Annex A

DESCRIPTIONS OF THE MODELS

This Annex contains the descriptions of POP models taking part in the intercomparison study.

A.1. HYSPLIT 4

Paul Bartlett

Persistent organic pollutants (POPs) emit into the atmosphere from near and distant sources, transport and deposit to land and marine surfaces, and enter the food chain through water, flora and fauna. Remedial policy must be directed to the reduction of emissions from the sources, but knowledge of source emissions, pollutant measurements, and distance alone is insufficient information to distinguish the sources most responsible for contamination. Numerical modeling of pollutant transport and environmental fate from individual sources to ecological receptors can close this information gap by taking into account weather patterns and the chemical characteristics of the pollutant affecting atmospheric destruction and deposition, but only when source-to-receptor information is preserved in the results. The approach we use with the HYSPLIT (Hybrid Single Particle Lagrangian Integrated Trajectory) atmospheric transport model can accomplish these objectives. HYSPLIT is a three dimensional Lagrangian model developed by Roland Draxler's team at the National Oceanic and Atmospheric Administration (NOAA). When simulated puffs enter new grids, they are split and follow their own trajectory. Meteorological data is interpolated between date time periods. HYSPLIT was adapted at CBNS (originally by Mark Cohen, presently at NOAA) for the persistent organic pollutants.

The (HYSPLIT) enables us to preserve source-to-receptor identity while simulating atmospheric transport, destruction and deposition of hypothetical emission puffs, from each source point to target receptor areas. The source-to-receptor relationship can be represented, as an output of HYSPLIT, by the ratio deposited to the receptor from one unit emission from the source, the atmospheric transport coefficient (ATC). When ATCs are mapped, the effect of weather patterns and pollutant chemical properties on transport can be evaluated. The product of the ATC and the quantity emitted is the amount deposited to the receptor from that source (ATC * Source Quantity Emitted = Receptor Deposition). Relative contributions of each source to receptor deposition can be determined and ranked. We are able to use this approach because we are modeling single-hop transport (no re-suspension; one-way deposition) and since the pollutants are transported in trace amounts, interactive effects between the pollutant is insignificant. HYSPLIT algorithms use pollutant chemical properties to estimate vapor-particle partitioning, destruction (hydroxyl radical and photochemical reactions), dispersion and deposition.

This method is made computationally feasible for a large number of sources and congeners by the use of a spatial and congener interpolation program, TRANSCO, which applies and emission inventory to a set of geographically represented standard point source-to-receptor HYSPLIT computer runs.

HYSPLIT has been used by CBNS for source-to-receptor transport modeling of HCB, dioxin, PCBs and atrazine.

A.2. EVN-BETR and UK-MODEL

Andrew Sweetman

Introduction: A fugacity-based, contaminant distribution model was developed at Lancaster University in order to simulate the fate of Persistent Organic Pollutants (POPs) in the entire European Continent. The model 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. GIS software was used to better describe geo-referenced data regarding landcover, water flows, soil organic carbon content, precipitation and temperature information.

Model segmentation: Europe was divided into 54 regions using a 5x5 degree grid. A total of 50 cells describe the main bulk of the European continent with four further perimetric boxes, namely: the Atlantic, Mediterranean, Eurasian and Arctic Boxes.

Flow balance: Inter-regional flows of air in the upper and lower atmosphere, fresh and coastal water connect the individual regional environments. The movement of air and water in both directions across all regional boundaries, thus, is described with the help of five matrices of volumetric flow rates. The five flow matrices have been compiled with the aid of Geographical Information System (GIS) analysis of available hydrological and meteorological data. Air-flow balances have been extrapolated from data gathered about wind speeds and directions, notably from the BADC trajectory service. The flow matrix for air specifies the 5-year average flow rates (m^3/h) of air between all connected regions in the upper and lower air compartments.

Mass balance equations: There are seven mass balance equations describing the fate of POPs in each region, and therefore 378 equations make up the 54 European regions. This system of seven equations and the seven unknown fugacities have been solved analytically using linear and matrix algebra algorithms.

Case studies: We are planning to model the environmental fate of a wide range of POPs, such as Polychlorinated Biphenyls (PCBs), Dibenzo-p-dioxins and Furans (PCDD/Fs), Polycyclic Aromatic Hydrocarbons (PAHs), Polybrominated Diphenyl Ethers (PBDEs) and organochlorine pesticides (OCs). Most of these chemicals are still emitted in considerable amounts into the European environment and constitute a growing hazard. Several emission scenarios will be tested for different chemicals and regions. Pollutants lying in the extreme ends of the physicochemical properties' range will be assessed in terms of persistence and transport potential. Emission estimates have already been compiled for a number of chemicals and the model's output will be tested against measurement data. The ultimate aim is to validate our model with the results of the PASAE (Passive Air Sampling Across Europe) campaign, Lancaster University and our collaborators have just concluded.

