

CHAPTER 2

Fate and Transport of Contaminants*

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Abstract: Release of toxic chemicals into the environment cannot always be avoided completely. As a result organisms, man included, will be exposed to chemicals *via* the environment. Given the release of certain chemicals into the environment, their exposure concentrations in air, water and soil would depend on the rates at which they are removed from the environment. This chapter deals with the transport and transformation processes that affect concentrations in the environment, with emphasis on the modeller's perspective. Being interested primarily in the effects that processes have on concentrations of chemicals in environmental media, we focus on a quantitative description of the rates at which losses from the environment take place, and on how these rates differ for different chemicals. We systematically formulate process rate constants for each transport or transformation process. Eventually, the rate constants combine into a mass balance model which allows us to describe and predict how releases into the environment result in exposure concentrations of organisms.

PROCESSES AND MECHANISMS

After entering the environment, chemicals are transported, distributed over the various environmental compartments and may be transformed into other chemicals. Transport can occur within a compartment, such as in air or in soil, or between compartments (e.g. between air and water, air and soil or water and soil). Transformation processes in the environment involve chemical degradation or biodegradation.

Process rates (*i.e.* the mass flows of substance that result from them) generally depend on two independent factors: (i) the concentration of the substance in the environmental medium (driving force) and (ii) the likelihood of occurrence of the process (rate constant). When process rates are directly proportional to concentrations, process kinetics are called first order (first power concentration). Non-linear relationships apply in cases of higher or lower order kinetics. In the case of first-order kinetics, the mass M of chemical in the environmental compartment of origin falls exponentially with time t :

$$\frac{dM}{dt} = -k_{loss} \cdot M \quad \text{or} \quad M = M_0 e^{-k_{loss} \cdot t} \quad (1)$$

The first-order loss process is characterized by one single parameter: the loss rate constant k_{loss} . The loss mechanism causes the mass of chemical in the compartment to fall from its original value M_0 to half of that value in a constant time period: the half-life time $t_{1/2}$ of the chemical in the compartment. Mass keeps falling at the same half-life until the chemical has disappeared entirely. It can be deduced from Eq 1, or seen from its graphical representation (Fig. 1), that in case of first-order kinetics the half-life time $t_{1/2}$ has a constant value throughout the loss process:

$$t_{1/2} = \frac{\ln 2}{k_{loss}} \quad (2)$$

Throughout this chapter, we shall assume first-order kinetics to apply to all transport and transformation process. Although in reality this is certainly not always true, usually too little information is available to better describe the process rate-concentration dependence. Moreover, even in cases where higher order kinetics apply, assuming first-order kinetics will not always lead to dramatically erroneous predictions, as often concentrations do vary only slightly, so that so-called pseudo-first-order kinetics apply.

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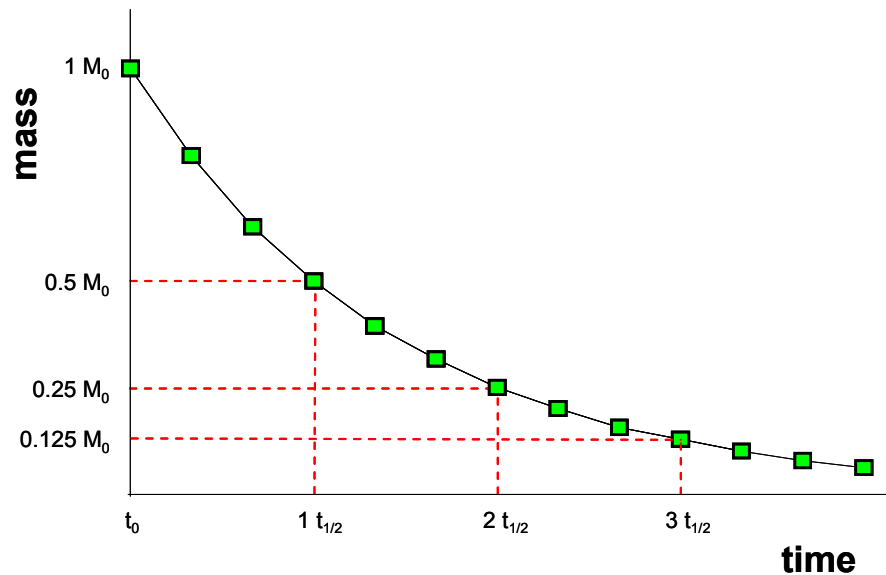


Figure 1: Loss of chemical from the environment through first-order kinetics results in constant half-life.

Equilibrium Partitioning Between Phases

Obeying general laws of thermodynamics, chemicals tend to spontaneously migrate from one phase (environmental medium: air, water, soil) to another if the phases are not in equilibrium. Migration in multi-phase systems continues until equilibrium has been reached. In thermodynamics, equilibrium is characterized as the state in which the chemical potential, and the chemical's activity and fugacity have the same value in the different phases. This principle has successfully been applied [2] in mass balance models of environmental fate of chemicals, that have become known as “fugacity models” or “Mackay models”. For most practical situations, the equilibrium condition can be expressed by stating that chemicals are driven towards equilibrium until the ratio of concentrations (C_1 and C_2) is equal to the intermedia equilibrium constant K , also known as partition coefficient:

$$K_{12} = \frac{C_1}{C_2} \quad (3)$$

Departure from thermodynamic equilibrium forms the main driving force of intermedia transport of chemicals. This is why intermedia equilibrium constants play such an important role in quantitative mathematical descriptions of transport and fate of chemicals in the environment.

Solids-Water Equilibrium

Equilibrium partitioning between water and solids is the result of adsorption of the chemical onto the surface of particles. For low concentrations of the chemical in water, the equilibrium ratio is usually a constant: K_{12} of Eq 3 is independent of the concentrations of the chemical. For higher concentrations, it is often observed experimentally that the equilibrium ratio does depend on the concentrations. In such cases, the equilibrium relationship between the concentrations is given by a non-linear sorption isotherm. The Freundlich-isotherm equation is often used (without making assumptions about the nature of the underlying mechanism) to fit experimentally observed non-linear sorption.

Commonly used estimation methods for solids-water partition coefficients K_p are based on the assumption that there is a “hydrophobic sorption” mechanism. This mechanism is generally modelled based on the organic carbon content of the soil, sediment or suspended solids f_{oc} and the octanol-water partition coefficient of the chemical K_{ow} , using simple regression equations:

$$\log K_p = \log(K_{oc} \cdot f_{oc}) = a \log K_{ow} + b + \log f_{oc} \quad (4)$$

where

K_{oc} = organic carbon referenced solids-water partition coefficient (L/kg)

a, b = constants, specific for chemical classes

Given a value of K_p , the extent to which partitioning from water to solids occurs depends on the amount of solids present. At equilibrium, the mass fraction of chemical dissolved in water $\Phi_{dissolved}$ can be calculated as

$$\Phi_{dissolved} = \frac{1}{1 + K_p \cdot TSS} \quad (5)$$

where

TSS = mass concentration of suspended solids in water ($\sim 10^{-5}$ kg/L)

Normalization to the organic carbon content of particulate matter has become standard procedure in this field of research. This procedure is based on the experimental observation that the K_p of organic chemicals is often proportional to the organic matter content of the solid phase. The estimation method was derived originally for hydrophobic chemicals [3]. The method was extended to apply to various other classes of non-ionic organic chemicals [4] and, more recently, to ionizing organic acids and bases [5]. The method cannot be applied to metals and other inorganic ionizing substances.

Solids-water partition coefficients are commonly reported in units L/kg. The physical meaning of this dimension can be understood by reading it as “the volume of water (L) which contains the same amount of the chemical as one kilogram of solid material does”. For many purposes, however, we are not just interested in the concentration ratio, but also in the mass distribution of the chemical over the phases. Obviously, this distribution depends on both the partition coefficient and the relative volumes of the phases. In surface water, the solids-water ratio is much smaller than in sediment and soil systems. As a result, the extent of partitioning of a certain chemical into the particle phase of sediment or soil is much greater than in surface water. Solids-water partition coefficients of chemicals K_p range from < 1 L/kg to $> 10^5$ L/kg, with resulting extents of partitioning into the solid phases ranging from negligible in surface water to near-complete in soil (Table 1).

Air-Water Equilibrium

Equilibrium between air and water is given by Henry's law, which states that in equilibrium, the partial pressure of a chemical in the gas phase is proportional to its concentration in water. The ratio of these, Henry's law constant H , can be obtained as the ratio of the saturated vapour pressure P^s and water solubility S of the pure compound, provided that P^s and S refer to the same physical state (liquid or solid) and to the same temperature T . The air-water concentration ratio K_{AW} can be derived from Henry's law constant by reworking it into a “dimensionless” partition coefficient. Dimensionless air-soil concentration ratios can be obtained in the same way:

$$K_{AW} = \frac{C_{air}}{C_{water}} = \frac{H}{RT} = \frac{P_{L,S}^s}{S_{L,S} \cdot RT} \quad (6)$$

where

R = gas constant (8.314 Pa.m³/mol/K)

T = temperature at the air-water interface (K)

Air-water equilibrium constants of chemicals K_{AW} range from $< 10^{-10}$ to > 1 (Table 1).

Table 1: Typical environmental values of intermedia partition parameters for selected chemicals.

| | units ¹ | Dichloroethane | Dieldrin | Benzo[a]pyrene | Cadmium ²⁺ |
|--------------------------------|--------------------|----------------|-------------|----------------|-----------------------|
| $K_{aerosol-gas}$ | - | 6.2E+02 | 3.5E+08 | 5.8E+10 | >>> ³ |
| $K_{air-water}$ | - | 4.9E-02 | 4.5E-04 | 1.9E-05 | <<< ³ |
| $K_{susp-water}$ | - | 5.0E+00 | 2.1E+03 | 2.5E+04 | 2.5E+04 |
| $K_{sed-water}$ | - | 2.5E+00 | 1.0E+03 | 1.2E+04 | 1.3E+04 |
| $K_{soil-water}$ | - | 1.0E+00 | 4.1E+02 | 4.9E+03 | 5.0E+03 |
| $K_{bio-water}$ | - | 3.8E+00 | 2.0E+04 | 1.4E+05 | 1.7E+02 |
| $\Phi_{gas}(air)^2$ | - | 100% (100%) | 99.6% (97%) | 25% (15%) | << (<<) ³ |
| $\Phi_{dissolved}(water)$ | - | 100% | 98% | 83% | 87% |
| $\Phi_{pore\ water}(sediment)$ | - | 62% | 0.4% | 0.03% | 0.03% |
| $\Phi_{pore\ water}(soil)$ | - | 25% | 0.1% | 0.01% | 0.01% |

¹"Dimensionless" ratios to be read as $m_{medium1}^3 \cdot m_{medium2}^{-3}$; for K-values, and as "mol_{phase1}/mol_{phase2}" for Φ -values;

² numbers in parentheses calculated according to Eq 8; ³ >>>: very large; <<<: very small

Air-Aerosol Equilibrium

The extent of association of chemicals with the aerosol phase of air is known to be inversely related to the chemical's vapour pressure. The fraction associated with the aerosol phase $\Phi_{aerosol}$ has successfully been described by Junge [6] with

$$\Phi_{aerosol} = \frac{c\Theta}{P_L^s + c\Theta} \quad (7)$$

where

Θ = aerosol surface area per volume unit of air (m²/m³)

P_L^s = vapour pressure of the pure compound in the liquid state (Pa)

c = constant (Pa.m)

The constant c depends on the heat of condensation and molecular weight for many organics, its value being approximately 0.17 Pa.m. The local pollution climate determines the aerosol surface density. A typical value for aerosol surface area under rural conditions is 3.5×10^{-4} m²/m³. For more polluted urban or industrialized areas Θ is estimated to be 1.1×10^{-3} m²/m³. Substitution of these values in Eq 7 shows that gas-particle partitioning is important for organic compounds with a P_L^s lower than approximately 10^{-3} Pa. Since P_L^s is strongly temperature dependent, the fraction of a substance absorbed to particles will also be temperature dependent. For certain organics this may imply that in tropical regions the pollutant will be in the gas phase, whereas in arctic regions it will be in the particle phase. More recently, it has been shown that for many (hydrophobic) chemicals, the octanol-air partition coefficient K_{OA} is a more accurate descriptor of aerosol-air partitioning [7].

$$\Phi_{gas} = \frac{1}{1 + K_{OA} \cdot (B \cdot TSP)} = \frac{1}{1 + (K_{OW} / K_{AW}) \cdot (B \cdot TSP)} \quad (8)$$

where

B = chemical- specific constant ($\approx 2 \times 10^{-12} \text{ m}^3/\mu\text{g}$)

TSP = mass concentration of aerosol in air ($\approx 50 \mu\text{g}/\text{m}^3$)

Eq 8 predicts significant partitioning to the aerosol phase for chemicals with K_{OA} greater than approximately 10^{10} , which is the case for many polyaromatic cyclic hydrocarbons PAH (Table 1).

