



MIGRATION AND FATE OF PERSISTENT ORGANIC POLLUTANTS IN THE ATMOSPHERE - A MODELLING APPROACH

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Abstract

Considering that the fate and behaviour of contaminants within the environment is an extremely complex issue, this paper analyzes the development of predictive models which can contribute to the understanding of the release of a contaminant. Different types of models concerning the atmospheric transport of POPs are examined, taking into consideration that these models can be used to simulate the behaviour of contaminants. A successful simulation, in which there is satisfactory agreement between observations and results derived from the models, suggests that a solid theoretical understanding of how chemicals move, react, and distribute among media is sufficient to explain their behaviour in real-world situations.

Keywords: intermedia transport; long range transport potential; multimedia models; multiple compartment models

1. Introduction

The occurrence, sources, transport and fate of xenobiotic chemicals into the environment and resulting effects are major issues that give rise to concerns at local, national, regional and global scales (Rieger et al., 2002; Baun et al., 2006). Synthetic organic chemicals are discharged into the environment through various processes which may possibly include: release during the production process, at some point in use (e.g. pesticides), or accidental emissions during combustion processes (e.g. dioxins).

Persistent organic pollutants are a group of chemical compounds with different origins but common characteristics: semi-volatility, lipophilicity, bioaccumulation and great persistence in the environment (Betianu and Gavrilescu, 2006; Gavrilescu, 2005; Jones and de Voogt, 1999; Bennett et al., 1999). They persist in the environment for a long time, being also able of long-range transport (Beyer et al., 2000), bioaccumulate in the food chain and human and animal tissue, biomagnifying in food chains, and to have potential significant impacts on human health and the environment being toxic to humans and/or wildlife. As a consequence of these

characteristics, POPs are found and measured in all environmental media, far from source regions, even in isolated areas with no usage or direct emissions of these compounds (Pacyna et al., 1995; Koziol and Pudykiewicz, 2001; Breivik et al., 2004; Gavrilescu, 2005).

Assessment of environmental pollution can be achieved by means of monitoring and modeling (linear and nonlinear regression, chemometric analysis, neural networks and artificial intelligence), which can identify which variables are likely to exert an influence on the seasonality of ambient POPs monitoring data, thereby providing indications as to the dominant processes and the reliability of emission inventories (Prevedouros et al., 2004).

2. Persistent organic pollutants in the atmosphere

The emergence and subsequent behaviour of POPs in the atmosphere proved to be processes, as once in the environment and based on their semivolatile character (P_v between 10^{-4} and 10^{-11} atm at 25 °C), owing to their ability to associate with atmospheric particles or distributed between these two phases as well (Aceves and Grimalt, 1993; Kaupp and McLachlan, 1999).

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Therefore, a complex interaction between the environmental compartments in relation with POPs transport and fate occurs, where the atmosphere is the main actor (Fig.1). Many researches revealed that the atmosphere is the main transport media for the global distribution of POPs in the environment, only days to weeks being necessary for an air bundle to mix completely in the northern hemisphere, while the transport times of ocean currents can be measured in years and decades (Finlayson-Pitts et al., 1999; Prevedouros et al., 2004). The scale of atmospheric transport of POPs depends on the meteorological conditions, POPs physical/chemical properties, removal processes which include photochemically driven reaction and physical depositional mechanism (Foreman et al., 2000). The transfer of chemicals from land surface to atmosphere consists of two steps (Beyer, 2000; Toose et al., 2004; Gavrilesu, 2005):

- change from liquid or solid state to vapors;
- subsequent dispersion by turbulent mixing.

Because several physico-chemical properties governing the environmental fate of POPs are temperature dependent, POPs atmospheric transport should be seen as *single-hop* pathways (a compound is emitted to the atmosphere, transported and deposited to earth's surface and never returns to atmosphere) or *multi-hop* pathways (a compound re-enters the atmosphere after initial deposition to the earth's surface, it can travel long distances via subsequent multiple atmospheric hops; also the so-called *grasshopper effect*) (Fernandez and Grimalt, 2003) (Fig. 2). This can occur passing through volatilizations from the earth's surface under high temperatures driven out by soil moisture, or sudden exposure of ocean water to the atmosphere after being covered by ice, or by resuspension of dust or snow by winds. Also, the transfer from low to high latitudes

takes place in successive condensation/volatilization steps (*the grasshopper effect*).

This way a mass transfer occurs between air and terrestrial surfaces according to seasonal temperature changes at mid-latitudes, when these compounds are exchanged (Fernandez and Grimalt, 2003) (Fig. 2). As a result of this phenomenon, POPs can undertake several cycles of deposition and re-emission (the so named *grasshopper* or *multi-hop* transport) before reaching their final destination (Hansen et al., 2004). Also, the transport of gas phase contaminants from the warm regions of the planet, that is tropical or temperate source areas, to colder, higher latitude regions can be predicted by the theory of the *global distillation effect* (Blais, 2005).

3. Modelling atmospheric transport of persistent organic pollutants

3.1. Premises for modelling the transport and fate of persistent organic pollutants

Modelling as the application of fundamental knowledge or experience to simulate or describe the performance of a real system to achieve certain goals has long been an integral component in organizing, synthesizing, and rationalizing observations of and measurements from real systems and in understanding their causes and effects (Barber et al., 2004; Gavrilesu, 2005).

Environmental studies have to be multidisciplinary, dealing with a wide range of pollutants undergoing complex biotic and abiotic processes in the soil, surface water, groundwater, ocean water, and atmospheric compartments of the ecosphere (Table 1).

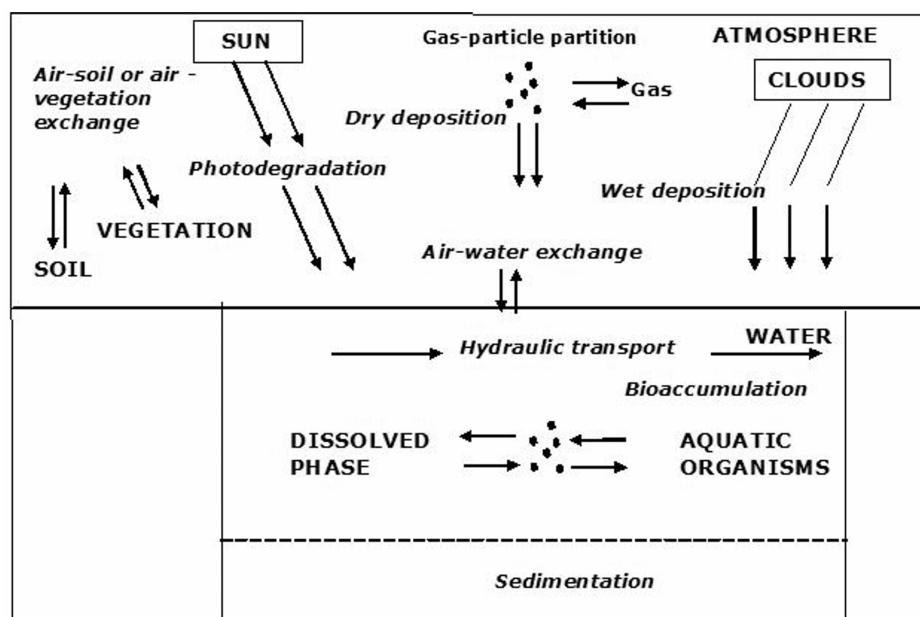


Fig. 1. Environmental processes occurring during long-range atmospheric transport of POPs (adapted upon Fernandez and Grimalt, 2003)

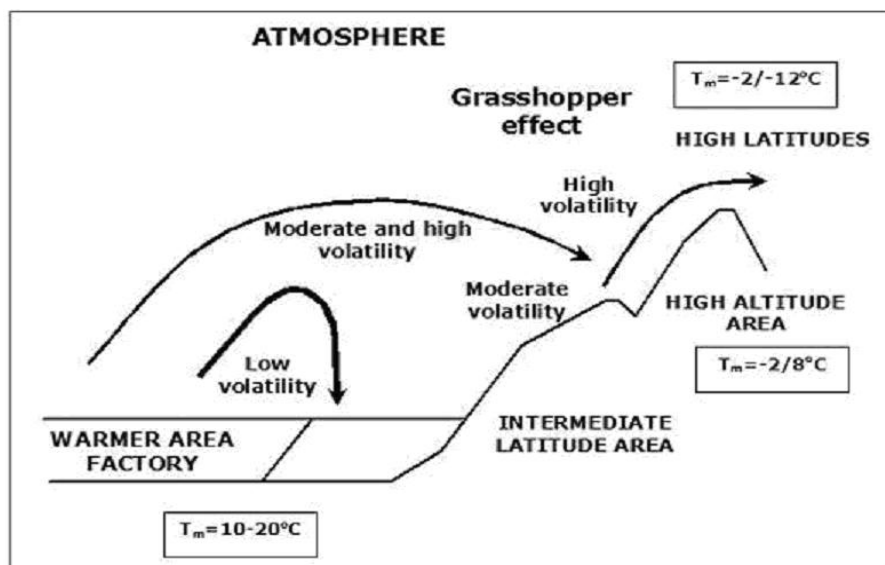


Fig. 2. Representation of the *global distillation effect* through the grasshopper mechanism (T_m – the mean air temperature in each region) (adapted upon Fernandez and Grimalt, 2003)