A.3. ELPOS

Michael Matthies

The model EUSES-SimpleBox 1.0 (a level III multimedia model) was expanded to calculate the overall persistence and the characteristic travel distance in air and water (long-range transport potential). The new model is called “Environmental Long-range transport and Persistence of Organic Substances” model (ELPOS). Both criteria describe inherent substance properties that can be used for screening, ranking, and chemical assessment. Both criteria account for the intermedia transfer and intramedia degradation and are independent of the chemical amount emitted. The criteria were calculated for 65 current-use pesticides, 23 industrial chemicals, and 21 persistent organic pollutants (POPs). The sensitivity analysis shows that the parameter sensitivity heavily depends on the characteristics of the chemicals as well as assumptions with respect to environmental conditions. The ranking of the chemicals can be affected if uncertainty of the parameters is taken into account, e.g. by using 90^{th}-percentiles instead of mean values. The criteria were assessed in relation to a reference scenario with respect to gas-particle partitioning, photo-oxidative degradation, degradability in water and soil (field and laboratory measurements), rain rate and possible degradation on foliage. The model was modified to account for temperature variations within a range of 5° to 30°C. The overall persistence as well as the characteristic travel distance are highly dependent on temperature. While the overall persistence always increases when temperature drops, the characteristic travel distance can increase or decrease, which is caused by opposing processes. The so-called cold condensation effect could be explained by these temperature dependent calculations. The characteristic travel distance was compared to monitoring data of pesticides in rain water, yielding a rough agreement between measurements and model results. A comparison of model results to observed spatial concentration gradients was possible for some PCB congeners, leading to the same chemical ranking in both cases. The 65 current-use pesticides (with the two exceptions Dicofol and Chlorothalonil) exhibit a lower persistence and long-range transport potential than typical POPs (such as hexachlorobenzene or DDT). The pesticides dicofol and chlorothalonil are therefore evaluated more in depth.

A.4. ChemRange and CliMoChem

Martin Scheringer and Fabio Wegmann

Compartments, coverage and resolution. Both models are multi-compartment box models and cover the global system, see Fig. A.1.Compartments included are soil, oceanic surface water and tropospheric air in the case of ChemRange and, in addition to these three, vegetation and vegetation soil in CliMoChem. ChemRange is a spatially homogeneous one-dimensional circular system (a "loop") while CliMoChem is a two-dimensional model containing a flexible number (typically: 20 to 30) latitudinal zones with different temperatures and compartment volumes (the vertical extension is not counted as a dimension here). CliMoChem does not have a spatial resolution in east-west direction; in north-south direction, the spatial resolution is given by the number of zones, *n* (the width of a zone is equal to 180/*n* degrees latitude).

ChemRange is a steady state model without temporal resolution. The temporal resolution of CliMoChem is between 1 month and 1 year.

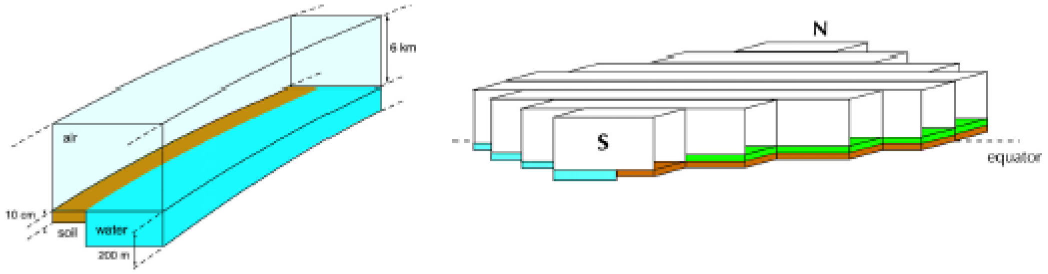


Fig. A.1. *Geometry of the global multi-compartment box models ChemRange (left) and CliMoChem (right)*

Processes and parameterization

Both models include:

1) degradation processes in all compartments, described as first-order processes;
2) transport in oceanic surface water and tropospheric air, described as macroscopic eddy diffusion with diffusion coefficients from measurements of large-scale oceanic diffusion and tracer experiments in the troposphere;
3) exchange processes between the compartments:
   - diffusive exchange of chemicals in the gas phase (gaseous deposition, volatilization)
   - dry deposition with aerosol particles of particle-bound chemicals
   - wet deposition with aerosol particles
   - rain washout of chemicals in the gas phase
   - deposition to the deep sea of chemicals associated with suspended particles in the ocean water.
   - runoff from soil to ocean water
   - leaf fall from the vegetation to the soil (only CliMoChem)

The diffusive processes are based on two-resistance models for the phase transfer of the chemicals. The advective processes are based on global and long-term averages of rain rates, particle fluxes etc. Association with particles is calculated from the chemicals' *K*OA (air) and *K*OC (water) partition coefficients.

In CliMoChem, degradation processes and processes influenced by partition coefficients are temperature dependent.

Chemicals. Both models can only be applied to non-polar organic chemicals, not to ionizing compounds or heavy metals. Interaction or conversion of different chemical species is not included in general. With ChemRange, the formation of transformation products such as DDE from DDT can be modeled. A similar extension is planned for CliMoChem.

