

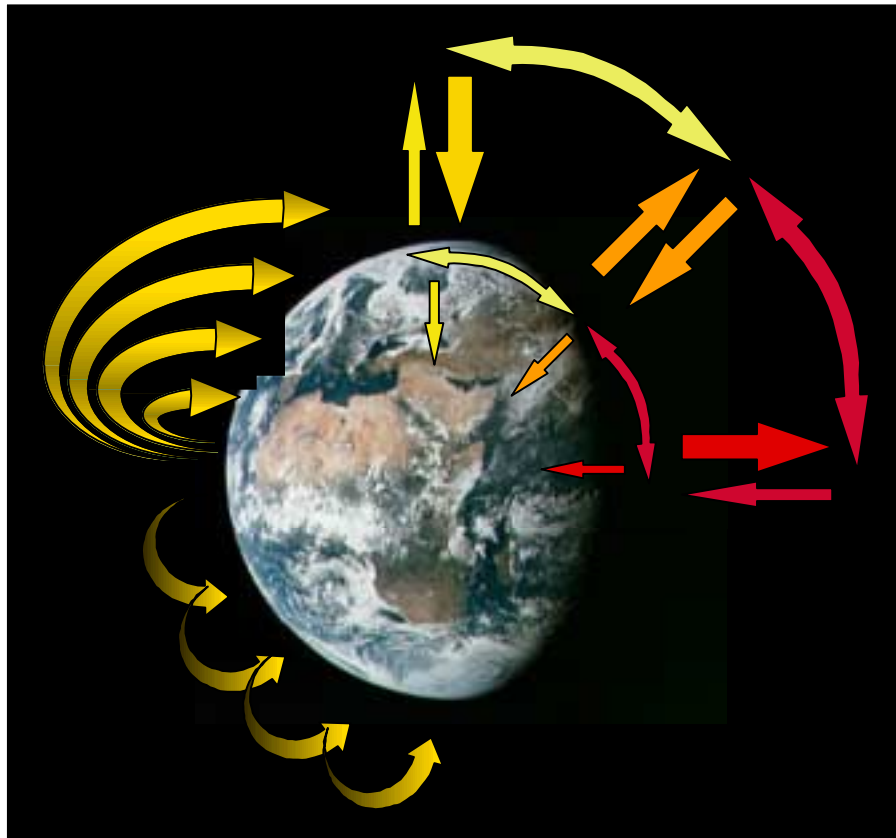
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# The Global Distribution Model

A Non-Steady State Multicompartment Mass Balance Model of the Fate of  
Persistent Organic Pollutants in the Global Environment

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Version 1.0 (July 2000)



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## Introduction

This document is NOT a detailed description of the global distribution model. The interested reader can find such a description in a number of journal publications, namely:

- Wania, F., D. Mackay **1993**. An approach to modelling the global distribution of toxaphene: A discussion of feasibility and desirability. *Chemosphere* **27**, 2079-2094.
- Wania, F., D. Mackay **1995**. A global distribution model for persistent organic chemicals. *Sci. Total Environ.* **160/161**, 211-232.
- Wania, F., D. Mackay, Y.-F. Li, T.F. Bidleman, A. Strand **1999**. Global chemical fate of  $\alpha$ -hexachlorocyclohexane. 1. Evaluation of a global distribution model. *Environ. Toxicol. Chem.* **18**, 1390-1399.

Another publication describes the use of the model for simulating the global fate of particular chemical, namely  $\alpha$ -hexachlorocyclohexane:

- Wania, F., D. Mackay **1999**. Global chemical fate of  $\alpha$ -hexachlorocyclohexane. 2. Use of a global distribution model for mass balancing, source apportionment, and trend predictions. *Environ. Toxicol. Chem.* **18**, 1400-1407.

As will be obvious from reading these publications, the global distribution model has undergone significant modifications and changes prior to this first public release of the computer program. The computer program version 1.0 reflects essentially the model version described in Wania et al. (1999), i.e. it includes ten climatic zones and a two-dimensional treatment of the global atmosphere. Most of the equations, and environmental input parameters are listed in Wania and Mackay (1995). However, there have been a number of updates and changes to the model and its input parameters. This document serves the dual purpose to document these modifications and to give brief instructions on how to use the computer program.

For an introduction into the basics of multi-compartmental chemical fate modelling see:

- Mackay, D. **1991**. *Multimedia Environmental Models: The Fugacity Approach*. Chelsea, MI: Lewis. 257 pp.

The global distribution model evolved from the GENERIC model, a description of which can be found in:

- Mackay, D., S. Paterson, W.Y. Shiu **1992**. Generic models for evaluating the regional fate of chemicals. *Chemosphere* **24**: 695-717.

## Acknowledgements

The development of this model has been financially support by the Natural Sciences and Engineering Research Council (NSERC) of Canada and the Northern Contaminants Program of the Department of Indian Affairs and Northern Development of the Canadian federal government. We further acknowledge the help of Dr. Asbjørn Strand of Norway for his assistance in incorporating a two-dimensional description of the global atmosphere into the model.

## Modifications to the Global Distribution Model

The modifications to the global distribution model are mostly related to facilitating the use of the model for simulating the global fate of a user-specified chemical. This requires the possibility to input the characteristics of a chemical in terms of its phase partitioning, degradation potential and release into the environment. A number of assumptions are required, among the most important of which are:

- The partitioning characteristics of the chemical in the environment can be approximated by the partitioning between the surrogate phases air, pure water and n-octanol.
- The degradation characteristics of the chemical in the environment can be described with first order kinetics, and the only zonal parameter that can influence degradation rates is phase temperature (exception: degradation in the atmosphere is additionally controlled by OH radical concentration).

### *Physical-Chemical Properties and their Temperature Dependence*

The input of the following physical-chemical properties for the substance of interest is thus required:

- Two out of the following three dimensionless equilibrium partition coefficients at the reference temperature  $T_{ref} = 25\text{ °C}$

Octanol-water partition coefficient  $\log K_{OW}$

Air-water partition coefficient  $\log K_{AW}$

Octanol-air partition coefficient  $\log K_{OA}$

The third partition coefficient is calculated from the other two using:

$$\log K_{OW} = \log K_{AW} + \log K_{OA}$$

- Two out of the following three heats of phase transfer in units of J/mol:

Heat of phase transfer between octanol and water  $\Delta H_{OW}$

Heat of phase transfer between air and water  $\Delta H_{AW}$

Heat of phase transfer between air and octanol  $\Delta H_{OA}$

The third heat of phase transfer is calculated from the other two using:

$$\Delta H_{OW} = \Delta H_{AW} + \Delta H_{OA}$$

When choosing these chemical properties, it is imperative to keep in mind that this model was developed for persistent organic pollutants, i.e. a fairly select group of chemicals that are highly apolar, persistent and have intermediate volatility. As will be pointed out shortly, the model relies on a few empirical regressions that relate the partitioning between water and natural organic matter in soils, sediments and suspended solids with that between water and octanol (Seth et al., 1999), and that between air and atmospheric aerosols with that between air and octanol (Finizio et al., 1996). The model should thus only be used for substances for which these empirical relationships are valid.