Table 1. Application of mathematical modelling for environmental processes (Nirmala Khandan N., 2002)

<i>Environmental component</i>	<i>Issues/Concerns</i>	<i>Use of models in</i>
Atmosphere	Hazardous air pollutants; air emissions; toxic releases; acid rain; smog; CFCs; particulates; health concerns; global warming.	Concentration profiles; exposure; design and analysis of control processes and equipment; evaluation of management actions; environmental impact assessment of new projects; compliance with regulations.
Surface water	Wastewater treatment plant discharges; industrial discharges; agricultural/urban runoff; storm water discharges; potable water source; food chain.	Fate and transport of pollutants; concentration plumes; design and analysis of control processes and equipment; wasteload allocations; evaluation of management actions; environmental impact assessment of new projects; compliance with regulations.
Groundwater	Leaking underground storage tanks; leachates from landfills and agriculture; injection; potable water source.	Fate and transport of pollutants; design and analysis of remedial actions; drawdowns; compliance with regulations.
Subsurface	Land application of solid and hazardous wastes; spills; leachates from landfills; contamination of potable aquifers.	Fate and transport of pollutants; concentration plumes; design and analysis of control processes; evaluation of management actions.
Ocean	Sludge disposal; spills outfalls; food chain.	Fate and transport of pollutants; concentration plumes; design and analysis of control processes; evaluation of management actions.

The difficulty at some stage in modelling process is to identify which models are the best appropriate to address a variety of tasks, how they should be tested and applied, and how their accuracy can be assessed (Sabjic and Peijnenburg, 2001).

Since atmosphere is the environmental component in which mass flows occur most rapidly on a global scale, mobility is generally reflected in volatility. Also, the release of a particular chemical depends to a large extent on its persistence.

These aspects lead to various model types for the fate and migration of persistent organic pollutants, by taking into account the temporal and spatial scales (Fig. 3).

Local scale air pollution models assess the impact of emissions to the atmosphere on ground level concentrations in the surrounding area of the emission source, which could be industrial stack discharges, fugitive emissions from factories, diffuse emissions from other areas such as landfill sites, and traffic emissions from roads, but they could be applied to predict concentrations in air over a wider scale. Two broad categories of local scale air pollution models are applied in the evaluation of local air pollution:

- *Eulerian* (plume and puff) models;
- *Lagrangian* particle dispersion models;
- *Gaussian* (plume and puff) models.

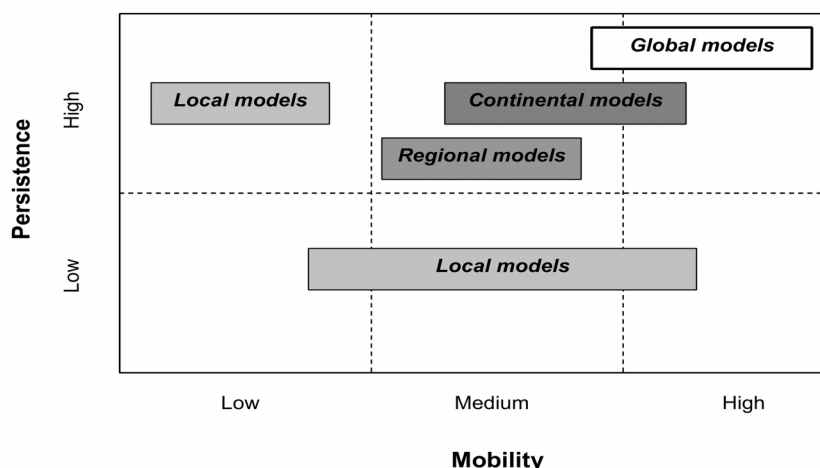


Fig. 3. Model categories depending on spatial scale determined by POPs persistence and mobility (adapted upon EEA, 2007)

Multimedia models have been developed to estimate fate and behaviour of a chemical in the environment on a large (regional or global) scale. Their particular application refers to assessing and managing the risks that persistent organic pollutants induce in the environment, even because of their potential for long range transport.

Currently, *multimedia box models and models based on atmospheric dispersion* are used to investigate the global behaviour of POPs.

Box models are simpler to construct and use, but they have only low spatial and temporal resolution. Several box models have been in use to understand the behaviour of persistent non-polar substances in the multimedia environment (Wania and Dugani, 2003; Wania et al., 2006). Models composed of meridionally connected boxes have been used to study long-range transport in two dimensions (Mackay et al., 1992; Wania and Mackay, 1995; van Jaarsveld et al., 1997).

Dispersion models have high resolution but also require high computational effort (van Jaarsveld et al., 1997).

In recent years, models have been used to simulate the observed behaviour of contaminants in a real situation and to address the following miscellaneous tasks (Scheringer et al., 2000; Frohn et al., 2002; Geels et al., 2004; Prevedouros et al., 2004):

- comparison of relative fates of different chemicals;
- identification of important fate processes;
- estimation of overall persistence and residence times;
- estimation of potential for Long Range Transport (LRT);
- estimation of environmental concentrations and exposures;
- determination of bioaccumulation in organisms and food webs;
- evaluation of likely recovery times of contaminated environments;
- checking the consistency of monitoring data;

- screening and prioritizing chemicals;
- in general, as a decision support tool documenting the sources and nature of contamination and feasible remedial strategies.

A successful simulation, in which there is satisfactory agreement between observations and model results, suggests that the degree of theoretical understanding of the way chemicals partition, move and react is sufficient to explain the observed behaviour in that environment. Some aspects are to be considered during modelling process, as is highlighted in Table 2 (Woodfine et al., 2001; Galiuulin et al., 2002; Macleold and Mackay, 2004).

3.2. POPs modelling framework

In order to get quantitative information on major sources, environmental concentrations, transport pathways and routes of exposure to humans and wildlife, several issues need to be investigated, such as:

- emission sources;
- global distribution;
- degradation processes;
- potential for long-range transport.

These properties are difficult to be evaluated in an accurate way, so that models were developed, based on measurements of the dispersion, toxicity, bioaccumulation or persistence, by analyzing samples taken from certain environmental areas (Mackay and MacLeod, 2002).

Other attributes cannot be measured directly, particularly fluxes such as evaporation rates, persistence and distance traveled (Totten et al., 2006).

3.3. Models

3.3.1. General structure

Models are able to evaluate the fate of compounds in the environment, for a wide range of chemicals and environments.

Table 2. Some important characteristics for modelling process

<i>Characteristic</i>	<i>Relevance</i>
<i>Transparency</i>	The assumptions and methodologies used for emission estimation should be clearly explained to facilitate replication and assessment of the data by users of the reported information.
<i>Consistency</i>	Emission data should be internally consistent in all their elements with data from other research. Emission data are consistent if the same methodologies are used for all stages and if consistent data sets are used to estimate emissions. Emission data using different methodologies for different years can be considered to be consistent if they have been recalculated in a transparent manner.
<i>Comparability</i>	Estimates of emissions reported by different researchers should be comparable.
<i>Completeness</i>	A certain emission report covers, at least all sources, as well as all compounds, as well as other existing relevant source categories that are specific.
<i>Accuracy</i>	A relative measure of the exactness of an emission estimate. Estimates should be accurate in the sense that they are systematically neither over nor under true emissions, as far as can be judged, and that uncertainties are reduced as far as practicable.

They can calculate transfers rates and quantities of different compounds between air, soil, water and living organisms, evaluate expected concentrations or relative proportions between environmental components and estimate persistence and potential for long range transport (Beyer et al., 2000; Scheringer et al., 2004).

A chemical released to the atmosphere can experience dry and wet deposition: it could be deposited onto the vegetation, soil and surface water. The transport processes between different environmental compartments are illustrated in Fig. 4.

In this situation, pollutant fate and transport can be assessed by means of multimedia models, which offer an attractive alternative for assessing the potential for multimedia impact of chemical pollutants (Taboas, 1993; Eisenberg et al., 1998).

These models can evaluate the exchange characteristics of a chemical based on its physical chemical properties and total air, water and soil concentrations.