Model input. ChemRange requires five chemical specific input parameters (degradation rate constants for soil, ocean and air as well as Henry's law constant and octanol-water partition coefficient). If possible, the partition coefficients should be internally consistent. If available, the chemical-specific input parameters should be chosen for a temperature around 280K because 298K is too high as a global average.

In addition to the chemical-specific parameters, several environmental parameters are required: concentration of aerosol particles, average aerosol deposition rate, rain rate, concentration of suspended particles in the oceanic surface water, organic carbon export from the surface ocean, fractions of air and water in the soil, several transfer velocities for two-film models, soil runoff rate.

CliMoChem requires degradation rate constants in soil, ocean water, air and vegetation and two partition coefficients (HLC and *K*OW). All of these parameters must be available as functions of temperature (mostly based on activation energies and enthalpies of phase transfer). Degradation rate constants in air should be second-order constants for reaction with OH radicals.

Environmental parameters required for each latitudinal zone are: fractions of ocean and land, fractions of three types of vegetation (grassland, deciduous and coniferous forests), monthly averages of air temperature at 2m height, OH radical concentrations as functions of temperature. In addition, the same environmental parameters as in ChemRange are required (transfer velocities, aerosol concentrations etc.). Further parameters are leaf fall rates and vegetation growth rates as functions of time and additional vegetation parameters (leaf surface index, fraction of organic matter in leafs, fraction of retained rainwater).

Emission scenarios. ChemRange can be used with any combination of continuous sources into one or more compartments and at different locations. Typically, a single point source is used because such a simple scenario is consistent with the evaluative and generic character of the model.

CliMoChem requires a single pulse emission or any combination of pulse emissions (spatially and temporally resolved) as emission scenario. Single pulse emissions are useful for evaluative calculations; temporally and spatially resolved emissions are required for calculations of absolute concentration levels.

Model results. ChemRange yields steady-state concentrations, mass fractions and mass flows of the chemical in each medium, the media-specific and overall persistence (calculated as residence times), and the spatial range in each medium (calculated as the 95^{th} interquantile distance of the spatial concentration distribution).

The CliMoChem output contains concentrations, mass fractions and mass flows in and between all compartments and latitudinal zones as functions of time. In addition, persistences, spatial ranges, cold condensation potentials are derived from the basic output.

A.5. CAM/POPs – Canadian Model for POPs

Sunling Gong

This model consists of four major components: (1) an active aerosol module (CAM), (2) a surface exchange module for PCBs between water and atmosphere and between soil and atmosphere (Emission), (3) a module to partition PCBs between gas and aerosol phases (Atmospheric Processes) and removal processes and (4) a transport module for tracers (Atmospheric Transport) as shown in Fig. A.2.

The Canadian Aerosol Module (CAM) developed for treating size segregated aerosols in both air quality and climate models [*Gong et al.*, 2003] simulates the mass and number distributions of five major aerosols: sea-salt, sulphate, soil dust, black carbon and organic carbon. CAM provides aerosol surface areas and removal rates for aerosol-bound PCBs

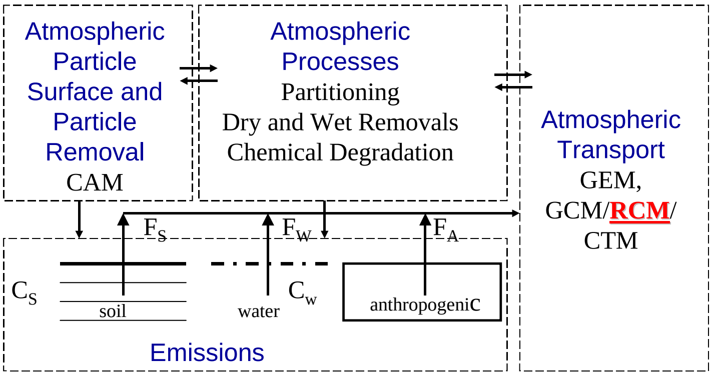


Fig. A.2. *Framework of POP model for simulating PCBs*

Air-water exchange of PCBs was treated with a method by *Liss and Slater* [1974] who asserts that a chemical must diffuse through layers of water and air in series at rates characterized by mass transfer coefficients k_w (water side) and k_a (air side). The dimensionless Henry's Law constant, K_{aw}, gives the ratio of the concentrations across the air-water interface. The soil-exchange model from [*Jury*, 1989; *Jury et al.*, 1983] was used for the calculating the soil PCB fluxes to the atmosphere. PCB/aerosol partition was simulated with the Junge-Pankow Partition [*Junge*, 1977; *Pankow*, 1987]. The PCB amount partitioned between gas and aerosol phase depends the aerosol surface area available for adsorption (m^2 aerosol/m^3 air), the liquid-phase saturation vapour pressure of pure compound (Pa). Atmospheric degradation of PCBs by OH has also been implemented.