From the input parameters, partition coefficients  $K_{AW}$  and  $K_{OA}$  at the environmental phase temperature  $T$  are calculated using the following relationships:

$$\log K_{AW}(T) = \log K_{AW}(T_{ref}) + \frac{\Delta H_{AW}}{2.303 \cdot R} \left( \frac{1}{T_{ref}} - \frac{1}{T} \right)$$

$$\log K_{OA}(T) = \log K_{OA}(T_{ref}) + \frac{\Delta H_{OA}}{2.303 \cdot R} \left( \frac{1}{T_{ref}} - \frac{1}{T} \right)$$

Temperature dependent Henry's law constants in units of Pa m<sup>3</sup>/mol and octanol-water partition coefficients are then derived using:

$$H(T) = R \cdot T \cdot K_{AW}(T)$$

$$K_{OW}(T) = K_{AW}(T) \cdot K_{OA}(T)$$

### ***Phase Partitioning in the Atmosphere***

Gas-particle partitioning in the atmosphere is calculated with a  $K_{OA}$ -based approach instead of the classical Junge-Pankow model, eliminating the need to specify a contaminant vapour pressure. The calculation of a Z-value for the entire aerosol  $Z_Q$  is based on an empirically derived regression between measured air-particle partition coefficients and the octanol-air partition coefficient  $K_{OA}$  (Finizio et al., 1997).

$$Z_Q(T) = 3.5 \cdot K_{OA}(T) \cdot Z_A(T) = 3.5 \cdot K_{OA}(T) / (R \cdot T)$$

### ***Phase Partitioning in the Aqueous Systems***

Z-values for particulate organic carbon in suspended solids, sediments and soils is calculated using the following empirical relationship (Seth et al., 1999):

$$Z_{POC}(T) = Z_W(T) \cdot K_{POC}(T) = Z_W(T) \cdot 0.35 \cdot K_{OW}(T) = 0.35 \cdot K_{OW}(T) / H(T)$$

### ***Description of Degradation Processes***

D-values for degradation processes in fugacity terms are calculated as the product of a Z-value, the compartment volume and a first-order degradation rate  $k$  in units of h<sup>-1</sup>. All degradation rates are calculated as function of the compartment temperature.

#### **DESCRIPTION OF ATMOSPHERIC DEGRADATION**

The reaction of the chemical in the gas phase with hydroxyl radicals is assumed to be the only significant degradation pathway for POPs in the atmosphere (Atkinson, 1996). The degradation rate  $k_{RA}$  is calculated as a function of seasonally variable atmospheric OH radical concentrations [OH] and temperatures T:

$$k_{RA} = k_{RAref} \cdot [OH] \cdot 3600 \frac{s}{h} \cdot e^{\frac{A_{EA}}{R} \left( \frac{1}{T_{ref}} - \frac{1}{T} \right)}$$

The contaminant-specific degradation rate  $k_{RAref}$  of vapor phase chemical with OH radicals at the reference temperature 25°C in units of cm<sup>3</sup>/(molecules·s) and the activation energy  $A_{EA}$  of that reaction in J/mol are model input parameters. The OH radical concentrations are a pre-supplied model parameters based on information in Rodriguez et al. (1992). The D-value is then calculated multiplying the reaction rate  $k_{RA}$ , the gas phase Z-value and the phase volume:

$$D_{RA} = k_{RA} \cdot V_A \cdot Z_A$$

## DEGRADATION IN OTHER MEDIA

Degradation rates in other compartments are calculated as a function of temperature using a contaminant-specific degradation rate  $k_{RXref}$  at the reference temperature 25°C and an activation energy  $A_{EX}$ . This degradation rate is assumed to include all degradation processes that the POP can undergo, including biodegradation, hydrolysis, and photolysis.

$$k_{RX} = k_{RXref} \cdot e^{\frac{A_{EX}}{R} \left( \frac{1}{T_{ref}} - \frac{1}{T} \right)}$$

Assuming that the degradation proceeds in all sub-phases of a compartment at the same rate, the D-values are calculated using the bulk-phase Z-values:

$$D_{RX} = k_{RX} \cdot V_X \cdot BZ_X$$

The model requires the input of a degradation half life at the reference temperature 25°C in hours for each of the environmental media, as well as an activation energy (i.e. temperature dependence slopes) in J/mol. Please note that the model is unsuitable for very short-lived chemical species for which the assumption of homogeneity within fairly large areas, which is inherent in compartmental box models, does not apply.

### ***Inputting Emission Data***

The global distribution model is a non-steady state model designed for the simulation of global distribution phenomena on the time scale of years to decades. It thus requires emission estimates covering such time scales. The primary emission information, which is read from file, are annual release rates for each climate zone in tons/year.

Emission is allowed to occur into the lowest air layer, agricultural soils and fresh water. The default assumption is that all emission occurs into the atmosphere. The user can specify fractions, which distribute the annual emission rates read from file among the compartments air, agricultural soil, and fresh water. Obviously, these fractions have to add up to one. These fractions are assumed fixed in time, but are allowed to vary from one zone to another.

The default assumption is that the annual emissions are distributed evenly across the entire year. However, it is possible to modulate this by superimposing a sinusoidal function on the emission rates. The user can specify the amplitude (as a fraction of the mean) and the month of maximum emission. Again, these parameters are fixed from year to year, but can vary between the various regions.

Finally, the model allows the user to specify a time-invariant scaling factor, which facilitates the modelling of contaminant mixtures. If the annual release rates are for a mixture of POPs (e.g. an Aroclor mixture), the scaling factor could be the fraction of that mixture, which is a certain constituent (e.g. a PCB congener or homologue).

From these input parameters, the model calculates time variant emission rates into 30 compartments in units of mol/h, which are parameters in the mass balance equations.

### ***Particle Settling Rate in the Ocean***

Whereas most environmental parameters are as listed in Wania and Mackay (1995), the particle settling rates in the surface oceans were updated. The model derives a contaminant loss rate to the deep sea by calculating a contaminant concentration on particulate matter within the surface ocean and applying a particle settling rate  $U_{9ocean}$  in units of m/h (Wania and Mackay 1995). Zonally variable settling rates were derived from information in Falkowski et al. (1998). Using the global map of photosynthetic carbon export to the deep sea in that publication, we estimated the

average carbon flux in each of the ten zones of the model, and from these deduced particle settling rates in m/h (Table 1).

**Table. 1** Oceanic particle settling rates derived from information in Falkowski et al. (1998).

<b>N-hemisphere</b>	<b>Polar</b>	<b>Boreal</b>	<b>Temperate</b>	<b>Subtropic</b>	<b>Tropic</b>
Average OC export in g OC/m <sup>2</sup> /a	75	55	121	44	33
Particle settling rate in m/h	2.25·10 <sup>-8</sup>	1.65·10 <sup>-8</sup>	3.60·10 <sup>-8</sup>	1.32·10 <sup>-8</sup>	1.00·10 <sup>-8</sup>
<b>S-hemisphere</b>	<b>Polar</b>	<b>Subpolar</b>	<b>Temperate</b>	<b>Subtropic</b>	<b>Tropic</b>
Average OC export in g OC/m <sup>2</sup> /a	5	33	55	55	33
Particle settling rate in m/h	0.15·10 <sup>-8</sup>	1.00·10 <sup>-8</sup>	1.65·10 <sup>-8</sup>	1.65·10 <sup>-8</sup>	1.00·10 <sup>-8</sup>

## Setting-up and Starting the Computer Program

The computer program with the Global Distribution Model is designed to run on personal computers with operating systems Windows 95 or higher. The model with a user-friendly interface is written in MicroSoft Visual Basic Version 5.0, but does not require the user to own a copy of that model development software. Much of the operation of the computer program should be self-explanatory, so this “manual” will only provide some guidance on how to get started.

In order to set up the program on your hard disk, run the set-up program by selecting “Run from the Windows “start” menu, browsing to “setup.exe”, clicking the OK button and following the instructions on the screen. After this sequence, the program should be successfully installed and ready to operate on your computer. If you experience the following error message: “Runtime error 13”, you will have to change the number setting on your computer from , (*comma*) to . (*dot*) because otherwise the program will not work. This can easily be done by following the sequence: *Start menu>Settings>Control Panel>Regional Settings>Number>Decimal Symbol*.