So, the distribution of the compound at defined, probably unsteady-state, conditions is described.

Because it is difficult to achieve the steady-state concentrations, for comparison, the fugacity in each medium is calculated from the other medium, assuming steady-state conditions (Shafi et al., 2006). Some information are required as input data, such as:

- chemical properties;
- environmental properties;
- concentrations.

The model outputs can be:

- all input data;
- chemical amounts in each medium;
- residence times in each medium;
- fugacity of each medium for the user-specified concentrations;
- fugacities at steady-state;
- intermedia transport and loss rates;
- concentrations in all subcompartments;
- a summary diagram.

The general structure of a model is presented in Fig. 5.

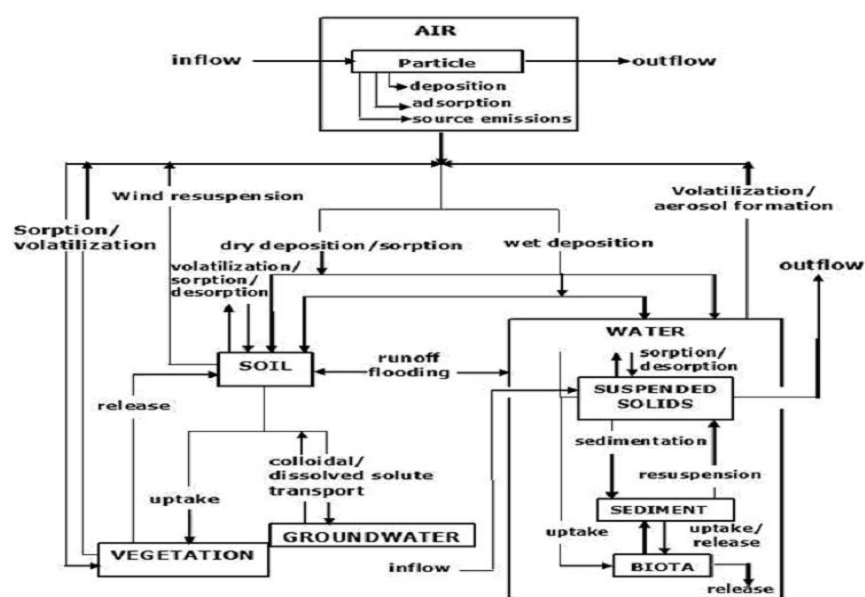


Fig. 4. Schematic representation of the transport processes between the environmental compartments (taken from Cohen and Cooter, 2002)

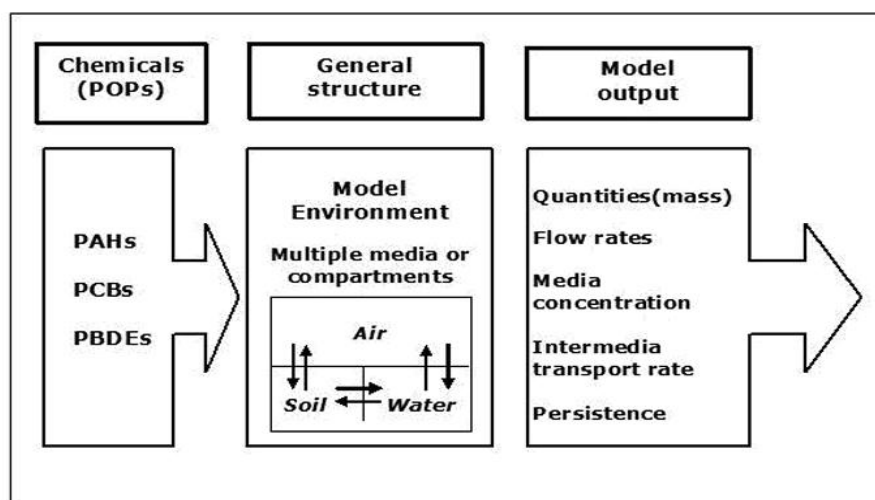


Fig. 5. The general structure of a model for intercompartmental transfer of chemicals in the environment

3.3.2. Model categories

A large and growing volume of literature exists on multimedia models.

Although these models can range greatly in complexity and can be elaborated in various ways, it is preferable to use the simplest model that can generate the desired result (Mackay and MacLeod, 2002).

Abbot et al. (2005) described two types of models for the atmosphere:

- *air quality models*, which include: *local air pollution models, photochemical models, acid deposition and eutrophication models*;
- *multimedia models*, ranging from *simple screening models to highly complex simulation models*.

External and internal exposure models

Mathematical models are being used to simulate actions in the exposure-response field, and to support quantitative predictions of risks to human health (Rosenbaum et al., 2007). The importance of contaminants to species, populations, and their ecosystems partly has been evaluated by measuring contaminant levels in air, water, and soil, and assumed effects in organisms.

Multimedia models of environmental fate and transport are mathematical tools that describe the entry, movement and distribution of chemicals within the environment, which includes both abiotic and biotic media, along with intermedia transport processes leading to chemical mass exchange among the various media (Cohen and Cooter, 2002; Shafi et al., 2006; Rosenbaum et al., 2007).

In the case of POPs, high trophic level organisms are vulnerable to accumulating high concentrations of POPs, but considerable variation exists among species (Kannan et al., 1995)

Integrated human and ecological risk assessment must be sufficiently flexible to be

applicable to a wide range of circumstances and target species, as a series of host factors have been demonstrated to affect bioavailability, fate, and effects of contaminants (Gavrilesu, 2006). Using external and internal exposure models from better understood species may be the most effective approach in many cases, but attention should be given to the ecological circumstances for the species or case in question.

Multimedia models

Four basically types of multimedia modelling approaches are relevant, such as (Paterson et al., 1994; McDonald and Gelston, 1998; Armitage et al., 2007):

- *integrated spatial multimedia models*, that describe chemical transport and fate in all the pertinent media *via* spatial models with interactions among media specified by well-posed boundary conditions and where the set of medium-specific transport equations are solved simultaneously;
- *linked spatial single-medium models*, which consist of serially-linked single-medium transport models (i.e., for air, water, soil and other media of interest) that first solve for concentrations in a given specific medium. Calculated intermedia fluxes (e.g., due to dry deposition) are then used as pseudo-source inputs to solve for contaminant concentrations in other adjoining media;
- *compartmental ("well-mixed" media) models*, being simpler and easy to execute relative to linked model systems and requiring fewer parameters. Literature makes a distinction between compartmental and fugacity-type multimedia models (Mackay and MacLeod, 2002);
- *integrated spatial-multimedia compartmental models (ISMCM)*, include both "well-mixed" and spatial compartments tightly integrated through well-posed intermedia physical boundary conditions.

Multimedia models (MMMs) have been set up for regions, nations, continents and even the global

system. These can be referred to as models of *real* systems. Another family of models consists of the *evaluative* models in which the environment is imaginary i.e. it does not correspond to a particular area (Mackay and MacLeod, 2002). These models do not explicitly attend to the likelihood of chemicals being transported from source regions and deposited to a specific target ecosystem, but they are required to estimate the relative contribution of different sources to the contaminant load present in a particular ecosystem (MacLeod and Mackay, 2004).

Multimedia models have often been limited to oversimplifications of the environmental processes governing the transport of chemicals, mainly because of the large uncertainty on the physical and chemical properties of substances, which discourage any refined computing exercise. Multimedia models require input data related to the properties and behaviour of the chemical under consideration, the environment into which it is released and the means of release (Margini et al., 2004). Some specific necessary inputs data are as follows:

- *meteorological data* (wind speed, direction, air temperature, depth of mixing layer);
- *hydrological data* - annual (or other time period) rainfall, runoff, infiltration, ground water recharge, surface water depth, sediment loads;
- *soil properties* – bulk density, porosity, water content, erosion rates and root zone depth.

Assessing concentrations of POPs in the atmosphere and their environmental fate relies also on modelling. Several groups, using various methods over the past two decades, have attempted numerical modelling of long-range atmospheric transport of persistent organic pollutants. Several approaches have been used such as: *generic box models based on the fugacity concept* (Mackay and Wania, 1995; Wania and Mackay, 1999) and *dynamic transport models* (Margini et al., 2004).

Multimedia mass balances

Multimedia are relatively simple mathematical descriptions of fate and transport of chemicals in the natural environment, which can provide a qualitative and quantitative understanding of the environmental behaviour of persistent organic pollutants, likely to be found in more than one environmental phase or medium (Margini et al., 2004; Foster et al., 2006).