A.6. G-Ciems

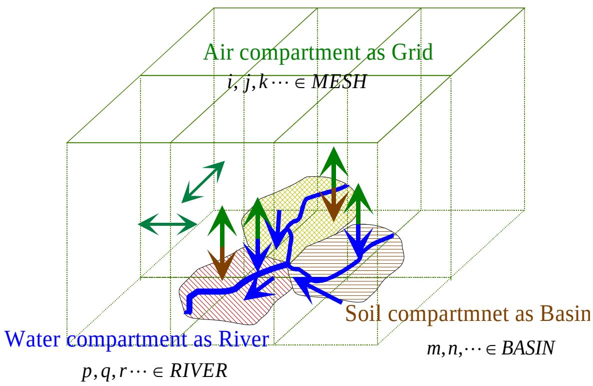
Noriyuki Suzuki

General description. Grid-Catchment Integrated Environmental Modeling System (G-CIEMS, tentative name) is a geo-referenced multimedia and river environmental fate model system for region-scale environment. The multimedia model is as an expansion of Mackay-type multimedia fate model to multi-box compartments with geo-referenced geographical resolution on GIS software. The model calculates multimedia environmental concentration on specified geographical environmental area.

Basic modeling items. Model consists of the following geographical/data items. Each item has relevant information like geographical/hydrological/meteorological and chemical datasets on database format.

Air: grid structure with layers, now 5x5 km size. River: GIS line items representing real geographical river. Soil: GIS polygon items including 7 land use categories and 1 forest vegetation compartment. Average size of soil polygon is around 10km^2 at present. Lake: GIS polygon item, Coastal area and Coastal sea.

Transport formulation. Inter-media transport between media are formulated based on basic transport phenomena (diffusive and advective processes). Transport between geographical items with different shape are formulated using projective area between the items.



User interface. The model is developed on GIS-based integrated information system as the data management system and the user interface, based on Microsoft Access database.

POPs modeling ability. The model can calculate the gross input and output between target area and outer boundary for each transport pathway. This is not directly show a specific transport index but could be a real estimation and reference of the transport potential of the chemicals within/outside the region.

A.7. INERIS

Regis FARRET

INERIS -French Institute for Industrial Risks and Environment- is a public institute which brings its scientific experience mainly to the Ministry of Environment. The Chronic Risks Division of INERIS covers experience in toxicology, ecotoxicology, modelisation of transfers in the environment, analytical chemistry. Through collaboration between these skills we developed our expertise in Risk Assessment, both at the local level – atmospheric emission of a factory, study of polluted sites– and at the national or international level, for supporting governmental actions.

Risk Assessment of chemical substances are carried out in the frame of the application of the European Directive 93/67 EEC (for new substances) and the Regulation 1488/94 (for existing substances). Therefore, following the Technical Guidance Document, INERIS has experience in the multi-media model EUSES, which includes a local and a regional model.

INERIS is also using other "generic" multimedia models like ELPOS (close to EUSES) and ChemCan. The results are not used directly for supporting national regulation for POPs, but they may be included in specific studies at a national level : For example I am presently performing a multi-criteria study aiming at prioritising pesticides considering their possible impact through atmospheric transport.

Besides, INERIS takes part in international programmes, such as:

- the UN-ECE Convention on Long-Range Transboundary Air Pollution.INERIS is the French National Focus Centre for Intagrated Assessment Modelling ; we also take part in the Task-Force on Measurement and Modelling and in several Task-Forces in the Working Group on Effects. We are developing together with the Laboratory of Dynamic Meteorology (Paris 6 University) the regional model CHIMERE with similar principles to EMEP (West) models. It is not a multi-media model, but particles are being included presently and future developments for including POPs and metals may be undertaken.
- the OECD Task-Force on Environmental Exposure Assessment. Here data, scenarios and models are discussed and exchanged, and INERIS is especially involved in the expert group on exposure reporting.
- the OECD expert group on multi-media modelling.
- the UNEP programme of regional evaluation of PTS for the Mediterranean region.

We also have to mention here that the multi-media model ChemFrance was developed in France by *Bintein and Devillers* [1996]. This model allows to choose between several options, each of them accounting for environmental conditions of a specific region of France. However this model is not used for national risk assessments, which are led in the frame of the European Union, as mentioned here above.

A.8. Globo-POP

Knut Breivik

The Globo-POP model is a zonally averaged global multimedia fate and transport model formulated in fugacity notation. Ten climate zones are distinguished based on a climatic classification of the world. The atmosphere is divided into four vertical layers. The top of the four vertical layers corresponds to pressure levels of 83.5, 50, 11 and 1 kPa or 1.3, 5, 16 and 33 kilometers of altitude. Vertical and horizontal atmospheric advective transport velocities and macro-diffusivities are defined with a monthly resolution, as are temperatures and the concentrations of OH radicals. Within each latitudinal zone, the Earth's surface is represented by two soil (agricultural and non-cultivated soil), a fresh water, a fresh water sediment and a surface ocean compartment (depth of 200 m). Chemical fate processes considered include: equilibrium phase partitioning between sub-compartments, advective and diffusive transport between compartments (including meridional transport in the atmosphere and ocean), first order degradation in each compartment (second order in atmosphere between vapor phase chemical and OH radical), transfer to the deep sea and fresh water sediment burial. Description of these processes follows standard practice in fugacity-based multimedia fate and transport models, but the impact of temperature on partitioning and degradation is accounted for through the use of activation energies and internal energies of phase transfer. Non-steady state mass balances are formulated over all 90 compartments of the model and solved step-wise by finite difference approximation. The model is programmed in Visual Basic, can be run from any Windows platform and downloaded free-of-charge from www.utsc.utoronto.ca/~wania. Various stages of the evolution of that model are documented in various publications [*Wania and Mackay*, 1993, 1995, 1999, 2000]. Using historical emission estimates the Globo-POP model has been applied to simulate the global fate of α-HCH [*Wania and Mackay*, 1999; *Wania et al*. 1999] and several PCB congeners [*Wania and Daly*, 2002] over the time frame of several decades. Using hypothetical scenarios it has also been used to assess the long range transport behaviour of persistent organic chemicals using the concept of Arctic Contamination Potential [*Wania and Dugani*, 2003].