TRANSPORT MECHANISMS

Two kinds of transport mechanisms may be distinguished: (1) *intramedia transport*, which is transport away from a source in one environmental medium, and (2) *intermedia transport*, which is transport from one environmental medium to another. Intramedia transport is important in relation to the mobile environmental media: air, water and groundwater; intermedia exchange takes place between all media, but is most important for transport of chemicals to and from the stationary media: sediment and soil.

Intramedia transport takes place through the mechanisms of advection and dispersion. Advection causes a chemical to travel from one place to another as a result of the flow of the medium in which it occurs; locally emitted packages or “puffs” of a chemical are carried as far as the wind or water current can take it during the residence time in that medium. Dispersion mechanisms (molecular diffusion, eddy diffusion) make the chemical move down concentration gradients until the gradients have disappeared. The residence time of the chemical in the medium is an important factor since besides this other removal processes occur at the same time. If, for example, a chemical is emitted into air and its degradation in air is rapid, the effective residence time of the chemical in air is short. Consequently, there is little time for the advective and dispersive processes to take place. In one medium, advection and dispersion always operate together. If a chemical is emitted continuously into air or water, the combined operation of advection and dispersion results in the formation of a plume. At short distances from emission sources, concentrations are usually affected most by intramedia transport. Intramedia transport of chemicals is observed as dilution, which in many situations is the most important process affecting environmental concentrations of chemicals. In this chapter, we shall account for the effect of intramedia dilution on the concentrations of chemicals by lumping it into rate constants for advective and dispersive loss of chemicals due to transport. However, explanation of the complex aerodynamic and hydrodynamic processes of advective and dispersive spread of chemicals within air, surface water and groundwater will not be discussed here. Interested readers are referred to specialized text books on mathematical modelling of air, surface water and groundwater [8].

Intermedia transport (air-water, water-sediment, *etc.*) also takes place by advective and dispersive mechanisms. Advective intermedia transport takes place if a chemical is transported from one environmental compartment to another by a physical carrier. Examples are deposition of fog, raindrops and aerosol particles from air to water or soil, sedimentation and resuspension of particulate matter across the water-sediment interface, and percolation of water through soil. Advective transport is a one-way phenomenon: the chemical is carried by the medium in which it resides in the direction of the medium flows. Intermedia dispersion is also diffusive in nature and follows concentration gradients. Examples are volatilization and gas absorption (air-water and air-soil), the direction depending on the concentration difference between the media, and diffusive exchange of chemicals between sediment and water. The driving force of intermedia transport is the tendency of chemicals to seek equilibrium between different phases. Transport from one environmental medium to another is commonly described by taking the box/compartment modelling approach. Theoretical backgrounds and detailed quantitative descriptions of intermedia exchange processes can be found in other texts [2, 9-13]. The most important interfaces are described below.

Air-Water and Air-Soil Exchange

Atmospheric deposition and volatilization processes transport chemicals between air and the earth's surface. It is customary to distinguish between wet (precipitation-mediated) deposition mechanisms and dry deposition mechanisms (Fig. 2). Wet deposition is further split into rain-out (in-cloud processes) and wash-out (below-cloud processes). Dry deposition is the sum of aerosol deposition and gas absorption. In multimedia environmental

chemistry, the latter mechanism is usually treated as one part of a bi-directional exchange mechanism. Rain-out, wash-out and aerosol deposition are one-way advective transport processes: the chemical is carried from the atmosphere to water and soil. This is true even if the chemical has a greater fugacity in water or soil. Gas absorption is a diffusive mechanism. There is only net absorption of chemicals from the gas phase by water or soil if the fugacity in air is greater than the fugacity in water or soil. If the fugacity in water or soil is greater, the result will be the reverse: net volatilization. This will generally be the case if a chemical is emitted to water or soil, in which cases fugacities in these media will be highest of all. Deposition from air to water and soil occurs at all times, even when net volatilization occurs (see below). It should be noted that absorption and volatilization occur simultaneously, and it is the net difference that accounts for the effective intermedia transport.

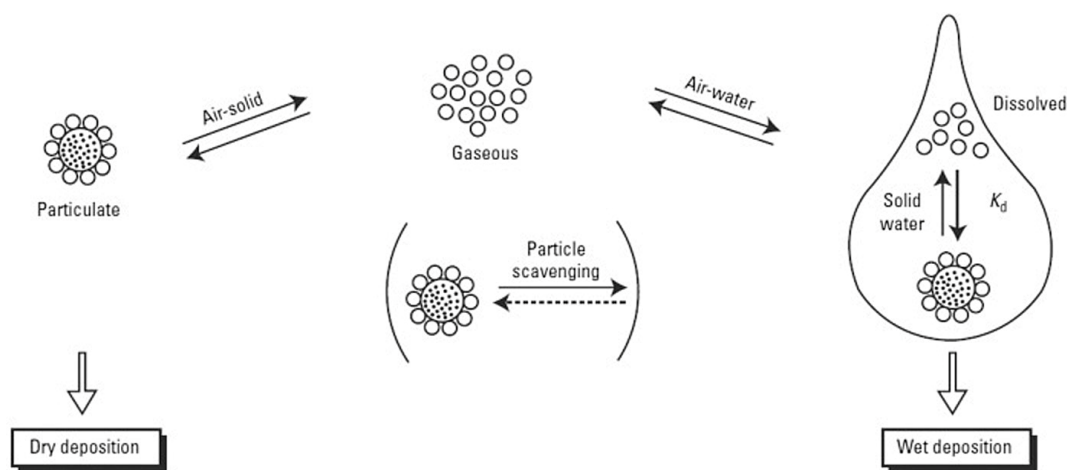


Figure 2: Exchange mechanisms between atmosphere and the earth's surface. From Schwarzenbach [14], as referred to by Sijm *et al.* [15].

Deposition with Aerosol and Rain

Chemicals adsorbed to aerosol particles are carried from the air compartment to the earth's surface by dry particle deposition. Aerosol particles can also be scavenged by rain drops as wet particle deposition. In addition, rain drops absorb chemicals from the gas phase and carry chemicals to the earth's surface by rain-out and wash-out.

Deposition rates depend on the physical parameters of the particle, of which the size is most important. Small particles tend to behave like gases; larger particles ($> 2 \mu\text{m}$) are efficiently removed from the atmosphere by deposition under the influence of gravity. Inertial impaction is important for particles with a diameter of between 0.1 and $10 \mu\text{m}$. This effect greatly depends on the velocity of the air and the intensity of the turbulence, which varies with the properties of the landscape. Larger particles ($> 10 \mu\text{m}$) are deposited primarily by sedimentation and chemicals associated with them will, in general, be deposited close to the source. Typical aerosol deposition velocities range from 10^{-4} to 10^{-2} m/s. Some chemicals are associated predominantly with the larger, rapidly depositing particles, whereas other chemicals bind predominantly to the smaller particles and stay airborne for much longer times.

The efficiency of wet deposition varies greatly. It depends on meteorological factors such as the duration, intensity and type of precipitation (snow, rain, hail), as well as on the size and the number of droplets. Other specific parameters, like solubility in rain and snow, are important too. Wash-out is an efficient removal mechanism for chemical substances with low Henry's law constants, and for aerosols with a diameter greater than $1 \mu\text{m}$. For less volatile chemicals (high Henry's law constants) the falling droplet will absorb only a very small amount of the compounds below the cloud. Wash-out plays an important role when concentrations below the cloud are much higher than the concentrations in the cloud, e.g., for plumes close to the source. In clouds the uptake of aerosols by cloud droplets is a very efficient process. For most purposes, it is sufficient to assume that the rain phase is in equilibrium with the gas phase. The extent of gas scavenging by falling rain drops can then be calculated from the air-water distribution ratio K_{AW} and the rain intensity. As a practical approach to estimating the extent of aerosol

scavenging, Mackay [2] has suggested that during rainfall in the atmosphere, each drop sweeps through a volume of air about 200,000 times its own volume. First-order rate constants for removal of chemicals from air by atmospheric deposition are given in Table 2.

Table 2: Influence of transport- and transformation processes on concentrations in AIR for selected chemicals, after a steady state has been reached.

| | Dichloroethane | | Dieldrin | | Benzo[a]pyrene | | Cadmium ²⁺ | |
|----------------|----------------|-----------------------------|----------------|-----------------------------|----------------|-----------------------------|-----------------------|-----------------------------|
| | <i>k</i> (1/s) | <i>t</i> _{1/2} (d) | <i>k</i> (1/s) | <i>t</i> _{1/2} (d) | <i>k</i> (1/s) | <i>t</i> _{1/2} (d) | <i>k</i> (1/s) | <i>t</i> _{1/2} (d) |
| advection | 7.1E-06 | 1.1 | 7.1E-06 | 1.1 | 7.1E-06 | 1.1 | 7.1E-06 | 1.1 |
| deposition | 9.1E-10 | 8852 | 1.2E-07 | 67 | 4.7E-06 | 1.7 | 5.5E-06 | 1.5 |
| gas absorption | 2.7E-06 | 3.0 | 2.9E-06 | 2.7 | 9.3E-07 | 8.6 | 3.8E-09 | 2089 |
| volatilization | 2.7E-06 | 3.0 | 2.0E-06 | 4.0 | 1.1E-07 | 72 | << | - |
| degradation | 1.0E-07 | 79 | 3.1E-06 | 2.6 | 2.5E-07 | 32 | << | - |
| total loss | 7.2E-06 | 1.1 | 1.1E-05 | 0.71 | 1.3E-05 | 0.63 | 1.3E-05 | 0.64 |

Volatilization and Gas Absorption

Transport of a chemical from water and soil into the gas phase of air and vice versa is commonly described by a two-resistance approach, as originally introduced 110 years ago by Whitman [16]. In this concept, the resistance to intermedia transfer is considered to be concentrated in two thin films on either side of the interface. Transport through this interfacial double layer has to take place by molecular diffusion and is, therefore, slow in comparison with transport to and from the interface. This concept was used by Liss and Slater [17] as a basis for modelling the transfer of gases across the air-sea interface. The direction of transport depends on the concentrations in air and water. In fugacity terminology: the net diffusion is from the compartment with the highest fugacity to the compartment with the lowest fugacity. The rate mass-transfer (depending on the direction referred to as either gas absorption or volatilization) is expressed by means of an “overall” mass-transfer coefficient k^{OV} , in which transfer resistances on either side of the air-water interface are accounted for, can be expressed in terms of air- or water concentrations. The mass-transfer coefficient (m/s) can be looked upon as the velocity of a piston, pushing the chemical through the interface. The driving force can be positive or negative, leading to absorption or volatilization. The overall mass transfer coefficients k^{OV} represent the resistance to mass transfer: the greater k^{OV} , the smaller the resistance. The magnitude of k^{OV} derives from the partial mass transfer coefficients of the stagnant films at either side of the air-water interface, through which the chemical must diffuse, and the intermedia equilibrium constant K_{AW} can be estimated as:

$$k_{air}^{OV} = \frac{kaw_{air} \cdot kaw_{water}}{kaw_{air} \cdot K_{AW} + kaw_{water}}, \quad (9)$$

$$k_{water}^{OV} = \frac{kaw_{air} \cdot kaw_{water}}{kaw_{air} + kaw_{water} / K_{AW}}$$

where

kaw_{air} = partial mass-transfer coefficient air side of the air-water interface (m/s)

kaw_{water} = partial mass-transfer coefficient water side of the air-water interface (m/s)

The partial mass transfer coefficients kaw represent the resistances of the stagnant air and water films. Thick films have greater resistances than thin films; substances with large diffusivities (small molecules) have smaller

resistances than substances with small diffusivities (big molecules). Since diffusivities of substances do not differ much, differences in k_{aw} originate mainly from differences in thickness of the stagnant film through which the molecules must diffuse. Film thicknesses vary from water body to water body due to differences in turbulence. Typical values of k_{aw} are 10^{-3} and 10^{-5} m/s for air and water films, respectively. As a result, differences in volatilization between substances arise from differences in the air-water equilibrium constant K_{AW} . It can be seen from Eq 9 that k^{OV} of water-loving chemicals ($K_{AW} \ll \sim 10^{-2}$) is proportional to K_{AW} ; resistance to volatilization for such chemicals originates entirely from slow diffusion through the air film. Air-loving chemicals ($K_{AW} \gg 10^{-2}$) volatilize independently of K_{AW} ; resistance to volatilization for such chemicals is limited only by slow diffusion through the water film. Advanced readers are referred to specialized textbooks on this subject [9, 10].

