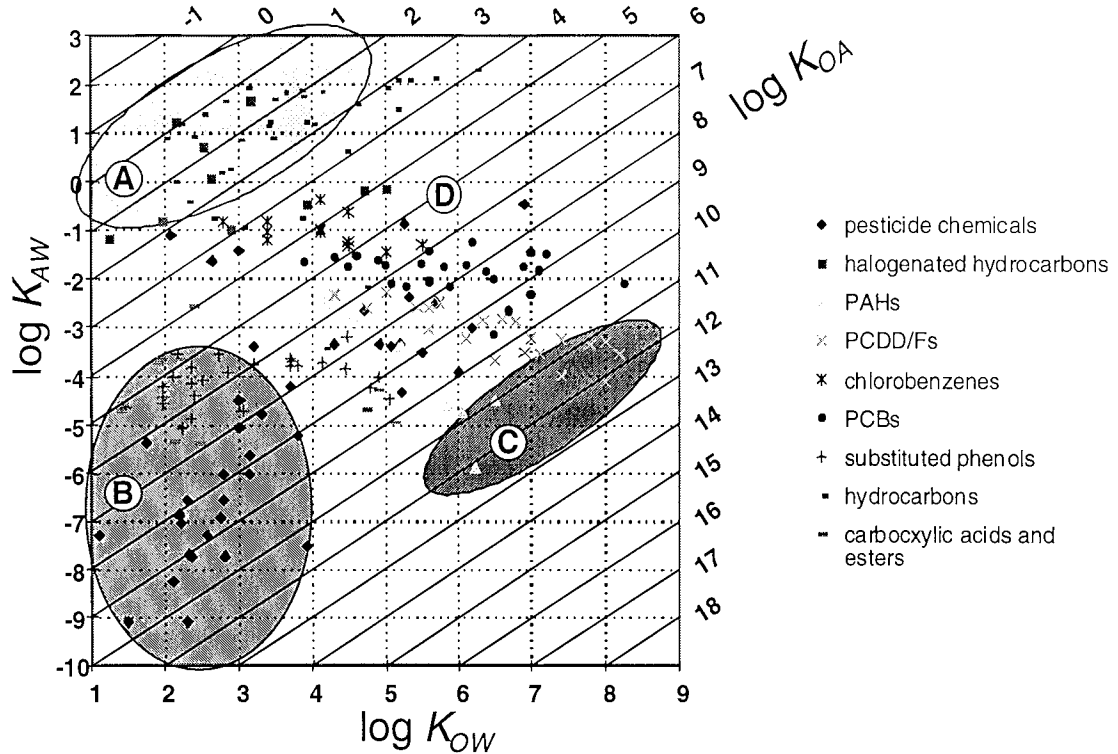


Figure 5-3 Plot showing the location of various organic chemicals in a two-dimensional space defined by the octanol-water and the air-water partition coefficients $\log K_{AW}$ and $\log K_{OW}$. Chemicals in group A partition exclusively into the gas phase, those in group B partition into the aqueous phase and those in group C partition into soils and sediments. Group D chemicals are multi-media substances. From Wania (1998)

5.1.3 Persistence Assessment for Single-Media Chemicals

Once classified as single media chemicals these compounds can be screened for persistence by comparing the degradation half-life in the medium of dominant occurrence T_X with a criteria value T_{Xcrit} . If $T_X < T_{Xcrit}$ the chemical is deemed non-persistent:

For class A chemicals: $T_A < T_{Acrit}$

For class B chemicals: $T_W < T_{Wcrit}$

For class C chemicals: $T_S < T_{Scrit}$

T_A , T_W , and T_S refer respectively to chemical half-life in air, water, and soil/sediment.

Single media chemicals that fail this screening tier as well all group D compounds proceed to further evaluative tiers.

The advantage of this first screening step is that degradation half-lives in media into which a chemical never partitions are not required in the screening process. It is likely that data for these half-lives would not be available or would be difficult to obtain. For example, the atmospheric degradation half-life of a chemical that is extremely non-volatile (e.g. a class C chemical) is very hard to determine experimentally, just as it is difficult, if not impossible to measure the degradation half-life in soil of an extremely volatile substance (e.g. a class A chemical). Consequently, this approach helps focus data collection efforts and decisions on the relevant degradation pathways that dictate persistence behavior.

In developing this first screening step, we note that there are a number of options for increasing the selectivity of this tier, including the following:

Option 1: If “mode of entry” information is available, it is feasible to screen out more chemicals in this first step. For example, the number of gas phase chemicals (class A) increases if the mode of entry is only into the atmosphere. In other words, the boundaries of the three groups A, B, and C can be moved further towards the center of Figure 3 if the mode of entry is to the same media that the chemical is expected to partition.

Option 2: Since class boundaries are somewhat dependent on environmental parameters, e.g. temperature, it is conceivable to define boundaries for different sets of environmental conditions. This means that the screening could be adjusted for site-specific conditions, e.g. for various climates.

Option 3: Under certain combinations of decay rates and partitioning behavior, a chemical can still be classified as non-persistent. This method eliminates some of the multi-media chemicals, as well as incorporating several of the previously mentioned rules. This can be completed using a model for persistence and a classification scheme, as discussed in section 5.5.

5.1.4 Persistence Assessment for Multi-Media Chemicals

For a chemical that is in category D, a *multimedia chemical*--which can partition in more than one environmental medium at least under some circumstances, the determination of persistence must be based on multimedia partitioning in combination with information on chemical half-lives in the various media. The relative distribution between compartments is influenced by:

- equilibrium partitioning of the chemical
- kinetics of chemical transfer between the media
- mode of emission into the environment
- nature of the environment (as it influences inter-compartmental partitioning and transfer).

Multimedia compartmental fate models (Cowan *et al.*, 1995) address all these issues in combination and thus are uniquely suited for the task of estimating the weighting factors, or chemical mass distribution. Persistence P is calculated as the overall residence time τ_{overall} of the chemical in the multi-media system (Webster *et al.* 1998):

$$P = \tau_{\text{overall}} = \sum M_i / \sum (M_i \cdot k_i) \quad (5.1)$$

Where M_i refers to the mass inventory (kg) and k_i refers to transformation rate constant (d^{-1}) in each of the i model compartments. The following different modeling approaches are suggested as tools for assessing persistence of multimedia chemicals (Figure 5-4).

Model A: a very simple global scale model with only three compartments (air, water, soil), five inter-compartmental transfer rates, three degradation loss and three permanent loss processes, as described by Wania (1998)

Model B: a global scale model similar to model A, but which additionally includes fresh water and fresh water sediments

Model C: a regional scale model similar to model B, but with regional rather than global dimensions (Webster *et al.* 1998, Beyer *et al.* 2000)

Model D: a continental model nested in global model, as described by Brandes *et al.* (1996). This would address the concern that only a small part of the chemical used on the continental scale interacts with the ocean.

Model E: a more complex model that includes either more nested compartments or a linked set of multimedia compartments as has been used by Wania and Mackay (1995) and Scheringer (1996, 1997)

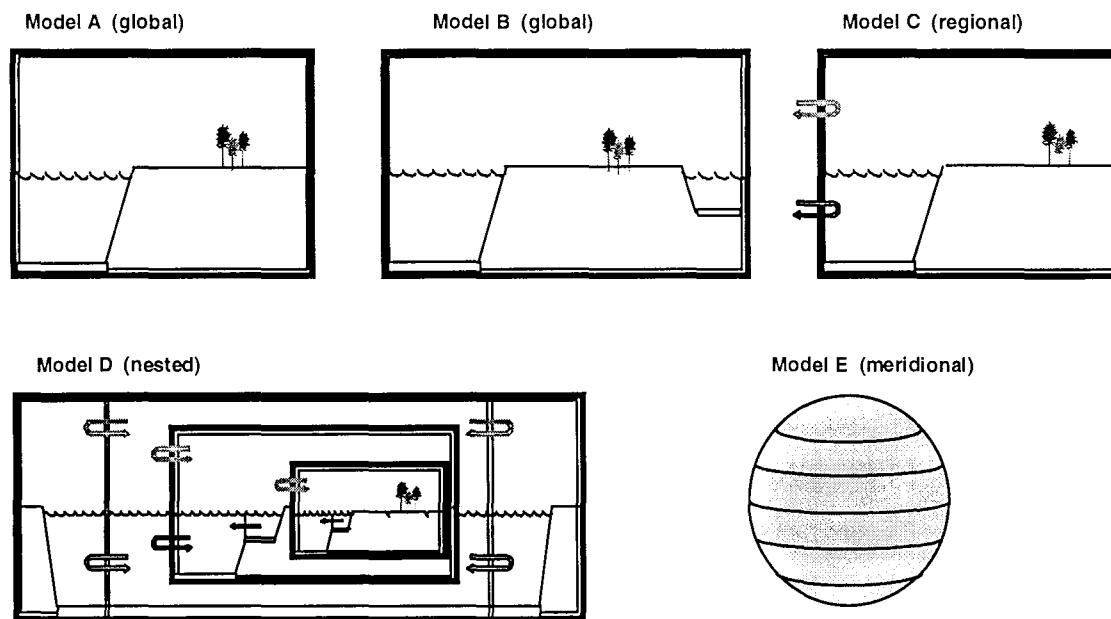


Figure 5-4 Multi-media model approaches for calculating overall residence time in the environment as a measure of persistence.

These modeling approaches should be evaluated by using them to determine the overall persistence values for a range of chemicals. The output from these different models should be compared based on the following criteria:

- The absolute scale of the calculated persistence values.
- The relative ranking of the chemicals according to persistence.
- The dependence of the calculated persistence values on the environmental parameters.
- The analysis of large deviations of persistence values between the various models, with an aim to identify the potential of a particular model to incorrectly categorize persistence.

