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# Screening Chemicals for Persistence in the Environment

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A method is suggested for rapid screening of chemicals for persistence in the environment. Physical–chemical equilibrium partitioning information between air, water, and octanol are used as a first screen to identify the media for which degradation half-lives are required and those for which half-lives may be unnecessary. An overall persistence under equilibrium conditions is then estimated using half-lives in air, water, soil, and sediment using a steady-state mass balance model. A graphical technique to identify the key half-lives is demonstrated using 233 chemicals. For chemicals of more extreme partitioning properties, some half-lives may not be needed.

## Introduction

As a result of international agreements to control chemicals (1), increasing efforts are being devoted to assessing the persistence, bioaccumulation, toxicity, and long-range transport potential of the many organic substances present in commerce and which may enter the environment. In Canada, for instance, 22 500 substances on the Domestic Substances List (2) are being evaluated, while in the United States, 4157 chemicals have been assessed for pollution prevention purposes (3). Similar efforts are presently under way in other jurisdictions. In view of the large number of chemicals in use, the frequent lack of complete data, and the probability that most of these chemicals are relatively innocuous as compared to the “priority pollutants”, there is an incentive to devise rapid and simple methods of assessing properties, such as persistence, that make minimal demands for physical–chemical and reactivity data.

It is likely that a tiered assessment process, in which chemicals of low priority can be screened out with minimal cost and effort, will prove most effective. A recent SETAC sponsored workshop (4) advocated such a system and stressed the need for a transparent, scientifically sound method. The method should be conservative, i.e., it should be designed to eliminate the clearly non-persistent chemicals with potentially persistent chemicals moving to higher tiers for more detailed assessment.

Two screening options exist; examination of individual, media-specific half-lives or as advocated by Webster et al. (5), evaluation of the single, overall half-life or persistence of a chemical in the environment. The overall persistence or residence time is a weighted mean of the media half-lives

and can be regarded as the ratio of the mass of chemical in the system at steady state to the total degradation rate. The related overall half-life is the time required for one-half of the chemical present in a system to be degraded under dynamic conditions.

A multiple half-life approach has been advocated by Environment Canada (6) in which a substance is declared to be persistent if **any one** of its half-lives in four environmental media exceed the following criteria: air,  $\geq 2$  days; surface water,  $\geq 182$  days (6 months); soil,  $\geq 182$  days (6 months); and sediment,  $\geq 365$  days (1 year). It must be appreciated that a chemical's degradation rate (usually expressed as a half-life) varies greatly between environmental media, and there is considerable variability with environmental conditions, such as temperature and microbial activity. As noted by Webster et al. (5), this strategy fails to recognize the partitioning tendency of a substance. A substance may be unnecessarily penalized and declared persistent because it fails the half-life criterion in a medium into which it does not appreciably partition. The medium in which most of a chemical is found in the environment, and therefore determines the persistence, and from which most exposure is likely is controlled by the chemical's half-lives in the various media and the proportions in each medium, as influenced by partitioning phenomena with the mode-of-entry and intermedia transport resistances also playing a role. It is possible for a chemical to be declared non-persistent using these multiple half-life criteria but to have a longer overall half-life than one that is declared persistent (5).

In summary, a tiered or multi-stage system is required in which the initial stage makes minimal data demands and which can screen out large numbers of less persistent chemicals using available data on media-specific half-lives and partitioning characteristics without the disadvantages of the multiple half-life approach. We propose here a screening level method for assessing persistence that satisfies these requirements.

## Graphically Identifying Key Half-Lives Using Partitioning Data

We propose that the most appropriate method is to deduce the chemicals' persistence under conditions of a constant discharge to an evaluative environment in which steady state is reached when total reaction rate equals the discharge rate. Equilibrium between media is assumed, and there are no advective losses. This is essentially a Level II model as described by Mackay (7). The evaluative environment is a hypothetical set of volumes of air, water, soil, and sediment of typical properties and reasonable proportions. Müller-Herold (8) has also suggested a similar approach but focused on the limiting conditions that may apply.