Within the directory that contains the executable program file “globopop.exe”, the set-up program creates four subdirectories named “\chemdata”, “\emitdata”, “\envdata” and “\results”. These directories, whose location and name should not be changed, contain auxiliary files, some of which can be modified or substituted by the user (see below).

The model is started by either going to *Start Menu>Programs>GloboPOP*, or by using *Start>Run* and then browsing to the “globopop.exe” file. While loading the program an introductory picture is displayed (Figure 1).

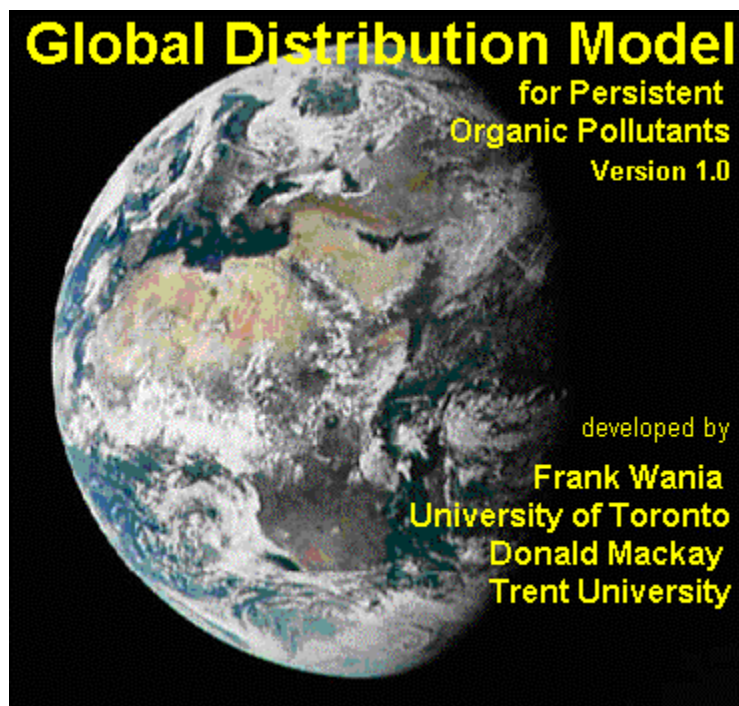


Figure 1



After a few seconds the main window of the computer program is displayed.

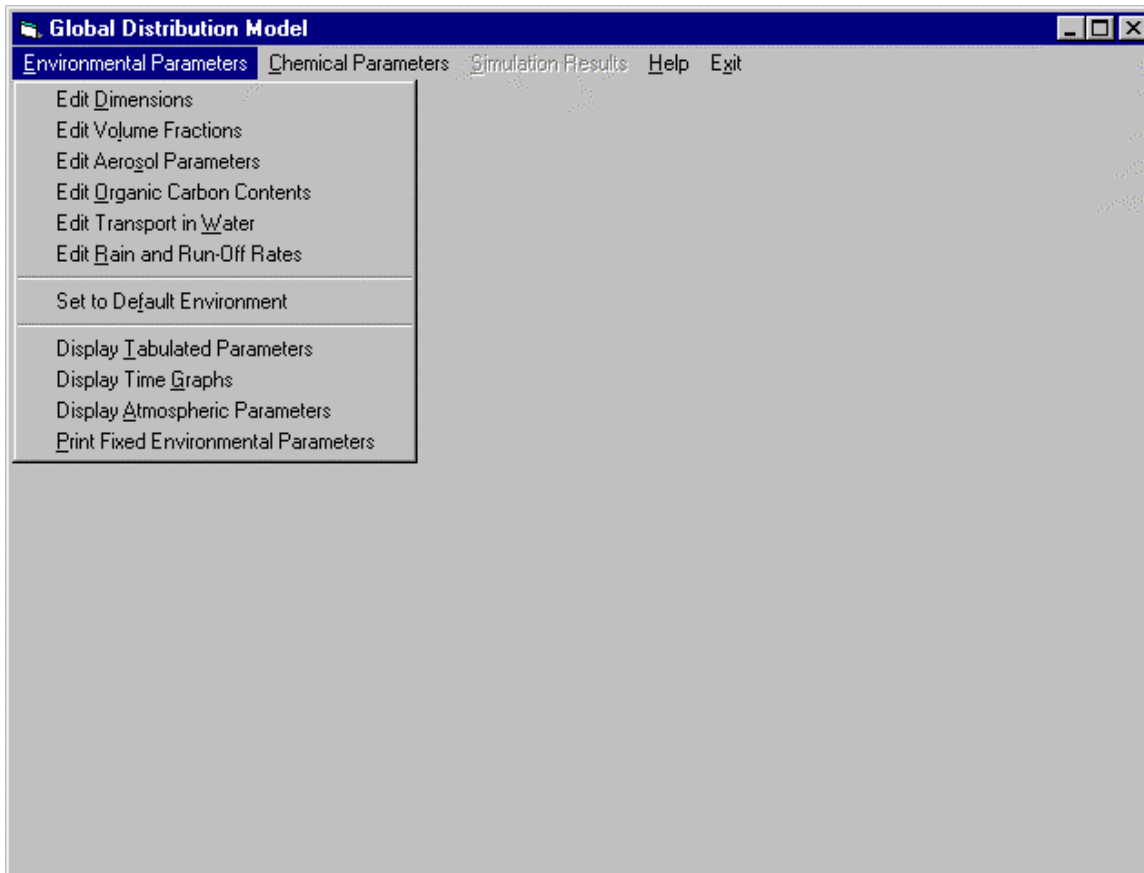


Figure 2

The model takes the user through three major, sequential steps of data processing:

1. Editing and Displaying Environmental Parameters (before selecting a chemical)
2. Selecting and Displaying Chemical Parameters (after selecting a chemical)
3. Displaying Model Results (after selecting run conditions and running a non-steady state simulation)

Each of these three steps is represented by a menu title in the menu bar of the main window (Figure 2). Initially some menu options are disabled, because they require the completion of preceding steps.

## Selecting and Displaying Environmental Input Parameters

The model requires a large number of parameters describing the global environment. When starting the model, default values are selected for these environmental parameters, and the user has the option to proceed directly to the next step of data processing by selecting a chemical of his/her choice (see below). Alternatively, the user has the possibility to:

1. edit these environmental input parameters
2. return the environmental input parameters to their default value
3. display and examine the environmental input parameters in tables and graphs.

### Editing Environmental Input Parameters

The user may wish to modify the default values for the environmental parameters, for example in order to test the sensitivity of a model result to a particular parameter, or if a better estimate becomes available. The procedure for editing environmental parameters is different for parameters that are fixed in time versus those that can fluctuate with season.

#### TIME-INVARIANT INPUT PARAMETERS

Six forms, one example of which is shown in Figure 3, allow the user to change environmental input parameters. These forms are displayed by selecting one of the first six menu options in the menu called <Environmental Parameters>.

Zones	Area Fractions		Depths in m				
	fresh water coverage of land area	cultivated fraction of land area	cultivated soil	uncultivated soil	surface ocean	fresh water	fresh water sediment
N-Polar	0.035	0.0001	0.02	0.02	200.0	20.0	0.05
N-Boreal	0.05	0.01	0.1	0.05	200.0	20.0	0.05
N-Temperate	0.05	0.15	0.2	0.05	200.0	20.0	0.05
N-Subtropic	0.025	0.1	0.2	0.05	200.0	20.0	0.05
N-Tropic	0.03	0.05	0.2	0.05	200.0	20.0	0.05
S-Tropic	0.05	0.05	0.2	0.05	200.0	20.0	0.05
S-Subtropic	0.025	0.1	0.2	0.05	200.0	20.0	0.05
S-Temperate	0.025	0.15	0.2	0.05	200.0	20.0	0.05
S-Subpolar	0.005	0.0001	0.02	0.05	200.0	20.0	0.05
S-Polar	0.005	0.0001	0.02	0.02	200.0	20.0	0.05

Figure 3

The values are simply edited by typing a modified value in the respective textbox. The model does NOT perform a check of the reasonability of the selected value, and it is the responsibility of the user to assure consistent and sensible parameter choices. Changes to the input parameters can not be stored permanently and upon restarting the program, the parameters are returned to their default values.