A.9. POPCYCLING-Baltic

Knut Breivik

The POPCYCLING-Baltic model is 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. A product of the EU-project POPCYCLING-Baltic project [*Pacyna et al*. 1999], a full description of the model is given in *F.Wania et al*. [2000]. Its 85 well-mixed compartments represent the atmosphere (4 boxes), the aquatic (26 water and 25 sediment boxes) and terrestrial environment (10 forest canopy, 10 forest soil and 10 agricultural soil boxes). Chemical fate processes considered include: equilibrium phase partitioning between sub-compartments, advective and diffusive transport between compartments, first order degradation in each compartment (second order in atmosphere between vapor phase chemical and OH radical), and fresh water sediment burial. Description of these processes follows standard practice in fugacity-based multimedia fate and transport models, but the impact of temperature on partitioning and degradation is accounted for through the use of activation energies and internal energies of phase transfer. Long term averaged monthly atmospheric advection rates between the four atmospheric compartments (Fig. A.3.A) were derived from a atmospheric transport model. Based upon a complete steady-state mass balance of water (Fig. A.3.B and C) and particulate organic carbon (Fig. A.3.D), a non-steady state contaminant mass balance equation is formulated over each of the 85 compartments and solved step-wise by finite difference approximation. The model is programmed in Visual Basic, can be run from any Windows platform and downloaded from www.utsc.utoronto.ca/~wania.

The model has been evaluated [*Breivik and Wania*, 2002a] and applied [*Breivik and Wania*, 2002b] to derive a quantitative understanding of the historical behavior of α- and γ-hexachlorocyclohexane from 1970 to 2000.

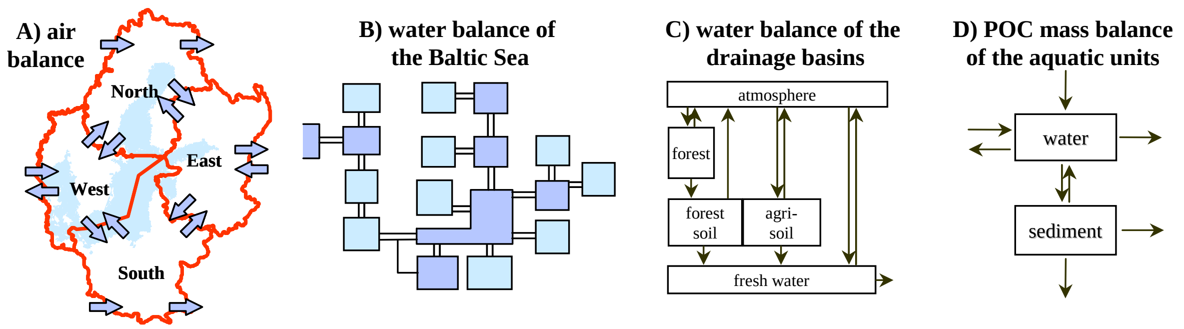


Fig. A.3. *Major components of the POPCYCLING-Baltic model*

A.10. MEDIA (MEDIA - Multicompartment Environmental DIagnosis and Assessment)