When the concentration in air is negligibly small, the net rate of volatilization depends only on the concentration in water, so that volatilization acts as a first-order removal process from water. Applying the mass balance concept of Eq 1, it follows that

$$VOL \approx A \cdot k_{water}^{OV} \cdot C_{water} = k_{vol} \cdot V_{water} \cdot C_{water},$$

$$\text{with } k_{vol} = \frac{A \cdot k_{water}^{OV}}{V_{water}} = \frac{1}{D_{water}} \cdot \frac{kaw_{air} \cdot kaw_{water}}{kaw_{air} + kaw_{water} / K_{AW}}, \quad (10)$$

where

k_{vol} = first-order rate constant for removal from water by volatilization (1/s)

V_{water} = volume of the water compartment (m^3)

D_{water} = depth of the water compartment (m)

Note that, while the volatilization rate (mol/s) depends on the area A of the water compartment, the effect that this volatilization has on the concentration C_{water} depends on the depth D_{water} of the water compartment. Similarly, gas absorption with negligible concentration in water acts as a first-order removal process from air. The rate constant for removal from air by gas absorption is left to be worked out by the reader. Volatilization from and gas absorption to soil can be deduced along the same lines and is not treated here. First-order rate constants for exchange of some chemicals between air and the Earth's surface are given in Tables 3 and 4.

Table 3: Influence of transport and transformation processes on concentrations in WATER for selected chemicals, after a steady state has been reached.

| | 1,2-Dichloroethane | | Dieldrin | | Benzo(a)pyrene | | Cadmium ²⁺ | |
|----------------|--------------------|---------------|-----------|---------------|----------------|---------------|-----------------------|---------------|
| | k (1/s) | $t_{1/2}$ (d) | k (1/s) | $t_{1/2}$ (d) | k (1/s) | $t_{1/2}$ (d) | k (1/s) | $t_{1/2}$ (d) |
| advection | 6.7E-08 | 119 | 6.7E-08 | 119 | 6.7E-08 | 119 | 6.7E-08 | 119 |
| deposition | 8.6E-12 | 936753 | 6.8E-11 | 118770 | 1.2E-10 | 68120 | << | >> |
| gas absorption | 2.1E-09 | 3795 | 1.5E-09 | 5218 | 2.3E-11 | 348458 | << | >> |
| volatilization | 1.8E-06 | 4.4 | 2.0E-07 | 40 | 1.0E-08 | 774 | << | >> |
| sedimentation | 1.2E-10 | 69613 | 1.2E-07 | 69 | 5.1E-07 | 16 | 1.3E-06 | 6.4 |
| resuspension | 2.5E-10 | 31566 | 9.4E-08 | 86 | 4.3E-07 | 19 | 1.1E-06 | 7.1 |
| adsorption | 9.2E-09 | 875 | 9.1E-09 | 884 | 8.3E-09 | 965 | 8.1E-09 | 996 |
| desorption | 9.0E-09 | 896 | 1.6E-08 | 496 | 1.6E-08 | 514 | 1.6E-08 | 502 |
| degradation | 4.6E-08 | 174 | 4.5E-09 | 1779 | 4.1E-08 | 194 | << | >> |
| total loss | 1.9E-06 | 4.1 | 2.9E-07 | 28 | 1.9E-07 | 42 | 1.9E-07 | 42 |

Table 4: Influence of transport and transformation processes on concentrations in SOIL for selected chemicals, after a steady state has been reached.

| | Dichloroethane | | Dieldrin | | Benzo[a]pyrene | | Cadmium ²⁺ | |
|----------------|----------------|---------------|-----------|---------------|----------------|---------------|-----------------------|---------------|
| | k (1/s) | $t_{1/2}$ (d) | k (1/s) | $t_{1/2}$ (d) | k (1/s) | $t_{1/2}$ (d) | k (1/s) | $t_{1/2}$ (d) |
| deposition | 2.2E-12 | 10036 | 1.0E-11 | 2167 | 1.5E-11 | 1504 | << | >> |
| gas absorption | 1.8E-12 | 12432 | 2.1E-11 | 1059 | 9.0E-13 | 24311 | << | >> |
| volatilization | 3.5E-08 | 0.63 | 3.7E-09 | 6.0 | 1.6E-10 | 136 | << | >> |
| run-off | 1.3E-08 | 1.8 | 4.4E-10 | 50 | 1.1E-10 | 194 | 2.8E-12 | 7847 |
| infiltration | 1.3E-08 | 1.8 | 4.2E-10 | 52 | 9.4E-11 | 233 | 1.8E-12 | 11883 |
| degradation | 1.4E-08 | 1.5 | 4.6E-09 | 4.8 | 4.6E-09 | 4.8 | << | >> |
| total loss | 3.9E-08 | 0.56 | 5.5E-09 | 4.0 | 4.8E-09 | 4.6 | 4.7E-12 | 4726 |

Soil Run-off

Part of the rainwater that reaches the soil runs off to surface water, *i.e.* rivers, estuaries and coastal waters. In urban areas, where most of the surface is paved, nearly all the precipitation is collected in sewerage systems, from where it may either be redirected to a waste water treatment facility or discharged into surface water. In rural areas the rainwater runs off directly into the surface waters. With the run-off, soil particles are washed away (eroded). Chemicals dissolved in water or associated with the soil particles, are transported by these mechanisms from soil to water. Assuming the water which runs off from soil is in equilibrium with the soil, the mass flow of a chemical resulting from run-off can be quantified. However, for most chemicals it is often more practical and accurate to conduct field measurements on contaminated sites than applying models.

Rates of net precipitation and fractions of water that run off and infiltrate into the soil are often well known from meteorological monitoring. Rates of soil erosion are much harder to obtain. There is extensive literature on the dependence of soil erosion on rainfall and terrain conditions (e.g. slope), which is not treated here [18]. First-order rate constants for removal of some chemicals from soil by run-off to surface water are given in Table 4.

Deposition and Resuspension of Sediment Particles

The transport of chemicals across the sediment-water interface can be treated in the same manner as air-water and air-soil exchanges. In this case there is an advective transport component *i.e.*, sedimentation and resuspension, and a diffusive transport component, *i.e.*, direct adsorption onto and desorption from the sediment. To estimate the rate of advective transport from water to sediment by sedimentation of suspended particles, we need to know the concentration of the chemical on the particles and the rate at which they settle. For most purposes it is sufficient to assume equilibrium between the suspended particles and water phase. The concentration in the particles is then proportional to the concentration in water and the can be derived by means of Eq 5. Settling rates of sediment particles can be obtained from field- or laboratory measurements, or can be estimated by theoretical means. Resuspension of freshly deposited sediment counteracts this removal from water. Resuspension rates are usually not known and must be derived as the difference between the sedimentation rate and the net sediment growth rate, which can be measured in the field, or deduced from mass balance calculations of incoming and outgoing sediment loads.

Exchange between Water and Sediment by Direct Adsorption and Desorption

Diffusive transport between sediment and water, by direct adsorption and desorption across that interface, is analogous to diffusive transport across the air-water and air-soil interfaces and can be described with a two-film resistance mechanism. A value of $\sim 3 \times 10^{-6}$ m/s (0.01 m/h) may be taken for the mass-transfer coefficient on the waterside of the sediment-water interface $kwSd_{water}$ [19]. The mass-transfer on the pore water side of the sediment-

water interface $kwsd_{sed}$ can be treated as molecular diffusion in the aqueous phase of a porous solid material, characterized by an effective diffusivity of $2 \times 10^{-6} \text{ m}^2/\text{h}$ and a diffusion path length of 2 cm. This gives kws_{sed} a value of $\sim 3 \times 10^{-8} \text{ m/s}$ (0.0001 m/h). It should be noted, however, that additional processes that are typically of a non-equilibrium nature, may greatly affect the net mass-transfer of all kinds of chemicals. For instance bioturbation and shipping can play a key role in the sediment side resistance, essentially eliminating it in some cases. As the extent of bioturbation is not governed by thermodynamic principles, and as, in general, very limited information is available on this and similar topics, it will not be extensively discussed here. Instead, readers are referred to the textbook by Thibodeaux [10]. First-order rate constants for exchange of some chemicals between water and sediment are given in Table 3.

Removal by Transport

Transport processes result in translocation of chemicals in the environment, but do not lead to their elimination. The advective exchange processes between environmental media as discussed above (e.g., sediment-water exchange by sedimentation and resuspension), are examples of such non-eliminating transport processes. Advective transport also occurs within environmental media (air, water). It is common to consider only a part of the environment, e.g., a world region or a layer of air, water or soil. In these open systems, transport does remove chemical from the environment. Transport across the system boundaries has the same effect on the concentration of chemical inside the system as real elimination (e.g., by chemical reaction).

Wind carries airborne chemicals out of the region considered to other parts of the world; water currents do the same function for waterborne chemical. First-order removal rate constants for the transport by advection processes that cause concentrations in air and water to decrease can be formulated by considering all incoming and outgoing air and water flows in relation to the volumes of their compartments.

Transport from the upper layer of the soil to the groundwater takes place through leaching with percolating water. If we choose to exclude groundwater from the system considered, soil leaching should be regarded as elimination from the system. Background information on transport in porous media can be found in Spitz and Moreno [20] and will not be considered in detail here. In many approximations, the process of soil leaching is simplified by assuming equilibrium between the solid phase and pore water phase at all times and in all places. It is clear that leaching is an important factor for chemicals with a small K_p value. Analogous transport phenomena take place in sediment. Surface water may seep into the sediment, thereby carrying the chemical from the upper sediment layer down and vice versa.

An additional phenomenon occurs in areas where there is continuous sedimentation. In this situation sediment is continuously being buried under freshly deposited material. It is common practice (e.g., in water quality management) to consider the (mixed) top few centimetres of sediment only. Regarded this way, the concentration of chemical in this sediment top layer can best be understood by regarding sediment burial as a mechanism that removes chemical from the top layer, transporting it to the deeper sediment. First-order rate constants for removal of some chemicals from air, water, sediment and soil by advection, burial and leaching are given in Tables 2-4.

Effect of Transport Processes on Concentrations of Chemicals in the Environment

As explained earlier (Fig. (1), Eqs 1 and 2), concentrations of chemicals in the environment are controlled entirely by the transport and transformation mass flows of chemical into and out of environmental compartments. As discussed above, transport rates vary greatly between chemicals in a way that can be understood and predicted from the differences in physical-chemical properties. In addition, transport rates vary with environmental conditions (geometry, temperature, wind, precipitation). The combined effect of all transport and transformation processes on concentrations of chemicals can be evaluated by comparing the rate constants for net transport from the compartment of interest. Tables 2-4 list the most important first-order rate constants for removal from (and addition to) air, water and soil, respectively, for a selection of different chemicals, together with the half-lives of change in concentration due to the process. For comparison, rate constants and half-lives for degradation (to be discussed in the following section) and rate constants and half-lives for all combined (net) losses are given. The process data in Tables 2-4 were derived from calculations with the multimedia fate model SimpleBox [12, 13], parameterized to reflect the regional spatial scale of EUSES.

It can be seen that

- The greatest rate constants are found in Table 2, for the air compartment. Half-lives for change in the concentrations in air are in the order of magnitude of days. The smallest rate constants are found in Table 4 for soil compartment. Note that $t_{1/2}$ values are expressed in years! Rate constants for water (Table 3) take positions in between those for air and soil, with half-lives of concentration changes in the order of weeks.
- Transport by advection out of the system takes a dominant position for all chemicals in air (Table 2) and to a lesser extent, also in water (Table 3). Note that removal by advection is independent of the properties of the chemical. One should bear in mind that the data given here reflect the relatively small regional spatial scale of the EUSES model. The effect of advection on concentrations at larger spatial scales (continental, global) is much smaller. There is no removal by advection of soil.
- The relative importance of the various processes on concentrations varies between chemicals and between environmental media.