Typically, a multi-media mass balance model separates the environment into a number of boxes or compartments of defined, well-mixed and homogeneous volume, with respect to both environmental characteristics and chemical contamination, then linked by a variety of inter-compartmental transfer processes (Shamsudeheen and Lammel, 2003; Wania et al., 2006). The model then calculates how a chemical is distributed within that simplified system. The distribution, and thus the concentration that is established in each medium, is influenced both by the chemical's intrinsic properties

and emission patterns and the characteristics of the environment into which it is released.

Multimedia models have variable numbers and types of compartments ranging from one or two, but more than a hundred could be connected. Several investigators suggest that the minimum number of compartments for a model aimed at estimating an overall persistence should be *three*, namely *air, water and soil* (Muller-Herold et al., 1997; Bennet et al., 1999; Margini et al., 2004).

The approach of Webster et al., (1998) is based on a model which additionally includes a sedimentation compartment. In the model proposed by Scheringer (1996), the basic three-compartment block is multiplied to additionally provide the possibility to assess a spatial range parameter.

The models could also integrate information on multiple and interacting processes of partitioning, transport and transformation into a comprehensive yet readily comprehensible picture of a chemical's fate in the environment (Hollander et al., 2007). A very clear description of the compartmental mass balance for multimedia models development was presented by Mackay et al., (2001) and Wania and Mackay (1999). Such models tend to include multiple environmental compartments, have a low spatial resolution, and involve simplifying assumptions of equilibrium and steady state (Mackay and MacLeod, 2002).

The single compartmental mass balance

Mackay et al., (2001) have considered first a single compartment as shown in Fig. 6, so that it was possible to set out the input and output processes such as:

- discharge or emission;
- convective inflow in air or water (and the corresponding convective outflow);
- diffusion to and from neighboring compartments;
- chemical species generation from other chemicals and degrading reactions.

According to the mass balance principles, the total rate of chemical input minus the total rate of output must equalize the rate of the chemical mass change in the given volume (Gavrilescu et al., 2005). Mathematically this can be expressed by Eq. (1):

$$\frac{dm}{dt} = \frac{d(VC)}{dt} = \text{input rate} - \text{output rate} \quad (1)$$

where $m[\text{kg}]$ is mass in the compartment, $V[\text{m}^3]$ - compartment volume, $C[\text{kg}/\text{m}^3]$ - concentration of chemicals.

Based on input and output fluxes from Fig. 5, Eq. (1) can be written in mathematical form as follows (Eq. 2) (Mackay et al., 2001):

$$\frac{dm}{dt} = T_{IN} + E + F_{IN} + S - (T_{OUT}) + F_{OUT} + R \quad (2)$$

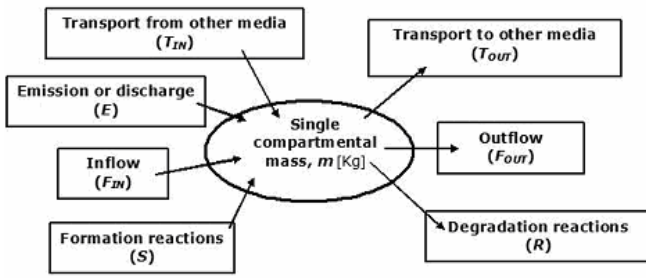


Fig. 6. Mass balance for single compartmental model (adapted upon Mackay et al., 2001)

If the following expressions for some terms in Eq. (2) are considered (Eqs. 3), then Eq. (2) can be written as (Eq. 4):

$$\begin{aligned} T_{OUT} &= VCk_T \\ F_{OUT} &= VCk_F \\ R &= VCk_R \end{aligned} \quad (3)$$

$$\frac{dVC}{dt} = T_{IN} + E + F_{IN} + S - VC(k_T + k_F + k_R) \quad (4)$$

An important quantity to be considered is the persistence of the chemical, which can be expressed as the residence time of the chemical in the box. It can be the best calculated at steady-state (Eq. 5) (Mackay et al., 2001):

$$\frac{dm}{dt} = \frac{dVC}{dt} = 0 \quad (5)$$

Thus the chemical concentration will be determined with (Eq. 6), while the residence time with Eq. (7):

$$C = \frac{T_{IN} + E + F_{IN} + S}{V(k_T + k_F + k_R)} \quad (6)$$

$$Residence\ time = \frac{Inventory}{Output\ rate} = \frac{m}{VC(k_T + k_F + k_R)} = \frac{1}{(k_T + k_F + k_R)} \quad (7)$$

Under unsteady-state, or dynamic conditions, a characteristic time (the average time that the chemical spends in the single compartment or box, as a first indication of persistence) can be calculated similarly as the mass divided by the output rate, as well as a residence time attributable to reaction and other loss processes (Mackay et al., 2001; Hollander et al., 2007).

Multiple compartments models

If the model consists of two connected boxes as in Fig. 7, the same approach can be applied to each box, as well as to the combination of the two boxes, i.e. the system as a whole (Mackay et al., 2001).

The individual residence times, for each compartment, can be calculated with Eqs. (8, 9):

$$\tau_1 = \frac{m_1}{F_{OUT_1} + R_1 + T_{12}} + \frac{1}{k_{F_1} + k_{R_1} + k_{12}} \quad (8)$$

$$\tau_2 = \frac{m_2}{F_{OUT_2} + R_2 + T_{21}} + \frac{1}{k_{F_2} + k_{R_2} + k_{21}} \quad (9)$$

while the residence time for the whole system with Eq. (10):

$$\tau_0 = \frac{(m_1 + m_2)}{F_{OUT_1} + F_{OUT_2} + R_1 + R_2} \quad (10)$$

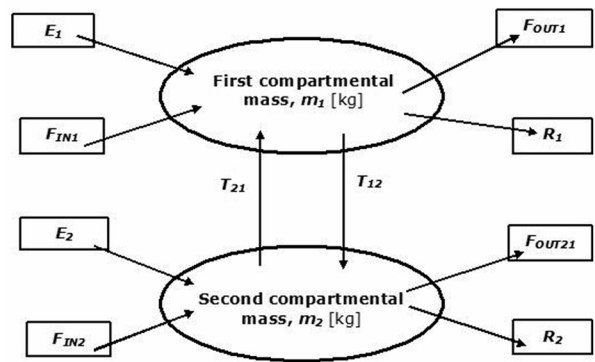


Fig. 7. Individual and overall media residence time of a chemical pollutant in a steady state multiple compartment system (E₁- emissions or discharge in the first compartment; F_{IN1}- inflow in the first compartment; E₂- emissions or discharge in the second compartment; F_{IN2}- inflow in the second compartment; F_{OUT1}- outflow from the first compartment; R₁- rate of degradation reactions in the first compartment; R₂- rate of degradation reactions in the second compartment; T₁₂- transport from the first to the second compartment; T₂₁- transport from the second to the first compartment) (adapted upon Mackay et al., 2001)

The overall residence time attributable only to reactions can be derived from Eq. (11):

$$\tau_{OR} = \frac{m_1 + m_2}{R_1 + R_2} = \frac{m_1 + m_2}{m_1 k_{R_1} + m_2 k_{R_2}} = \frac{m_1 + m_2}{f_1 k_{R_1} + f_2 k_{R_2}} \quad (11)$$

By following the same procedure, other compartments can be added, assuming that they are in chemical equilibrium with an existing compartment. Examples are aerosol particles added to the air, or suspended solids and biota to water (Mackay and MacLeod, 2002).

The overall persistence in a multimedia system including *n* compartments results by using the residence time in the system without considering advective losses (Eq. 12) (Mackay et al., 2001; Hollander et al., 2007):

$$\tau_{OR} = \frac{m_{total}}{R_{total}} = \frac{m_{total}}{m_1 k_{R_1} + m_2 k_{R_2} + \dots + m_i k_{R_i} + \dots + m_n k_{R_n}} = \frac{1}{\sum_{i=1}^n (f_i k_{R_i})} \quad (12)$$

where $f_i = m_i / m_{tot} =$ mass fraction in compartment i and R_{total} is the total rate of reaction.

The number of mass balance equations is given by the number of independent compartments (those that are not at equilibrium). If the concentrations differ significantly between two locations, they could be treated as separate compartments.

Connected multimedia models for evaluation of long-range transport

The global environment is treated as a series of connected multimedia environments of various configuration (e.g. circular), where the spatial distribution of concentrations can be calculated and expressed as a distance within which most of the chemicals are located (Mackay et al., 2001; Hollander et al., 2007). The description of LRT can be also made by using a Lagrangian system applied to a volume of air (or water) containing chemical as it is transported. This case is illustrated in Fig. 8, where long-range transport calculations in Lagrangian coordinate considers that the changing concentrations in a segment of the atmosphere is followed as it travels over soil (Mackay et al., 2001). The mass balance equations for this system are as bellow. The fraction retained is given by (Eq. 13):

$$S = \frac{k_{RS}}{(k_{RS} + k_D S)} \quad (13)$$

where $k_D S$ is the net deposition.