Janusz Pudykiewicz

<table>
<tr><td>Type of the model</td><td colspan="3">Three dimensional, global scale multicompartment environmental transport model including atmosphere, soil, cryosphere and ocean compartments</td></tr>
<tr><td rowspan="5">Description of compartments taken into account in the model</td><td>Atmosphere</td><td colspan="2">▪ Three-dimensional atmospheric transport model written in the spherical Gal-Chen terrain following coordinates, horizontal resolution can vary between 0.5 x 0.5 and 2 x 2 degrees, vertical resolution is variable with 15-25 levels
▪ Advection is solved using the semi-Lagrangain algorithm
▪ Diffusion is solved using a semi-implicit Crank-Nicholson scheme</td></tr>
<tr><td>Soil</td><td colspan="2">▪ Column soil model based on advection diffusion equation which is used to simulate water flow and the transport of chemicals in porous medium, typical resolution is of the order of 10 to 15 levels; the first level is located at the surface, the last corresponds to the soil depth
▪ Transport of water and chemical species in soil is simulated using Multidimensional Positive Definite Advection Transport Algorithm MPDATA</td></tr>
<tr><td>Cryosphere</td><td colspan="2">The equilibrium partition model</td></tr>
<tr><td rowspan="2">Ocean</td><td>Static version</td><td>The values of the concentration of chemical species in ocean are kept constant</td></tr>
<tr><td>Dynamic version of the ocean</td><td>The modified version of High-Latitude Exchange Interior Diffusion-Advection (HILDA) model described originally by Siegenthaler and Joos [1992]</td></tr>
<tr><td rowspan="5">Description of processes included in the model</td><td>Atmosphere</td><td colspan="2">▪ Mixing in vertical direction based on the similarity theory
▪ Horizontal and vertical advection
▪ Scavenging by clouds and precipitation
▪ Decay of chemical species with the rate evaluated as a function of temperature and a solar zenith angle
▪ Exchange of mass between atmosphere and soil. The exchange is represented by the lower boundary condition at the interface between atmosphere and soil.</td></tr>
<tr><td>Soil</td><td colspan="2">▪ Convective and diffusive transport of chemicals (in three phases) in soil
▪ Exchange of mass between the soil system and the atmosphere. The exchange is represented by the lower boundary condition at the interface between soil and atmosphere.
▪ Water flow in soil taking into account the forcing at the surface associated with evaporation and precipitation
▪ Decay of chemical species with a rate evaluated as a function of temperature</td></tr>
<tr><td>Cryopshere</td><td colspan="2">The equilibrium partition of organic compounds in a layer of ice (or snow) takes place between two phases: adsorbed on the surface of ice particles and mixed with interstitial air.</td></tr>
<tr><td rowspan="2">Ocean</td><td>Static version</td><td>Exchange of pollutant with the atmosphere based on Henry law</td></tr>
<tr><td>Dynamic version</td><td>Advection in the surface layer and exchange of mass with deep water reservoir, exchange of pollutant with the atmosphere</td></tr>
<tr><td>Chemicals included in the simulation</td><td colspan="3">alpha-HCH and gamma-HCH (lindane)</td></tr>
<tr><td rowspan="3">Model data base</td><td>Meteorological data</td><td colspan="2">The NCEP/NCAR 40-year reanalysis project [Kalnay et al., 1996]</td></tr>
<tr><td>Soil and Cryosphere data</td><td colspan="2">Global data sets for land-atmosphere models [Sellers et al., 1995]</td></tr>
<tr><td>Oceanographic data</td><td colspan="2">Ocean Circulation Experiment [WOCE, 1998]</td></tr>
<tr><td>Usage data</td><td>Seasonal usage inventory</td><td colspan="2">The information about usage of HCH was obtained from: Li et al [1996]</td></tr>
<tr><td>Model evaluation</td><td>Evaluation was perforedd for 1993 and 1994</td><td colspan="2">Model evaluation was performed for the selected stations in the Arctic</td></tr>
<tr><td>Future work</td><td>Improve model parameterizations</td><td colspan="2">Improvement of the wet scavenging scheme. Additionally we plan also to perform the simulation of environmental cycling of other chemical species. The time frame of the future work with the model is to be determined</td></tr>
<tr><td>Model status</td><td>Research model</td><td colspan="2">MEDIA was developed between 1997 and 2000. The model was used for the assessment of the global scale transport of HCH on the grid with resolution of 2 x 2 degrees. Subsequently it was applied for the evaluation of the transport of lindane from Canadian sources (on a finer grid with the resolution of 1 x 1 degree). Description of the model: Koziol and Pudykiewicz, 2001</td></tr>
</table>

Explanation of acronyms:

MEDIA – **M**ulticompartment **E**nvironmental **DI**agnosis and **A**ssessment
MSC – **M**eteorological **S**ervice of **C**anada
NCEP – **N**ational **C**enter for **E**nvironmental **P**rediction
NCAR – **N**ational **C**enter for **A**tmospheric **R**esearch
WOCE – **W**orld **O**cean **C**irculation **E**xperiment

A.11. ADOM-POP

Gerharg Petersen

A comprehensive mercury modelling system using the Eulerian reference frame of the Acid Deposition and Oxidant Model (ADOM) has been developed under the Canada-Germany Science & Technology Co-operation Agreement and applied within various projects funded by the European Commission to study the regional transport and deposition fluxes of atmospheric mercury species [*Petersen et al*., 2001]. As a first step in extending this model system for POPs the cloud mixing, scavenging, chemistry and wet deposition modules of ADOM, originally designed for regional-scale acid precipitation and photochemical oxidants studies have been restructured to accommodate recent developments in atmospheric processes of benzo[a]pyrene (B[a]P). A stand-alone version of these modules referred to as the Tropospheric Chemistry Module (TCM) was designed to simulate the meteorology and chemistry of the entire depth of the troposphere to study cloud mixing, scavenging and physico-chemical processes associated with precipitation systems that generate wet deposition fluxes of B[a]P).

