

3.3: Pathways and processes determining chemical fate

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Learning objectives:

You should be able to

- explain how emission of chemicals into the environment leads to exposure of ecosystems, populations, and organisms including man.
- understand how quantitative knowledge of process kinetics is of use in mathematical modeling of environmental fate
- understand the concept of characterization of fate processes in terms of rate constants and half-lives
- give examples of relevant fate processes and briefly describe them

Keywords: fate processes, degradation, transport, partitioning

Characterizing 'fate'

Chemicals can escape during all steps of their life cycle, e.g. manufacturing, processing, use, or disposal. Release of chemicals into the environment necessarily leads to exposure of ecosystems, populations, and organisms including man. Exposure assessment science seeks to analyze, characterize, understand and (quantitatively) describe the pathways and processes that link releases to exposure. Chemicals in the environment undergo various transport, transfer and degradation processes, which can be described and quantified in terms of loss rates, i.e. the rates at which chemicals are lost from the environmental compartment into which they are emitted or transferred from adjacent compartments. Exposure assessment science aims to capture the 'environmental fate' of chemicals in process descriptions that can be used in mass balance modeling, using mathematical expressions borrowed from thermodynamic laws and chemical reaction kinetics (Trapp and Matthies, 1998).

The 'fate' of a chemical in the environment can be viewed of as the net result of a suite of transport, transfer and degradation processes (see Section 3.4 on [partitioning and partitioning constants](#), Section 3.6 on [availability and bioavailability](#), Section 3.7 on [degradation](#)) that start to act on the chemical directly after its emission (see Section 3.2 on [sources of emission](#)) and during the subsequent environmental distribution. Environmental fate modeling (see Section 3.8 on [multimedia mass balance modelling](#)) builds on this knowledge by implementing the various degradation, transfer and transport processes derived in exposure assessment science in mathematical models that simulate 'fate of chemicals in the environment'.

First-order kinetics

In chemical reaction kinetics, the amount of chemical in a 'system' (for instance, a volume of surface water) is described by mass balance equations of the kind:

$$\frac{dm}{dt} = i - k m \quad (\text{eq. 1})$$

where $\frac{dm}{dt}$ is the rate of change ($\text{kg}\cdot\text{s}^{-1}$) of the mass (kg) of chemical in the system over time t (s), i is the input rate ($\text{kg}\cdot\text{s}^{-1}$) and k (s^{-1}) is the reaction rate constant. Mathematically, this equation is a **first-order differential equation** in m , meaning that the loss rate of mass from the system is proportional to the **first power** of m . Equation 1 is widely applied in description and characterization of environmental fate processes: environmental fate processes generally obey first-order kinetics, and can generally be characterized by a first-order reaction rate constant k^{1st} :

$$\frac{dm}{dt} = -k^{1st} m \quad (\text{eq. 2})$$

Such loss rate equations can also be formulated in integral format, which is obtained by integration of equation (2) over time t with initial mass $m_0 = m(0)$:

$$m_t = m_0 e^{-k^{1st} t} \quad (\text{eq. 3})$$

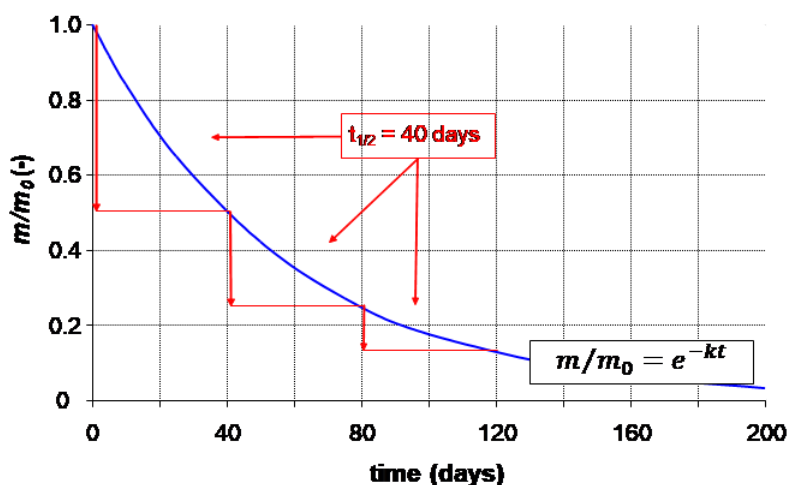


Figure 1. Graphical representation of equation 3. Decrease of relative mass of a chemical in an environmental compartment would follow the blue curve when the loss process is given by a first-order differential loss equation. Loss processes that obey first-order kinetics have constant half-lives (here time $t_{1/2} = 40$ days).