Characteristic travel distance (CTD) can be expressed with (Eq. 14):

$$CTD = \frac{U}{(k_{RS} + k_D S)} \quad (14)$$

If the residence time in air is given by Eq. (15), CTD could be determined using Eq. (16):

$$\tau_A = \frac{1}{(k_{RS} + k_D S)} \quad (15)$$

$$CTD = \tau_0 U f_A \quad (16)$$

where:

τ_0 - overall residence time; f_A - fraction of the chemical in air;

so that the residence time in air results as (Eq. 17):

$$\tau_A = \tau_0 f_A \quad (17)$$

Hybrid multimedia compartmental models

An integrated hybrid spatial-compartmental modelling approach was presented by Cohen and Cooter (2002) for analyzing the dynamic distribution of chemicals in the multimedia environment, which may consist of both uniform (air, water, suspended solids, vegetation, biota, suspended solids, and atmospheric aerosols) and nonuniform (soil and sediment) environmental compartments.

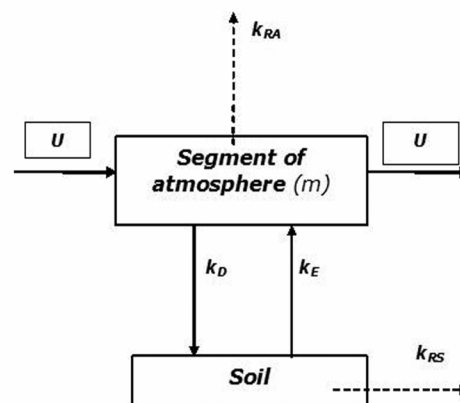


Fig. 8. Scheme for long-range transport in Lagrangian coordinates, between air and soil (U - velocity; k_{RA} - reaction constant rate in air; k_D - deposition rate constant; k_E - evaporation rate constant; k_{RS} - reaction rate constant in soil) (adapted upon Mackay et al., 2001)

The resulted information includes temporal chemical concentration profiles in various media, mass distribution, and intermedia chemical mass fluxes.

The interactive system of model equations for the uniform compartments (ordinary differential equations) and nonuniform compartments (1D partial differential equations) must be solved simultaneously to ensure conservation of mass (Cohen and Cooter, 2002).

Fugacity-based modelling

The fugacity concept can be applied to a model unit world to gain valuable information about a chemical's behaviour in the natural environment (Abbott et al., 2005). This information can be of significant value in designing a chemical with desired environmental characteristics, managing environmental emissions, ranking chemicals, and environmental policy-making (Mackay and Fraser, 2000; Gavrilescu, 2006).

This kind of models is also based on the intercompartmental approach. A basic configuration of the unit world proposed by Mackay and MacLeold, (2002) consists of the water, soil, air, and sediment compartments. Compartmental fugacity-type models express the driving forces for diffusional interfacial mass transfer (among compartments) in terms of fugacity (or chemical potential) instead of concentration driving forces (Berding et al., 2000; Mackay and MacLeold, 2002).

The fugacity concept can be applied at various levels of complexity by including more detailed compartments in the unit world, inter- and intraphase transport and reactive processes, emissions etc. (Mackay and Fraser, 2000; Berding et al., 2000):

- *Level I model* is based on a closed system mass balance of a defined quantity of chemical, without reaction, as it partitions at equilibrium between compartments. They consider the steady state in a closed system. The equilibrium distribution of a fixed quantity of conserved chemical occurs in a closed environment at equilibrium, with no degrading reactions, no advective processes, and no intermedia transport processes (no wet deposition, or sedimentation).

Level I models cannot be used to calculate persistence and LRTP because they don't take degradation into account, and rely on mass balancing by equilibrium partitioning alone.

- *Level II model* is a steady-state open system description of chemical fate at equilibrium with constant chemical emission rate. It includes reaction and advection as loss processes. It can describe a situation in which a chemical is continuously discharged at a constant rate, achieving equilibrium condition at the steady-state, at which the input and output rates are equal. Degrading reactions and advective processes are the loss or output processes treated. Intermedia transport processes (no wet deposition, or sedimentation) are not quantified. They are the simplest models to calculate persistence and LRTP (EEA, 2007).

- *Level III model* is a steady-state description of the fate of a chemical between a number of well-mixed compartments, which are not at equilibrium. This level thus includes intermedia mass transport expressions. Similar to the Level II model, the chemical is continuously discharged at a constant rate and steady state condition is achieved, when input and output rates are equal.

The loss processes are degrading reactions and advection. Unlike the Level II model, equilibrium between media is not assumed and, in general, each medium is at a different fugacity. These models include the rates of intermedia transport. Mass balance conditions are applied to each environmental compartment (EEA, 2007).

Rates of intermedia transport are calculated using information on mass transfer coefficients, areas, deposition and resuspension rates, diffusion rates, and soil runoff rates. In this situation, it is necessary to define inputs to each medium separately, whereas in Level II only the total input rate was requested (Berding et al., 2000).

- *Level IV model* is an unsteady-state version of Level III. The obtained information refers to the influence of mode of emission on P_{ov} and LRTP, as well as to the time course of response of contaminant inventory by compartment to any time varying conditions (EEA, 2007). In addition to the four levels of sophistication of multimedia models referred to above, models may also be classed according to how

they reflect the environmental properties. Removal rates and rates of intermedia transport between environmental compartments are used to define a time dependent description of mass distribution. This makes assessment of transient effects possible, such as seasonal variations in emissions and/or climate and soil conditions. A general multimedia environmental fate model is presented by Cahill et al. (2003) for simulating the fate of up to four interconverting chemical species. It is an extension of the existing equilibrium criterion (EQC) fugacity model, which is limited to single-species assessments.

It is suggested that multispecies chemical assessments are warranted when a degradation product of a released chemical is either more toxic or more persistent than the parent chemical or where there is cycling between species, as occurs with association, disassociation, or ionization. The model is illustratively applied to three chemicals, namely chlorpyrifos, pentachlorophenol, and perfluorooctane sulfonate, for which multispecies assessments are advisable (Berding et al., 2000; Baker et al., 2000).

3.4. Particular models for POPs transport and fate

Different models are applied in order to estimate atmospheric travel distance of POPs (Mackay et al., 1992; van de Meent, 1993; Scheringer, 1996; Brandes et al., 1996; Scheringer, 1997; Bennett et al., 1998; Wania, 1998; van de Meent et al., 2000; Wania et al., 2000; Beyer et al., 2000), and those are presented in Table 3.

Several of the models listed in Table 3 are highly complex models requiring substantial computing resources to operate, with typical run times extending to several hours or even days.

3.4.1. DEHM-POP Model

DEHM-POP is developed based on the Danish Eulerian Hemispheric Model (DEHM) as a 3-D Eulerian dynamical atmospheric transport model.

DEHM was originally developed to study the atmospheric transport of sulphur into the Arctic (Christensen, 1997). DEHM has also been expanded to study the atmospheric transport of lead (Christensen, 1999), CO₂ (Geels et al., 2004) and a chemical scheme with 60 components (Frohn et al., 2002); it has been validated for these compounds (Hansen et al., 2004).

The DEHM-POP model is coupled with a weather prediction model, such as MM5v2 (Fig. 9). The model is based on the continuity equation (Eq. 18):

$$\frac{\partial q}{\partial t} = -\left(u \frac{\partial q}{\partial x} + v \frac{\partial q}{\partial y} + \sigma \frac{\partial q}{\partial \sigma}\right) + K_x \frac{\partial^2 q}{\partial x^2} + K_y \frac{\partial^2 q}{\partial y^2} + \frac{\partial}{\partial \sigma} \left(K_\sigma \frac{\partial^2 q}{\partial \sigma^2} \right) + P(t, x, y, \sigma, q) - Q(t, x, y, \sigma, q) \quad (18)$$

Table 3. Models applied to evaluate and predict the persistent organic pollutants persistence and long range transport (Mackay et al., 2001; EEA, 2007)