## TIME-VARIANT INPUT PARAMETERS

A number of environmental input parameters are functions of time, namely temperature, sea ice cover, atmospheric hydroxyl radical concentrations and atmospheric transport parameters. These data are read as monthly values from files upon starting the computer program and can not be edited as readily as the parameters that are fixed in time. Namely, in order to edit these parameters the user has to open and edit the respective data files prior to starting the program. All of these files are located in subdirectory “\envdata”, are in ASCII format and can for example be edited in NOTEPAD. When editing these files, it is important that the location, name and the formatting of the files stays the same. It is recommended that the user makes copies of the original data files before making changes.

“TK.txt”, “W.txt” and “KZ.txt” have each a total of 120 lines, i.e. a line for each month and zone. The sequence is as follows

```
Jan: N-Polar
Jan: N-Boreal
...
Jan: S-Polar
Feb: N-Polar
...
```

Each line in “TK.txt” has five five-digit temperature entries, giving temperature values in Kelvin in the sequence: sea water surface, air layer 1, air layer 2, air layer 3, air layer 4 (no delimiter).

The lines in “W.txt” and “KZ.txt” contain the vertical atmospheric advection velocities and eddy diffusivities between the atmospheric layers in m/h and m<sup>2</sup>/h, respectively. Positive values of w indicate downward, negative values upward advection. Each line has three 13-digit entries in the sequence: layer 1/layer 2, layer2/layer 3, and layer 3/layer 4.

“V.txt” and “KY.txt” contain the horizontal atmospheric advection velocities and eddy diffusivities between the zones in m/h and m<sup>2</sup>/h, respectively. Positive values of v indicate northbound, negative values southbound advection. Each of these files has 108 lines with four 13-digit entries in the sequence: layer 1, layer 2, layer 3, and layer 4.

```
Jan: N-Polar/N-Boreal
Jan: N-Boreal/N-Temperate
...
Jan: S-Subpolar/S-Polar
Feb: N-Polar/N-Boreal
...
```

“SIC.txt” contains the fractions of sea ice coverage on a total of 12 lines, one for each month. Each line has three four-digit entries, in the sequence N-Polar, S-Subpolar, S-Polar (no delimiter).

“OHconc.txt” contains monthly OH concentrations in each of the 40 atmospheric compartments. Each of the 48 lines has ten nine-digit entries giving the concentration of OH radicals in molecules/cm<sup>3</sup> in the sequence: N-Polar, N-Boreal, N-Temperate, ... S-Polar.

```
Layer 1-Jan
Layer 1-Feb
...
Layer 1-Dec
Layer 2-Jan
...
```

### Returning Environmental Input Parameters to their Default Value

Selected groups of time-invariant environmental parameters that have been edited in one of the six forms as described above can be returned to their default values by clicking the respective command button on these forms. By selecting the menu choice *<Set to Default Environment>* under the menu option *<Environmental Parameters>* all environmental input parameters are returned to default values. They are also automatically returned to their default value when the program is started again. A permanent change of the time-invariant parameters is only possible in the source code.

### Displaying Environmental Parameters in Tables and Graphs

The forms displaying environmental parameters are called up by using various options under the menu option *<Environmental Parameters>*. These forms allow the user to inspect the effect of changing and editing environmental input parameters on the environmental parameters derived from these.

#### DISPLAYING ENVIRONMENTAL PARAMETERS IN TABULAR FORM

By selecting the heading *<Display Tabulated Parameters>* a form (Figure 4) is displayed that allows the user to inspect the monthly temperature and ice cover values in a table. Also, calculated phase residence times can be displayed. The month for which parameters are shown is selected by using the arrow buttons in the upper left corner of the form.

	Polar	Boreal	North Temperate	North Subtropic	North Tropic	South Tropic	South Subtropic	South Temperate	Subpolar	Polar	Globe
Air layer 1	-18.40	-4.00	8.600	18.20	26.40	26.75	21.10	13.60	4.300	-7.30	-
Air layer 2	-29.70	-20.45	-10.35	0.650	10.25	10.55	5.600	-1.75	-11.45	-21.00	-
Air layer 3	-51.95	-48.65	-44.40	-35.65	-25.55	-24.80	-30.05	-36.10	-41.40	-43.55	-
Air layer 4	-63.95	-58.20	-57.65	-61.90	-66.70	-66.20	-61.20	-55.05	-46.05	-38.80	-
Sea water	-0.50	1.250	6.700	17.35	26.30	26.80	22.00	14.50	5.900	-1.50	-
Agri-soil	-18.40	-4.00	8.600	18.20	26.40	26.75	21.10	13.60	4.300	-7.30	-
Uncult-soil	-18.40	-4.00	8.600	18.20	26.40	26.75	21.10	13.60	4.300	-7.30	-
Freshwater	-2	-2	8.600	18.20	26.40	26.75	21.10	13.60	4.300	-2	-
Sediment	-2	-2	8.600	18.20	26.40	26.75	21.10	13.60	4.300	-2	-
Total Zone	-	-	-	-	-	-	-	-	-	-	-

Figure 4

#### DISPLAYING ATMOSPHERIC PARAMETERS

By selecting the heading *<Display Atmospheric Parameters>* a form (Figure 5) is displayed that allows the user to inspect a variety of atmospheric parameters, including temperature, volume, density, aerosol content, and air residence time for the forty atmospheric compartments. Also, the atmospheric transport parameters  $v$ ,  $w$ ,  $K_y$  and  $K_x$ , which are read from file (see above), as well as the total air flows which are calculated from these can be displayed. Again, it is possible to display the values for each month by using the arrow buttons.

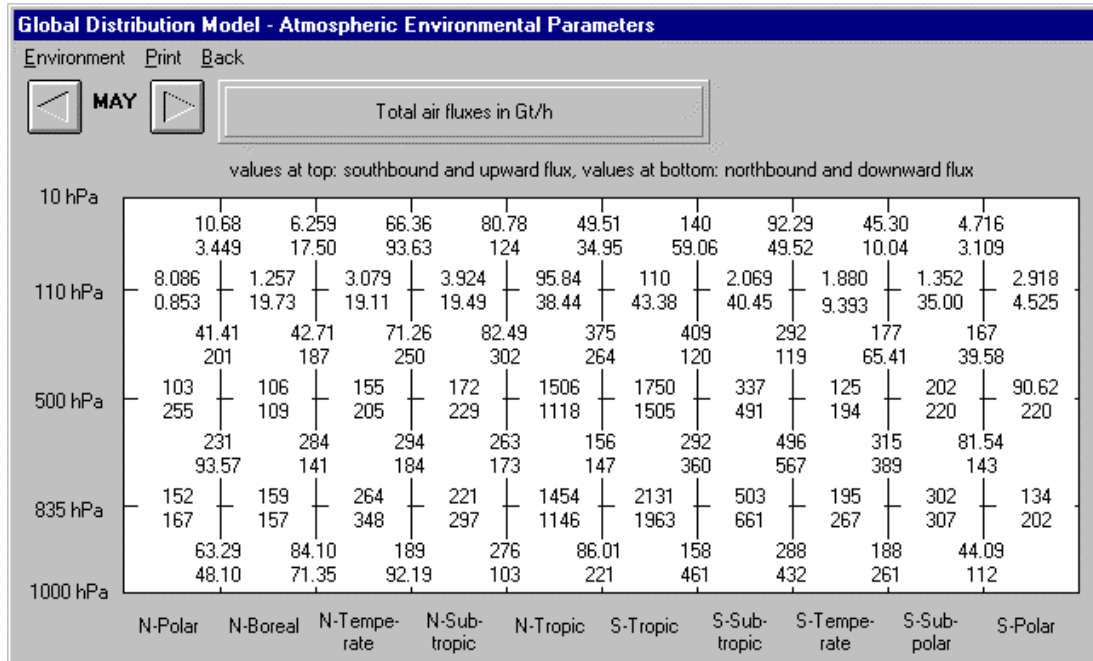


Figure 5

DISPLAYING TIME-VARIANT ENVIRONMENTAL PARAMETERS

The time variant environmental parameters (temperatures, OH radical concentration, and sea ice cover) can be displayed by selecting <Display Time Graphs> from the menu entitled <Environmental Parameters>. Upon selecting one of the menu options provided the parameters are displayed as a function of time for a one-year period. Figure 6 gives an example.