An existing evaluative model such as the Equilibrium Criterion, or EQC model (9), could be used; however, it is simpler to view the environment as volumes of air, water, and octanol where octanol represents the organic matter found in soils and sediments. It is well-established that octanol is the best surrogate for organic matter, with numerous linear or near-linear correlations between the octanol–water and organic carbon–water partition coefficients. The environmental volumes of air ( $10^{14}$  m<sup>3</sup>) and water ( $2 \times 10^{11}$  m<sup>3</sup>) in EQC can be used directly. These represent reasonable volumes for an area of 100 000 km<sup>2</sup>, an atmospheric height of 1000 m, with 10% of the area covered by water to a depth of 20 m. Soil having a depth of 10 cm and sediment 1 cm deep can also be included (9). Volumes of soil

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and sediment can be converted to equivalent volumes of octanol as follows:

$$V_{\text{octanol}} = V_{\text{soil}} \Phi \times 0.35 \rho \quad (1)$$

Here  $\Phi$  is the fraction of organic carbon in the soil (0.02),  $\rho$  is the density of the soil (2.4 g/cm<sup>3</sup>),  $V_{\text{soil}}$  is the volume of the soil compartment ( $9 \times 10^9$  m<sup>3</sup>), and  $V_{\text{octanol}}$  is the equivalent volume of octanol ( $151 \times 10^6$  m<sup>3</sup>). This assumes that  $K_{\text{OC}}$ , the organic carbon partition coefficient is correlated as  $0.35 K_{\text{OW}}$  (10). Often the coefficient of 0.41 as suggested by Karickhoff in 1981 (11) is used, but as Seth et al. (10) have shown, a coefficient of 0.35 plus or minus a factor of 2.5 is more appropriate. The volume of octanol equivalent to the sediment compartment can be calculated similarly (assuming  $\Phi$  is 0.04,  $\rho$  is 2.4 g/cm<sup>3</sup>, and  $V_{\text{sed}}$  is  $10^8$  m<sup>3</sup>) to be  $3.4 \times 10^6$  m<sup>3</sup>. The ratio of air:water:octanol volumes is approximately 650 000:1300:1, with octanol being 97.8% from soil and 2.2% from sediment.

At equilibrium, the total mass of chemical,  $M$ , will be distributed as follows:

$$M = V_{\text{W}}C_{\text{W}} + V_{\text{A}}C_{\text{A}} + V_{\text{O}}C_{\text{O}} = C_{\text{W}}(V_{\text{W}} + K_{\text{AW}}V_{\text{A}} + K_{\text{OW}}V_{\text{O}}) \quad (2)$$

where  $V$  is volume (m<sup>3</sup>),  $C$  is concentration (g/m<sup>3</sup>),  $K_{\text{AW}}$  is the air–water partition coefficient,  $K_{\text{OW}}$  is the octanol–water partition coefficient, and the subscripts A, W, and O refer to air, water, and octanol, respectively. The mass fractions of the chemical in each medium are thus

$$\text{air: } F_{\text{A}} = K_{\text{AW}}V_{\text{A}}/(V_{\text{W}} + K_{\text{AW}}V_{\text{A}} + K_{\text{OW}}V_{\text{O}}) \quad (3)$$

$$\text{water: } F_{\text{W}} = V_{\text{W}}/(V_{\text{W}} + K_{\text{AW}}V_{\text{A}} + K_{\text{OW}}V_{\text{O}}) \quad (4)$$

$$\text{octanol: } F_{\text{O}} = V_{\text{O}}K_{\text{OW}}/(V_{\text{W}} + K_{\text{AW}}V_{\text{A}} + K_{\text{OW}}V_{\text{O}}) \quad (5)$$

or in general

$$F_i = V_iK_{iW}/(K_{\text{WW}}V_{\text{W}} + K_{\text{AW}}V_{\text{A}} + K_{\text{OW}}V_{\text{O}}) \quad (6)$$

where  $i$  is A, W, or O and  $K_{\text{WW}}$  is 1.0. The ratio of environmental volumes can be adjusted in eqs 3–6 to suit local requirements, when the EQC volume ratios are inappropriate.  $F_i$  values are controlled by the volume ratios, not the absolute volumes. In this study the approximate ratios given above are used.

