MULTIMEDIA FATE AND TRANSPORT OF ORGANIC POLLUTANTS

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Keywords: environmental fate, exposure, exposure assessment, multimedia modeling, environmental and health risk, persistence, long range environmental transport potential, mass balance equation, characteristic travel distance, environmental transport

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Summary

Environmental transport and fate of organic chemical pollutants are described by a system of mass balance equations which take into account the various physical, chemical and biological exchange and transformation processes in and among the environmental compartments. In multimedia models, the total environment is represented as a set of spatially homogeneous boxes; one box for each environmental compartment in which the chemical is assumed to be evenly distributed. The number, size, properties etc. of boxes, e.g. air, water and soil, can vary. Four levels of increasing complexity are defined, depending on the assumptions of thermodynamic equilibrium, steady and nonsteady state or intermedia mass transfer. Mass transfer is modeled by advective transport, e.g. deposition, and diffusive exchange, e.g. volatilization. Multimedia models give insight into the dynamics of environmental transport and transformation of organic substances independent of the emission compartment. They are used to determine the overall persistence and long-range transport of organic pollutants and to estimate the concentrations/doses to which human population or

ecosystems are or may be exposed. Multimedia models are an essential part of risk assessment of new and existing chemicals.

1. Introduction

Organic chemical substances with different physical and chemical properties are emitted into the environment due to the production, manufacturing, use and disposal of man-made chemical products. In order to understand and quantify the fate and distribution of organic pollutants in the environment, the main dynamic processes of substance transport and transformation in and between environmental media need to be described quantitatively. The environment is a spatially multi-structured, temporally changing system made up of abiotic and biotic components, which interact via physical processes, such as air flow and water flow, and chemical processes, such as nutrient consumption and excretion. A common, pragmatic procedure is to divide the system into the environmental compartments air, water and soil, which are composed of various amounts of gaseous, liquid, amorphous and solid phases, and which exchange substances and energy. This division is based on the assumption that environmental systems can be perceived as mixed phases. The transport and conversion processes such as advection, diffusion and degradation, which lead to a temporal change and spatial distribution of substances, take place both within and between phases. Environmental media are frequently understood as compartments, in other words, as spatial sections, volumes or boxes, which are homogenous within themselves. Chemical substances are intermixed within them with negligible temporal delay. The assumption upon which this approach is based, which stipulates that the intramedia intermixing occurs much more quickly than intermedia exchange, however, has to be examined in each individual case. The environment (or a section of it) is described as a multi-compartment system (or multimedia system). The spatial complexity is reduced to an interlinked system of environmental compartments with distinct geometric, physical, chemical and biological properties, which interact with the chemical substances and exchange them over the compartment boundaries.

Multimedia fate models are used for understanding and quantifying the distribution and transport of organic substances between air, water, soil, and other compartments. They describe the relations between emissions and exposure concentrations by solving the mass balance equations for these compartments. In order to do so quantitative expressions for the mass transfer and degradation process rates need to be formulated. This chapter adopts the approach of Donald Mackay to multimedia mass balance models including definition of increasing levels of complexity.

2. Mass Balance Models

The basis for modeling the distribution of substances in the environment is the principle of mass conservation, which states that the rate of change of mass in a system equals the difference of inputs and outputs. It is assumed that adverse ecotoxic effects that may occur only negligibly affect the environmental distribution, in other words, feedback between the effects, and distribution can be neglected. Following the proposal of the pioneering work of Donald Mackay, four levels I to IV of increasing complexity are defined. These levels differ in their consideration of exchange and degradation processes, as well as dynamics (see Table 1.). The most significant aspect is the differentiation between steady state and (thermodynamic) equilibrium. Steady state means that everything in the system remains constant. The substance masses of all environmental compartments do not change with time, i.e. $\frac{d}{dt}m_i = 0$ where i is the number of mixed compartments. (Thermodynamic) equilibrium is a special case when the concentration ratios between all media (compartments) are at their equilibrium partition ratio.