As shown in Figure 1, first-order loss processes are expected to result in exponential decrease of mass from which concentration can be calculated by dividing m with the compartment volume. Using the value $t_{1/2}$ for t in equation 3, it follows directly that the value of $t_{1/2}$ is inversely proportional to the first-order loss rate constant k^{1st} :

$$\frac{m_t}{m_0} = \frac{1}{2} = e^{-k^{1st} t_{1/2}} \rightarrow \ln\left(\frac{1}{2}\right) = -k^{1st} t_{1/2} \rightarrow t_{1/2} = \frac{\ln(2)}{k^{1st}} \quad (\text{eq. 4})$$

which shows that half-life time constant, i.e. independent of the concentration of the chemical considered. This is the case for all environmental loss processes that obey first-order kinetics. First-order loss processes can therefore be sufficiently characterized by the time required for disappearance of 50% of the amount originally present.

The disappearance time $DT50$ is often used in environmental regulation but is only identically with the half-life if the loss process is of first order. Note that the silent assumption of constancy of half-life implies that the process considered is assumed to obey first-order kinetics.

Abiotic chemical reactions

Occurrence of true first-order reaction kinetics in chemistry is rare (see Section 3.7 on [degradation](#)). It occurs only when substances degrade spontaneously, without interaction with other chemicals. A good example is radio-active decay of elements, with a reaction rate proportional to the (first power of) the concentration (mass) of the decaying element, as in equation 3.

Most chemical reactions between two substances are of second order:

$$\frac{dm}{dt} = -k^{2nd} m_1 m_2 \quad (\text{eq. 5})$$

or, when a chemical reacts with itself:

$$\frac{dm}{dt} = -k^{2nd} m_1^2 \quad (\text{eq. 6})$$

because the reaction rate is proportional to the concentrations (masses) of both of the two reactants. It follows directly from equation 2. As the concentrations (masses) of both reactants decrease as a result of the reaction taking place, the reaction rate decreases during the reaction, more rapidly so at high initial concentrations. When second-order kinetics applies, half-life is not constant, but increases with ongoing reaction, when concentrations decrease. In principle, this is the case for most chemical reactions, in which the chemical considered is transformed into something else by reaction with a transforming chemical agent.

In the environment, the availability of second reactant (transforming agent) is usually in excess, so that its concentration remains nearly unaffected by the ongoing transformation reaction. This is the case, for oxidation (reaction with oxygen) and hydrolysis (reaction with water). In these cases, the rate of reaction decreases with the decreasing concentration of the first chemical only:

$$\frac{dm}{dt} = -(k^{2nd} m_2) m_1 = k^{1st} m_1 \quad (\text{eq. 7})$$

and reaction kinetics become practically first-order: so-called *pseudo* first-order kinetics. Pseudo first-order kinetics of chemical transformation processes is very common in the environment.

Biotic chemical reaction

Chemical reactions in the biosphere are often catalyzed by enzymes. This type of reaction is saturable and the kinetics can be described by the Michael-Menten kinetic model for single substrate reactions. At low concentrations, there is no effect of saturation of the enzyme and the reaction can be assumed to follow (pseudo) first order kinetics. At concentrations high enough to saturate the enzyme, the rate of reaction is independent of the concentrations (masses) of the reactants, thus constant in time during the reaction, and the reaction obeys zero-order kinetics. This is true for catalysis, where the reaction rate depends only on the availability of catalyst (usually the reactive surface area):

$$\frac{dm}{dt} = -k^{zero} m^0 = \text{constant. (eq. 8)}$$

One could say that the rate is proportional to the zero-th power of the mass of reactant present. In case of zero-order kinetics, the half-life times are longer for greater initial concentrations of chemical.

An example of zero-order reaction kinetics is the transformation of alcohol (ethanol) in the liver. It has been worked out theoretically and experimentally that human livers remove alcohol from the blood at a constant rate, regardless the amount of alcohol consumed.