Figure 1 is a plot of  $\log K_{\text{AW}}$  vs  $\log K_{\text{OW}}$  including points representing the partitioning properties of 233 selected substances representing chemicals of environmental concern. This selected group should not be construed as representing the universe of chemicals of commerce, but it is useful for illustrative purposes. Physical, chemical, and reactivity data for these substances were obtained from Mackay et al. (12), Brubaker and Hites (13), Wania (14), and Wania and Mackay (15). A list of the chemicals and their properties is available in the Supporting Information. It should be noted that the half-lives are reported in ref 12 as ranges and are subject to considerable temporal and spatial variability but are used here as single values. The 45° diagonals are lines of constant  $\log K_{\text{OA}}$ , the octanol–air partition coefficient, because  $K_{\text{OA}} = K_{\text{OW}}/K_{\text{AW}}$  or  $\log K_{\text{OA}} = \log K_{\text{OW}} - \log K_{\text{AW}}$ . Lines of constant  $F_{\text{A}}$ ,  $F_{\text{W}}$ , and  $F_{\text{O}}$  are drawn in Figure 1 using the above volume ratios. The lines corresponding to one-third in each compartment converge at the point where  $\log K_{\text{OW}}$  is 3.1;  $\log K_{\text{AW}}$  is –2.74; and  $V_{\text{W}}$ ,  $K_{\text{AW}}V_{\text{A}}$ , and  $K_{\text{OW}}V_{\text{O}}$  are equal, i.e.,  $K_{\text{AW}}$  is  $V_{\text{W}}/V_{\text{A}}$  or 1300/650 000 or 0.002 and  $K_{\text{OW}}$  is  $V_{\text{W}}/V_{\text{O}}$  or 1300/1. If the ratios of the volumes change, for example, if the water volume is increased, the location of this central point will move upward along the 45° diagonal changing the location of the lines of constant  $F_i$ .