<i>Model</i>	<i>Reference</i>	<i>Description</i>
BENNX	Bennett et al., 1998; Bennett et al., 1999	<i>Persistence and long-range transport models</i>
CalTox	McKone, 1993	<i>Level III evaluative model developed in California, includes exposure.</i>
ChemCAN	Mackay et al., 19991	<i>A level III regional model with a database of Canadian regional environments, which can represent 24 Canadian regions, providing information on average concentrations in air, fresh surface water, soils, vegetation, fish and marine coastal water.</i>
ChemFrance	Devillers et al., 1995	<i>A level III regional model applied for 12 regions of France and France itself, for generic chemical fate. Assessment, giving information on steady state concentrations in air, water, soil and vegetation.</i>
ChemRange and SCHE	Scheringer, 1996; Scheringer, 1997	<i>Circular multi-box model for calculating persistence and long-range transport. ChemRange is an evaluative, one-dimensional steady-state (level III) model.</i>
ChemRange-CliMoChem	Scheringer et al., 2000; Scheringer et al., 2004	<i>Combines ChemRange model with a two-dimensional model with different temperatures, land/water ratios and vegetation types in different latitudinal zones.</i>
CoZMo-POP	Wania et al., 2006	<i>Regional model specifically for large drainage basins or costal environments, providing information on average concentrations in air, fresh surface water, soils, vegetation, fish and marine coastal water; it's level IV model, including up to 19 compartments, incorporating the forest, soils and fresh water bodies of the drainage basin, and a variable number of sequentially arranged marine water units</i>
DEHM-POP	Christensen, 1997	<i>A 3-D dynamical atmospheric transport model developed to describe the long-range transport. It has a horizontal resolution of 150 km x 150 km and 20 unevenly distributed vertical layers in terrain-following sigma-coordinates extending to about 18 km height.</i>
ELPOS	Beyer and Matthies, 2001	<i>A level II or III modified EUSES/SimpleBox to calculate overall persistence and characteristic travel distance, CTD in air and water (Environmental Long-Range Transport and Persistence of Organic Substances)</i>
EQC	Mackay et al., 1996	<i>Level I, II and III calculations in a single model, fixed environment, evaluative - especially for chemical to chemical comparison; it provides steady state concentrations in air, water, sediment and soil.</i>
EVN-BETR and UK-MODEL	Prevedouros et al., 2004	<i>Calculates steady and non-steady state (dynamic) mass balances of chemical contaminants from inputs describing the environmental characteristics of Europe, the physicochemical properties of the chemical of interest, and contaminant emission rates; the focus is on describing pollutant fate and transport, including transfer, transport and cycling in and between air, vegetation, soil, surface water, sediments and coastal water.</i>
G-Ciems	Suzuki et al., 2004	<i>Grid-Catchment Integrated Environmental Modeling System, is a geo-referenced multimedia and river environmental fate model system for region-scale environment; it is as an expansion of Mackay-type multimedia fate model to multi-box compartments with geo-referenced geographical resolution on GIS software and calculates multimedia environmental concentration on specified geographical environmental area.</i>
GloboPOP	Wania and Mackay, 1993; Wania et al., Wania and Mackay, 1999	<i>A zonal averaged global multimedia fate and transport model formulated in fugacity notation.</i>
HELD	Held, 2001	<i>3D version of the SCHE model</i>
HYSPLIT 4	Draxler and Rolph, 2003	<i>Hybrid Single Particle Lagrangian Integrated Trajectory atmospheric transport model by taking into account weather patterns and the chemical characteristics of the pollutant affecting atmospheric destruction and deposition; the source-to-receptor relationship can be represented; it can be applied on any scale; .</i>
MEDIA	Koziol and Pudykiewicz, 2001	<i><u>M</u>ulticompartment <u>E</u>nvironmental <u>D</u>iagnosis and <u>A</u>ssessment, a three dimensional, global scale multicompartment environmental transport model including atmosphere, soil, cryosphere and ocean compartments</i>
PENX	Pennington and Ralston, 1999; Pennington, 2001	<i>PEN1: Steady-state concentration based model, has been used by the EPA PEN2: Heuristic-based approach</i>

POPCYCLING-Baltic	Pacyna et al., 2003	A regional multimedia fate and transport model formulated in fugacity notation. Its aim is to describe the long-term, large-scale fate of persistent organic pollutants in the drainage basin and water body of the Baltic Sea
SimpleBox	van de Meent, 1993	A nested multi-media fate model of the "Mackay type" Level III regional model: the environment is modelled as consisting of a set of well-mixed, homogeneous compartments (air, two water compartments, sediments, three soil compartments and two vegetation compartments) in regional, continental and global scales
TAPL3	Beyer et al., 2000; Webster et al., 1998	Transport and persistence Level III model with user-defined environment, fixed emissions; evaluation of long range transport and persistence for chemical to chemical comparison. Lack of advection means that it is unsuitable for absolute assessments. Provides information on steady state concentrations in air, water, sediment and soil, persistence and characteristic travel distances.
VDMX	Van de Meent, 1993; Brandes et al., 1996	Persistence and LRT models based on SimpleBox
WANIA	Wania, 1998	Three compartment (air, water, soil) Level III fugacity model
WANX	Wania, 1998	WAN1: Includes global scale advective loss processes WAN2: Does not include advectons

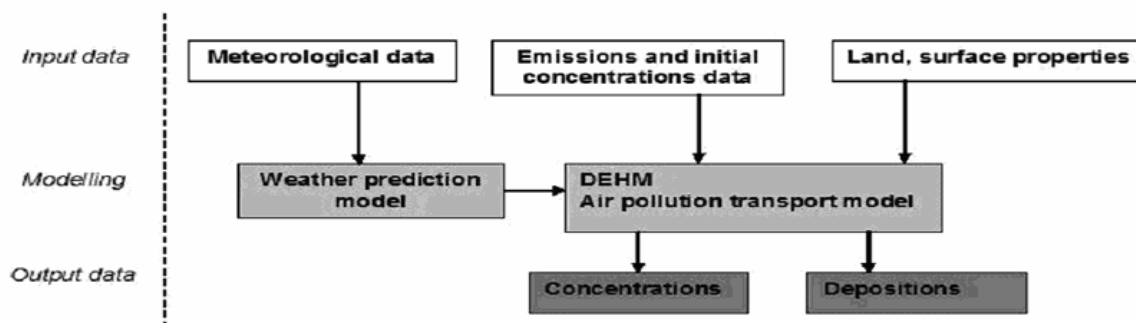


Fig. 9. Tiers of DEHM model (Hansen et al., 2004)

where q is the mixing ratio of the modeled compound, t is time, x , y , and z are the horizontal and vertical coordinates, u and v are the components of the horizontal wind field and w is the generalized vertical velocity, K_x , K_y , and K_z are the horizontal and vertical diffusion coefficients, and P and Q are sources and sinks.

Time integration of the continuity equation is done by splitting it into five sub-models, which are then solved successively in each time step.

The first sub-model is the three-dimensional advection, sub-models two to four are diffusion in the three dimensions and the fifth sub-model is sources and sinks including the special air-surface exchange processes for POPs (Hansen et al., 2004; Hansen et al., 2006). The time step is calculated using a Courant-Friedrich-Levy stability criterion on the basis of the horizontal and vertical wind fields and the horizontal boundary conditions are non-periodic (Frohn et al., 2002). The boundary conditions are free at the top of the domain (Christensen, 1997), and are given by the air-surface exchange fluxes at the ground. The model was used by Hansen et al. (2004) to study the atmospheric transport and environmental fate of the α -HCH for the years 1991–1998. Wet

deposition of α -HCH is calculated in DEHM-POP using a simple parameterization based on a scavenging coefficient formulation (Christensen, 1997), while the reaction with OH radicals is assumed to be the most important transformation of α -HCH in the atmosphere. A first order degradation rate is calculated in the model using an estimated mean residence time in the atmosphere due to reactions with OH radicals of $k_{\text{air}} = 1/(118 \text{ days})$.

The model include also equations for the change in α -HCH concentration in soil, C_s , with time, input and flux out of the soil due to evaporation of water, the air-soil gas exchange flux, the excess run-through, α -HCH biodegradation in soil.

Meteorological data and emissions, initial concentrations in the three media are used as input to the model simulations, high spatiotemporal resolution being also developed to address these issues (Hansen et al., 2006).

3.4.2. ChemRange-CliMoChem Models

The long-range transport of persistent organic pollutants (POPs) could be investigated with two multimedia box models of the global system mainly developed by Scheringer et al. (2004):

ChemRange - an evaluative, one-dimensional steady-state (level III) model, and CliMoChem - a two-dimensional model for different temperatures, land/water ratios and vegetation types in different latitudinal zones (Scheringer et al., 2000), (Fig. 10).

Modelling was applied for different case studies (Scheringer et al., 2004; Abbott et al., 2005), which aimed to obtain information on:

- (i) the effect of atmospheric aerosol particles on the long-range transport of POPs;
- (ii) the effect of oceanic deposition on the long-range transport of different PCB congeners;
- (iii) the global fractionation of different PCB congeners.

Formation or transformation of various POPs, such as DDE from DDT can be modeled, under the influences of varying environmental conditions on the physico-chemical properties and the degradation rate constants of POPs (Scheringer et al., 2004).