TRANSFORMATION PROCESSES

Following its release into the environment, a chemical may undergo various biotic and abiotic processes which modify its chemical structure. Degradation or transformation of a compound refers to the disappearance of the parent compound from the environment by a change in its chemical structure. When this change is brought about by micro-organisms, the degradation process is called primary biodegradation or biotransformation. When chemicals are converted entirely to simple molecules and ions, such as carbon dioxide, methane, water and chloride, biodegradation is referred to as mineralization. Transformation of chemicals in the environment can also occur by abiotic processes. Four categories of abiotic transformation processes are distinguished:

- *Hydrolysis*: alteration of the chemical structure by direct reaction with water.
- *Oxidation*: a transformation process in which electrons are transferred from the chemical to the oxidant species accepting the electrons
- *Reduction*: the reverse of oxidation; electron transfer takes place from a reductant to the chemical to be reduced.
- *Photo degradation*: transformation due to interaction with sunlight.

Transformation and mineralization processes alter the physicochemical and toxicological properties and can reduce exposure concentrations of chemicals in the environment. The rate of degradation of a specific chemical depends on its intrinsic sensitivity to undergo chemical transformation (reactivity), the presence of reactants and the availability of the chemical to undergo reaction, *i.e.* the presence of the chemical in the gas phase of air or dissolved in water. Generally, the availability and reactivity of both the chemical and the reactant depend to a large extent on environmental conditions like pH, temperature, light intensity and redox conditions.

Hydrolysis

In a typical hydrolysis reaction a hydroxyl group replaces another chemical group in a molecule. However, certain functional groups, including alkanes, alkenes, benzenes, biphenyls, (halogenated) polycyclic aromatics (e.g., PAHs and PCBs), alcohols, esters and ketones, are often inert to hydrolysis.

The importance of hydrolysis stems from the fact that the products formed are more polar and, consequently, more water soluble and less lipophilic than the parent compound. Hydrolysis reactions are commonly catalysed by hydrogen or hydroxide ions. Because the concentrations of hydrogen ion $[H^+]$ and hydroxide ion $[OH^-]$ change with the pH of the water, the rate of hydrolysis directly depends on the pH. Hydrolysis rate constants k_h , which generally obey pseudo first-order kinetics, are measured experimentally in laboratory tests, in which a known quantity of the compound is introduced into a solution of fixed pH and the disappearance of the compound is followed over time. As in Eq 1 and Fig. (1), the mass (and hence the concentration) of the chemical typically declines exponentially with increasing time. When plotted logarithmically, the loss rate constant is observed as the slope of the concentration-time plot

$$\ln(C_t / C_0) = -k_h \cdot t \quad (11)$$

where

C_t = time-dependent observed concentration of the chemical (mol/m³)

C_0 = concentration of the chemical at the beginning of the experiment (mol/m³)

k_h = observed pseudo first-order hydrolysis rate constant (1/s).

From the results of a series of such experiments at different pH levels, a pH rate profile can be constructed by plotting the logarithms of the observed rate constants as a function of the pH of the experimental solutions. Fig. (3) shows the pH rate profile of the hydrolytic transformation of phenyl acetate to yield acetic acid and phenol. Under acid conditions (pH < 3), specific acid catalysis is the predominant mechanism. In this pH region, the logarithm of k_{obs} decreases by a unit slope -1 with increasing pH. At less acidic pH (pH > 4), the hydrogen ion concentration is so small that the specific acid catalysed hydrolytic reaction is too slow to be seen in the profile. Between pH 4 and 6, the neutral mechanism (independent of pH) predominates. Finally, at pH > 8, due to base catalysis, an increase of k_h directly proportional with increasing OH⁻ concentration, becomes visible.

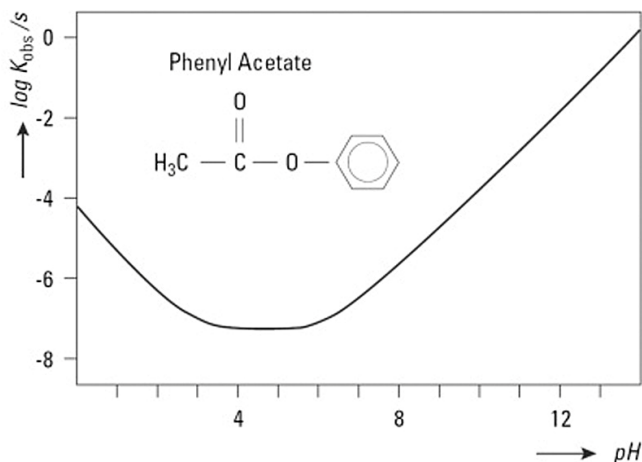


Figure 3: Hydrolysis pH rate profile of phenyl acetate. From Burns and Baughman [21] and Mabey and Mill [22], as referred to by Sijm *et al.* [15].

Oxidation

Oxidation is the chemical process in which an electron-deficient particle (the oxidant) accepts electrons from the compound to be oxidized. Examples of oxidants that occur under environmental conditions in sufficiently high concentrations and also react rapidly with organic compounds are: alkoxy radicals (RO[•]), peroxy radicals (RO₂[•]), hydroxyl radicals (HO[•]), singlet oxygen (¹O₂) and ozone (O₃).

Most of these oxidants are directly or indirectly generated from chemicals that interact with solar radiation, forming an “excited state” of the molecule; oxidation with photochemically formed reactive oxidants is usually referred to as photo oxidation. Oxidations are the main transformation routes for most organic compounds in the troposphere and also transform various micro pollutants in surface waters [23]. Most radical oxidants exhibit similar chemistry for aliphatic and aromatic structures.

Although many different kinds of RO₂[•] or RO[•] radicals may be present in a natural system, the simplifying assumption can be made that the structure of R has little effect on its reactivity [24]. Rate constants for reactions of most radical oxidants are known for a large number of organic molecules. The concentrations of the major oxidants

in less heavily polluted aquatic and atmospheric systems are also known. By combining these data it can be derived that, in general, the hydroxyl radical is the only oxidant of importance in atmospheric systems. In aquatic systems the concentration of $\cdot\text{OH}$ is so low that its contribution is negligible compared with $\text{RO}_2\cdot$ or $\text{RO}\cdot$. To illustrate the differences in reactivity of the hydroxyl radical to various organic chemicals, the half-lives for gas-phase oxidation of various classes of chemicals in the northern hemisphere are given in Table 5.

Table 5: Half-lives (days) for tropospheric oxidation of various classes of organic compounds in the northern hemisphere.

| | |
|--------------|--------------|
| Alkanes | 1 – 10 |
| Alcohols | 1 – 3 |
| Aromatics | 1 – 10 |
| Olefins | 0.06 – 1 |
| Halomethanes | 100 – 47,000 |

From this table it is clear that chlorofluorohydrocarbons (CFCs or halomethanes), in particular, may remain in the troposphere for prolonged periods of time. This enables them to reach the stratosphere, where they pose a threat to the ozone layer.

Reduction

Reduction is the chemical process by which electrons are transferred from an electron donor (reductant) to the compound to be reduced. The redox half-reactions leading to reduction of a 1,2-substituted alkane are shown as a diagram in Fig. (4). In this example, Fe^{2+} is used as the reductant. Following the transfer of 2 electrons from 2 molecules of Fe^{2+} to the halogenated compound, Fe^{3+} , the free halide ion and the product of reduction (in this case ethene) are formed.

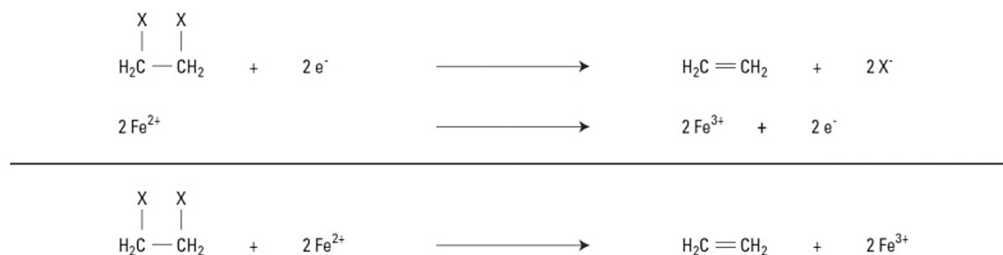


Figure 4: Example of a reductive transformation: electron transfer from Fe^{2+} to 1,2-dihalogen substituted ethane (X denotes a halogen atom).

It has been shown that reductive reaction pathways can contribute significantly to the removal of several micro pollutants. Nitro aromatics, azo compounds, halogenated aliphatic and aromatic compounds (including PCBs and even dioxins) can be reduced under certain environmental conditions [25].

Reduction can take place in a variety of reducing (non-oxic) systems, including sewage sludge, anaerobic biological systems, saturated soil systems, anoxic sediments, reducing iron porphyrin systems, solutions of various chemical reagents, as well as in the gastronomic tract of invertebrate species. It has also been shown that the reduction rate of specific halogen compounds depends on environmental factors, such as the prevailing redox potential, temperature, pH and the physical and chemical properties of the micro pollutant to be reduced. As in hydrolytic transformation, usually more polar products are formed from the parent compound by reduction, which makes them more susceptible to further chemical attack and less likely to accumulate.

At present, insufficient information is available on the nature of the reductants responsible for the main reductive transformations in natural systems. Nevertheless, it has been shown in most studies that reductive transformations generally follow pseudo first-order reaction kinetics.

Photochemical Degradation

Interaction with sunlight can initiate a wide variety of photolytic processes. The primary requirement for photochemical processes is the penetration of radiation (light, in particular UV light) in aqueous and atmospheric environments. Various categories of photochemical conversions can be distinguished:

- Direct photoreaction, in which the reacting molecule itself directly absorbs light;
- Indirect or sensitized photolysis, in which a light-absorbing molecule transfers its excess energy to an acceptor molecule causing the acceptor to react;
- Photo oxidation, in which molecules react with photochemically formed oxidative species (see above).

Following absorption of a photon by a compound, the photon energy either needs to be transferred to the reactive site within the molecule or transferred to another molecule, which may subsequently undergo a photochemical transformation. Not every photon that is absorbed by a molecule induces a chemical reaction. The proportion of absorbed photons which causes reaction is the quantum yield, a number between 0 and 1. Quantum yields may vary largely, depending on the chemical structure of the molecule. In direct photoreactions, the reaction rate is proportional to the absorption of light at a specific wave length and the quantum yield. The rate of light absorption depends on the light intensity and the specific absorptivity (molar absorption coefficient) of the chemical. Both the molar absorption coefficient and the quantum yield are intrinsic properties of the chemical; light intensity is a property of the environment. Since the rates of all photochemical reactions are proportional to light intensity, it is evident that the significance of the photo-transformation of a certain chemical will change with time and place. In this process factors such as time of the day or year, location (climate) and weather (cloud cover) play a major role.

In the aquatic environment, an important fraction of sunlight is absorbed by dissolved and particulate matter. This clearly reduces the rates of direct photo-transformation, and changes the solar spectrum in deeper water layers. However, this dissolved and particulate matter is also capable of initiating indirect photo-conversions. Given the complexity of these indirect conversions, and the many variables that influence the rate of indirect photolysis, it has so far only been possible, to a limited extent, to derive general, mathematical equations for rate constants in natural water systems.

Given the various direct and indirect transformations that can take place due to interaction with solar radiation, a variety of primary and secondary photoproducts is often observed. Since penetration of light is usually only possible in oxic systems, most photo-products formed are in an oxidized state, compared with the parent compound.

Biodegradation

For most xenobiotic organic chemicals, microbial degradation plays a key role in their removal from the environment. By contrast with non-biological elimination processes such as hydrolysis or photochemical degradation, biodegradation in the oxygen-containing biosphere is, generally, equivalent to conversion into inorganic end-products, such as carbon dioxide and water. This has been named ultimate biodegradation or mineralization and may be regarded as a true sink in aerobic compartments. In the anaerobic environment, microbial degradation processes are generally much slower and may not always result in complete mineralization. Transformation of the parent compound into another organic product (metabolite) is often referred to as primary degradation.