On the basis of such a comparative model evaluation, it should be feasible to identify the simplest model approach that will minimize the likelihood that persistent chemicals are misclassified².

5.1.5 Important Issues in Multimedia Model Selection

A number of important issues must be considered in the process of selecting the multimedia model used for persistence calculations.

Level II or III: Equilibrium Partitioning vs. Steady-State?

The main requirement for such a model is to be as simple as possible, yet estimate the relative media distribution of a chemical as realistically as possible. In principle, several approaches to estimating the relative media distribution exist:

Assumption of equilibrium partitioning among all compartments. This approach implies that the resistances to inter-compartmental transfer are zero and that there are no effects from advective processes between compartments, often referred to as a “level II” calculation. There is no need to define the mode of emission or the environmental parameters that influence inter-compartmental transfer such as deposition velocities and mass transfer coefficients, but environmental parameters that define size and composition of the environmental media are still required.

Assumption of a system in steady state, with mass transfer resistances between the compartments. This implies that no change in time occurs and at any point in time, inputs and outputs are balanced. This is often labeled a “level III” calculation. This method is more realistic because the mass distribution reflects the shift from equilibrium resulting from both transport and the mode of entry.

² Late 1998, F. Wania initiated a comparative study by modellers to find out how sensitive the computed *P*-value is to model settings. Multimedia modellers were asked to compute *P* with their own favorite model for 180 chemicals, based on a distributed table of properties and half lives. No results are available at this time.

More complex approaches could be envisaged that require neither the assumption of equilibrium nor steady state. Existing approaches to calculating overall persistence have been either at level II (Müller-Herold 1996, Müller-Herold *et al.* 1997), level III, (Webster *et al.* 1998, Bennett *et al.* 1999) or for a pulse input (Scheringer 1996 and 1997).

Model Scale

With regard to the scale of the modeled environment, the two basic options are (1) a model describing the entire global environment or (2) a defined regional subsection. Each model scale has advantages and disadvantages:

Global scale:

- + System boundaries are well defined, thus there is only one overall persistence value. This system is naturally closed, i.e. no atmospheric or oceanic advection out of the global system occurs; choice of environmental parameters are constrained to global averages.
- Many chemicals, particularly less persistent ones, do not “experience” the whole global environment, but tend to be limited to a smaller scale. Namely, the water volume will tend to be over-represented in a global model for such chemicals.

Regional scale:

- + Scale, media composition and environmental descriptors of modeled system better reflect the environment in which a chemical is likely to occur. System boundaries flexible, so overall persistence value will depend on selected system. System is open, i.e. atmospheric or oceanic advection occurs. (This system can either be artificially closed by setting advective terms to zero, or left open with the half-life calculated based on degradation processes only. With an open system, the overall persistence value is dependent on the selected size of the modeled system.)

Number of Compartments

Although there are numerous possibilities in selecting compartment types, two primary alternatives emerge: (1) using a minimum of three compartments, namely air, water and soil, whereby “water” lumps the fresh water and marine environment (Scheringer, 1996 and 1997, Wania, 1998) or (2) a slightly more complex structure that includes fresh water, fresh water

sediment and ocean water compartments and possibly vegetation (in addition to air and soil) (see chapter 4).

Non-Degradation Losses

The overall residence time of a chemical in a system is dependent not only on degradation, but also on translocation beyond the system boundaries, e.g. by advection in water and atmosphere. Some models simply set any advective transport beyond system boundaries to zero, making degradation the only loss process (Webster *et al.* 1998). While the artificiality of this assumption is not appealing, the alternative of allowing for advection and calculating an overall persistence only based on the degradation processes is problematic as this persistence value will be scale dependent. On a global scale, atmospheric and oceanic advection beyond system boundaries ceases to exist. In order to avoid unrealistically high overall residence times in a global scale model, it may still be desirable to include processes that lead to loss of chemical out of the sphere accessible to organisms, such as burial in sediments, transfer to the deep sea and the stratosphere, and immobilization in soils (Wania 1998). However, it should be reiterated that overall persistence is always to be based solely on processes that lead to an irreversible chemical conversion.

Environmental Parameter Selection

What environmental parameters should be employed in the model calculations? Namely, which media volumes (e.g. relative volumes of air, water and soils, depth of compartments), phase composition (e.g. organic carbon content in soil and water), kinetic (intermedia mass transfer coefficients, etc.) and climatic conditions (e.g. temperature) should be used in the calculations? Although there is large choice of environmental parameters, it is believed that the ranking of chemicals according to persistence will not significantly change for a different scale or set of environmental parameters. The lack of dependence on the choice of environmental parameters is demonstrated in the results of the CART (Classification And Regression Tree) analysis presented in section 5.4.

5.2 Transport Potential in a Multimedia Environment

5.2.1 Framework for Defining Transport Potential

Persistence is a necessary condition for long-range transport: without persistence there is no opportunity for transport. However, persistent chemicals are not necessarily subject to long range transport unless the residence time of the chemical in the mobile media (air or water) is sufficiently long to allow adequate travel time. With an absence of spatial structure, the closed global model used to determine persistence provides little insight with respect on the spatial range. Chemicals released into the environment from a fixed point or area may be transported away from the source over large distances. Such persistent organic chemicals that exhibit this behavior are now the focus of various national and international regulatory initiatives.

We define the transport potential of a chemical by balancing advective transport in air and water with transformation losses in an open system, an approach conceived of by this working group and independently by Hertwich (1999) and Beyer (1999). In such a model each chemical has a spatial scale at which losses by transformation in the system equal advective transport out of the system. Given a set of system properties (model), this characteristic scale is a function of the properties (intermedia transfer coefficients, rates of degradation) of the chemical. The major forces that facilitate regional and continental transport are air and water flows, e.g. winds and water currents (mobility in soil and groundwater are several orders of magnitude slower and thus not considered). Since advective transport fluxes are controlled by air and water velocities, mobility is not scale-dependent. However, transformation losses are proportional to system volume. Therefore, the proportion of the total chemical budget that is transported out of a system is a function of system scale. This fact provides the mathematical basis for establishing quantitative measures to characterize transport potential.

5.2.2 Characteristic Scale

Mixed-compartment approach

As a first tier approach, the characteristic spatial scale can be determined using the mixed-compartment multi-media models as described in the previous section. The closed system (as used for calculating persistence in Figure 5-2) has to be opened to account for advective inflow and outflow (Figure 5-5).

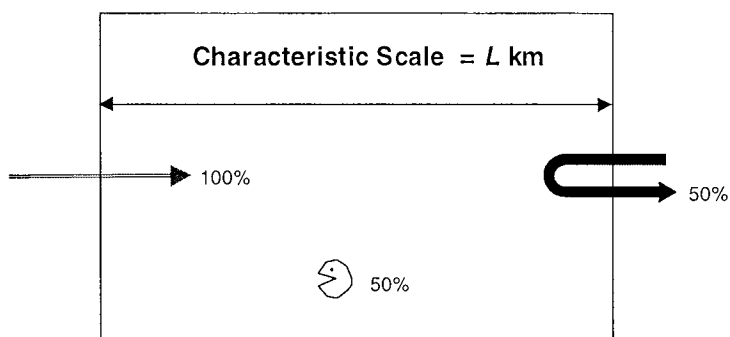


Figure 5-5 A regional, open model (advective transport equal to transformation) is proposed for calculating the characteristic spatial scale, L , as a measure of transport potential. The closed system (no transport, transformation only) was described in section 5.1.1 to define the overall residence time in the environment as a measure of persistence, P .

The scale represented by balancing the advective and transformation loss results from the non-dimensionalization of the equations describing chemical behavior. Using the global multimedia model, one can “open” the system by allowing for advective transport. Instead of using the global dimensions, the size of the system is reduced to precisely the size that meets the criteria that half of the chemical is transported from the system by advection with air and water, and the other half is eliminated by transformation. If only advection in air is considered, this is equivalent to the Lagrangian method, discussed below. In this approach, the advective and reactive mass losses can easily be calculated with an open multimedia model (Mackay 1991). Let us assume a standard regional multimedia environment with substance input into air (only for simplification) and mass export and degradation. Then, under steady

state conditions, the advective outflow F_{adv} [kg/d] and the reactive loss F_{rea} [kg/d] are constant and their sum is identical with the mass import E [kg/d]. Both mass losses can be calculated from the multimedia model:

$$F_{adv} = u_A \cdot C_A \cdot A_A + u_W \cdot C_W \cdot A_W \quad (5.2)$$

$$F_{rea} = k_A \cdot C_A \cdot V_A + k_W \cdot C_W \cdot V_W + k_S \cdot C_S \cdot V_S \quad (5.3)$$

Where:

u_A = wind speed [m/day]

u_W = water speed [m/day]

C_i = concentration in i [kg/m³]

A_A = cross-section of wind flux [m²]

A_W = cross-section of water flux [m²]

k_i = degradation rate in i [1/day]

V_i = volume of i [m³]

A, W, S = subscripts for air, water, and soil, respectively

To calculate the characteristic scale L_A , F_{adv} is set equal to F_{rea} :

$$k_A \cdot C_A \cdot V_A + k_W \cdot C_W \cdot V_W + k_S \cdot C_S \cdot V_S = u_A \cdot C_A \cdot A_A + u_W \cdot C_W \cdot A_W \quad (5.4)$$

If we include only input into and transport in air, convert the equation to a mass based equation, use equation (5.1) and define (Beyer *et al.* 2000):

$$k_{overall} = \frac{\sum_i k_i M_i}{M_A} = \frac{\sum_i k_i M_i}{M_t} \cdot \frac{M_t}{M_A} = \frac{1}{\tau_{overall} \cdot F_A} \quad (5.5)$$

where $k_{overall}$ is the mass weighted decay rate, mass weighted by the chemical mass distribution in an open level III system (Bennett *et al.* 1999, see 5.9 Appendix), M_i is the mass of chemical in compartment i , M_t is the total mass of chemical in the system and F_A denotes the proportion the chemical in the atmosphere, equal to M_A/M_t . we can solve Equation 5.4 which yields:

$$L_A = \frac{u_A \cdot \tau_{overall} \cdot M_A}{M_t} = u_A \cdot \tau_{overall} \cdot F_A = \frac{u_A}{k_{overall}} \quad (5.6)$$

Equations 5.5 and 5.6 enable the effect of inter-media transfer on transport potential to be examined. For class A chemicals which reside essentially all in air, the effective degradation rate simplifies to the atmospheric degradation rate since $M_A \cdot k_A \approx \Sigma(M_i \cdot k_i)$. As a result, the characteristic travel distance is directly related to the atmospheric half-life. However, for chemicals that partition to other compartments, the effective degradation rate increases as transport is retarded thereby allowing more time for reaction. A similar approach can be used to determine a characteristic travel distance in water, L_W (Beyer et al. 2000).