3.4.3. General Circulation ECHAM Model

Three dimensional atmosphere global general circulation model types (ECHAM3, ECHAM4 and ECHAM5, which differ through the horizontal resolution), were used by to study the long-range transport of POPs, and their fate in the multimedia environment (Lohmann et al., 1993; Lorenz et al., 1996).

The models comprise a fully developed atmospheric compartment, soil with a 'bucket model' hydrology, two-dimensional vegetation surface and a mixed layer ocean. The process of volatilization plays an important role in the increase of concentration of pesticides in the atmosphere away from the exploitation area. The physico-chemical properties relevant to pesticide volatilization from the soil surface are molecular mass, vapour pressure, solubility in water, adsorption and half-life values.

The model incorporates atmosphere, soil, vegetation and ocean compartments (Fig. 11). Transports only occur in the atmosphere. Soil, vegetation and the ocean mixed layer are represented as two-dimensional compartments. The parameters used to describe the intra- and inter-compartmental processes of mass exchange and conversion are listed

in Table 4 (Semeena and Lammel, 2003; Shamsudheem, 2005).

The global multicompartamental fate and long-range transport of two persistent semivolatile organic pollutants, DDT and γ -HCH were studied on a time scale of 10 years (Shamsudheem, 2005).

The scenarios were selected such as to address questions on:

- the environmental fate for the same substance but changing over time, as a function of geographic regions of entry, or
- function of mode of entry and for two substances under the same application scenario.

Semeena et al. (2005) applied the global multicompartamental model which is based on a 3-D atmospheric general circulation model (ECHAM5) coupled to 2-D soil, vegetation and sea surface mixed layer reservoirs to simulate the atmospheric transports and total environmental fate of DDT and γ -HCH.

- The global environment is predicted to be contaminated by the substances within about 2 years.

The model is based on an atmosphere general circulation model (AGCM) which had been shown to be well suited to represent the large scale atmospheric dynamics and, the hydrological and aerosol cycle, ECHAM. By addition of 2-D ground compartments, a multicompartamental model is complemented.

3.4.4. EMEP/MSCE POPs Model

A three-dimensional Eulerian transport model ASIMD (**AS**ymmetric **I**mproved **Mo**del) used for calculations of the long-range transport of persistent organic pollutants was developed in EMEP/MSCE (Munthe and Palm, 2003).

A simplified scheme of the EMEP/MSCE POPs model (Fig. 12) indicates that it is a multi-compartmental Eulerian-type advection scheme model with spatial resolution 150×150 and 50×50 km. It includes atmosphere, soil, sea water and vegetation. The model is able to assess the redistribution of POPs between these media and estimate concentration levels in them. Obviously, many uncertainties remain of concern, such as: emission rates, degradation rates and the role of sediments.

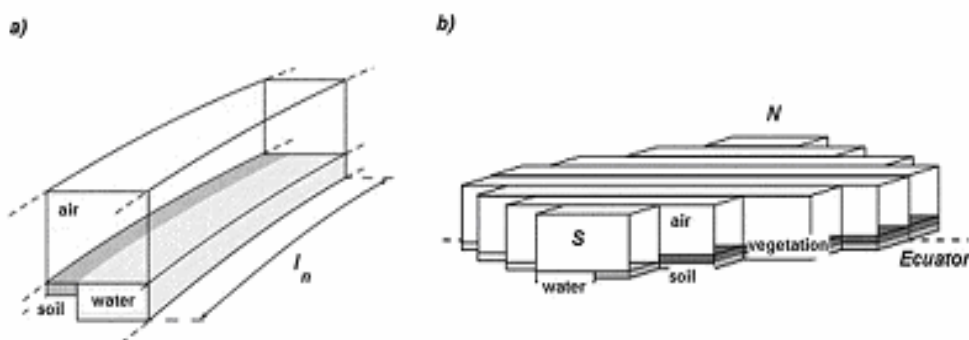


Fig. 10. Geometry of the multimedia box models ChemRange (a) and CliMoChem (b)

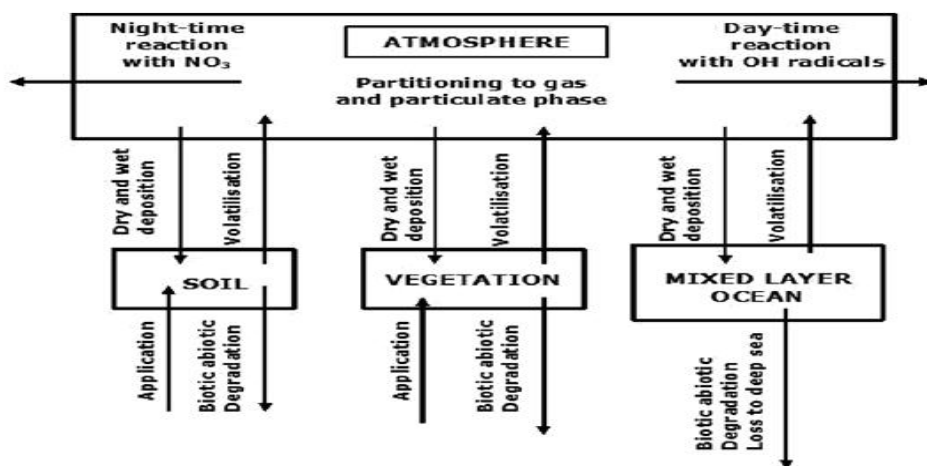


Fig. 11. Multicompartmental approach, processes involved in substance cycling (Shamsudheen, 2005)

Table 4. Intra- and intercompartmental mass exchange and conversion processes (Semeena and Lammel, 2003)

Process	Process description	Parameter representation
Partitioning between gas-phase and atmospheric particulate matter, θ	Assumed to be determined by absorption into organic matter, empirically based on the octanol-air partition coefficient (Finizio et al., 1997), K_{oa} ⁽¹⁾ prescribed spatially and temporally variable aerosol concentration	Diagnostic
Chemical degradation in the atmosphere	Reaction with hydroxyl radical, similar in the gaseous and particulate-bound state; prescribed spatially and temporally variable oxidant concentration (Roelofs et al., 1997)	Prognostic
Degradation in soil, vegetation and in ocean	Overall first-order rates, assumed to double per 10 K temperature increase ⁽²⁾	Prognostic
Partitioning in soils	Phase equilibrium in 3-phase soil system, temperature dependent, soil hydrology represented by bucket model (Roekner et al., 1996)	Diagnostic
Volatilisation from soils	Loss of gaseous substance from the soil pore space using an empirically derived rate from pesticide application studies	Prognostic
Volatilisation from vegetation	Loss of gaseous substance from plant surfaces using an empirically derived rate from pesticide application studies	Prognostic
Flux of trace substances from the ocean to the atmosphere	Two-film model (Wania et al., 2000), temperature dependent	Prognostic
Atmospheric dry deposition	Fixed deposition velocities “vdep” for gaseous molecules ⁽³⁾ and according to the particle mass (Slinn, 1982) median diameter for particulate-bound molecules	Prognostic
Atmospheric wet deposition	In-cloud and below-cloud scavenging from stratiform and convective clouds according to water solubility (gaseous molecule) and wet-scavenging coefficient, ϵ ⁽⁴⁾ (particulate-bound molecule)	Prognostic

⁽¹⁾ $c_{gas}/(c_{gas}+c_{particulate})=\theta=[1/(K_p c_{TSP})+1]^{-1}$; $\log K_p=0.55 * \log K_{oa}-8.23$; particulate mater concentration $c_{TSP}(cm^{-3})$, gas-particle equilibrium constant; K_p , temperature dependence of θ assumed to be similar to polycyclic aromatic hydrocarbons;

⁽²⁾ $k_{soil}=k_{vegetation}$; in the case of γ -HCH the contribution of the hydration reaction to the degradation in ocean water is accounted for, too;

⁽³⁾ dry deposition velocities are 1.4 and 1.38 $cm s^{-1}$ over land and 0.08 and 1.38 $cm s^{-1}$ over sea for DDT and γ -HCH, respectively;

⁽⁴⁾ $\epsilon=1.0$ and 0.1 for in-cloud and below-cloud scavenging, respectively.

3.4.5. CoZMo-POP Model

The Coastal Zone Model for Persistent Organic Pollutants (CoZMo-POP) is a non-steady state multimedia mass balance model which can describe the long term fate of persistent organic pollutants (POPs) in a coastal environment or the drainage basin of large lakes (Wania et al., 2006).