Heterotrophic micro-organisms are characterized by a high catabolic versatility. Mixed micro florae, rather than monocultures, are responsible for the elimination of substances from the biosphere, and because adaptation of the microbial ecosystem to a xenobiotic compound is so important, a more operational definition would be useful. Adaptation can be described as a change in the microbial community that increases the rate of biodegradation of a chemical as a result of prior exposure to that compound. This definition does not distinguish between mechanisms such as gene transfer or mutation, enzyme induction and population changes. The enzymatic machinery of micro-organisms consists of constitutive enzymes, which are involved in fundamental metabolic cycles (e.g., hydrolysis), and adaptive or induced enzymes. These enzymes enable bacteria to utilize organic compounds which are not appropriate for immediate use.

Environmental factors affect the population distribution and biochemistry of bacteria. Sediment and soil are more or less aerobic unless the oxygen consumption by micro-organisms, due to an abundance of substrate, is higher than the oxygen supply by diffusion. Aerobic bacteria use oxygen both as a reactant for the oxidation of organic compounds, and as a terminal electron acceptor. The latter is necessary for the conversion of the organic compound into carbon dioxide. This reaction, also known as dissimilation, produces the energy required during the formation of biomass from the organic compound (assimilation). Facultative anaerobic bacteria use oxygen but have the capability to change to another electron acceptor if their environment turns anaerobic. Other electron acceptors are nitrate, utilized by denitrifying bacteria and sulphate, used by sulphate-reducing bacteria particularly in marine and wetland environments. Oxygen is very toxic to the obligate anaerobic bacteria, which can only use alternative electron acceptors. The methanogens (methane-producing bacteria) derive energy from the conversion of hydrogen and carbon dioxide into methane. The considerable decrease in energy supply by the different electron acceptors from oxygen to the organic compound itself explains why microbial processes are faster in the aerobic world.

Biodegradation of synthetic chemicals does not always result in bacterial growth. When exponential growth does not occur the degradation process is called co-metabolism, in which micro-organisms - while growing on another, widely available, substrate - also have the capacity to transform other compounds (xenobiotics) without deriving any benefit from that transformation [26].

Biodegradation Kinetics

In first approximation, removal of chemicals from the environment by microbial degradation can be treated similar to other removal processes, *i.e.* by describing the process as following pseudo first-order kinetics and by formulating pseudo first-order reaction rate constants for it. In fact, the so-called second-order rate concept of microbial degradation in water was proposed as early as 1981 [27]. More recently, this almost forgotten concept has been re-introduced to quantitatively treat the subject of persistence of chemicals in the environment [28]. Following the assumption that the removal by microbial degradation obeys pseudo first-order kinetics, the pseudo first-order rate constant postulated to be proportional to the concentration of bacteria in the system:

$$k_{bio} = k^{2nd} \cdot [Bact] \quad (12)$$

where

k_{bio} = pseudo first-order rate constant for biodegradation (1/s)

k^{2nd} = second-order rate constant for biodegradation (L/CFU/s)

$[Bact]$ = number of colony-forming units of bacteria in water (CFU/L)

Although of attractive conceptual simplicity, this approach has limited predictive power. Quantitative bacterial counts can be made, but the degrading power of the microbial colonies is hard to assess or predict; the second-order rate constants obtained from field observations or laboratory experiments are not nearly as constant as required for extrapolating observed biodegradation rates to other environmental situations, let alone to other chemicals. Reality of biodegradation kinetics is complex.

Biodegradability and Biodegradation Rates

Biodegradation rates are hard to predict. Despite major efforts, it has so far proved difficult to formulate generally applicable predictive theory, even for aerobic biodegradation in water and soil. At present, the re-interpretation of experimental studies is the only way to estimate rates of aerobic biodegradation. Most experimental data on microbial degradation originate from the standard tests of biodegradability of chemicals, as required by many regulatory agencies, *e.g.*, the European Chemicals Agency ECHA. Biodegradability testing is commonly done according to standard methods published by the OECD [29, 30]. In the OECD hierarchy, three different levels of testing are distinguished as follows:

- Ready biodegradability tests (RBT), are designed for a quick selection of “soft” chemicals to avoid further costly and time-consuming research. To meet the demands of simplicity and cost efficiency, there are six different methods in the OECD scheme [30], which are all based on the principle that biodegradation is monitored as the degree of mineralization.
- Inherent biodegradability tests (IBT) are designed to demonstrate the potential biodegradability of a compound, using much higher population densities. IBT methods have a screening function as persistent chemicals are also detected. A negative result indicates that a chemical is clearly persistent and, tentatively, that no further research on biodegradation has to be done.
- Simulation tests (aerobic and anaerobic) provide data for biodegradation under specified environmentally-relevant conditions. These tests simulate the degradation in a specific environment used by indigenous biomass, media, relevant solids (*i.e.*, soil, sediment, activated sludge or other surfaces) to allow sorption of the chemical, and a typical temperature which represents that particular environment.

Recalcitrance

So it seems that microbial communities in the natural environment are catabolically so versatile, that always one or more species capable of degrading any chemical is present in a specific environment. Why then do some man-made chemicals persist in the environment for such a long time? The rate and extent of biodegradation of a chemical depends on both its chemical structure and the prevailing environmental conditions. In general, the following properties or conditions have a significant influence on the biodegradation of synthetic chemicals:

Chemical structure. Type, number and position of substituents on aliphatic or aromatic structures may cause “violation of comparative biochemistry and enzyme specificity”, as described by Alexander [31]. Effects of substitution of radicals have already been discussed in the three examples of major metabolic pathways for biochemical oxidation; aromatic rings, however, are hard to break and substitute. The influence of the molecular structure on its biodegradability in the aerobic environment is clear.

Environmental conditions. Temperature is an important factor and especially around and below 4°C, microbial processes become very slow. The optimum temperature for psychrophilic (cold-loving) bacteria is between 0 and 20°C and for mesophyllic (moderate temperature loving) bacteria it is between 20 and 40°C. In seawater 15°C is the borderline between different microbial ecosystems. The inorganic nutrient status of the surface water affects the biodegradation rate and in some coastal waters may even exceed the temperature effect. The presence of auxiliary organic nutrients may also play a role, and the occurrence of co-metabolism has already been mentioned. Failure of biodegradation may be due to the presence of other, more easily degradable compounds used in preference to the specific xenobiotic compound. This phenomenon is known as diauxism. Unlike seawater, which is a well-buffered system of pH 8, inland waters can vary up to 5 pH units in acidity, thereby determining the form in which some chemicals exist. The availability of some natural organic substrates may also facilitate co-metabolism of the pollutant. However, even if it were possible to find two aquatic ecosystems characterized by similar environmental parameters, the outcome of a biodegradability experiment might be quite different for the same chemical. The presence and influence of high population densities of “specialized” degraders is evident. Some aquatic ecosystems may have been previously exposed to a chemical or another pollutant which shares a common enzyme system of such a specific degrader. The presence and density of specific degraders is often highly decisive for biodegradation to occur within a limited period of time.

Bioavailability. If a chemical is trapped in micro sites, e.g., in inorganic material such as clay minerals or the organic matrix of sediment or soil, interaction with micro-organisms may be physically impossible, which impedes biodegradation.

Biodegradation in Sediment and Soil

Biodegradation in sediment or soil is commonly reported to obey first-order kinetics. Experimentally observed half-lives and first-order rate constants can be found in the literature for many chemicals in many sediment and soil systems. It is often claimed that biodegradation in sediment- and soil systems is described and explained best from the theory that degradation takes place entirely in the water phase; chemical bound to the solid phase is considered

unavailable for attack by microbes and, therefore, non-reactive. Several studies have provided evidence that a chemical associated with sediment or soil particles is not available for biodegradation because micro-organisms only utilize dissolved chemicals [32]. Therefore, the overall rate of biodegradation in a solids-water system greatly depends on the extent of partitioning to the solid phase:

- Partitioning of a compound between the particle and the aqueous phase is governed by a thermodynamic equilibrium occurring at a fast rate with respect to degradation processes. The rate of elimination will then become strongly dependent on the organic carbon-water partitioning constant (K_{oc}) of a substance (see Eq 4). With increasing K_{oc} the concentration of a substance in the pore water subsequently becomes very low, and hence the elimination rate due to biodegradation becomes proportionally low.
- Biodegradation in the aqueous phase is relatively fast but overall elimination (and hence the biodegradation kinetics) from the solids-water system is controlled by slow desorption.

This again illustrates the difficulties associated with extrapolation of a laboratory-derived degradation rate to an environmental half-life of a laboratory-derived degradation rate. When assessing the environmental risk of a chemical, it is important to realize that even a relatively easily biodegradable chemical can become more or less persistent when it ends up in an environmental compartment where its bioavailability becomes limited.

MODELLING CONCENTRATIONS IN THE ENVIRONMENT

Distribution of chemicals in the environment can be determined by measurement of concentrations in air, water, soil and sediments. Such measurements are expensive, since they usually include analyses of many chemicals at different places and usually over long periods of time. Modelling the fate of chemicals in the environment is a feasible alternative which renders similar results at much cheaper cost. Moreover, modelling is necessary when measurement is no option, e.g., when predictions are to be made of expected results of environmental management measures, or when making predictions for new chemicals that have not been released yet, so they can be used in regulatory risk assessment.

Many of the models used in risk assessment of toxic substances are compartment models, also referred to as box models or mass balance models. The environment is thought to be made up of homogeneous, well-mixed compartments. Compartments can represent segments of the environment, or even entire environmental media. Examples of the former are the spatially segmented air and water transport models and layered soil models. The latter is used in multimedia (air, water, soil, *etc.*) fate models and in physiology-based pharmacokinetic models (blood, tissue, *etc.*). Compartment models apply the principle of mass conservation: the mass of a substance in a compartment appears or disappears only as a result of mass flows of a substance into or out of the compartment. What compartment models have in common is that the mass balance equation is used as their basic instrument. Because mass balance modelling is used so widely in the environmental risk assessment of toxic substances, its principles will be explained here. We shall first derive a mass balance equation for one compartment, then a mass balance model for more compartments.

One Compartment

If a substance is added to or taken from a compartment, the mass of that substance in the compartment changes. This change can be quantitatively expressed in a mass balance equation, in which all incoming and outgoing mass flows of the substance are accounted for

$$\frac{\Delta M}{\Delta t} \left(= V \frac{\Delta C}{\Delta t} \right) = \text{gains} - \text{losses} = \sum \text{mass flows} \quad , \quad (13)$$

where ΔM and ΔC are changes in mass and concentration within a time interval Δt , respectively, and V is the (constant) volume of the compartment. Note that the change is in unit mass per unit time (e.g., kg/s): a sum of mass flows. If nothing is added or taken away, or if gains and losses match exactly, the mass of substance in the compartment does not change: a steady state. If ΔM , ΔC and Δt are infinitesimally small, Eq 13 becomes what is

mathematically known as a differential equation. Differential equations describe at what rate a variable (here: mass of a substance in a compartment) changes. If the mass at starting time ($t=0$) is known (the initial condition), a differential equation can be used to derive the mass at other times. The art of mass balance modelling is thus to properly quantify the mass flows of a substance going into and out of the compartments. For the purpose of mass balance modelling it is useful to distinguish between mass flows that take place independently of what happens in the compartment and mass flows that do depend on the conditions within the compartment. Emissions and imports are examples of the first category. The rate at which mass is brought into the compartment by these processes may be constant or time-dependent, and may relate to the mass of a substance outside the compartment, but bears no relationship to the mass of a substance within the compartment. These mass flows need to be specified to the model as so-called “forcings”. If a constant emission of E (kg/s) is forced upon a compartment, which contains M_0 kg of the substance at $t = 0$, and nothing else happens, the mass balance equation becomes:

$$\frac{dM}{dt} \left(= V \frac{dC}{dt} \right) = E, \quad (14)$$

of which the integral form or solution is

$$M = M_0 + E \cdot t. \quad (15)$$

How this solution is obtained is not further explained here. Readers may want to refresh their knowledge of this mathematical calculation method by reviewing a standard text on differential calculus, e.g. Wikipedia [http://en.wikipedia.org/wiki/Differential_equation]. The result of a constant inflow of a substance is that its mass in the compartment continuously increases. Note that this occurs at the constant rate of E kg/s (Fig. 5).