The characteristic travel distance in air (L_A) may be interpreted as the distance required to reduce the initial source concentration by 63% (Figure 5-6).

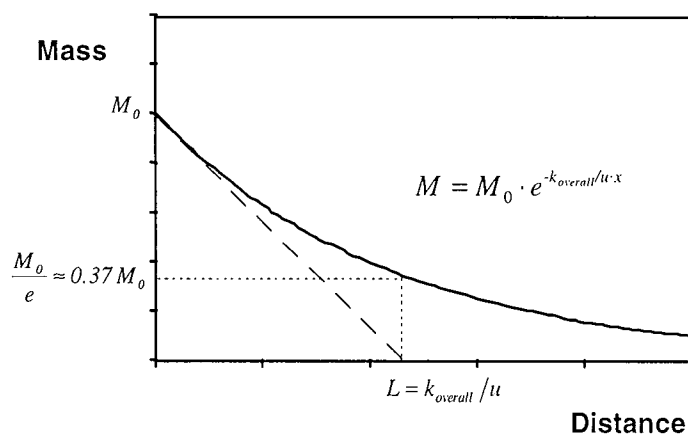


Figure 5-6 Characteristic scale (length) or travel distance.

From L all other spatial range values can be calculated, e.g. the half-length ($L_{0.5} = \ln 2 * L$) or the distance where 95% (or 5%) of the mass is decayed. While the absolute scale of the different travel distance measures varies depending on the percent of mass decayed any of these definitions will provide a consistent basis for persistence classification.

Lagrangian approach

The transport distance obtained from an open system in which advection by wind equals degradation is equivalent to that derived from the previously derived Lagrangian approach

(Figure 5-7; the details of this calculation are in section 5.9). The latter approach considers the movement of a compound driven by the advective flow, e.g. wind velocity, over a non-moving phase, e.g. soil (Bennett et al. 1998). The approach is the same as plug-in flow in hydrology (Schnoor 1996, Trapp and Matthies 1998).

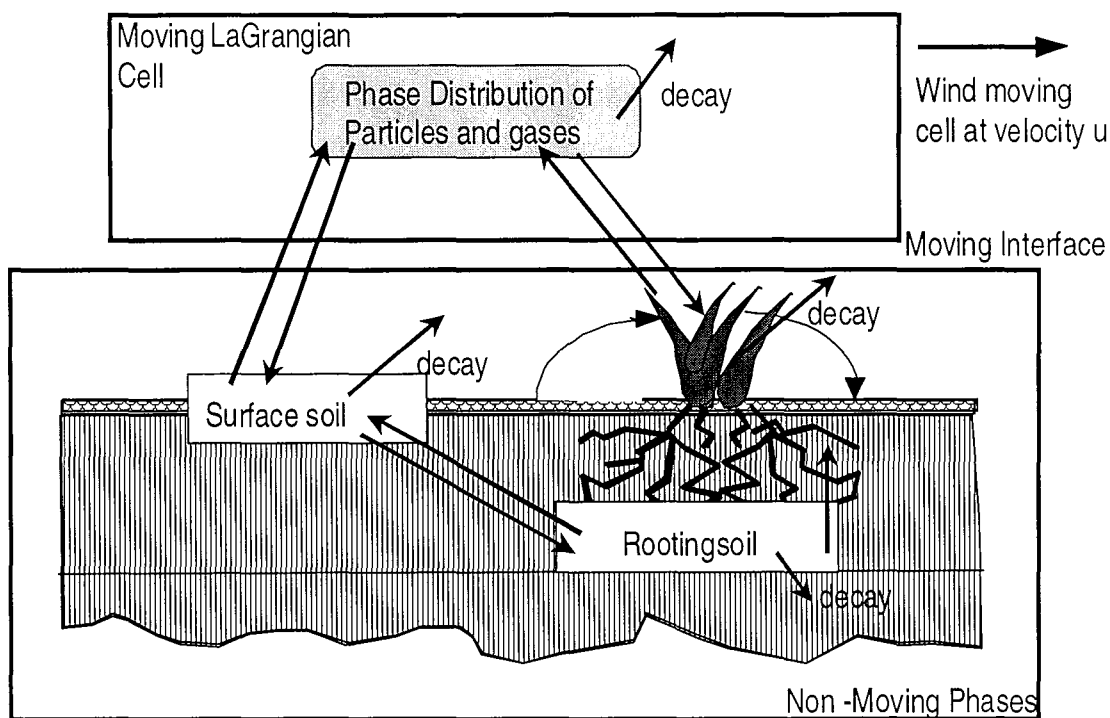


Figure 5-7 Regional multimedia environment used by Bennet et al. (1998) for calculation of the characteristic travel distance

During transport a compound undergoes mass transfer between all media. If the compound is degraded in any of these media the chemical mass is reduced depending on the travel time and distance. At steady state, there is one distance at which the concentration in air has been reduced by 63%, at this point, the reaction losses balance the advective transport losses. This distance is defined as the characteristic scale or characteristic travel distance (L). This quantity describes the spatial range of a compound in a given open model system. At one characteristic travel distance from the source, the degradation losses equal the advective losses.

The Lagrangian approach has been used by Bennett et al. (1998), and by Van Pul et al. (1998), to define a Characteristic Travel Distance L and to calculate a half-length of travelling, respectively. Although different in the way they are worked out, the methods are essentially equivalent. While Bennett et al. use a coupled multi-media level III model to account for the intermedia mass transfer and intramedia degradation processes (Figure 5-7), Van Pul et al. use effective net deposition velocities to account for revolatilization from soil and water. Bennett et al. included air, soil, and vegetation, whereas van Pul et al. excluded vegetation but included fresh surface water and also determined the travel distance for the air movement over the ocean. In both investigations, the compound is degraded by assuming first order or pseudo-first order reaction rate constants for the various media.

Other important assumptions include:

- The source term is a continuous emission into air and/or water from an area source (e.g. city, region, country, or latitudinal zone).
- The system has reached steady state.
- The lateral and longitudinal dispersion is neglected. (This can be easily be introduced if needed (see Matthies and Trenkle 1988)).
- The wind blows at a steady state in one direction, which is orthogonal to the area cross section.
- The water flows in the same direction as the wind blows (only for simplification).
- The landscape properties do not vary spatially or they are spatially averaged.

All environmental parameters (wind and water velocity, rain fall, temperature, height of atmospheric layer etc.) are kept constant or they are temporally and spatially averaged.

Eulerian approach

A more comprehensive approach uses the global circulation system divided into a number of latitudinal (or meridional) zones which exchange matter by interzonal wind and ocean current streams. Scheringer (1997, 1996) used a closed loop of zones and calculated the spatial range,

R , and the characteristic time, τ , of a pulse emission in this system. This approach enables the global circulation to be reduced to a one-dimensional system as illustrated in Figure 5-8.

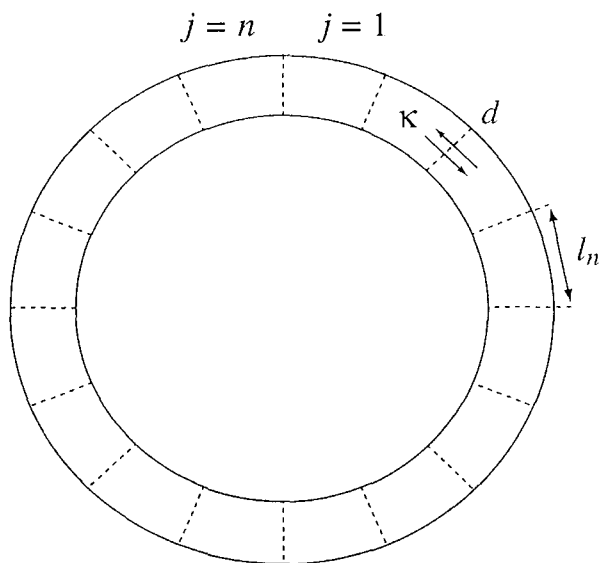


Figure 5-8 Geometry of the global model used by Scheringer (1996, 1997) to determine the spatial range of an organic chemical.

The influence of temperature on partitioning and degradation, as was done by Wania and Mackay (1995) in their global model, is not considered in this circular model, but is studied in an updated version of this model (Scheringer *et al.*, 2000a).

This model is based on the following concepts:

- Each zone consists of homogeneous boxes for air, water, and soil with corresponding first-order degradation rates.
- The zones are connected by air and water flows representing eddy diffusion in the troposphere and ocean.
- The amount M_0 of a chemical is released at time $t=0$ to one of the zones (pulse emission) and the chemical's partitioning, degradation, and travelling between the zones are calculated simultaneously in a dynamic multimedia model.