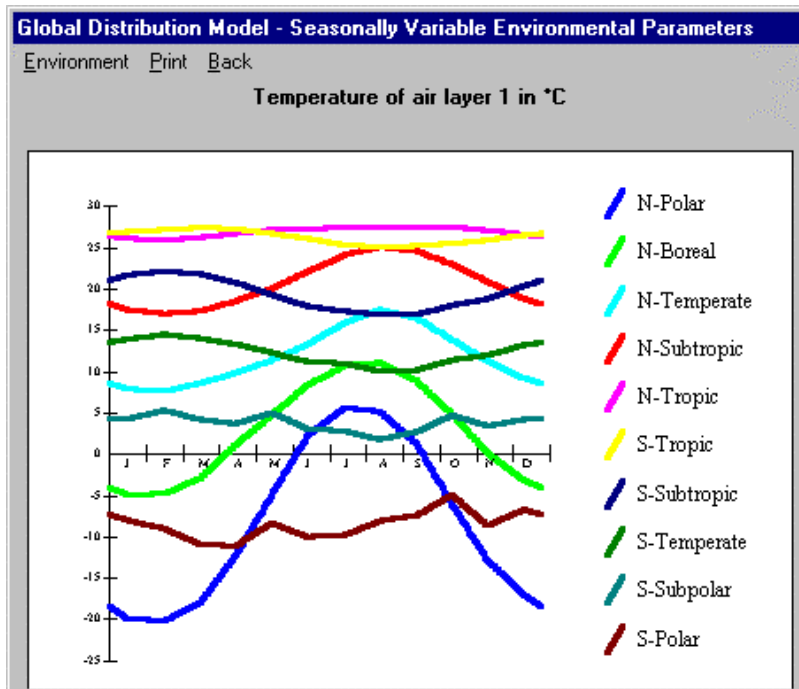


Figure 6

## Selecting and Displaying Chemical Parameters

### Selecting Chemical Parameters

To facilitate the task of selecting chemical parameters, the model contains a database, which allows the user to retrieve and store these data for a large set of chemicals. Access to this database is provided through a form (Figure 7) that is displayed upon choosing *<Input Chemical Properties>* from the menu named *<Chemical Properties>*. On this form the user can (1) use the chemical properties provided for a number of chemicals by selecting the respective choice in the drop-down menu, (2) modify these chemical properties temporarily by editing the data displayed in the text boxes, or (3) permanently store modified or entirely new chemical property profiles in the database. It should be self-explanatory how that is done. By clicking the *<OK>* button on that form, the user accepts the values displayed in the text boxes for use in the simulation.

In addition to the chemical properties, the fate of a chemical is influenced by some emission-related parameters, namely the mode of emission, i.e. the compartment(s) into which the chemical is being release/discharged, and the seasonal variability of the discharge. Since these parameters are often different for different chemicals, they are stored together with the true chemical property parameters in the chemical property database. These are default values that can be modified for each of the 10 individual zones (see below).

**Chemical Properties**

Chemical Name:  Molecular mass (g/mol):

**Equilibrium Partitioning between Air, Water and Octanol**

Partition Coefficients at 25°C (dimensionless)

log Kaw and log Kow log Kow:

log Kaw and log Koa log Kaw:

log Kow and log Koa log Koa:

Heats of Phase Transfer in J/mol

dHaw and dHow dHow:

dHaw and dHoa dHaw:

dHow and dHoa dHoa:

**Reaction Half Lives**

	air	uncult. soil	agri. soil	fresh water	sea water	fw sediment
half-life at 25 °C in h	<input type="text" value="2190"/>	<input type="text" value="2190"/>	<input type="text" value="8760"/>	<input type="text" value="8760"/>	<input type="text" value="17520"/>	
activation energy in J/mol	<input type="text" value="10000"/>	<input type="text" value="30000"/>	<input type="text" value="30000"/>	<input type="text" value="30000"/>	<input type="text" value="30000"/>	<input type="text" value="30000"/>

reaction rate of vapour with OH in cm<sup>2</sup>/(molecules.s)

**Default Emission Parameters**

fraction emitted into a compartment in %

air:  agri-soil:  fresh water:

seasonality of emissions

amplitude as fraction of mean:

month of maximum emission:

**DB Operations**

Figure 7

### Displaying Chemical Parameters

Upon making a selection for the chemical properties, the menu choices *<Display Tabulated Parameters>*, *<Display Time Graphs>*, and *<Display Atmospheric Parameters>* from the menu named *<Chemical Properties>* become enabled. Clicking these menu options opens windows very similar to those described above (Figures 4 to 6). These forms now additionally allow the

display of time-dependent chemical properties over a one-year period. The environmental parameters continue to be included among the menu options of that window. The time variant chemical parameters that can be displayed this way, are the equilibrium partition coefficients at various model temperatures, the degradation half-lives and rates in all compartments, the pure phase and bulk Z-values, the products of the bulk Z-values and compartment volumes, the D-values, and the characteristic times for each process  $VZ/D$ .

## Performing a Simulation

With environmental and chemical properties being specified, additional information is required before a simulation can be performed. An emission scenario has to be specified, and the simulation conditions such as simulation period, step size and results storage intervals have to be specified.

### Specifying an Emission Scenario

Upon making a selection for the chemical properties, the menu choice *<Input Emission Scenario>* from the menu named *<Chemical Properties>* becomes enabled, and allows to call up a form (Figure 8) to specify the emission scenario.

**Global Distribution Model - Global Chemical Discharge**

**alpha-HCH**

**Specifying an Emission Data File**  
 release period and total annual release rates in t/a are read from

**Specifying a Scaling Factor**  
 the annual release rates read from the file are multiplied with this factor

**Compartments Receiving the Emissions**  
 fraction into air (top) and agricultural soil (bottom). The remaining fraction is emitted into fresh water.