Loss rates generally depend on the mass of a substance in the compartment (see Eq 2 and accompanying text). It should be noted that first-order reaction kinetics (see Eq 1) are the exception, rather than the rule. Zero-order kinetics, in which the reaction is independent of C (formally proportional to C^0), second-order kinetics (reaction rate proportional to C^2) and broken order kinetics (proportional to $C^{1.5}$) commonly occur. Second-order kinetics will generally apply when a substance reacts with a chemical agent: the reaction is first-order in relation to both the substance degraded and the reactant. It is only because the concentration of the reactant is often approximately constant that the reaction appears proportional only to C^1 . This is called pseudo first-order reaction kinetics. For instance, the loss due to reaction with chemical or microbial agents (degradation) is often characterized by pseudo first-order kinetics.

If degradation is the only process, the mass balance equation becomes:

$$\frac{dM}{dt} \left(= V \frac{dC}{dt} \right) = -k \cdot M, \quad (16)$$

the solution of which results in an exponential decrease of mass in the compartment (Fig. 5):

$$M = M_0 \cdot e^{-k \cdot t}. \quad (17)$$

If both emission and degradation act on a compartment, the combined result will be:

$$\frac{dM}{dt} \left(= V \frac{dC}{dt} \right) = E - k \cdot M; \quad M = M_0 \text{ at } t = 0, \quad (18)$$

the solution of which is:

$$M = M_0 \cdot e^{-k \cdot t} + \frac{E}{k} (1 - e^{-k \cdot t}) \quad (19)$$

(see Fig. 5). Eq 18 and 19 illustrate how the mathematical solution of the mass balance equation yields a mass-time profile of a substance in a compartment as a function of the initial conditions (here: mass M_0 at $t = 0$), forcings (here: emission rate, E) and the parameters of the mass flow rate equations (here: the degradation rate constant, k). Note that eventually (at $t = \infty$), the mass of substance in the compartment will reach a level at which the loss by degradation, $k \cdot M$ (kg/s), exactly matches the constant emission, E (kg/s), so that the mass of substance in the compartment is maintained at the steady-state level of E/k (kg).

There are many other loss mechanisms that need to be accounted for in the mass balance equation, such as advective or diffusive outflow. Because losses due to all mechanisms i are proportional to M , and can each be represented by a first-order rate constant k_i (1/s), the full mass balance equation keeps the same simple format of Eq 18:

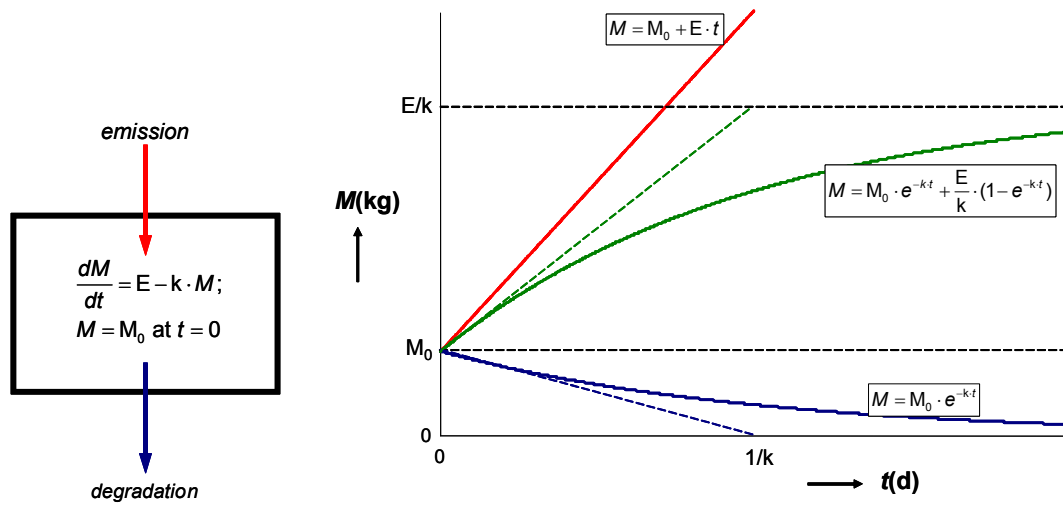


Figure 5: Elementary form of a one-compartment mass balance model, showing the differential mass balance equation and its solution for the cases of emission only (red), degradation only (blue) and both (green).

$$\frac{dM}{dt} \left(= V \frac{dC}{dt} \right) = \text{gains} - \text{losses} = E - \sum_i k_i \cdot M; \quad M = M_0 \text{ at } t = 0 \quad (20)$$

and its solution takes the same format as Eq 19:

$$M = M_0 \cdot e^{-\sum_i k_i \cdot t} + \frac{E}{\sum_i k_i} (1 - e^{-\sum_i k_i \cdot t}) \quad (21)$$

More Compartments

Models usually comprise many compartments and describe the transport of a substance in and between these compartments. Such multicompartment mass balance models contain one mass balance equation for each compartment in the model. As in the above situation for one compartment, losses are all assumed to obey first-order kinetics. Where more than one compartment is involved, losses may be due to degradation or export, but losses may also represent mass flows from one compartment to another.

For a set of n compartments, this leads to a set of n mass balance equations, all of which will have the same format as Eq 20, with n unknown masses M_i and a suite of first-order rate constants which describes the losses from the compartments. An example for three compartments is shown in Fig. (6). Each of the compartments receives an emission – for the sake of simplicity, emissions will be assumed to be constant and imports considered to be included in the emission flows. The emission flows into the compartments i are denoted by E_i (kg/s). Degradation

occurs in the three compartments – again, in the interests of readability, the degradation flows will be considered to include possible exports. The resulting mass flows from the compartments i , out of the system are characterized by pseudo first-order loss rate constants k_i and denoted by $k_i \cdot M_i$ (kg/s).

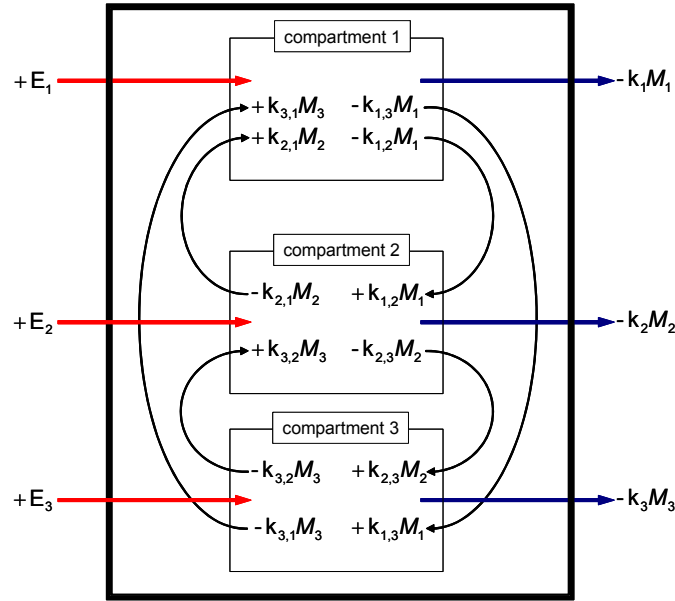


Figure 6: Diagram of a three-compartment mass balance model. Intercompartment mass-transfer represents a loss to the source compartment and a gain to the receiving compartment.

There are six intercompartment mass-transfer flows, each proportional to the mass in the source compartments denoted by $k_{i,j} \cdot M_i$ (kg/s). On this basis, and assuming all initial masses to be zero, the three differential mass balance equations become:

$$\begin{aligned} \frac{dM_1}{dt} &= E_1 - (k_1 + k_{1,2} + k_{1,3}) \cdot M_1 + k_{2,1} \cdot M_2 + k_{3,1} \cdot M_3; \quad M_1 = 0 \text{ at } t = 0 \\ \frac{dM_2}{dt} &= E_2 + k_{1,2} \cdot M_1 - (k_2 + k_{2,1} + k_{2,3}) \cdot M_2 + k_{3,2} \cdot M_3; \quad M_2 = 0 \text{ at } t = 0 \\ \frac{dM_3}{dt} &= E_3 + k_{1,3} \cdot M_1 + k_{2,3} \cdot M_2 - (k_3 + k_{3,1} + k_{3,2}) \cdot M_3; \quad M_3 = 0 \text{ at } t = 0 \end{aligned} \quad (22)$$

For this system of three compartments there is an equation equivalent to Eq 19, *i.e.* the analytical solution of the one-compartment system, which expresses the mass of the substance at all times. It is not possible to formulate precisely how the three masses in the three compartments change with time. Solutions can be approximated quite well, however, with computer-based numerical techniques which will not be described here. As in the one-compartment system, the three-compartment system will eventually (at $t = \infty$) reach to a steady state in which emission is equally balanced by degradation ($dM_i/dt = 0$) and masses reach their constant steady state level, M_i^* :

$$\begin{aligned} \text{balance}_1 &= E_1 - (k_1 + k_{1,2} + k_{1,3}) \cdot M_1^* + k_{2,1} \cdot M_2^* + k_{3,1} \cdot M_3^* = 0 \\ \text{balance}_2 &= E_2 + k_{1,2} \cdot M_1^* - (k_2 + k_{2,1} + k_{2,3}) \cdot M_2^* + k_{3,2} \cdot M_3^* = 0 \\ \text{balance}_3 &= E_3 + k_{1,3} \cdot M_1^* + k_{2,3} \cdot M_2^* - (k_3 + k_{3,1} + k_{3,2}) \cdot M_3^* = 0 \end{aligned} \quad (23)$$

The set of steady-state masses for which the mass balance equations become zero can be derived directly from Eq 23 quite easily through simple algebraic manipulation. Solving sets of equations algebraically becomes increasingly tedious for larger sets, so linear algebra (matrix calculus) is used to obtain solutions to large sets of linear equations, as follows:

$$\mathbf{m} = \begin{bmatrix} M_1 \\ M_2 \\ M_3 \end{bmatrix}, \quad \mathbf{e} = \begin{bmatrix} E_1 \\ E_2 \\ E_3 \end{bmatrix}, \quad \mathbf{A} = \begin{bmatrix} -(k_1 + k_{1,2} + k_{1,3}) & k_{2,1} & k_{3,1} \\ k_{1,2} & -(k_2 + k_{2,1} + k_{2,3}) & k_{3,2} \\ k_{1,3} & k_{2,3} & -(k_3 + k_{3,1} + k_{3,2}) \end{bmatrix} \quad (24)$$

Using this, the three mass balance equations of Eq 23 can be rewritten into a one-line linear-algebraic equation:

$$\mathbf{m} = -\mathbf{A}^{-1} \cdot \mathbf{e}. \quad (25)$$

Various standard software packages, such as Microsoft Excel, can be used to carry out matrix inversion.

Multimedia Modelling

If a chemical is released into one medium and resides there until it is removed by degradation or advection, single-media models may be perfectly suitable for estimating the environmental concentration. If, however, a chemical is released into several compartments simultaneously, or after release into one compartment is transported to other compartments, it becomes necessary to account for the intermedia transport processes so that its ultimate fate in the overall environment can be assessed. Multimedia models are specifically designed to do this. This section on multimedia models starts with a short description of their features and the explicit and implicit assumptions usually made. The use of these models in exposure assessment is described together with their limitations. Subsequently, some information on data requirements and on the different models available is given, following which a number of sample calculations are presented to illustrate the use of these models.

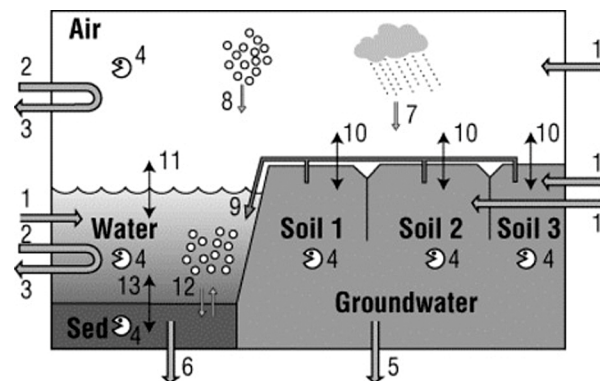


Figure 7: Diagram of a multimedia mass balance model concept. 1 = Emission, 2 = Import, 3 = Export, 4 = Degradation, 5 = Leaching, 6 = Burial, 7 = Wet deposition, 8 = Dry aerosol deposition, 9 = Run-off, 10, 11 = Gas absorption and volatilization, 12 = Sedimentation and resuspension, 13 = Sorption and desorption.