- The model parameters (partition coefficients, degradation rates, intermedia transfer parameters such as deposition velocities) do not vary in space and time, i.e. the model in its present state consists of many identical replicates of a dynamic model.

Since this is a dynamic calculation, i.e. pulse input, the chemical's total amount in the system decreases with time. For each compartment (soil, water, air) in each zone (indicated by the index j), the exposure

$$e_j = \int_0^{\infty} c_j(t) dt \quad (5.7)$$

is calculated, and from the resulting spatial exposure distributions $\{e_j\}_{j=1,\dots,n}$, the spatial range R is derived as the 95%-interquantile range, i.e. as the distance that contains 95% of the weight of the exposure distribution.

It is important to point out that while these different approaches will yield different estimates of transport potential on an absolute scale it is expected these methods will yield similar rankings of transport potential on a relative scale. This hypothesis needs to be tested by a comparative model exercise. For a first comparison of the characteristic travel distance L and the spatial range R , see Scheringer *et al.* (2000b).

5.3 Benchmark Chemicals in the Persistence/Distance Diagram

Persistence (P) and transport potential (L) as indicated by the characteristic travel distance or the spatial range are considered basic quantities describing a chemical's tendency to be persistent and widely dispersed, i.e. mobile. For different routes of release (soil, water, air), different results may be obtained so that up to three pairs of persistence and transport potential values may need to be considered for each chemical.

The persistence and transport behavior of various chemicals can be conveniently visualized with the aid of a two-dimensional plot with P on the horizontal axis and L on the vertical axis. In Figure 5-9, the results for some benchmark chemicals calculated using a dynamic model are shown (Scheringer 1997) including the presently identified 12 POPs (Persistent Organic

Pollutant), e.g. DDT (DichloroDiphenylTrichloroethane), hexachlorobenzene, dieldrin, chlordane, mirex, lindane, etc., chlorinated benzenes and halogenated and non-halogenated solvents such as tetrachloromethane (tetra), tetrachloroethylene (per), CFC-11, HCFC-142b (Chlorinated and Fluorinated HydroCarbons), cyclohexane, and dioxane (in Figure 5-9 and in this subsection, the symbols R and τ are used instead of L and P).

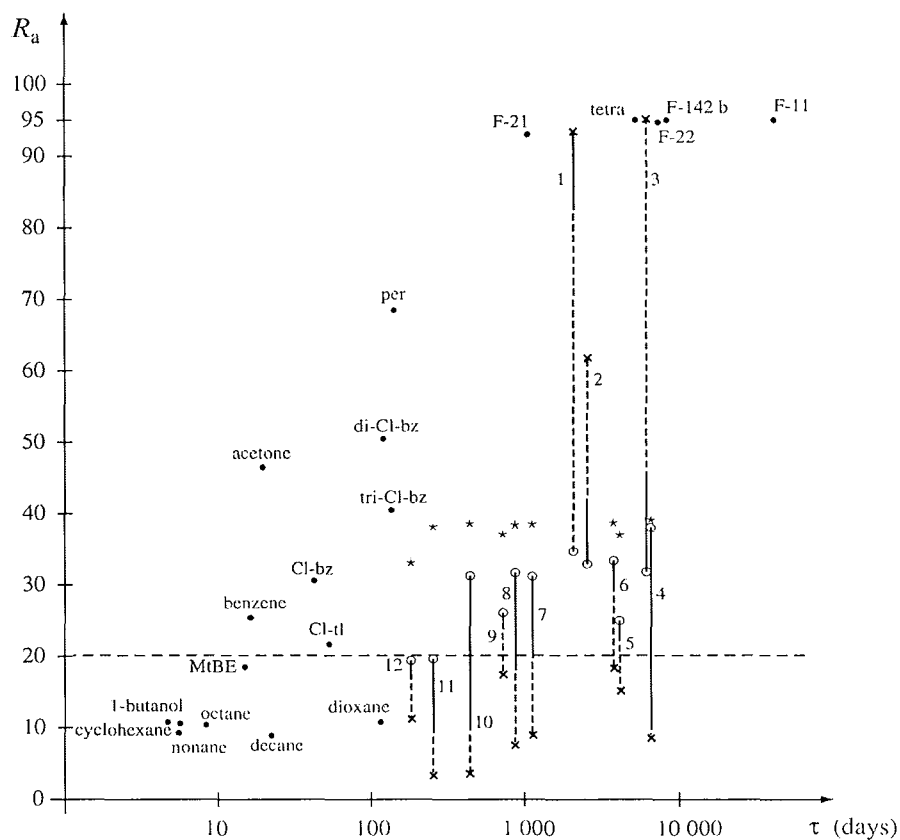


Figure 5-9 Spatial range R (normalized to the earth's circumference), and persistence τ of various chemicals based on the results of the global model proposed by Scheringer (1996, 1999).

a: cyclohexane, b: nonane, c: 1-butanol; 1: hexachlorobenzene (HCB), 2: hexachlorobiphenyl, 3: mirex, 4: endrin, 5: DDT, 6: toxaphene, 7: chlordane, 8: dieldrin, 9: TCDD, 10: aldrin, 11: heptachlor, 12: lindane.

(With permission from Scheringer (1999, p. 133)). See Scheringer *et al.* (2000b) for a more detailed interpretation of this kind of plot.

The diagram shows very high persistence and nearly global spatial ranges for highly volatile and chemically stable compounds such as CFC-11, HCFC-142b, and tetra. The chlorinated benzenes show an increase from intermediate R - and τ -values (monochlorobenzene; cl-bz) to high (di- and trichlorobenzene; di-cl-bz, tri-cl-bz) and very high values (HCB).

Low values for both R and τ are found among the non-halogenated solvents (cyclohexane, butanol, and alkanes). The semivolatile organic compounds (e.g. DDT) are a special case, with high τ -values, more than 100 days, and high or very high spatial ranges (more than 25% of the perimeter of the earth). For the R -values of semivolatile organic compounds, intervals are given (full and dotted lines) because the atmospheric degradation rates k_A of these compounds are not well characterized. This analysis indicates that the atmospheric degradation rate k_A is the crucial parameter which determines long range transport potential. Thus the uncertainty in k_A leads to considerable uncertainty in R . With respect to the identification of POPs among a variety of semivolatile organic compounds, the determination of k_A , or at least the range for k_A , is paramount. In particular, the influence of adsorption onto and absorption into aerosol particles on the degradation rates has to be investigated (this is discussed in detail in Chapter 2). In addition to k_A , the Henry's law constant H and the octanol-air partition coefficient K_{OA} have a strong influence on the long-range transport potential because they determine a chemical's volatility, i.e. its tendency to enter the gas phase (Harner and Mackay 1995). These partition coefficients are often known with higher accuracy than the atmospheric degradation rates, at least in the case of semivolatile organic compounds.

If cut-off values for persistence and transport potential are assigned, the diagram can be divided into the four regions of mobility/persistence properties. These cut-off values are to some extent arbitrary and might be chosen differently for different purposes. A possible choice for the shown diagram is 100 days for persistence, and 1000 km for transport distance. The cut-off values can be chosen differently to reflect specific regulatory objectives. To illustrate the categorization of chemicals shown in Figure 5-9, an arbitrary criterion of 100 days for P and 1000 km for L is selected. In the next section, CART analysis is used to identify physical chemical properties that lead to exceedance of such criteria.

5.4 Application of CART Analysis for Chemical Prioritization

5.4.1 *The Use of a Multimedia Framework for Classification*

As discussed, task of assessing the persistence and transport potential of both new and existing chemicals would be a major undertaking, requiring the collection of chemical properties for use in multimedia model simulations for each chemical or the world-wide collection of data in multiple environmental media at each sample site. As an alternative, we present a classification system that considers sets of chemical properties that would result in the classification of a chemical as “persistent” and as having the potential for long-range transport.

A multimedia modeling framework can be integrated with limited data on chemical properties to understand the temporal behavior of a broad spectrum of chemicals. We describe how simple but informative models can be used to develop effective strategies to classify both existing and new chemicals with respect to persistence in the environment.

The framework developed is part of the second tier, and follows after the elimination of non-persistent, single media chemicals. The classification scheme used can successfully determine sets of chemical properties that will lead to a non-persistent chemical. However, those that do not fall into the non-persistent classification are not necessarily persistent. They need to go into a higher tier of testing, requiring the use of a multi-media model with most of the chemical properties known.

In order to gain broad insight on how chemical properties can be used to classify a chemical as persistent, there is a need to consider how the chemical properties relate to the persistence calculated for a defined environmental system. One method for conducting such an analysis involves the use of a set of binary classification trees. To construct binary classification trees we considered the use of the Classification and Regression Trees (CART) approach. In the next subsection, we provide an introduction to CART and a simple illustration of how CART

can be applied to a multimedia model to assess the link between an output classification such as “persistence” and the range of input values that give rise to this classification.

5.4.2 CART Methodology

CART is an acronym for **C**lassification **a**nd **R**egression **T**rees. The CART methodology is an example of binary recursive partitioning. The results are concise and easy to understand, geared toward decision making, and the analysis is largely automatic. CART is a non-analytic, computer intensive procedure which leads to classification rules based on inequality constraints applied to individual parameter values or to linear combinations of parameters (Breiman, 1984). This technique has been used for over twenty years in fields such as engineering, public health, medicine, and economics (Breiman, 1984). The CART analysis can be used to determine sets of parameters that lead to a non-persistent classification of a chemical. Often, only a few parameters are used to reach a classification. Identifying these parameters can better facilitate the decision-making process for persistent chemicals.