Level	**Thermodynamic equilibrium**	**In- and Outflow**	**Degradation**	**Intermedia mass transfer**	**Steady state**	**Output**
I	Yes	No	No	No	Not applicable	Equilibrium mass distribution
II	Yes	Yes	Yes	No	Yes	Steady state input/output balance
IIdyn	Yes	Yes	Yes	No	No	As II, but dynamic mass and concentration course
III	No	Yes	Yes	Yes	Yes	Steady state input/output balance with intermedia exchange
IV	No	Yes	Yes	Yes	No	As III, but dynamic mass and concentration course

Table 1: Mass balance models of increasing complexity

In Level I, an isolated system that exchanges neither mass nor chemical potential with its environment is described. The substance mass within the system is merely distributed to the compartments. This equilibrium state occurs immediately and without delay, since it is assumed that the system is in thermodynamic equilibrium at all times.

In Level II, the assumption of thermodynamic equilibrium is retained, but continual inflows and outflows, as well as losses through degradation, are additionally taken into account. The original Level II, which assumes steady state, was later extended to the dynamic, nonsteady-state case of Level IIdyn, which simulates the fate of concentrations over the whole time scale. In Levels III and IV, additional internal advective and diffuse exchange processes, such as deposition, volatilization and sedimentation, are taken into account. These processes lead to a temporal delay and to a deviation of any state from the thermodynamic equilibrium, due to resistances at the phase boundaries. Level III models look only at steady state, while Level IV models deal with the general nonsteady-state solution over the whole time-scale.

In order to be able to compare the four levels with one another, Donald Mackay introduced the “Unit World” concept. The environment is divided into the main compartments air, soil, surface water, and sediment. Volumes, boundary areas and other environmental properties are parameterized for either a global or regional environment. EUSES (European System for the Evaluation of Substances) assumes area of 200 by 200 kilometers, which is divided into 97 percent soil and 3 percent fresh water. The height of atmospheric mixing layer is 1000 meters; depth of the water is 3 meters, that of soil is 10 centimeters, and that of sediment 3 centimeters. These lead to the volumes given in Figure 1. For simplification purposes, the three soils, considered in EUSES, were combined into one.

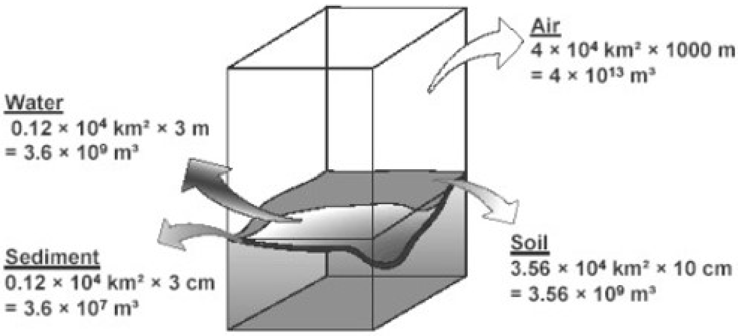


Figure 1: Regional multimedia distribution model with four compartments; modified from EUSES – the European Union System for the Evaluation of Substances, European Chemicals Bureau, Ispra (1996)

Mass balance models can equivalently be formulated by using fugacity and fugacity capacities. Fugacity corresponds to the partial pressure in a compartment and can be viewed as the “escaping tendency” of a substance. The following basic equation applies

$$C = f \times Z \tag{1}$$

where C is the concentration of a substance (here: mol m^{-3}), f is the fugacity (Pa) and Z is the fugacity capacity (mol m^{-3} Pa^{-1})). In thermodynamic equilibrium the fugacities f_i and f_j of two adjacent phases i and j are equal. This leads to:

$$C_i / C_j = \left(f_i \times Z_i \right) / \left(f_j \times Z_j \right) = Z_i / Z_j = K_{ij} \tag{2}$$

The partition coefficient K_{ij} can therefore be expressed by equilibrium concentration ratio or the quotient of the fugacity capacities. Different fugacities in adjacent phases show that the system is not in equilibrium. The fugacity concept enables the differences of the varying model types Level I to IV to be shown clearly (see Figures 2, 4 and 5).