After comprehensive testing under different environmental conditions the TCM has been implemented into the full ADOM-POP model. Within the constraints of the available computer resources and input data, this model incorporates an up-to-date understanding of the detailed physical and chemical processes in the atmosphere. The vertical grid consists of 12 unequally spaced levels between the surface and the top of the model domain at 10 km. The model is run for a grid cell size 55 by 55 km (High Resolution Limited Area Model (HIRLAM) grid) over a 76 by 76 domain.

The transport and diffusion module uses a sophisticated cell-centered flux formulation solver for the 3-dimensional advection-diffusion equation. Dry deposition is modelled in terms of a deposition velocity for gaseous and particle associated mercury species, which is calculated as the inverse of the sum of the aerodynamic, deposition layer and surface canopy resistance. The mass transfer, chemistry and adsorption component of the model has a potential for incorporating numerous species and reactions including mass transfer, aqueous phase and gas phase chemical reactions and adsorption processes on particles. However, this component is restricted at present to the mass transfer of B[a]P from ambient air to cloud droplets and back evaporation after cloud dissipation.

The cloud physics module simulates the vertical distribution of mercury species in clouds. Two different modules are incorporated: one describes stratus (layer) clouds and the other simulates cumulus (convective) type clouds. One or the other or a combination (cumulus deck embedded in a stratus cloud) is used in the calculation depending on the characteristics of the precipitation observed.

The meteorological input data needed by ADOM are three-dimensional fields of wind speed, wind direction, pressure, temperature, relative humidity, vertical velocity and vertical diffusivity, and two-dimensional fields of surface winds, surface pressure, surface air temperature, friction velocity, Monin-Obukhov length, mixing height, cloud base and top height, amount of cloud cover and the amount of precipitation at every one hour model time step. These data sets are derived diagnostically using the weather prediction model HIRLAM.

The geophysical data include files for 8 land use categories (i. e. deciduous forest, coniferous forest, grassland, cropland, urban, desert, water and swamp) and 12 soil categories. The database also includes information on terrain height and the growing season. This geophysical data affects meteorology, dry deposition processes and air-surface exchange of gaseous mercury species.

Initial and boundary conditions are needed for all advected species in the model. Due its relative short atmospheric residence time and due to anthropogenic emissions occurring near the ground concentrations B[a]P is allowed to decrease with height to a value of about 10 % of the boundary value at the model top. In the absence of reliable measurement data, a very low initial value of $1.5 \cdot 10^{-3}$ ng/m^3 at ground level is used for both B[a]P initial and boundary concentrations.

A.12. Danish Eulerian Hemispheric Model (DEHM-POP)

Kaj Mantzius Hansen and Jesper H. Christensen

The Danish Eulerian Hemispheric Model (DEHM) is a 3-D dynamical atmospheric transport model initially developed to describe the long-range transport of sulphur into the Arctic [*Christensen*, 1997]. The model has since been further developed to describe the atmospheric transport of lead and CO_2, and the model results have been thoroughly validated for these compounds [*Christensen*, 1997; *Christensen*, 1999; *Geels et al*., 2001]. The recent development has been to include a scheme with 54 chemical species (e.g. O_3, NH_3, and NO_x) and 110 reactions, mercury, and persistent organic pollutants (POPs) in the model.

The model 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. It covers the majority of the northern hemisphere, and is driven by meteorological data from the numerical weather prediction model MM5V2 [*Grell et al*., 1995]. It is possible to run the model with a two-way nest covering the EMEP region with a resolution of 50 km x 50 km. A full model description can be found in *Christensen* [1997] and *Frohn et al*. [2002].

A description of the exchange processes between the land/ocean surfaces and the atmosphere is included in the model to account for the multi-hop transport of POPs. The environmental parameters for the surface compartments and the parameterisation of the air/surface exchange processes have been adapted from a multimedia box model [*Strand and Hov*, 1996]. The processes described by DEHM are atmospheric advection, diffusion and wet deposition, air/surface gas exchange and degradation in the three media.

The model has been used to study the atmospheric transport of α-HCH for the years 1991 to 1998. Input to this model run were emissions of α-HCH from 1990 [*Li et al*., 2000] and a background concentration in water interpolated from measurements from the late 1980s and early 1990s. The model results are currently being evaluated against measured data.

A.13. SimpleBox

Dirk van de Meent

“SimpleBox is a nested multi-media fate model of the “Mackay type”. The environment is modeled 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. The model takes emission rates and rate constants for transport and transformation of micropollutants as input and computes steady-state concentrations as output. SimpleBox is a generic model in the sense that it can be customised to represent specific environmental situations. The default settings of the regional and continental scales of the model are set to match the EU procedures for evaluation of substances…

SimpleBox follows the Mackay concept of sequentially carrying out the modelling procedure at different stages of conceptual sophistication or “levels” (Mackay, 1991). In SimpleBox, the non-equilibrium, steady-state computation (level 3) and the quasi-dynamic non-equilibrium, non-steady-state computation (level 4) can be performed. Unlike the fugacity approach as adopted by Mackay, computation of mass flows and concentration levels in SimpleBox is done with concentration-based "piston velocity" type mass transfer coefficients [m.s-1]… As is done in the Mackay models, transfer and transformation phenomena are treated as simple pseudo first-order processes.” - cited from [Brandes et al., 1996].