CART is a set of rules for splitting each node in a binary decision tree, deciding when the tree is complete, and assigning each terminal node to a class outcome. For every model input, CART tests every value as a split point to try to maximize the reduction in variance between the parent node and the resultant two sub-nodes. We have chosen to assign the classification of non-persistent only when 95% of the chemicals in that parameter grouping are non-persistent, leading to less false negative decisions. The system is set up to minimize false negatives while allowing for false positives. This implies that a negative result is not necessarily persistent, but is identified as a chemical that needs to be evaluated in a higher tier.

5.4.3 Application to a Two-Compartment Model

In order to illustrate how one would classify pollutants based on their chemical properties, we consider the simple two-compartment closed system in Figure 5-10 consisting of air (compartment 1) and water (compartment 2) at equilibrium with a source to the air, S mol/y (a level II system). The chemical can only be removed from this system by a transformation reaction in the water compartment.

$$\text{Relative solubility} = C_A/C_W, \quad \text{Persistence} = \frac{\text{Inventory}}{\text{Loss rate}}$$

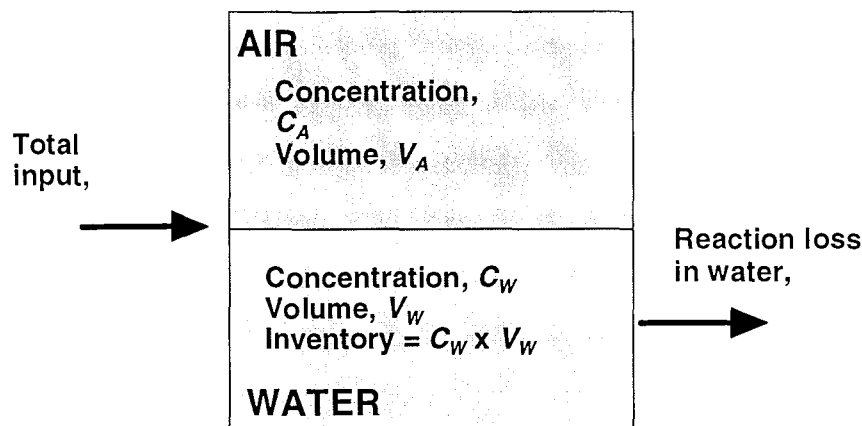


Figure 5-10 A simple two-compartment system used to illustrate the CART analysis.

The mass-balance condition for this system is:

$$S = f_W Z_W V_W k_W \quad (5.8)$$

and the mass in each compartment is given by:

$$M_A = f_A Z_A V_A ; M_W = f_W Z_W V_W \quad (5.9)$$

Where S is the source term (mol/y), f_i is the fugacity in compartment i (Pa), V_i is the volume of compartment i (m³), M_i is the chemical mass in compartment i (mol), k_W is the reaction half life in water (1/y), Z_W is the fugacity capacity in water (mol/m³-Pa), defined as $1/H$, where H is the Henry's law ratio (Pa-m³/mol), and Z_A is the fugacity capacity in air (mol/m³-Pa), defined as $1/RT$, where T is the temperature.

Using the above equations with the definition for persistence, Equation 5.1, the persistence P (or characteristic time τ) for this system is:

$$P = \tau = (f_A Z_A V_A + f_W Z_W V_W) / f_W Z_W V_W k_W \quad (5.10)$$

We define the system such that $V_A = V_W$. Since the system is in equilibrium, $f_A = f_W$. K_{AW} , the air/water partition coefficient, is equal to H/RT . Simplifying the above equation, we obtain:

$$P = \tau = (1/k_W) x (1 + K_{AW}) \quad (5.11)$$

Under the assumption that $P > 1$ year will result in a classification of "persistence", the above equation was calculated with a broad spectrum of K_{aw} and k_w values to determine what sets of

K_{AW} and k_W exceed the cutoff criteria. Solving this analytically, it is apparent that if k_W is less than 1, the chemical will be persistent. If K_{AW} is greater than 1, k_W must be greater than two to be non-persistent, since less than half of the chemical will be in water undergoing transformation processes. The more chemical pollutant in the air, the shorter the half-life in water must be for the chemical to remain in the system for less than a year. Regions of chemical properties resulting in a classification "persistent" ($P > 1$ yr) are shown in Figure 5-11.

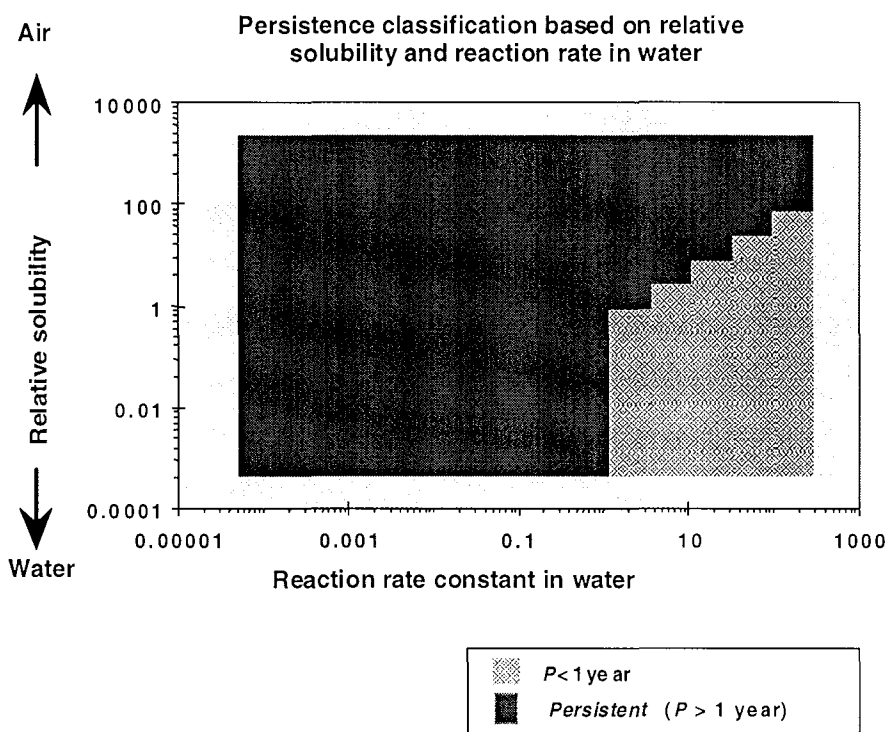


Figure 5-11 Dependence of the joint occurrence of k_a and K_{aw} on persistence classification. This figure illustrates that there are large regions in which either the “persistence” or “non-persistence” classification dominates.

The results in this figure can be used to develop a binary classification tree, such as the one shown in Figure 5-12. From this tree, we can determine if a chemical is likely to be persistent based on the series of questions asked in the tree. This example yields a straightforward method for defining and classifying chemicals based on whether or not they persist for more than a year in the defined system. However, as the number of compartments in the model

increases and as the number of independent parameters increases, the complexity and tractability of this process increases substantially.

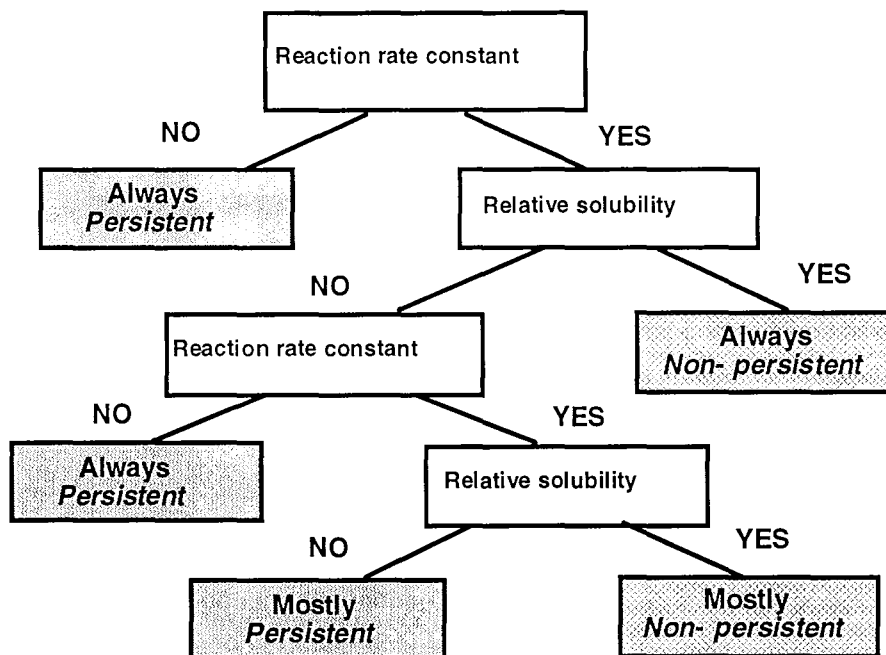


Figure 5-12 The binary decision tree obtained from the results of the two-compartment case study with the overall persistence criterion set to >1 year.

5.4.4 Application for Classifying Persistence in a Multimedia Environment

Now that we have demonstrated how CART can be applied to a two compartment system, we expand this to a more complete environmental system. We focus on hypothetical chemicals, with the range of each chemical property falling within the feasible range for organic chemicals. These chemicals are released to the air compartment in a multi-media unit world as presented in Figure 5-4, model A with the proportions of water and soil equaling global averages. A measure of persistence is calculated for each hypothetical chemical. A CART analysis is then completed with the goal of determining what sets of chemical parameters lead to a persistent chemical. The analysis could also be completed for releases into other environmental media.