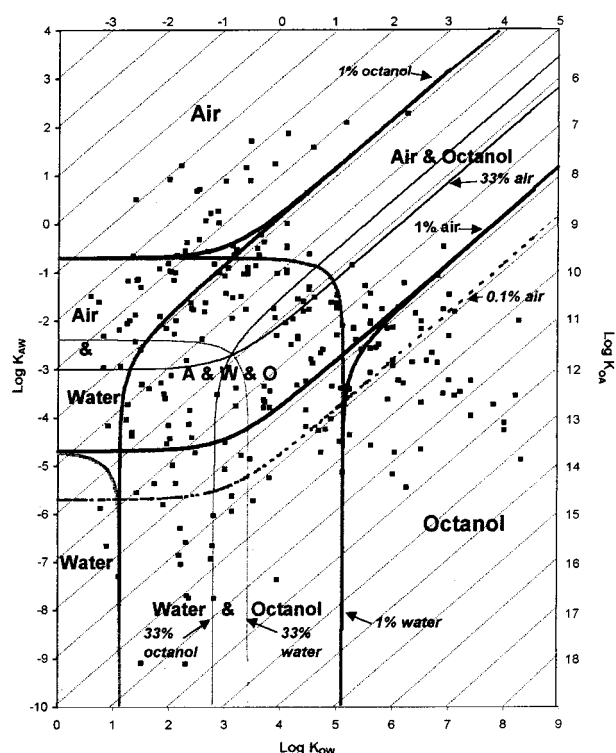


FIGURE 1. Plot of  $\log K_{\text{AW}}$  vs  $\log K_{\text{OW}}$  showing the distribution of 233 chemicals and lines of equal  $F_{\text{A}}$ ,  $F_{\text{W}}$ , and  $F_{\text{O}}$ . Data from ref 12. The 45° diagonals are lines of constant  $\log K_{\text{OA}}$ , the octanol–air partition coefficient. The region to the upper left, where more than 99% is in air, shows that persistence is controlled by the air half-life. Similarly, the region to the lower left, where more than 99% is in water, shows that persistence is controlled by the water half-life; the region to the lower right, where more than 99% is in octanol, shows that persistence is controlled by the octanol half-life. The lines corresponding to one-third in each compartment converge at the single point where  $\log K_{\text{OW}}$  is 3.1 and  $\log K_{\text{AW}}$  is –2.74. Substances in this region are multimedia, and all half-lives will be required.

The 1% and 99% lines divide the  $K_{\text{AW}}/K_{\text{OW}}$  space into regions in which partitioning is predominately into one medium and in which it is likely that degradation in that medium is most important. In the region to the upper left, where more than 99% is in air, the air half-life probably controls the persistence, and it is unlikely that half-lives in water, soil, or sediment are required. To the lower right of the 99% octanol line, substances are strongly sorbed, and only data for soils and sediments are likely to be needed. To the lower left, water is the dominant medium of partitioning. As is discussed later, half-lives in air are generally shorter than those in water, soil, and sediment, largely because of relatively rapid hydroxyl radical reactions. As a result, even 0.5% partitioning to air can represent an appreciable fraction of the overall degradation. The 0.1% air line (also shown) may be a better limit. Approximately 34% of the substances are “multimedia” because there is more than 1% of the substance in each medium. For these substances, all half-lives will be required. If the substances that fall between 1% and 0.1% of air are included, then approximately 40% of the substances become multimedia. Similarly there are regions where only two half-lives may be required.

Figure 1 provides a rapid method of identifying the key degradation data requirements and can avoid the need to obtain data of marginal utility.

### Individual and Overall Half-Lives

Figure 2 A–C gives histograms showing the distribution of half-lives in air, water, and soil for the 233 chemicals, with

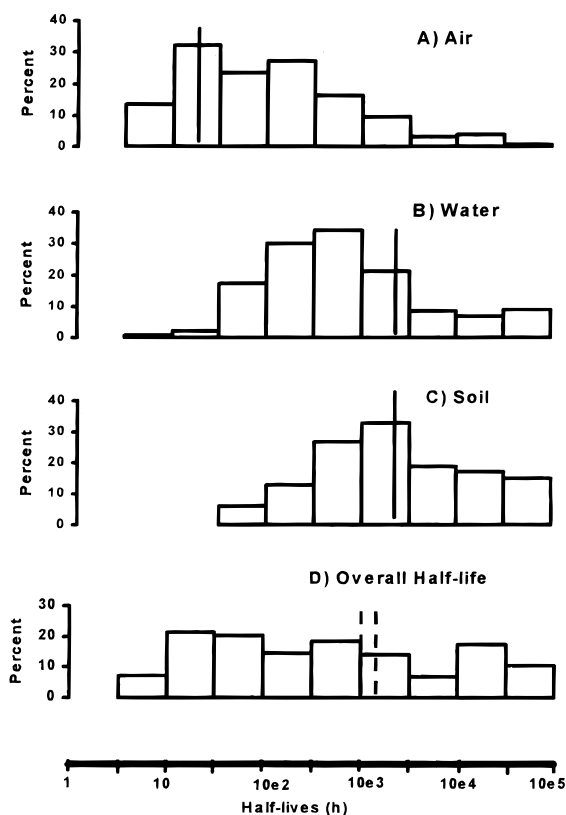


FIGURE 2. Distribution of reported half-lives (h) in (A) air, (B) water, (C) soil, and (D) overall half-lives calculated from eq 8 of 233 chemicals in logarithmic increments. Data from refs 12–15. The solid vertical lines in panels A–C show the Environment Canada cut-off criteria. 65% of the 233 chemicals are “persistent” due to their air half-lives, 18% are persistent due to their water half-lives, and 39% are persistent due to soil half-lives. The vertical lines in panel D define the suggested range of overall criteria. Using these criteria, 36% to 28% are declared persistent.