N-Polar	N-Boreal	N-Temp.	N-Subtr.	N-Tropic	S-Tropic	S-Subtr.	S-Temp.	S-Subpol.	S-Polar
<input type="text" value="17.5"/>	<input type="text" value="17.5"/>	<input type="text" value="17.5"/>	<input type="text" value="17.5"/>	<input type="text" value="17.5"/>	<input type="text" value="17.5"/>	<input type="text" value="17.5"/>	<input type="text" value="17.5"/>	<input type="text" value="17.5"/>	<input type="text" value="17.5"/>
<input type="text" value="80"/>	<input type="text" value="80"/>	<input type="text" value="80"/>	<input type="text" value="80"/>	<input type="text" value="80"/>	<input type="text" value="80"/>	<input type="text" value="80"/>	<input type="text" value="80"/>	<input type="text" value="80"/>	<input type="text" value="80"/>

**Seasonality of the Emissions**  
 amplitude as fraction of mean and month of maximum emission

N-Polar	N-Boreal	N-Temp.	N-Subtr.	N-Tropic	S-Tropic	S-Subtr.	S-Temp.	S-Subpl.	S-Polar
<input type="text" value="0"/>	<input type="text" value="0"/>	<input type="text" value="0"/>	<input type="text" value="0"/>	<input type="text" value="0"/>	<input type="text" value="0"/>	<input type="text" value="0"/>	<input type="text" value="0"/>	<input type="text" value="0"/>	<input type="text" value="0"/>
<input type="text" value=""/>	<input type="text" value=""/>	<input type="text" value=""/>	<input type="text" value=""/>	<input type="text" value=""/>	<input type="text" value=""/>	<input type="text" value=""/>	<input type="text" value=""/>	<input type="text" value=""/>	<input type="text" value=""/>

Figure 8

### READING FILE WITH ANNUAL ZONAL EMISSION RATES

Annual emission rates are read from a file by pressing the button called *<Select File>*, browsing for, and selecting the name of an emission file, and pressing the *<OK>* button. A pre-supplied emission file for the chemical  $\alpha$ -HCH is located in the subdirectory entitled "emitdata". The user can also construct such files, but these have to have a prescribed format. The first line contains four digits indicating the number of years for which emission rates are supplied, e.g. 0051. The second line contains four digits indicating the first year, for which emission rates and fugacity ratios are supplied, e.g. 1947. Then follow as many lines as have been specified in the first line.

All these lines have 10 eleven-digit entries (without delimiters) corresponding to the emission rate into the ten zones in t/a starting with the most northerly zone.

#### SPECIFYING OTHER PARAMETERS RELATED TO THE EMISSION SCENARIO

On the same form several parameters related to the emission scenario have to be specified.

**Scaling factor:** a fixed multiplication factor scaling the emission rates is meant to help modelling individual constituents of chemical mixtures for which only composite emission data are available. The scaling factor then is the fraction of the total release that applies to a constituent, e.g. the fraction of a single congener in a PCB mixture.

For each zone, the following information is required:

**Seasonality of the release:** The total annual release can be distributed over the year using a sinusoidal function. The amplitude of the seasonal fluctuation has to be specified as a fraction of the annual mean. An amplitude of "0" means no seasonal variability, whereas an amplitude of "2" implies the maximum possible variability. Additionally, the month during which maximum release occurs needs to be specified.

**Mode of emission:** the compartment distribution of the emissions is defined by giving fractions of the total release, which are entering a certain compartment. These fractions obviously have to add up to 1 within each zone.

Defaults for the latter two are already chosen on the form selecting chemical properties (Figure 7), but can now be modified for individual zones. The default options are a scaling factor of 1, no seasonal fluctuation, and release into the air compartment only.

#### *Specifying the Simulation Conditions and Performing the Simulations*

When the emission scenario has been accepted, a frame, which allows the specification of the simulation conditions, appears on the main window (Figure 9).

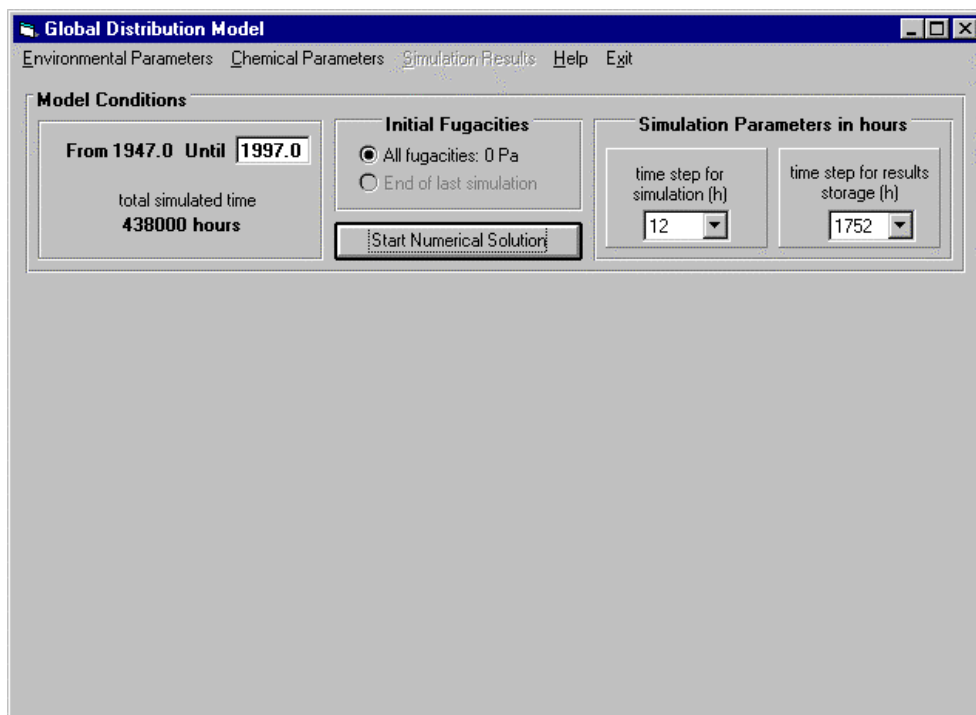


Figure 9



Namely, the following parameters are required to perform a non-steady state simulation:

**Date when simulation starts:** This date can not be changed. For the first simulation it has to be the year when emissions started. This year has been specified in the second line of the emissions file (see above). Every first simulation starts on a January 1.

**Date when simulation ends:** Selecting the date when the simulation should stop controls the length of the simulation. That date is to be entered into the respective textbox as a year. Obviously the number has to be larger than the starting date. The simulation length does not have to be a multiple of full years, but the date when the simulation ends could also be an uneven number, e.g. "1995.3". The default ending date is the last year for which emission data have been read from file.

**Time Step for Simulation:** The default time step used for the step-size numerical solution is 12 hours. The user may specify a smaller or higher step size among the provided options (1, 3, 6 and 24 hours). A step size smaller than 12 results in increased calculation times, but usually provides only marginal reductions in the numerical errors, if any.

**Time Step for Results Storage:** After certain predefined intervals during the simulation, the calculated fugacities in all model compartments are stored for later retrieval and processing. The user can specify this interval from among the choices provided (24 h, 120 h, 1752 h, and 8760 h). The selection of that parameter affects for how the model results can be displayed. A shorter storage interval provides high temporal resolution, but time graphs can only be displayed for fairly short simulation times. A larger storage interval results in a loss of temporal resolution, namely on seasonal or shorter time scale, but allows the plotting of time curves over several decades. To display the results in graphical form, there needs to be a minimum of 2 storage events.

Clicking the button *<Start Numerical Solution>* starts the simulation. The progress of the numerical solution is displayed in a window until the simulation has been completed (Figure 10).

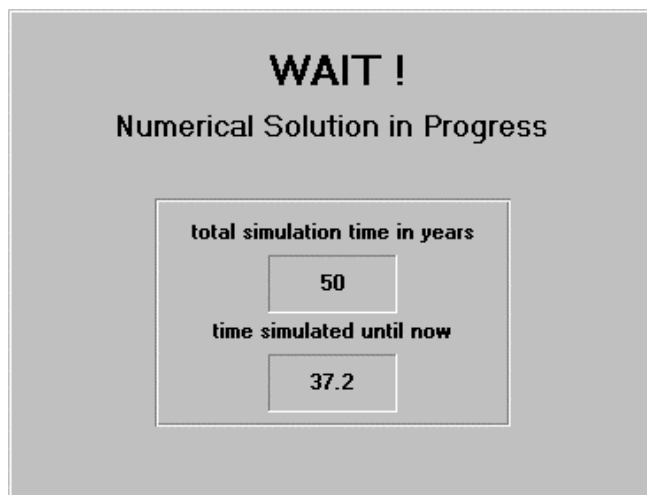


Figure 10

Then the menu choice *<Simulation Results>* will become enabled. Note that if the environmental or chemical parameters are changed after a simulation has been performed, this menu choice *<Simulation Results>* becomes disabled again. This reflects the fact that the simulation has to be repeated with changed input conditions to look at the results.