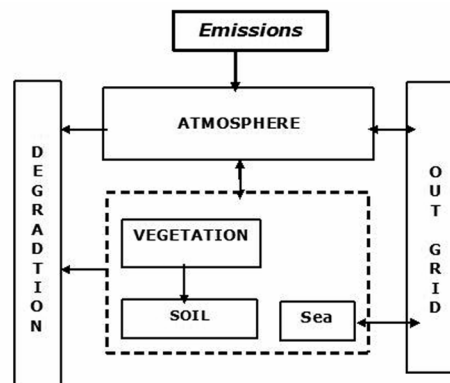


Fig. 12. Simplified scheme of the EMEP/MSCE POPs model (adapted upon Munthe and Palm, 2003)

The main focus is on quantifying the relative importance of the riverine and atmospheric pathway for delivering POPs to the aquatic ecosystem as well as to distinguish the fraction of the riverine load which is atmospherically derived vs. being emitted directly to the soils, plants and rivers of a drainage basin. The aim of the model is to describe the rates of release (and the seasonal change of this release) of POPs from the main terrestrial storage media, i.e. soil and vegetation, into the two transport media delivering POPs to the aquatic environment, i.e. atmosphere and fresh water, considering two processes (Wania et al., 2000; Wania et al., 2006):

- the two-directional exchange, or cycling, of POPs between the atmosphere and aquatic and terrestrial surfaces;
- the uni-directional run-off of chemical from soil to fresh water and further to the marine system.

Also, degradation and deposition in the atmosphere, and degradation, net sedimentation to fresh water sediments, and volatilization in the fresh water system are considered.

The model is driven by historical emission estimates and the inflow of contaminated air and water across the model boundaries. The default assumption is that all emission occurs into the atmosphere. CoZMo-POP may consist of eight boxes or compartments: atmosphere (A), forest canopy (F), forest soil (B), agricultural soil (E), fresh water (W), fresh water sediment (S), coastal water (C), and coastal sediment (L), but up to 19 compartments can be assumed within CoZMo-POP 2 model, which takes into account seasonably variable wind speeds, temperatures, canopy developments and OH radical concentrations, and allows for the definition of time-variant emission scenarios (Wania et al., 2006).

3.4.6. BETR North America Model

The Berkeley–Trent North American contaminant fate model (BETR North America) was applied by some researchers to model intermedia transfer processes (Betts, 2001; Woodfine et al., 2001; MacLeod et al., 2001; Dahl, 2002). Twenty-four ecological regions are considered in BETR model for evaluation of the North American environment, where the fate of environmental contaminants is described using a seven-compartment fugacity model including a vertically segmented atmosphere, vegetation, soil, freshwater, freshwater sediments and coastal water (MacLeod and Mackay, 2004). Contaminants can be transported between adjacent regions of the model in the atmosphere and in flowing rivers and near-shore ocean currents.

Contaminant fluxes between all regions and environmental compartments are constant at steady state, such that emissions are balanced by removal processes for the entire continental environment (MacLeod and Mackay, 2004). The emission rate used as input to the BETR North America model represents primary emissions only (Toose et al., 2004). Revolatilization of chemical from the terrestrial and aquatic surfaces is calculated by the

mass balance equations in the model. A transfer efficiency (TE) was calculated as a percentage from the steady-state solution with Eq (19) (MacLeod and Mackay, 2004):

$$TE = \frac{\text{rate of contaminant flux to the target ecosystem (kg/year)} \times 100}{\text{emission rate in the source region (kg/year)}} \quad (19)$$

The BETR North America model uses first-order kinetics to describe all transport processes. If a competing degrading reaction with half-time t_R is introduced in the atmosphere in all regions of the model, the fraction of chemical that survives to deposit to the Lakes (F), relative to a perfectly persistent chemical will be (Eq. 20):

$$F = \frac{t_R}{t_R + t_A} \quad (20)$$

where t_A is the time or half-life to the transport and deposition process that represents the atmospheric residence time between emission and deposition, while t_R is a competing degrading reaction half-time.

The model allowed for identification of combinations of physico-chemical properties that favour efficient transport and deposition to the Great Lakes, and estimated the time-scale required. Also, it was found that for an ecosystem to become contaminated from distant sources of chemicals two processes must occur: (i) transport from the source region and (ii) deposition to the target ecosystem. Efficient transport and deposition to specific ecosystems is only possible for chemicals with certain combinations of partitioning properties and sufficient environmental persistence to survive the journey (MacLeod and Mackay, 2004).

A regionally segmented multimedia fate model for the European continent has been developed to provide fate and behaviour information for POP compounds on a continental scale, built on the regionally segmented BETR North America model structure. The European continent is described by a $5^\circ \times 5^\circ$ grid, leading to 50 regions together with 4 perimeter boxes representing regions buffering the European environment¹¹. Each zone comprises seven compartments including: (i) upper and lower atmosphere, (ii) soil, (iii) vegetation, (iv) fresh water and sediment and (v) coastal water. Inter-regions flows of air and water are described, exploiting information originating from GIS databases and other georeferenced data.

3.4.6. POPCYCLING-Baltic Model

The POPCYCLING-Baltic model is a MFTM that aims to distinguish and quantify the environmental pathways of selected persistent organic pollutants (POPs) in the Baltic Sea environment, which are inaccessible to measurements (Wania et al., 2000; Pacyna et al., 2003; Wania et al., 2001) (Fig. 13).

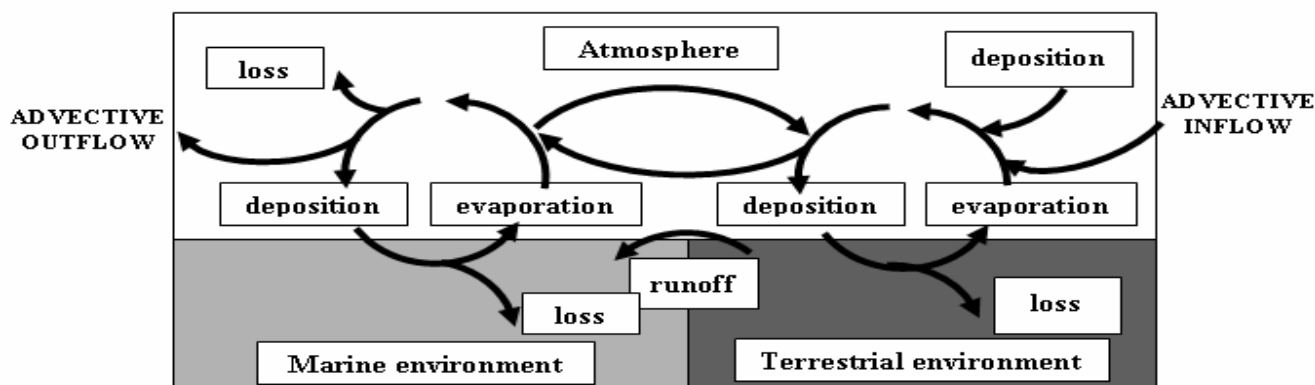


Fig. 13. Representation of POPCYCLING model of POPs migration from the terrestrial environment to the marine environment via atmosphere and rivers (adapted upon Wania et al., 2000)

In particular, it aims to estimate the fractions of the POPs currently present in various parts of that environment, which are derived from (i) recent releases within the drainage basin, (ii) past emissions in the drainage basin and (iii) contaminated air masses being advected into the area (Wania and Mackay, 1999)

Within the model region, a main focus is on the relative importance of the riverine and atmospheric pathway for delivering POPs to the marine ecosystem of the Baltic Sea. The model was developed as part of the POPCYCLING-Baltic project funded by the European Union, a detailed description of the project has been provided by Wania and McLachlan, (2001). It traces its origin to the QWASI model (Mackay et al., 1983) as well as the generic model (Mackay et al., 1992).

The focus of the model evaluation was on the absolute concentration levels, on the spatial and temporal concentration patterns in various media and biota, and on atmospheric depositional in the Baltic Sea fluxes to the drainage basin (Fig. 13).

4. Concluding remarks

The application of modelling to estimate the environmental fate of chemicals at local and global scales proved to be a very valuable tool because of the impossibility to measure the chemical concentrations in various environmental media and locations.

Atmosphere can be considered the most favorable environmental component for a rapid mass flow of persistent organic pollutants, with a great potential to transport them over long distances.

A large number of models are now available for predicting environmental concentrations of chemicals in single or multiple environmental media. Because a wide range of factors determines the fate of chemicals in the environment, especially persistence and mobility, they have to be included as input data in the model. For this reason, models range from highly

complex spatially and temporally resolved models capable of predicting small scale variations in chemical concentrations in one or more environmental media, to simpler screening tools that predict concentrations averaged over wider spatial and temporal domains.

Acknowledgements

This paper has been elaborated within the National Research, Development and Innovation Program, PNCDI - II, IDEI Program, Project ID_595, contract 132/01.10.2007.

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