Multimedia fate models are typical examples of compartment mass balance models. The total environment is represented as a set of spatially homogeneous (zero-dimensional) compartments; one compartment for each environmental medium in which the chemical is assumed to be evenly distributed (Fig. 7). Typical compartments considered in models are: air, water, suspended solids, sediment, soil and aquatic biota. Multimedia mass balance modelling was initiated in the early 1980s by Mackay and co-workers [2, 33-36]. The example was soon followed by others [11, 37-39]. In Europe, the model SimpleBox used in The Netherlands was adopted as the basis for the risk assessment model EUSES [12, 13]. While the early models described a fixed, “unit world”, which was meant to represent a global scale, later models have enabled users to customize the environment and define smaller and more open spatial scales. More recently, the use of spatially resolved multimedia fate models has become more common [40-50].

A typical regional multimedia model describes a region between 10^4 and 10^5 km². In this generic form, the models can account for emissions into one or more compartments, exchange by import and export with compartments “outside” the system (air and water), degradation in all compartments and intermedia transport by various mechanisms (Fig. 7). Mass flow kinetics, formulated slightly differently in models by different authors, are usually defined as simply as possible: mass flows are either constant (emission, import) or controlled by (pseudo) first-order

rate constants (degradation, intermedia transport), as in Eq 15. In all the models, the user has to set parameter values for these mass flows to provide input for the model.

Using a number of criteria, such as equilibrium or non-equilibrium, steady-state or non-steady-state, and based on whether to take the degradation of the chemical into account in the calculation or not, Mackay and Paterson introduced a classification of multimedia models [34]. This classification begins with a Level I model which describes the equilibrium partitioning of a given amount of a chemical between the above media. The Level II model simulates a situation where a chemical is continuously discharged into a multimedia environment in which partitioning, advection and degradation take place. Transport between the media is assumed as infinitely rapid, so that thermodynamic equilibrium between the media is maintained. At Level III, realistic intermedia transport kinetics are assumed, so that media may not be in thermodynamic equilibrium. Level III models calculate steady-state concentrations in all compartments. Finally, Level IV models assume a non-steady-state and yield time-related chemical concentrations.

Level I calculation requires knowledge of intermedia partition coefficients (air-water, water-solids) only. Calculation at level II and above requires additional knowledge of degradation rate constants in air, water, sediment and soil. Unfortunately, measured partition coefficients and rate constants are not always available. In the absence of measured data, partition coefficients can be estimated from basic substance properties, using quantitative structure-activity relationships (Q)SAR. Easy to use software is available to support such estimates. The consequence of using estimated model input data is that the accuracy of the model output will also depend on the quality of the (Q)SAR methods that have been used. Very often biodegradation rate constants are extrapolated from standard degradation tests, or even estimated using (Q)SARs (e.g., BIOWIN). This may introduce another uncertainty into the outcome of the calculation, especially if precise data is not available for the degradation rate constants in compartments that serve as a “sink” for a specific chemical.

The principal utility of multimedia models, as a first step in exposure assessment, is to determine to what extent intermedia partitioning may occur. If it appears that no significant partitioning into secondary compartments is expected, further exposure assessments may focus on the primary compartment(s) only. As intermedia transfer is usually relatively slow, its effect on the fate of chemicals is significant only over longer periods of time, *i.e.* if the spatial scale is large or the chemical does not degrade rapidly. This brings us to one of the major applications of these models, which is the exposure assessment of chemicals on regional (usually 10^4 to 10^5 km²) and larger spatial scales. These models are particularly useful for calculating the predicted environmental concentration (PEC) especially of chemicals with a very diffuse release pattern. Results from Level III multimedia models are used in EU risk assessments for new and existing chemicals. In addition to calculating the regional concentration of a chemical, the results of Level III models can also be used as input for local models. When using such models, the actual concentration is greatly underestimated if the concentration of the chemical in air or water from “outside” is set to zero, especially in relation to high production volume chemicals with a widely distributed use pattern. Regional concentrations estimated from the release rates for a larger region fed into a regional multimedia model can then be used as boundary concentrations in local model calculations.

One of the key processes in multimedia models is the partitioning between aqueous and solid phases. Most models follow in the footsteps of the original Mackay models and estimate solids-water partitioning from the octanol-water partition coefficient K_{OW} . This means that the models are particularly useful for organic chemicals whose K_{OW} values can be accurately measured or estimated. Applying these models to ionisable compounds, surface-active chemicals, polymers, or inorganic compounds (including metals) should be done with great care. However, the models can be used for these chemicals, provided certain adaptations to specific physicochemical properties are made. Mackay and Diamond, for instance, used an “equivalent” based model to describe the fate of lead in the environment [50], while in the example calculation for cadmium parameters such as soil-water and sediment-water partition coefficients or the fraction of the chemical associated with aerosols, must be specifically entered by the user in order to overrule the standard estimation routines.

Naturally, representing the environment in the form of a unit world or unit region with homogeneous boxes is a major simplification of reality. However, this extreme degree of simplification in this model concept is both a weakness and a strength at the same time. By disregarding spatial variation, the modelling effort can focus on intermedia distribution and

understanding the ultimate fate of a chemical. The concentrations calculated with multimedia models should therefore be interpreted as “spatially-weighted averages” of the concentrations that would be expected in real situations. However, the assumption of homogeneity brings with it a considerable risk that potentially more localized effects may be overlooked. The disadvantage of zero-dimensionality becomes evident with larger areas since, other than for air, it is difficult to identify any large-scale situations where the homogeneity of compartments would seem to be a realistic assumption. To overcome this problem the SimpleBox has introduced the concept of “nesting” [12]. In a nested model the input and output flows of a regional or smaller scale model are connected to a continental scale model which in turn, is connected to a global scale model. In this way, the specific environmental characteristics of the region can be taken into account when the overall fate of the chemical is assessed. While spatial scale nesting was originally introduced as a tool for assessing the overall persistence of a chemical in the environment, the concept soon found wider application in regional exposure assessment in EUSES [13].

Testing the validity of multimedia models is difficult and, until recently, had not been seriously addressed [51]. If a common evaluation environment with agreed fixed environmental characteristics is used, validation of the outcome becomes almost paradoxical since this generic environment does not actually exist in reality. However, the regional generic characteristics can be modified at a later stage and region-specific information on environmental parameters, as well as information on specific discharge rates can be introduced in order to “validate” a specific model setting [35, 52].

Multimedia Models in Use

Multimedia fate models of the Mackay type have been produced by different authors, most of them for their own scientific use. Many of these have been documented and made available for end users, e.g., HAZCHEM [53], SimpleBox [12, 13] CemoS [38], CalTOX [39], ChemCAN [40], EQC [41], ChemRange [42], ELPOS [43], Globo-POP [44], CliMoChem [45], BETR North America [46], BETR World [47], IMPACT 2002 [48] and MSCE-POP [49]. The similarities between these models are more striking than the differences. When fed the same input, the models were shown to yield the same results [51]. The main differences lie in the number of compartments or sub-compartments included and how they are handled in terms of computer calculation.

Table 6: Parameters used for steady-state calculations with SimpleBox

| Parameter | Value in SimpleBox | Parameter | Value in SimpleBox |
|--|--------------------------------|--|--------------------|
| Area of the system | $3.8 \times 10^4 \text{ km}^2$ | Organic carbon content in suspended matter | 0.1 |
| Area fraction of water | 0.125 | Atmospheric mixing height | 1000 m |
| Area fraction of natural soil | 0.415 | Mixing depth of water ^a | 3 m |
| Area fraction of agricultural soil | 0.45 | Mixing depth of sediment ^a | 0.03 m |
| Area fraction of industrial/urban soil | 0.01 | Average annual precipitation | 792 mm/year |
| Mixing depth of natural soil ^a | 0.05 m | Wind speed | 5 m/s |
| Mixing depth of agricultural soil ^a | 0.2 m | Residence time air ^b | 0.40 days |
| Mixing depth of industrial/urban soil ^a | 0.05 m | Residence time water ^b | 54.5 days |
| Organic carbon content in soil | 0.029 | Fraction of rain water infiltrating soil | 0.4 |
| Organic carbon content in sediment | 0.029 | Fraction of rain water running off soil | 0.5 |
| Concentration suspended solids | 15 mg/L | Temperature | 285 K (12°C) |

^a The mixing depth represents the thickness of the soil, water or sediment box.

^b Residence time for air or water represents the time needed for air or water to flush through the air or water compartments, respectively.

ENVIRONMENTAL FATE OF CHEMICAL SUBSTANCES

Examples of how to perform Level I, II and III calculations for a range of different chemicals have been presented by Mackay and others [2, 35, 36, 40, 41, 54]. To illustrate the utility of Level III and IV type multimedia modelling, let us consider the use of three chemicals, 1,1,1-trichloroethane, dieldrin and cadmium, in a system resembling The Netherlands, as simulated with SimpleBox [12, 13].

The system parameters are summarized in Table 6. Let us assume that the background concentrations of these chemicals in air and water outside The Netherlands are equal to the quality standards or objectives set for environmental protection. After 10 years, with these background concentrations, domestic emissions of 1000 tonnes/year for each chemical start to occur: dieldrin to water, cadmium to air, and 1,1,1-trichloroethane to air, water and soil simultaneously (ratio 1:1:1). This situation continues for 40 years and then suddenly stops. What concentrations may be expected in the different environmental compartments, how are the chemicals distributed, and how long does it take to return to the original situation after the emissions stop? In order to evaluate the change in concentrations of the three chemicals in the different environmental compartments some chemical-specific information is needed. This is summarized in Table 7.

Table 7: Input parameters used in the multi-media model calculations for 1,1,1-trichloroethane, dieldrin and cadmium

| | | 1,1,1-Trichloroethane | Dieldrin | Cadmium²⁺ |
|----------------------|------------------|------------------------------|----------------------|-----------------------------|
| Background (air) | g/m ³ | 10 ⁻⁸ | 10 ⁻⁹ | 10 ⁻⁹ |
| Background (water) | g/L | 10 ⁻⁸ | 10 ⁻⁷ | 10 ⁻⁷ |
| Emission (air) | tonnes/year | 333 | - | 1000 |
| Emission (water) | tonnes/year | 333 | 1000 | - |
| Emission (soil) | tonnes/year | 333 | - | - |
| K_h (air-water) | - | 1.1 | 1.7x10 ⁻⁴ | 10 ^{-10a} |
| Frac (aerosol) | - | 0.0 | 0.25 | 0.9 |
| Scavenging ratio | - | 0.96 | 5.5x10 ⁴ | 10 ⁵ |
| K_p (susp.solid) | L/kg | 3.1x10 ¹ | 6.3x10 ² | 10 ⁴ |
| K_p (sediment) | L/kg | 1.6x10 ¹ | 3.2x10 ² | 10 ⁴ |
| K_p (soil) | L/kg | 1.6x10 ¹ | 3.2x10 ² | 10 ³ |
| Half-life (air) | days | 200 | 200 | ∞ |
| Half-life (water) | days | 1000 | 1000 | ∞ |
| Half-life (sediment) | days | 1000 | 1000 | ∞ |
| Half-life (soil) | days | 2000 | 100000 | ∞ |

^a Substitute for zero-value.

The Level III mode of the SimpleBox program is then used to generate the concentrations and intermedia distribution at steady-state. The concentrations in and distribution over the environmental compartments at steady-state are summarized in Table 8. The mass flows that support these steady-states are also shown in Fig. (8). The model calculation emphasizes the high volatility of 1,1,1-trichloroethane. Approximately all emissions to soil and water go to air through diffusive transport. Of the total mass in the system, however, a high percentage still resides in the soil.