After the first simulation is completed, the user has two options:

- Continue the simulation by clicking the option button *<End of last simulation>* in the frame entitled *<Initial Fugacities>* and then entering a new date when the simulation should end. The year when simulation starts is automatically updated. The continuation can have simulation parameters (step size, results storage interval, etc.) that differ from those used in the initial part of the simulation. A simulation can be continued several times.
- Conduct a new simulation starting in the year the emission started.

Please note that whenever a new simulation is started or a simulation is continued, the stored results from the previous simulation are lost.

## Displaying Model Results

The program provides a multitude of ways to display the simulation results. As was mentioned above, the fugacities in all model compartments are stored at user-defined intervals during the simulation. Naturally, it is only possible to display results for these storage events. When results other than fugacities are being displayed, these are calculated from the stored fugacity values.

In addition to these instantaneous results, the model calculates cumulative fluxes, i.e. it sums up the rates and fluxes for the entire simulation period. Please note that if the simulation is a continuation of a previous simulation, these cumulative fluxes only refer to the last part of the simulation. The results display options are accessible through various menu options under the main menu title *<Simulation Results>*.

### Displaying the Simulation Results in Tables

Selecting *<Tabulated Results>* under the menu heading *<Simulation Results>* opens a window, on which the values of selected parameters at the storage events can be displayed in a table (Figure 11).

Global Distribution Model - Simulation Results											
Environment Chemical Simulation Results Print Back											
<div style="display: flex; justify-content: space-between; align-items: center;"> <div style="display: flex; align-items: center;"> <span>◀</span> <div style="border: 1px solid black; padding: 2px 10px; margin: 0 5px;">209</div> <span>▶</span> </div> <div style="margin: 0 20px;">NOV1949</div> <div style="border: 1px solid black; padding: 2px 10px; margin: 0 20px;">VZ-values for bulk phases in mol/Pa</div> <div style="text-align: right;">             24960 hours    34 months    2.8 years              alpha-HCH           </div> </div>											
	North						South				
	Polar	Boreal	Temperate	Subtropic	Tropic	Tropic	Subtropic	Temperate	Subpolar	Polar	Globe
Air layer 1	1.59E+13	1.33E+13	2.67E+13	2.52E+13	5.68E+13	5.66E+13	2.73E+13	1.64E+13	2.61E+13	1.18E+13	2.76E+14
Air layer 2	3.75E+13	3.06E+13	6.00E+13	5.50E+13	1.23E+14	1.22E+14	5.93E+13	3.65E+13	5.79E+13	2.84E+13	6.10E+14
Air layer 3	1.33E+14	1.12E+14	2.24E+14	2.12E+14	4.77E+14	4.75E+14	2.29E+14	1.37E+14	2.19E+14	9.89E+13	1.59E+15
Air layer 4	2.11E+14	1.78E+14	3.55E+14	3.35E+14	7.55E+14	7.52E+14	3.63E+14	2.18E+14	3.47E+14	1.57E+14	1.90E+16
Sea water	6.60E+16	7.68E+15	2.83E+16	1.49E+16	2.15E+16	2.26E+16	1.89E+16	2.56E+16	9.40E+16	2.89E+16	3.28E+17
Agri-soil	2.27E+10	2.22E+13	2.58E+14	3.91E+13	1.53E+13	1.65E+13	2.64E+13	1.60E+13	1.04E+8	2.55E+10	3.94E+14
Uncult-soil	2.51E+14	1.22E+15	4.06E+14	9.78E+13	8.08E+13	8.69E+13	6.61E+13	2.52E+13	2.87E+12	2.83E+14	2.52E+15
Freshwater	1.13E+14	2.93E+14	1.45E+14	1.96E+13	2.08E+13	3.69E+13	1.25E+13	4.35E+12	2.67E+11	2.76E+13	6.73E+14
Sediment	1.12E+13	2.64E+13	1.99E+13	2.22E+12	2.09E+12	3.83E+12	1.50E+12	6.02E+11	2.30E+10	2.73E+12	7.05E+13
Total Zone	6.68E+16	9.57E+15	2.98E+16	1.57E+16	2.31E+16	2.41E+16	1.97E+16	2.61E+16	9.46E+16	2.95E+16	2.95E+16

Figure 11

The menu options allow choosing which parameters should be displayed. The event, i.e. the point in time for which results should be displayed, is selected either by using the arrow buttons, or by entering the number of the storage event into the text box between the arrow buttons and using the return key. On the upper right corner, three labels indicate the number of hours, months, and years that have passed since the beginning of the simulation. Other forms displaying simulation results show a similar layout.

### Displaying Atmospheric Results

When choosing the menu option *<Display Atmospheric Results>* under the menu heading *<Simulation Results>* a form similar to that showing atmospheric parameters (Figure 5) is displayed. However, different menu options allow the display of atmospheric fugacities, concentrations, amounts, fluxes and rates for the various storage events.

### Displaying Flux Diagrams with Zonal and Global Mass Balances

When choosing the menu option *<Mass Balances>* under the menu heading *<Simulation Results>*, a form (Figure 12) is displayed, which shows the emission, degradation, intercompartmental and interzonal transfer rates for each climate zone and the total globe - either instantaneous at the storage events or cumulative for the entire simulation period. In instantaneous mass balance diagrams the figures within the boxes indicate the fraction of the total amount of contaminant in a zone (or on the total globe) which is present in one of the six environmental media. In cumulative mass balance diagrams the figures in the boxes indicate the amount of contaminant in that medium at the beginning (bottom number) and at the end (number at the top) of the simulation period. It is possible to change the units of the fluxes and amounts displayed by selecting the respectively labelled option buttons on the upper right corner of the form.