We calculate the mass distribution in the evaluation unit based on fugacity principles, a

common approach for describing partitioning in multimedia systems (Mackay, 1991). The steady-state concentrations in each environmental compartment are determined from the interactions between the three environmental compartments and the decay rate in each compartment. The chemical parameter value ranges with examples of chemicals near the minimum and maximum of that range are presented in Table 5-1. All of the distributions used were log-uniform. This will yield the same number of chemicals having that property value in that range for each order of magnitude. Using the Monte Carlo package Crystal Ball, 10,000 simulations were completed (Decisioneering, 1996). These 10,000 outputs were input to the CART program. Six months was chosen to define a persistent chemical in this study. Branches not yielding a different result for a significant number of simulations were trimmed.

Table 5-1 Ranges of Chemical Properties

Property	Symbol	Distribution type	Lower End	Upper End	Example of Chemical with Property at Lower End of Range	Example with Property at Upper End of Range
Henry's law constant (Pa·m ³ /mol)	H	log uniform	1×10^{-3}	1×10^5	Phenol	Nitrogen gas
octanol-water partition coefficient	K_{OW}	log uniform	1	1×10^9	Butanol, Methylchloride	Di-n-octyl-phthalate
decay rate in air (1/day)	k_A	log uniform	4×10^{-4}	1×10^2	Toxaphene, Bromodichloromethane	Benzo(a)Pyrene
decay rate in water (1/day)	k_W	log uniform	1×10^{-5}	1×10^2	hexachloroethane	Pyrene
decay rate in soil (1/day)	k_S	log uniform	1×10^{-5}	1×10^2	PCB	Anthracene
vapor pressure in (Pa)	VP	log uniform	1×10^{-6}	1×10^5	Chrysene, TCDD	Atmospheric Pressure
melting point (K)	T_m	uniform	100	600	Vinyl Chloride	Chrysene, beta - HCH, TCDD
Diffusion coefficient in pure air (m ² /d)	D_A	uniform	.2	1.7	Toxaphene	2,4 - Dinitrotoluene
Diffusion coefficient; pure water (m ² /d)	D_W	uniform	3.00E-05	1.00E-4	Endrin	Vinyl Chloride

As an example, we considered a system with source term to air and defined persistence as a chemical with a characteristic time of more than 6 months. In the tree, shown in Figure 5-13, all of the chemical and landscape properties are used as possible predictor variables.

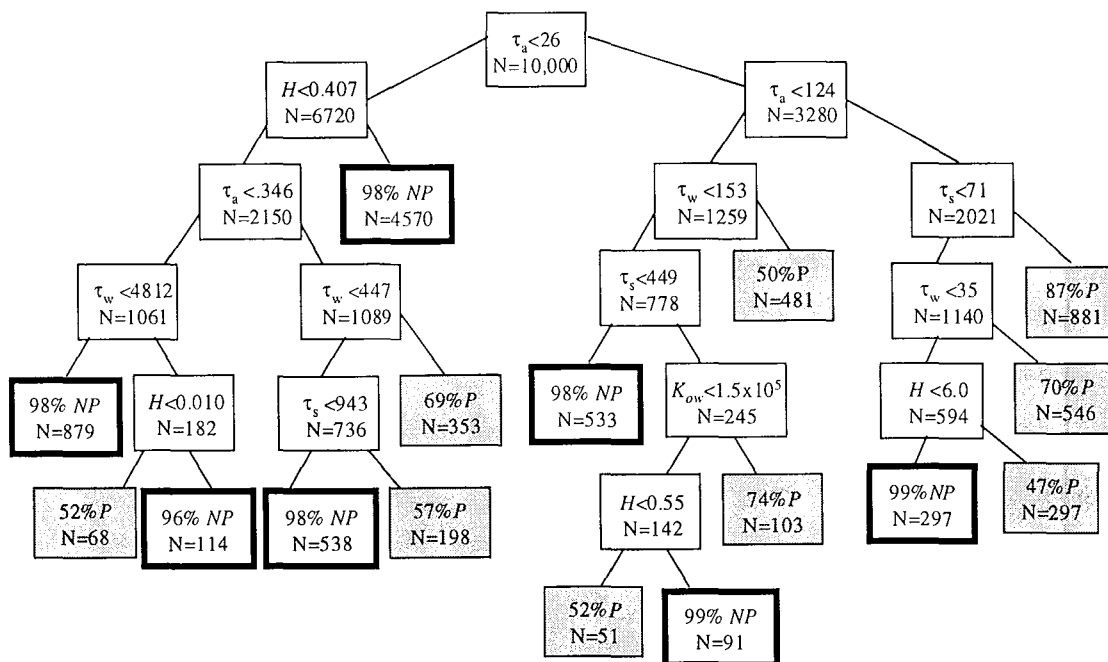


Figure 5-13 CART tree for emissions to air, persistence defined as one year, all chemical and landscape properties used as predictor variables. The tree is read by asking a question regarding the inequality listed. If the answer is yes, the user follows the left branch while if the answer is no, the user follows the right branch. The user follows this procedure until a terminal node is reached, which indicates if the chemical can be classified as non-persistent or if the chemical needs to be evaluated in a second tier evaluation. N defines the number of chemical realizations in that node. The terminal nodes indicate the percent of the realizations that are either persistent, P, or non-persistent, NP.

The first split point on the tree is associated with the question “is the half-life in air less than 22 days?”. If the answer is yes, the user follows the left branch of the tree and asks “is the Henry’s law constant less than 0.42 Pa m³/mol?”. If the answer is no, the user follows along the right branch and learns that 98% of the chemicals with these two properties are non-persistent. It makes sense that the first question is about the half-life in air because the release is to the air compartment and thus a significant portion of the chemical can be found in this phase. With a high Henry’s law constant, the chemical is more likely to remain in the air, rather than partition to the water, and thus be influenced by the short half-life in air.

The user reads the tree and answers the questions to reach the terminal nodes. An alternate view of the results of this process, the regions of persistence and non-persistence are plotted based on the half-life in air and the Henry's law constant in Figure 5-14. Light gray regions are non-persistent, medium gray regions are non-persistent if they meet the qualifications listed in that region, and dark gray regions are persistent.

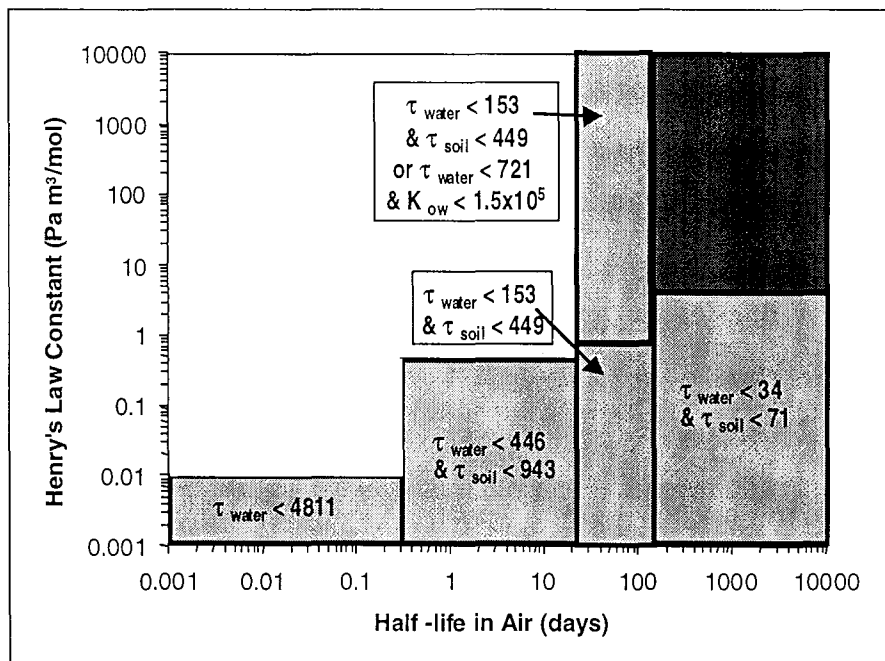


Figure 5-14 Results of CART analysis for emissions to air; persistence defined as 6 months; all chemical and landscape properties used as predictor variables. Light gray regions are classified as non-persistent; dark gray regions are classified as persistent. Medium gray regions are classified as non-persistent if the chemical meets the additional inequalities specified in the region or caption, otherwise second tier testing is needed. Each medium gray region (as defined by the black boarder) is separate, and must meet only the specifications in that region.

5.4.5 Implications of CART Classification Example

A screening level classification system is proposed for determining if a chemical compound is persistent or non-persistent. The method can also be used for transport potential. This provides a regulatory advantage by allowing the classification of numerous parameters

without needing to run a simulation model. Classification of persistence is determined by comparing the overall residence time of a compound in a multimedia evaluation environment to a reference time value. The multimedia model is used with ten-thousand simulations to capture a broad range of chemical-property sets, allowing us to identify sets of properties that result in a “non-persistent” residence time in the multimedia model.

The CART analysis reveals that the most important chemical parameters for classifying the persistence of chemicals released to the air is the decay rate in the air. Other important parameters are Henry’s law constant and the decay rate in water. When the source medium is changed from air to soil, both the resulting classification trees and the importance rankings change.

Although the process of generating the classification trees requires an understanding of multimedia interactions, CART reduces the results to a classification diagram that does not require an understanding of multimedia models for interpretation. In the case study here, the multidimensional response surface of a model can be reduced to a two-dimensional plot with two classifier parameters on the axes. The importance of other parameters shows up in the sub-regions of this plot.

5.5 Use of Persistence and Transport Potential in Decision-Making

Application of the modeling tools described in this chapter provide a transparent, scientifically-sound approach for characterizing the relative persistence and long range transport potential of different chemicals in a multimedia context. These attributes serve as the key attributes that can be used to rank chemicals and thus identify candidate POPs. However, it is important to point out that the models cannot be used to establish recommended criteria for decision-making since criterion selection depends upon the specific regulatory goals. Nevertheless, it is possible to use modeling tools to ensure proposed criteria are coherent.