Table 8: Steady-state distribution of 1,1,1-trichloroethane, dieldrin and cadmium in The Netherlands, calculated with SimpleBox [12, 13]. Numbers in parentheses represent a percentage of the total mass in the environment at steady-state.

| | 1,1,1-Trichloroethane | Dieldrin | Cadmium ²⁺ |
|-------------------------|----------------------------|----------------------------|------------------------------|
| Air (g/m ³) | 3.9x10 ⁻⁸ (19%) | 1.5x10 ⁻⁸ (0%) | 2.7x10 ⁻⁸ (0%) |
| Water (g/L) | 4.5x10 ⁻⁸ (8%) | 5.1x10 ⁻⁶ (3%) | 2.1x10 ⁻⁷ (0%) |
| Suspended matter (g/kg) | 1.2x10 ⁻⁶ (0%) | 2.8x10 ⁻³ (0%) | 2.1x10 ⁻³ (0%) |
| Sediment (g/kg) | 7.5x10 ⁻⁷ (1%) | 2.1x10 ⁻³ (7%) | 2.1x10 ⁻³ (0.5%) |
| Soil (g/kg) | 1.6x10 ⁻⁶ (73%) | 6.1x10 ⁻⁴ (90%) | 9.2x10 ⁻³ (99.5%) |

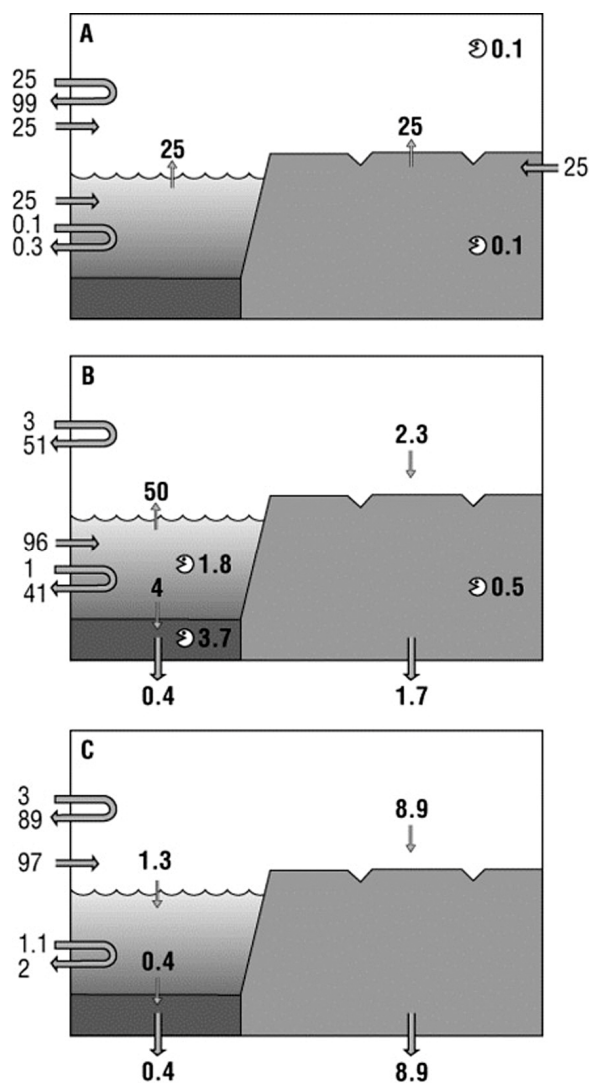


Figure 8: Steady-state mass flows of trichloroethane (A), dieldrin (B) and cadmium (C), as a percentage of the total throughput of the system.

Remarkably, the relatively high volatility of dieldrin causes more than half of the total load of the water compartment to be transported to air, from where it is exported out of the system. The high hydrophobicity and low biodegradation rates of the chemical produce relatively high concentrations in sediment and soil. Cadmium does not

degrade at all. When emissions go to air the most important fate process is advection out of the air compartment. However, due to atmospheric deposition, some 10% of the total load of the atmosphere is transported to soil and water. Atmospheric deposition to soil leads to a build-up of cadmium in the soil, from where it is eventually leached to the ultimate sink: the deeper groundwater. It should be borne in mind that this build-up may be slow. If, as in the case of cadmium in soil, all mass flows are small, it may take an extremely long time before the steady-state is achieved. This can be demonstrated with Level IV calculations using the SimpleBox model. Fig. (9) shows the change in concentrations in the different compartments according to the above emission scenario relative to the background concentrations which result when there are no domestic emissions. For cadmium, the compartments air, water and sediment are expected to respond relatively quickly, whereas a near linear increase in the concentration in soil is predicted over the 40-year exposure period.

After reducing the emissions, the soil concentration of cadmium shows little response (Fig. 8C). For dieldrin exposure, for 40 years is almost long enough to reach a steady-state, even in the “slow” soil compartment; after reducing the emission to 10% of its original value, the concentrations decrease at the same rate (Fig. 8B). For trichloroethane the situation is completely different. The steady-state situation is reached so quickly that plotting the concentrations against time on a 100-year scale would yield a block diagram. Therefore, the Level IV calculation was repeated over a time-scale of one year. The results as presented in Fig. (8A) show that concentrations in air, water and soil reach steady-state within one month. For sediment this takes a little longer, though probably not much longer than a year. These results demonstrate the usefulness of Level III and Level IV multimedia box model calculations. Where steady-state calculations can give information on the concentrations and distribution in the environment at a constant emission scenario, the results of a Level IV calculation elucidate the time scale in which this situation may be reached. In addition, changes in the emission scenario as a result of evolving risk reduction strategies can be evaluated in this way.

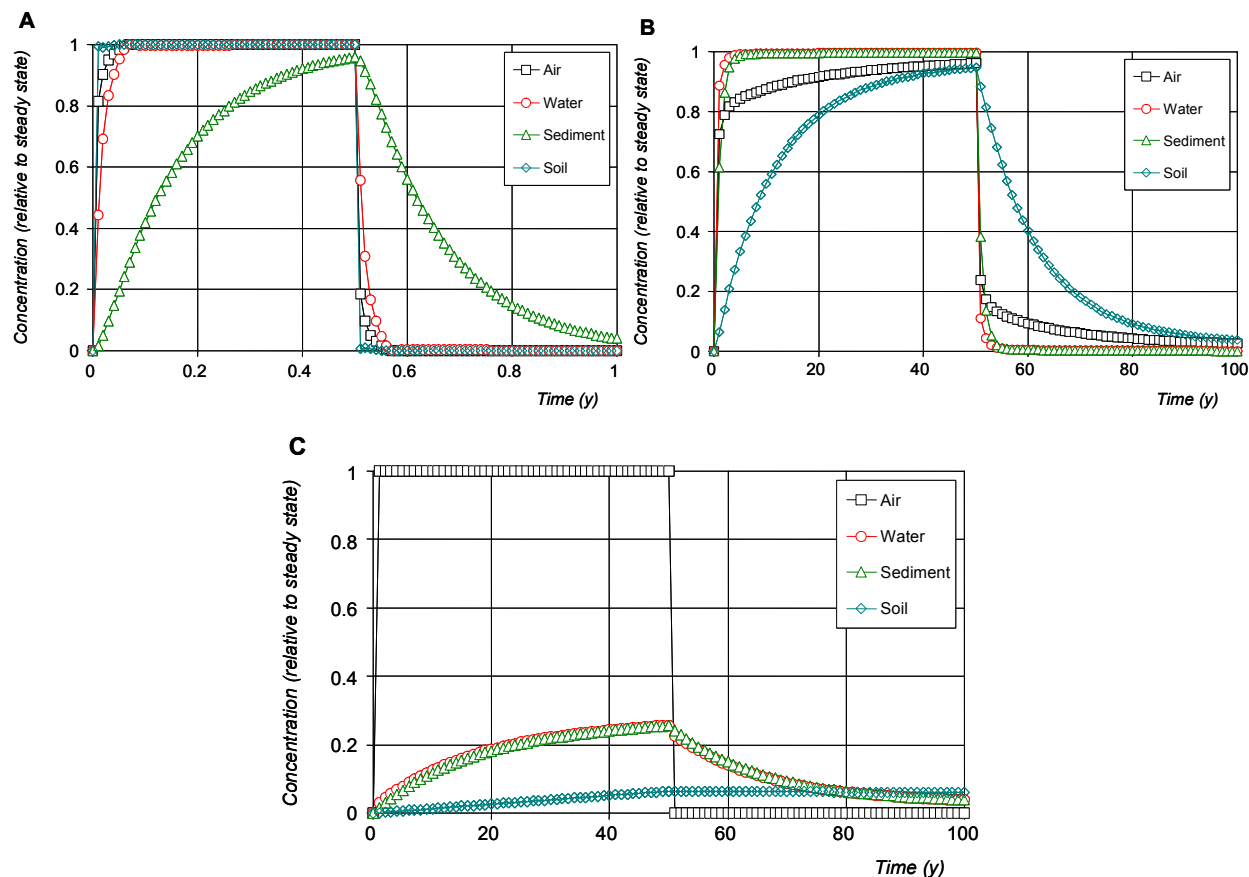


Figure 9: Change in concentrations of trichloroethane (A), dieldrin (B) and cadmium (C) after a change in emission rates. Note the shorter time scale in graph A.

Calculation of Overall Persistence in the Environment and Long-Range Transport Potential

It is clear that the physical and chemical properties of substances greatly influence their concentrations and distributions in the environment. Not only does this have implications for the risks posed to humans and ecosystems, there are other ethical and scientific consequences to be considered [55]. Slow degradation and great mobility mean that substances disperse throughout the entire globe. This has been recognized internationally. Two international conventions: the UNEP Stockholm Convention [56] and the UN ECE POP protocol [57] now regulate substances on the basis of their persistence in the environment and their long-range transport potential. Both of these are indirect or “derived” substance properties.

Persistence reflects the resistance of a substance to degradation. This is indicated by the dynamic response to changes in emissions, as shown above. Alternatively, persistence can be quantified by the degradation half-life or reactive residence time during an emission episode [58, 59]. As degradation half-lives in air, water and soil differ greatly, it needs to be decided how to combine the different single-medium half-lives. Calculation of overall persistence in the environment P_{OV} as the reciprocal of the overall degradation rate constant k_{OV} , or the mass-weighted average reactive residence time in the environmental media M_i , has been proposed for this purpose [58-60]:

$$P_{OV} = \frac{1}{k_{OV}} = \frac{\sum_i M_i}{\sum_i M_i \cdot k_i} \quad (26)$$

In this derivation of P_{OV} , k_i 's are the first-order degradation rate constants in pure media and M_i 's are the masses in the media at steady-state. According to this derivation, substance properties other than degradation half-lives (partition coefficients and mass-transfer velocities) play a role in determining the “derived property” P_{OV} . Applied to the calculation results of the previous paragraph, this would yield P_{OV} values of 2.8 years, 20.8 years and ∞ for trichloroethane, dieldrin and cadmium, respectively.

The long-range transport potential (LRTP) reflects the tendency of a substance to be transported away from the location where it was emitted. There are different ways to capture this in a “derived property” [59, 60]. One is to take the fraction of the total emission exported out of an open regional environment, as shown in the previous paragraph:

$$LRTP = \frac{adv_{air} + adv_{water}}{E}, \quad (27)$$

with adv_{air} and adv_{water} denoting the advective mass flows by air and water, respectively and E the sum of emissions. The LRTP values (dimensionless) for trichloroethane, dieldrin and cadmium would be 0.99, 0.92 and 0.91, respectively, based on example model used. Another method is to use the Lagrangian characteristic travel distance. The distance travelled by a parcel in the period that the original mass is reduced exponentially to 37% ($=1/e$) of its original value is calculated as [59, 60]

$$LRTP = \frac{u}{k_{OV}^*}, \quad (28)$$

in which u is the average velocity at which the parcel travels. Here, k_{OV}^* considers non-reactive losses to ultimate sinks such as sediment burial, groundwater or deeper ocean layers as well as abiotic and biotic degradation processes.

What P_{OV} and LRTP have in common is that they cannot easily be determined by observation, but must be calculated from substance properties that can be measured (degradation rate constants, partition coefficients, mass-transfer velocities), using a multimedia environmental fate model. This has raised the concern that the choice of model could play a role in the calculation result, which would be undesirable if P_{OV} and LRTP are to be used as a property of the substance in a regulatory context. This issue has been thoroughly studied by an international group of modelling experts for the OECD [60]. The experts concluded that indeed the absolute values of P_{OV} and LRTP obtained from different models differ greatly, as a result of different modelling objectives and model

parameterization. However, the rankings of substances obtained appeared to be relatively insensitive to the model choice: models tend to put chemicals in roughly the same order of P_{OV} and LRTP. If properly processed, output of any well-designed multimedia model can be used to derive P_{OV} and LRTP [61, 62]. This was concluded from a comparison of the performance of existing models with respect to P_{OV} and LRTP calculation, which demonstrated that a simplified version of existing models could be constructed that differed as little from the existing models as the models differed among themselves. This consensus model is available from the OECD on their website [63].

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