2.1. Level I: Equilibrium, No Inflow or Outflow, No Degradation

With this level it is assumed that the whole substance amount in the system is infinitely rapid distributed to all compartments in accordance with the partition coefficients. The substance mass in the system remains constant, since there are neither inflows, outflows nor degradation. The result is the equilibrium distribution of a substance in an evaluative environment, as it would tend to adapt itself if exchange were uninhibited. The compartment of entry is unimportant, because redistribution is assumed to be instantaneous.

If the whole substance mass in the system m_{t} (kg) consisting of n compartments with the volumes $V_1,..,V_n$ (m^3) is known, the masses $m_1,...,m_n$ and concentrations $C_1,...,C_n$ need to be determined. The following serves as a mass balance equation

$$m_{\mathrm{t}} = C_1 \times V_1 + C_2 \times V_2 + \ldots + C_n \times V_n \,. \qquad (3)$$

In (thermodynamic) equilibrium the following applies: $C_i / C_1 = K_{i1}$, where i is from 1 to n and K_{11} is 1. This leads to:

$$m_{\mathrm{t}} = C_1 \times V_1 + C_1 \times K_{21} \times V_2 + \ldots + C_1 \times K_{n1} \times V_n \qquad (4)$$

$$C_1 = m_{\mathrm{t}} \big/ \left(V_1 + K_{21} \times V_2 + \ldots + K_{n1} \times V_n\right). \qquad (5)$$

From this the partition coefficients K_{ij} can be used to calculate all other concentrations C_i, and the masses can also be determined with the use of

$$m_i = V_i \times C_i \,. \qquad (6)$$

The principle is portrayed in Figure 2. Compartments $1, 2, ..., n$ are assumed to be communicating pipes or boxes. Uninhibited exchange is possible between the boxes. All boxes are filled to the same height (h). The system is in equilibrium. Analogously, a system of communicating pipes filled with water can be imagined. The substance masses m_i are represented by the volumes in the pipes. The height h is the fugacity f and, as the measure of the equilibrium state, is the same height in all pipes. The fugacity capacity Z_i is represented by width b. According to Eq. (1), the areas from height h (= fugacity f) multiplied by width b (= fugacity capacity Z_i) lead to concentrations C_i. The depths l_i correspond to the compartment volumes V_i.

The only substance properties, which are required for calculation by Level I model, are the partition coefficients K_{ij} between adjacent compartments. Partition coefficient between air and water, K_{AW} , can be computed from Henry's law constant H by dividing it by a factor $R \times T$, where R is the gas constant and T is the absolute temperature. For organic substances, H is given by the ratio of vapor pressure $p°$ and water solubility S_W of the pure compound. Partition coefficient between soil and water, K_{SW} , can be estimated from n-octanol/water partition coefficient K_{OW} , which is based on the assumption that sorption to soil particles is governed by lipophilic soil organic carbon content OC. Many regressions revealed a close relation between K_{OW} and K_{OC} , which is the partition coefficient between OC and water. Finally, K_{SW} is estimated by multiplying K_{OC} with the fraction of OC and the ratio of the bulk soil density and soil water content. Similar approach is applied to the estimation of the partition coefficient between sediment and water. Partition coefficient between air and soil is immediately given as the ratio of K_{AW} and K_{SW} (*see Ecological Chemistry*).