For example, consider the proposed air half-life criterion of 2 days. If this criterion is applied to a class A chemical application of Equation 5.6 yields a characteristic travel distance of 750 km if an average wind speed of 3 m s^{-1} is assumed. Alternatively, if a half-life criterion in water of 180 days is adopted the characteristic travel distance for a class B chemical is less than 0.1 km assuming a representative hydraulic residence time of 10 days and an average water depth of 3 m. This simple calculation reveals that the proposed air half-life criterion can be used to establish a benchmark for assessing transport potential of multimedia chemicals which exhibit various partitioning and degradation properties. Further, this calculation suggests class B chemicals are not susceptible to long range transport. Due to the non-mobile nature of the soil compartment a similar argument can be made for class C chemicals. This however does not imply that the persistence behavior of such compounds does not present local concerns. However, based on application of screening level modeling tools such chemicals should not be given high priority for international initiatives.

Another important issue related to the classification of a chemical as persistent or susceptible to long-range transport is the influence of model input variability on model output. In comparing calculated persistence/transport measures to a proposed criterion, it should be kept in mind that the calculated values are not to be looked at as single deterministic values, but rather as distributions of possible outcomes. The variance in outcome can be simulated with Monte-Carlo analysis. Instead of doing the calculation with single input values, distributions of possible input values, reflecting natural variability and parameter uncertainty, can be used as input to the model. The outcome would be a distribution, reflecting the operational margins of certainty. In a recent study on persistence assessment, it was suggested that media specific half-lives be defined in terms of log normal distributions with defined standard deviations rather than fixed single values. The model result would then be expressed as a distribution of overall persistence values, 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).

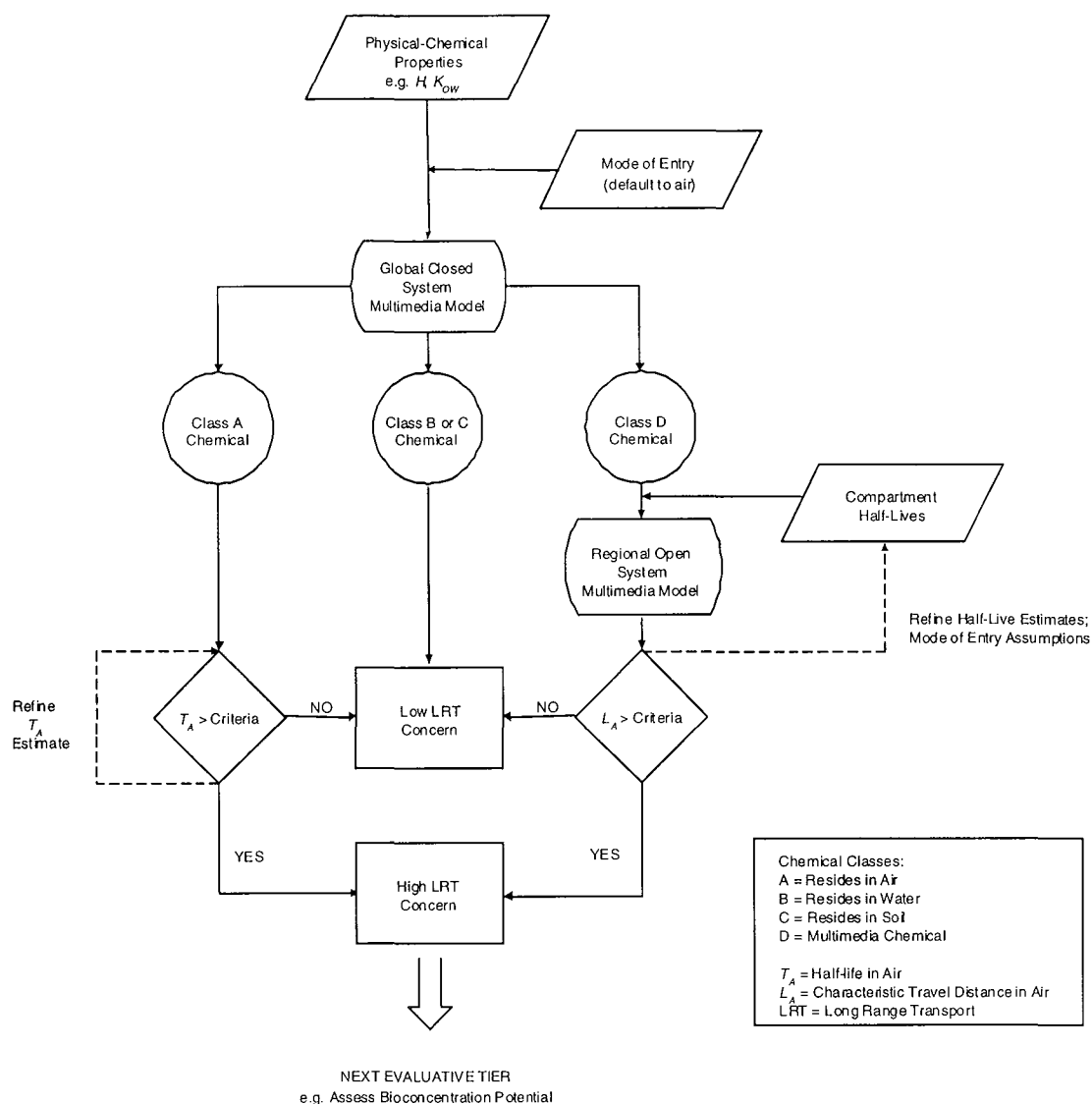


Figure 5-15 Example Decision Framework for Identifying Candidate POPs

Based upon the above insights, a proposed scheme for identifying candidate POPs subject to long range transport could rely on the following tiered framework. In tier I, physical chemical properties are used to classify chemicals as described in section 5.1. Class A chemicals are compared to the proposed single media air half-life criterion. If the chemical exceeds this criterion the chemical is identified as a candidate POP and moves to the next evaluative tier (e.g. bioaccumulation potential). Since class B and C chemicals do not exhibit long range transport potential these compounds are dropped from further consideration. Class D

chemicals proceed to a second evaluative tier in which transport potential is determined using a multimedia model as described in section 5.2 that allows the variability in media-specific degradation rates to be included. The model calculated distribution of transport potential is then compared to the transport potential criterion that is coherent with the value derived for a class A chemical and the prescribed air half-life criterion. Alternatively, CART analysis could be used to define the combination of chemical properties for class D chemicals that exceed the transport potential criterion. Class D chemicals that fail this decision point move to the next evaluative tier. This scheme is illustrated in Figure 5-15.

It is important to highlight some limitations in assessing persistence and long range transport using the approaches presented in this chapter. If a chemical is used in only very small quantities and/or in uses that translate into very limited emissions into the environment this chemical may in fact pose a low concern despite incriminating persistence and long range potential properties. Similarly, a less persistent and mobile chemical may pose higher concern if emitted in very large quantities. Furthermore, increased persistence does not necessarily imply increased exposure potential. For example, if a hydrophobic chemical is emitted to soil persistence may be greater than if released to air. However, human exposure potential may be greater because air may serve as a more efficient transport medium to secondary compartments (e.g. plants) that determine indirect exposure pathways (i.e. vegetable ingestion). Consequently, additional information must be examined in higher evaluative tiers (e.g. emission quantity, mode of entry, exposure potential) to ensure effective management decisions. Often such information is poorly characterized and provides a basis for future data collection especially for high production volume chemicals.

5.6 Higher tiers

Input variance is only one aspect of the total model uncertainty. To a great extent, the uncertainty in the predicted persistence and transport potential originates from our fundamental doubts about the correctness of the modeling concept applied. Other, equally plausible modeling concepts could have been applied that may have yielded different results.

Without further quantitative analysis of the fundamental concepts, this part of the uncertainty cannot be addressed.

The models presented above have been developed for screening and are not applicable for more precise modeling. They are average global models. After a chemical has been identified using criteria including the above global models, it is expected that more data such as toxicity and release modes will be obtained for a risk evaluation. Part of this evaluation is likely to involve the use of models that more accurately reflect reality. The above models are simplified for ease of computation and to be useful for a wide variety of conditions. These more specific models can be chosen and parameterized to reflect the conditions of the environment in the locale and/or region of release. The models can be set to reflect levels of UV radiation, wind speed, degradation rates, temperature variations, amount of vegetation, proportion of water, soil types, spatial scale, temporal scale, seasonal changes, marine systems, and other properties. It will likely be useful to use a model such as the global meridional model to explain transport from tropical to polar regions to evaluate the degree of global distillation (Wania and Mackay, 1996). The models used can be either the fugacity type or one of the many other types available. The model chosen will depend on the chemical, its properties, release conditions and location of release. The decision of what model(s) to use and the modeling will probably be done by experts associated with the authority or group that will do the risk evaluation.

It is possible to combine a fate model and effects information into one model that can give an indication of risk. Both the EUSES model (Vermeire et al. 1997) and CalTOX (McKone 1993) do this and are already accepted by the European Union and the state of California, respectively.

Caution is advised when deciding to use a more complex model. They do not necessarily give better information. This is because more complex models have more components in them. The more components, then the higher the likelihood that part or the entire model may be

poorly calibrated. The added components are often pushing the cutting edge of science, thus there may be insufficient data to adequately calibrate the model component and the model.