TABLE 1: Distributions of Air, Water, and Soil Half-Lives (h) for 233 Chemicals from Ref 12<sup>a</sup>

media <i>i</i>	ratio of mean half-lives	half-life (h) $\tau_i$		SD about mean log $\tau_i$		% of chemicals tested “persistent” by Environment Canada criteria
		mean of log $\tau_i$	mean $\tau_i$	log	factor	
air	1	1.98	96	0.89	7.7	65
water	7	2.81	649	0.86	7.2	18
soil	23	3.34	2202	0.82	6.7	39

<sup>a</sup> Exceptions: half-lives in air for HCHs and HCB: Brubaker and Hites (13); half-life in water and soil for  $\alpha$ -HCH: Wania (14) and Wania and Mackay (15).

the half-life statistics being summarized in Table 1. The mean half-life in air is 96 h, whereas for water it is 649 h, and for soil it is 2202 h. The ratios of the mean half-lives are air, 1; water, 7; and soil, 23. Clearly air is the most reactive medium. For example, for degradation in air, the mean of the log half-lives is 1.98, corresponding to 96 h, or 4 days, with a log standard deviation of 0.89, i.e., a factor of  $10^{0.89}$  or 7.8. A total of 76% of all air half-lives lie within a factor of 7.8 of 96 h, i.e., between 12 and 749 h.

If the total mass of chemical in the system is  $M$ , the masses in each medium are  $F_A M$ ,  $F_W M$ , and  $F_O M$ , and the rate constants are respectively  $k_A$ ,  $k_W$ , and  $k_O$ , then the total rate of reaction  $N$  (which equals the rate of emission at steady state) will be  $M(F_A k_A + F_W k_W + F_O k_O)$  and the residence time of the chemical in this system, i.e., the persistence, will be

#### Pentachlorobenzene

Properties:	$K_{AW} = 0.0339$	$K_{OW} = 100\,000$	$K_{OA} = 2.951 \times 10^6$
Half-Lives, $\tau_i$ (h)	Air = 5 500	Water = 17 000	Soil = 17 000
Volume fractions, $F_i$ (from equations 3, 4, 5)	$F_A = 0.179$	$F_W = 0.011$	$F_O = 0.810$

Overall Half-life (hours)  $\tau_R = 12\,400$

If  $\tau_A$  is infinite (hours), overall half-life is 20 700

If  $\tau_W$  is infinite (hours), overall half-life is 12 500

If  $\tau_O$  is infinite (hours), overall half-life is 30 100

FIGURE 3. Specimen calculation of persistence for pentachlorobenzene; data from ref 12.

$M/N$  or  $1/(F_A k_A + F_W k_W + F_O k_O)$ . The overall rate constant  $k_R$  is  $N/M$  and is a weighted mean of the individual rate constants, namely:

$$k_R = F_A k_A + F_W k_W + F_O k_O \quad (7)$$

If half-lives ( $\tau$ ) are used instead of rate constants ( $k$ ),  $\tau$  is  $0.693/k_i$  and the overall half-life ( $\tau_R$ ) is

$$1/\tau_R = F_A/\tau_A + F_W/\tau_W + F_O/\tau_O \quad (8)$$

Using the key half-lives as identified by a plot such as Figure 1 and assuming unimportant half-lives to be infinite, a value of  $\tau_R$  can be calculated. If the resulting value of  $\tau_R$  is large, because of this assumption, the missing half-life data can be experimentally determined and the overall half-life correspondingly reduced. Thus, efforts are focused on only those half-lives that will have a significant effect on the overall persistence, reducing the need for costly experiments. Figure 3 gives a specimen calculation for a typical multimedia chemical and shows the implications of missing data.