For the three substances 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD), linear alkylbenzene sulfonate (LAS) and benzene, the mass distribution to the media of air, water, soil and sediment are calculated for the simplified regional scenario from Figure 1. Substance data are given in Figure 3 together with the results of the Level I model. The predominant percentage of 2,3,7,8-TCDD accumulates in the soil and sediment, while LAS mainly resides in water, and benzene accumulates in the air. This leads to the conclusion that benzene is mainly dispersed by wind, LAS is carried with water flow, while 2,3,7,8-TCDD is rather immobile.

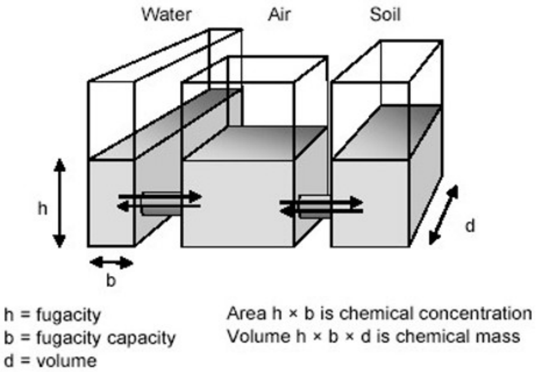
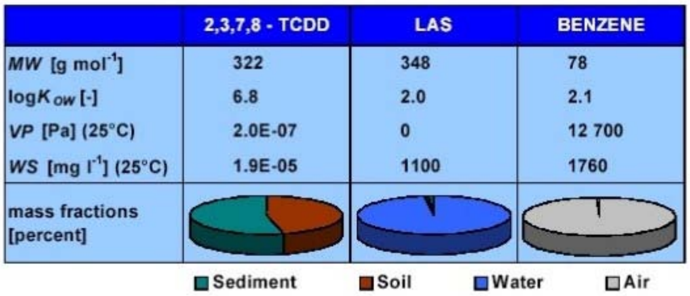


Figure 2: Multimedia mass balance model Level I



	2,3,7,8 - TCDD	LAS	BENZENE
MW [g mol^{-1}]	322	348	78
logK_{OW} [-]	6.8	2.0	2.1
VP [Pa] (25°C)	2.0E-07	0	12 700
WS [mg l^{-1}] (25°C)	1.9E-05	1100	1760
mass fractions [percent]			

■ Sediment ■ Soil ■ Water □ Air

Figure 3: Mass percentages for three sample compounds calculated with Level I and the model presented in Figure 1; 2,3,7,8-TCDD (2,3,7,8-tetrachloro-dibenzo-p-dioxin), LAS (linear alkyl benzene sulfonate)

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Biographical Sketch

Professor Michael Matthies studied physics at the Universities in Münster and München, Germany. In 1971 he finished his undergraduate studies with B.Sc. thesis in Medical Physics. In 1975 he received his

Ph.D. in Physical Chemistry from the University of München, Faculty of Chemistry. His Ph.D. thesis was on hydrogen bonds in energy rich biochemical compounds. From 1976–1977 he worked as a research associate in at Institute of Biophyics, University of Giessen. Two years later he became a research associate at the National Centre of Environment and Health in München-Neuherberg. He worked on radiation risk analysis, radioecology and chemical exposure and risk assessment. In 1987 he became the head of the Project Group on Hazard Assessment of Chemicals. In 1992 he was appointed as a full professor of Applied Systems at the University of Osnabrück. He founded the Institute for Environmental Systems Research in 1994 and is its director since then. His major interests are environmental systems science, systems ecology and biogeochemical cycles, transport modeling of pollutants in air, soil and water, exposure and risk assessment, integrated modeling and assessment. Professor Matthies participated in several national and international projects on exposure modeling, comparative risk assessment, long-range transport modeling of persistent organic pollutants and geo-referenced exposure assessment. The results of his research are documented in over 150 articles in scientific journals, proceedings and handbooks and 40 scientific reports and books. He served as a consultant for international organizations (OECD, EU) and various national agencies such as the German Federal Environmental Protection Agency and Federal Ministry of Research and Technology.