It might be desirable to use one model or set of models for consistency in the risk assessment. If that is the case and the risk assessors consider fugacity modeling to be appropriate, the approaches of Bennett et al. (1998) and Scheringer (1996, 1997) provide a suitable starting point for this task. These papers cover regional transport and global dispersion in complementary ways. These models would be used in two steps. The first contains the calculation of a chemical's regional travel distance where the model contains a moving parcel of contaminated air, which is in contact with soil, surface water, and vegetation as stationary phases. If this distance exceeds a threshold of regional dimensions, e.g. some 500-1000 km, the second step is taken. The second step is to use the global circulation model. This model consists of many replications of the regional level III fugacity model to form a closed loop that can be looked upon as a one-dimensional representation of the global circulation system (see Figure 5.8 (Scheringer 1996)). The model calculates the spread of the chemical along this closed chain of regional models. The overall persistence and spatial range on a global scale are based on macroscopic (turbulent) diffusion in the troposphere and the oceanic surface water. The upper limit of the spatial range is the earth's perimeter, 40,000 km, which is equivalent to a uniform global distribution as observed for CFCs. The lower limit is given by the size of the regional models for which the loop is made. This "block size" is the spatial resolution of the global model. For a consistent use of both the regional and global model, the maximum dimension of the regional model and the block length of the global model should be of the same order of magnitude. For a proper and consistent application, these models have to be refined and harmonized to some extent.

5.7 Conclusions and Recommendations

The following summarize the conclusions and recommendations of the workgroup:

- Separate measures of both persistence and transport potential are both needed to classify chemicals with respect persistence and long-range transport

- Useful measures of persistence and transport potential can be derived from half-lives in specific media and intermedia partition coefficients, using a level III multimedia model.
- Given cut-off criteria, the parameter domains that would give rise to undesired persistence and transport potential can be derived using a Classification and Regression Tree (CART) analysis.
- Two-dimensional “Scheringer plots” of persistence versus transport potential for determining agreed-on concern and no-concern chemicals are useful!
- Although there are no scientific rationale for criteria selection, science can help in the process of developing criteria that are coherent.

5.8 References

- California Environmental Protection Agency (Cal-EPA) 1997. Department of Toxic Substances Control (DTSC) 1997. *Draft Concept Paper RSU Task D.3, California's Non-RCRA Waste Classification System: Analysis and Proposed Revisions*. California Environmental Protection Agency, Department of Toxic Substances and Control, Human and Ecological Risk Division. Available from <http://www.cwo.com/~herd1/-caltox.htm>
- Bennett DH, McKone TE, Matthies M, Kastenber WE. 1998. General Formulation of Characteristic Travel Distance for Semivolatile Chemicals in a Multimedia Environment. *Environ Sci Technol* 32:4023-4030.
- Bennett, D.H., 1999. Semivolatile Organic Chemicals in a Multimedia Environment: Characteristic Travel Distance, Characteristic Time, and Human Exposure, Ph.D. Dissertation, Mechanical Engineering, University of California, Berkeley.
- Bennett, D.H., Kastenber, W.E., McKone, T.E., 1999. General Formulation of Characteristic Time for Persistent Chemicals in a Multimedia Environment, *Environ Sci Technol*, 33:503-509.
- Beyer, A., 1999. *Assessment of Long-range Transport of Persistent Organic Pollutants*. Diplom Thesis, Applied Systems Science, University of Osnabrück.
- Beyer, A., Mackay, D., Matthies, M., Wania F., Webster E., 2000. Assessing Long-range Transport of Persistent Organic Pollutants. *Environ Sci Techn (accepted)*.
- Brandes LJ, den Hollander H, van de Meent D. 1996. SimpleBox 2.0: a nested multimedia fate model for evaluating the environmental fate of chemicals. RIVM report 719101 029.
- Breiman, L, J Freidman and S Olshen (1984). *Classification and Regression Trees*. Monterey, CA, Wadsworth, Inc.
- Cowan C, Mackay D, Feijtel T, van de Meent D, Di Guardo A, Davies J, and Mackay N. 1995. *The multi-media model: A vital tool for predicting the fate of chemicals*. Pensacola, FL: SETAC Press.
- Decisioneering, 1996, *Crystal Ball*. 4.0 ed. Decisioneering: Boulder, CO.

- ECETOC (1994). HAZCHEM. A mathematical model for the use in risk assessment of substances. Special report no. 8, October 1994. European Centre for Ecotoxicology and Toxicology of Chemicals, Brussels, B.
- Harner, T, Mackay, D. 1995. Measurement of Octanol-Air Partition Coefficients for Chlorobenzenes, PCBs, and DDT. *Environmental Science and Technology* 29: 1599-1606.
- Hertwich, E.G., 1999. *Toxic Equivalency: Accounting for Human Health in Life-Cycle Impact Assessment*, Ph.D. Dissertation, Energy Resources Group, University of California, Berkeley.
- Klein, A., (1985), in *Handbook of Environmental Chemistry*, O. Hutzinger, Editor. Springer: Berlin. p. 1-28.
- Mackay, D (1991). *Multimedia Environmental Models, The Fugacity Approach*. Chelsea, MI, Lewis Publishers.
- Mackay, D. and S. Paterson, (1991) *Evaluating the Multimedia Fate Of Organic Chemicals - a Level-III Fugacity Model*. *Environ. Sci. Technol.*, **25**(3): p. 427-436.
- Matthies M, Trenkle R. 1988. Variability of Exposure Estimations for Hazardous Chemicals released to the Environment. *Chemosphere* 17:1471-1486.
- McKone T.E. 1993. CalTOX, A Multi-media total-exposure model for hazardous wastes sites Part II: The dynamic multi-media transport and transformation model. Lawrence Livermore National Laboratory Report no. UCRL-CR-111456PtII., Livermore, CA.
- 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, 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. 1996. Persistence and spatial range as endpoints of an exposure-based assessment of organic chemicals. *Environ. Sci. Technol.* 30: 1652-1659.
- Scheringer M. 1997. Characterization of the environmental distribution behavior of organic chemicals by means of persistence and spatial range. *Environ. Sci. Technol.* 31:2891-2897.

- Schering, M. 1999. Persistenz und Reichweite von Umweltchemikalien. Wiley-VCH, Weinheim.
- Schering, M., Wegmann, F., Fenner, K., Hungerbühler, K. 2000a, Investigation of the Cold Condensation of Persistent Organic Pollutants with a Global Multimedia Fate Model, *Environmental Science & Technology*, 34, in press.
- Schering M., Bennett, D.H., McKone, T.E., Hungerbühler, K. 2000b. Relationship between Persistence and Spatial Range of Environmental Chemicals. In: Lipnick, R.L., Mackay, D., Jansson, B., Petreas, M. *Persistent Bioaccumulative Toxic Chemicals: Fate and Exposure*. American Chemical Society, in press.
- Schnoor J. 1996. Environmental Modelling. New York: J.Wiley.
- Tell, J.G., T.F. Parkerton (1997). A Comparison of Multi-Media Models Used in Regulatory Decision-Making, *SAR and QRAR Environmental Research* 6:29-45.
- Trapp S, Matthies M. 1998. Chemodynamics and Environmental Modeling. An Introduction. Heidelberg: Springer.
- U.S. Federal Register, Persistent Bioaccumulative Toxic (PBT) Chemicals; Proposed Rule, Vol. 64, No 2, Tuesday, January 5, 1999
- Van de Meent D, Peijnenburg W, Struijs J, Govers HA. 1992. Towards a QSAR-driven computation of persistence of chemicals in the environment. Poster, 5th International Workshop on QSAR in Ecotoxicology, Duluth, MN, USA.
- Van de Meent D. 1993. SimpleBox, a generic multimedia fate evaluation model. RIVM report no. 672720 001.
- Van Pul WAJ, de Leeuw FAAM, van Jaarsveld JA, van der Gaag MA, Sliggers CJ. 1988. The Potential for Long-Range Transboundary Atmospheric Transport. *Chemosphere* 37:113-141.
- Vermeire TG, Jager DT, Bussian B, Devillers J, Den Haan K, Hansen B, Lundberg I, Niessen H, Robertson S, Tyle H, Van der Zandt PTJ. 1997. European Union System for the Evaluation of Substances EUSES. Principles and structure. *Chemosphere* 34:1823-1836
- Wania F, Mackay D. 1995. A global distribution model for persistent organic chemicals. *Sci. Total Environ.* 160/161:211-232.

- Wania F, Mackay D. 1996. Tracking the Global Distribution of Persistent Chemicals. *Environ Sci Technol* 30:A390-A396.
- Wania F. 1998. An integrated criterion for the persistence of organic chemicals based on model calculations. WECC-Report 1/98, Toronto.
- Webster E, Mackay D, Wania F. 1998. Evaluating Environmental Persistence. *Environ. Toxicol. Chem.*, 17:2148-2158.

5.9 Appendix

Characteristic travel distance derived from a transport model is equivalent to that derived from a multimedia model that matches degradation losses are to advective losses to characterize the transport scale, a method derived by Hertwich (1999) if only advection in air is considered.

This equivalence was demonstrated by Bennett (1999) and is repeated here:

$$\text{Advective Losses} = \text{Degredation Losses} \quad (5.12)$$

We write the equation for a two compartment system expressing the masses as concentrations and defining the depth of each compartment as h_i .

$$\frac{M_1}{h_1 L_A^2} u_A \times h_1 \times L_A = \frac{M_1}{h_1 L_A^2} k_1 \times h_1 \times L_A^2 + \frac{M_2}{h_2 L_A^2} k_2 \times h_2 \times L_A^2 \quad (5.13)$$

Solving for L yields:

$$L_A = \frac{M_1 u}{M_1 k_1 + M_2 k_2} = \frac{u_A}{k_{overall}} \quad (5.14)$$

This is equivalent to the characteristic travel distance. This alternative approach may be more intuitive for some individuals.

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