It is noteworthy that persistence is an intensive property of the substance and the model environment, i.e., the value is independent of the quantity of chemical emitted. Obviously chemicals emitted in greater quantities are of greater concern because concentrations will be higher and the risk of adverse effects more likely, but this is a separate issue from the evaluation of persistence.

Equation 8 was applied to the 233 chemicals to determine the distribution of overall persistence as shown in Figure 2D. Establishing cutoff criteria for persistence is a regulatory issue and beyond our scope here; however, the distribution in Figure 2D provides an indication of the range of options. The median is 471 h or 20 days. One approach is to set a criterion based on a defined fraction of the chemical surviving in the environment (i.e., in all three compartments combined) to the next year. Overall half-lives in the range of 1400–2000 h, i.e., 58–83 days, result in 6.3–4.4 half-lives per year. If these half-lives applied throughout the year, this would result in only 1.3–4.7% of the chemical surviving to the next year. In practice, because of slower degradation in winter, these percentages would increase somewhat, making a more detailed temperature-dependent evaluation necessary in some cases after the initial screening. Using these criteria, 36% to 28% are declared persistent.

On the other hand, using the multiple half-life approach, of the 233 chemicals selected, 65% would be declared persistent because their half-lives in air exceed the 2-day criterion suggested by Environment Canada. Clearly the single medium approach can capture a large fraction of the substances as a result of its multiple criteria, and screening-out can be inefficient.



It is important to set out the assumptions inherent in this approach, the limitations, and the key sensitivities. The overall persistence depends on the ratio of air, water, and octanol volumes; the accuracy of the partition coefficients; the assumed  $K_{OC} - K_{OW}$  relationship; and the assertion that the assumed half-lives apply to all chemicals in each compartment at all times and, most importantly, that equilibrium is achieved. There is no treatment of aerosols, suspended sediment in water, vegetation, biota, deep sediments, or groundwater. The approach will fail for substances that speciate (e.g., ionize) or have sorptive properties that are not described by  $K_{AW}$  or  $K_{OW}$ . Fortunately, the approach is likely to be most valid for persistent hydrophobic substances that are the subject of most concern. Since this is a first screen, it would be useful to assess a group of chemicals using this screen and a second, more detailed assessment to determine if any persistent substances are wrongly screened out. This will minimize the risk of failure.

### Proposed First-Stage Screening Method

We suggest that, for the first stage screening of persistence, partitioning data be obtained, i.e., any two of  $K_{OW}$ ,  $K_{AW}$ , and  $K_{OA}$ . Using Figure 1, the key media are identified and half-lives sought in these media. The chemical fractions  $F_A$ ,  $F_W$ , and  $F_O$  in air, water, and octanol are calculated using eqs 3–5. The overall persistence is calculated using eq 8. If a half-life is unavailable for a non-key medium, infinity is substituted. If desired, the half-life can be determined experimentally. Criteria for overall persistence can be developed based on observations of the performance of a large number of chemicals.

By using this simple and rapid screening process, it may be possible to eliminate a large fraction of the chemicals of commerce from further consideration. The principal criticism that can be leveled at this method is that it may be lax for a chemical, such as a pesticide, that is discharged to a medium in which it is persistent and from which it is only slowly transported. If this "mode-of-entry" information is available, the simple and conservative expedient is to assume that the overall half-life equals the single medium half-life. This approach may also wrongly penalize a compound that has a short half-life in the medium into which it is discharged, and it has little tendency to enter other media in which it has a longer half-life. For those substances that are deemed to be potentially persistent, as calculated by eq 8, or for which mode-of-entry is important, it is suggested that a more detailed second stage evaluation be done, as described by

Webster et al. (5), using a nonequilibrium level III model in which intermedia transport processes are quantified.

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### Supporting Information Available

One table giving the physical–chemical properties of selected chemicals (4 pages). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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