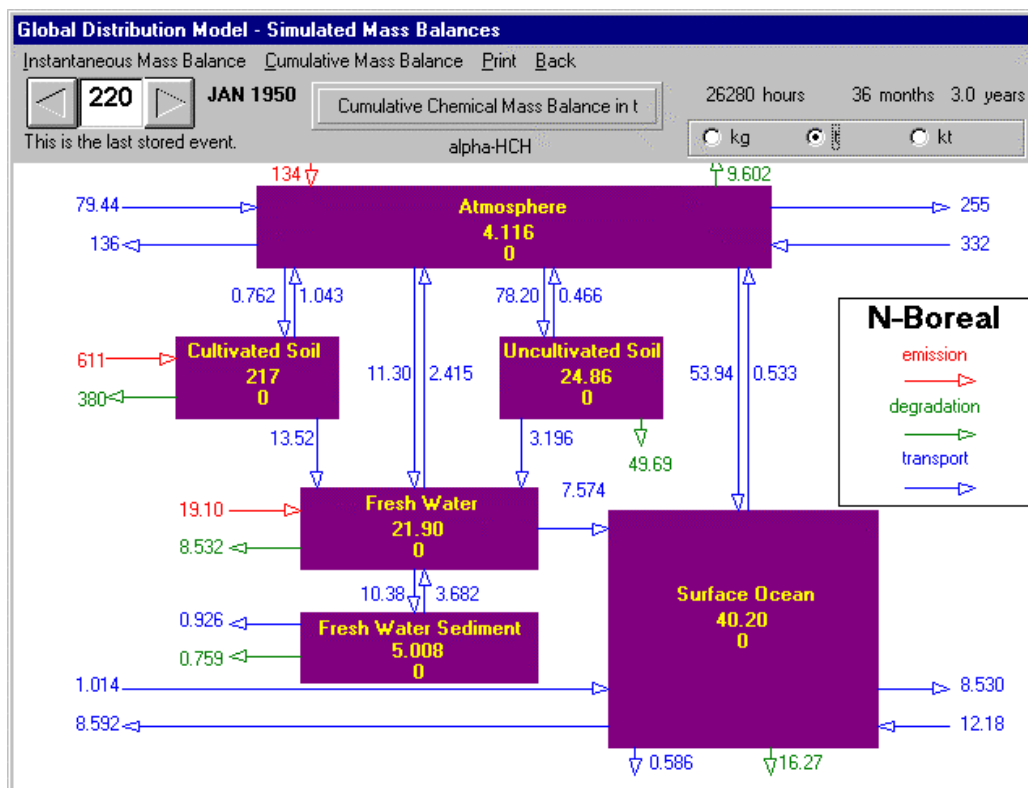


Figure 12

### Displaying Zonal Concentration Profiles

Zonal concentration profiles at the storage events can be displayed by selecting option <Zonal Distribution> under the menu heading <Simulation Results>. On the window that appears (Figure 13), the menu options allow to choose for which compartment the concentration profiles should be displayed. It is also possible to display the zonal distribution of emissions and total accumulated amount. As is the case for all other forms displaying simulation results, the event, i.e. the point in time for which results should be displayed, is selected either by using the arrow buttons, or by entering the number of the storage event into the text box between the arrow buttons, or by entering the number of the storage event into the text box between the arrow buttons and using the return key.

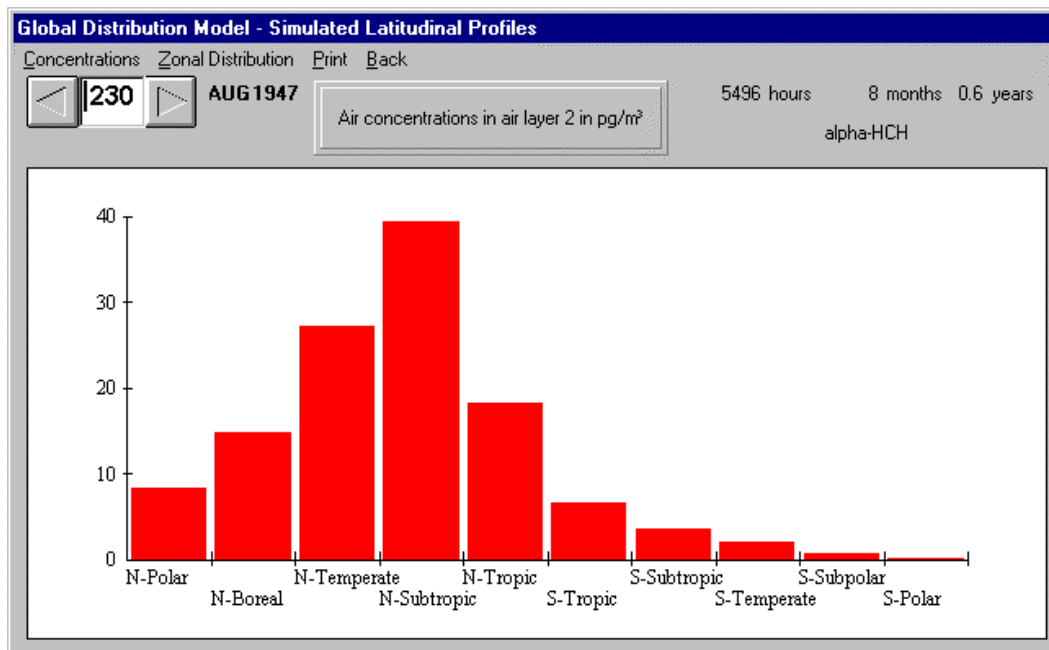


Figure 13

### Displaying the Simulation Results as Time Graphs

The choice <Time Response> under the menu heading <Simulation Results> opens a window (Figure 14) that allows the display of many model parameters as a function of time for the simulation period. As usual, the menu options allow choosing which parameters should be displayed. The parameters that can be displayed are: fugacities, fugacity ratios, concentrations, amounts, fluxes and rates, net fluxes. Please note that if the simulation is a continuation of a previous simulation, these graphs show only the last part of the simulation. The temporal resolution of the graphs is obviously determined by the chosen storage interval (see above). The number of data that can be displayed in this form is limited. Simulations stretching over many years can only be displayed, when a fairly long storage interval is being selected (e.g. 1752 hours or five storage events per year). Simulations over many decades can be performed with high temporal resolution (i.e. small storage event intervals), but then this form will be disabled.

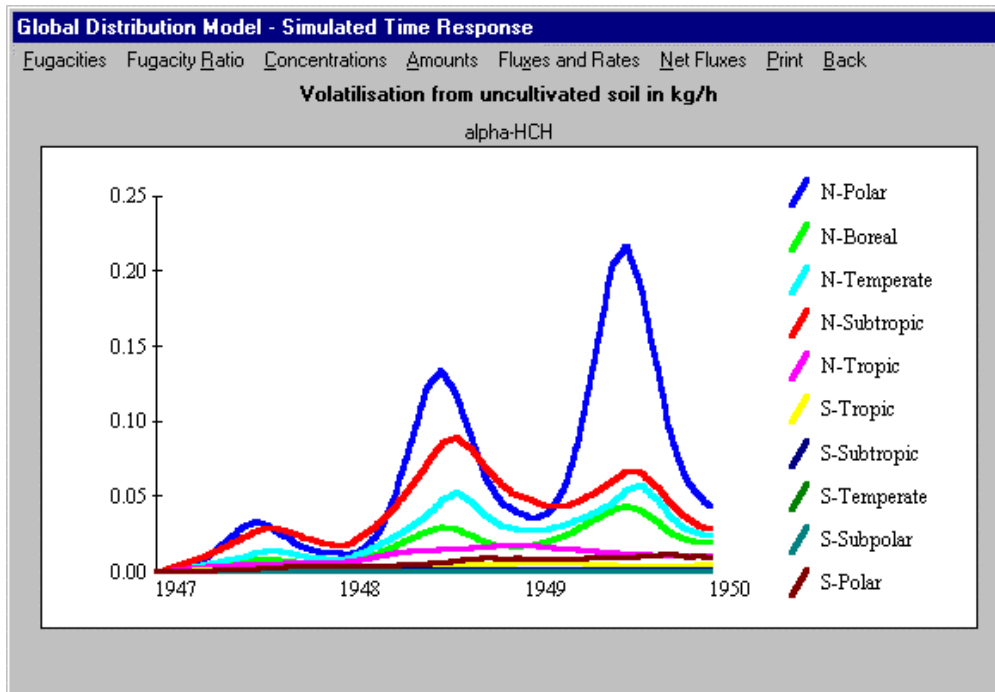


Figure 14

### Writing Results to File

Selected results, namely the fugacities and concentrations, can also be written to ASCII files for further processing. Selecting menu option *<Write Results To Files>* displays a window (Figure 15), that allows choosing which parameters to write to ASCII files (by clicking the respective checkmarks), and what names these files should have (by writing the respective names into the textboxes provided). By clicking the buttons *<Write to File>* the files will be saved in the subdirectory "results".

Figure 15

The files have one line for each storage event. The number of lines is thus determined by both simulation length and time step for result storage. Only the data for the last simulation (in the case of a continued simulation only the results for the last section of the simulation) will be saved to file. Whereas the first entry of each line gives the simulation time in hours (with respect to the year when emissions first started), the following entries are the respective concentrations or fugacities. Commas delimit the entries. The first line in each file provides information on the content of the file and the units used for the concentration values. The second line indicates to which region the values refer. The files can be opened in spreadsheet programs such as MS Excel for further processing.

Clicking the menu option <Exit> closes the program.

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