Microbial degradation

Microbial degradation (often referred to as [biodegradation](#)) is a special case of biotic transformation kinetics. Although this is an enzymatically catalysed process, the microbial transformation process can be viewed of as the result of the encounter of molecules of chemical with microbial cells, which should result in apparent second-order kinetics (first order with respect to the number of microbial cells present, and first order with respect to the mass of chemical present):

$$\frac{dm}{dt} = -(k^{2nd} m_{bio}) m = -k_{deg} m \quad (\text{eq. 9})$$

where m_{bio} stands for the concentration (mass) of active bacteria present in natural surface water, and k_{deg} represents a pseudo-first-order degradation rate constant.

Advective and dispersive transport

Chemicals can be moved from one local point to another by wind and water currents. Advection means transport along the current axis whereas dispersion is the process of turbulent mixing in all directions. Advective processes are driven by external forces such as wind and water velocity, or gravity such as rain fall and leaching in soil. In most exposure models these processes are described in a simplified manner, e.g. the dispersive air plume model. An example of a first-order advective loss process is the outflow of a chemical from a lake:

$$\frac{dm}{dt} = -\frac{Q}{V} m = -k_{adv} m \quad (\text{eq. 10})$$

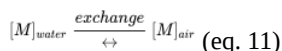
where Q stands for the flow rate of lake water [m^3/s] and V is the lake volume [m^3]. Q/V is known as the renewal rate constant k_{adv} of the transport medium, here water. More sophisticated hydrological, atmospheric, or soil leaching models consider detailed spatial and temporal resolution, which require much more data and higher mathematical computing effort (see sections [3.1.2](#) and [3.8.2](#)).

Transfer and partitioning

Due to Fick's first law the rate of transfer through an interface between two media (e.g. water and air, or water and sediment) is proportional to the concentration difference of the chemical in the two media (see section 3.4 on [partitioning](#), and Schwarzenbach et al., 2017 for further reading). As long as the concentration in one media is higher than in the other, the more molecules are likely to pass through the interface. Examples are volatilization of chemicals from water (to air) and gas absorption from air (to water or soil), adsorption from water (to sediments, suspended solids and biota) and desorption from sediments and other solid surfaces.

When two environmental media are in direct contact, (first-order) transfer can take place in two directions, in the case of water and air by volatilization and gas absorption: Each at a rate proportional to the concentration of chemical in the medium of origin and each with a (first-order) rate constant characteristic of the physical properties of the chemical and of the nature of the interface

(area, roughness). This is known as physical intermedia partitioning (see section 3.4 on [partitioning](#)), usually represented by a chemical reaction formula:



where $[M]$ stands for a (mass) concentration (unit mass per unit volume) and the double arrow represents forward and reverse transport. Intermedia partitioning proceeds spontaneously until the two media have come to thermodynamic equilibrium. In the state of equilibrium, forward and backward rates (here: volatilization from water to air and gas absorption from air to water) have become equal. At equilibrium, the total (Gibbs free) energy of the system has reached a minimum: the system has come to rest, so that

$$k_{\text{abs}} [M]_{\text{air}} = k_{\text{volat}} [M]_{\text{water}} \rightarrow K_{\text{AW}} = \frac{[M]_{\text{air}}}{[M]_{\text{water}}} = \frac{k_{\text{volat}}}{k_{\text{abs}}} \quad (\text{eq. 12})$$

and the ratio of concentrations of the chemical in the two media has reached its (thermodynamic) equilibrium value, called equilibrium constant or partition coefficient (see section 3.4 on [partitioning](#)).

Challenge

Challenge to environmental chemists is to describe and characterize the various processes of chemical and microbial degradation and transformation, of intra-media transport and intermedia transfer rate constants and of equilibrium constants, in terms of (i) physical and chemical properties of the chemicals considered and (ii) of the properties of the environmental media.

References

Schwarzenbach, R.P., Gschwend, P.M., Imboden, D.M. (2017). Environmental Organic Chemistry, Third Edition, Wiley, ISBN 978-1-118-76723-8.

Trapp, S., Matthies, M. (1998). Chemodynamics and Environmental Modeling. An Introduction. Springer, Heidelberg, ISBN 3-540-63096-1.

3.3. Question 1

Name and explain in your own words the essential environmentally relevant property of (pseudo) first-order kinetics.

3.3. Question 2

Give examples of transformation or transport processes that obey zero-order, first-order, second-order and pseudo first-order kinetics.

3.3. Question 3

Why is it useful to formulate environmental fate processes in terms of process rates and rate constants and equilibrium constants?

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