A.14. MSCE-POP

Victor Shatalov and Mikhail Fedyunin

Here we present a short description of EMEP/MSCE-POP model. This model is a multicompartment one describing processes in and exchange between basic environmental compartments (atmosphere, soil, seawater, vegetation). Spatial resolution of the model is 150 km x150 km. At present hemispheric version of the model with resolution 2.5ºx2.5º is under development.

Model structure. Fig. A.4 presents the structure of the model showing environmental media and processes included.

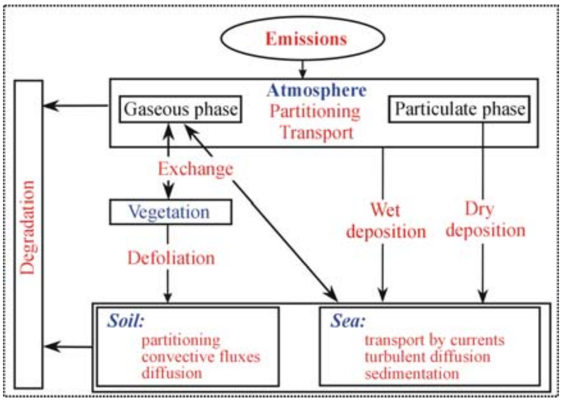


Fig. A.4. The scheme of the multicompartment transport model MSCE-POP

In particular, apart from atmospheric transport the model takes into account the transport of pollutants by sea currents. This can be essential for the pollutants, which tend to be accumulated in the marine environment (e.g. HCB and γ-HCH). Vegetation is considered to describe their transport from vegetation to soil, forest litter as an intermediate media between vegetation and soil was introduced.

Model parameterizations are elaborated for PAHs (B[a]P, B[b]F and B[k]F), HCHs (γ-HCH), PCBs, HCB, and PCDD/Fs. At present there exists a modification of the model for evaluation of B[a]P and PCDD/Fs transboundary transport by country-to-country scheme with resolution 50 km x 50 km.

In the model, such media as the atmosphere, soil, and sea are separated vertically into a number of layers to describe the vertical transport of a pollutant in question. To describe variability of soil and vegetation properties in the horizontal direction the corresponding land-use and leaf area index information is taken into account.

Time scale. Due to large accumulation capacities of soil and sea compartments and long periods required for establishing equilibrium, for correct evaluation of POP environmental pollution levels long-term calculations are to be performed. This can be illustrated by plots of long-term dynamics of PCB accumulation in media (Fig. A.5) calculated for the period from 1970 to 2010 under the assumption that emissions from 1995 are constant.

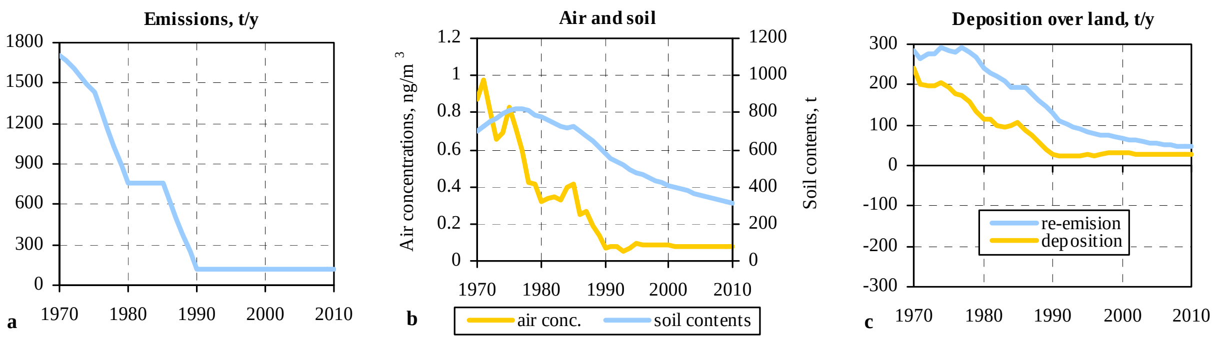


Fig. A.5. Long-term dynamics of emissions (a), air concentrations and soil content (b), and re-emission and particle deposition over land (c) for the period from 1970 to 2010 under the assumption that emissions are constant beginning from 1995

From these plots it is seen that contamination levels in soil are determined by a long-term process and can support pollution of other media for a long time period.

Model reliability. At present the discrepancies between measured and calculated data for all the pollutants considered are within the order of magnitude. More detailed information on comparison of calculated data against measurements can be found in [*Shatalov et al.,* 2000, 2001, 2002, 2003].

Detailed description of regional version of MSCE-POP model is published in MSC-E Report 4/2000 (vol.2) and of hemispheric version – in MSC-E Report 8/2002 [*Malanichev et al.,* 2002]. Recent model modification can be found in MSC-E Report 4/2003 [*Shatalov et al.,* 2003]; see also MSC-E web site: www.msce@msceast.org.