Chapter 1

APPROACHES TO POP MODELLING WITH EMPHASIS ON MSCE-POP MODEL

The aim of this Chapter is to compare modelling approach to the evaluation of POP behaviour in the environment used in MSCE-POP model with the approaches of other models. There exist a number of different approaches to POP modelling elaborated for different purposes (for the assessment of environmental pollution by POPs, for the risk assessment, for the evaluation of new pollutants as potential candidates to be implemented in the regulatory control activity, etc). One of the possible ways to evaluate reliability of MSCE-POP model estimates is their comparison with results obtained by other existing POP models. To do that we use some results obtained in the course of POP model intercomparison study, which is now ongoing under the UN ECE Convention on Long-Range Transboundary Air Pollution, see [*Shatalov et al.,* 2004, *Shatalov et al.,* 2005]. The full text of both technical reports devoted to the POP model intercomparison study is available at the MSC-E website: www.msceast.org.

The POP model intercomparison study was initiated under EMEP/MSC-E in 2002 in accordance with the recommendations of the Executive Body for the Convention [*ECE/EB.AIR/75*]. The main aim of the study is to exchange scientific experience between different groups of POP modelers in order to improve understanding of POP fate in the environment. National experts from a large number of countries take part in this study. Three EMEP expert meetings on intercomparison of POP models have been held since that year (Moscow, Russia, 2002; 2003; 2005).

The POP model intercomparison study is performed within three stages:

Stage I. Comparison of descriptions of main processes determining POP behaviour in various environmental compartments.

Stage II. Comparison of mass balance estimates and calculated deposition and concentration fields of POPs in different environmental compartments. Sensitivity study with respect to physical-chemical parameter values used in basic process descriptions and mass balance estimates.

Stage III. Comparison of calculated overall environmental persistence and long-range transport potential for evaluation of new substances

Stage I of the intercomparison study was launched in 2002 and completed in 2004. Fourteen scientific groups from Canada, the Czech Republic, Denmark, France, Germany, Japan, the Netherlands, Norway, Switzerland, the United Kingdom, the USA and representatives of the OECD and MSC-E took part in the first stage. At Stage I model parameterizations and model approaches to the description of such processes as gas/particle partitioning, dry deposition of particulate phase, wet deposition, gaseous exchange between the atmosphere and different types of underlying surface (soil, water, vegetation) and degradation processes were considered. This implied the comparison of process descriptions as well as results of relevant computation experiments. Main outcome of Stage I was published in the joint Technical Report 1/2004 “POP Model Intercomparison Study. Stage I. Comparison of descriptions of main processes determining POP behaviour in various environmental compartments” [*Shatalov et al*., 2004].

Stage II of the POP model intercomparison study has been ongoing since 2004. The third EMEP expert meeting on intercomparison of POP models (Moscow, February, 2005) devoted to discussion of Stage II results was attended by national experts from Canada, Germany, Japan, the Netherlands, Norway, Switzerland, the United Kingdom, the USA and MSC-E. Eleven models participating in the intercomparison study at Stage II are given in Table 1.1.

Table 1.1. *The list of participating models*

	Model name	Experts	Institution
1	HYSPLIT 4	P. Bartlett	CBNS, Queens College, USA
2	EVN-BETR and UK-MODEL	K. Jones, A. Sweetman	Lancaster University, UK
3	CliMoChem	M. Scheringer, J. Stocker, K. Hungerbühler, F. Wegmann	ETH Zürich, Switzerland
4	CAM/POPs	S. Gong, P. Huang	Air Quality Research Branch, Canada
5	G-CIEMS	N. Suzuki	National Institute for Environmental Studies, Japan
6	ADOM-POP	G. Petersen	GKSS, Germany
7	DEHM-POP	J. Christensen, K.M. Hansen	National Environmental Research Institute, Denmark
8	SimpleBox	D. van de Meent, A. Hollander	RIVM Laboratory for Ecological Risk Assessment, the Netherlands
9	LOTOS	M.G.M. Roemer, A.C. Baart	TNO-MEP, the Netherlands
10	ADEPT		Delft Hydraulics, the Netherlands
11	MSCE-POP	S. Dutchak, V. Shatalov , A. Gusev, E. Mantseva	EMEP/MSC-E

Computational experiments on calculation of mass balance and spatial distribution of depositions and concentrations together with a comparison of model results with monitoring data were performed by the participants in the framework of Stage II. Sensitivity of each model to variation in physical-chemical parameter values used in mass balance estimates as well as in descriptions of basic processes was also evaluated. At this stage PCB-153 (first priority), and PCB-28, PCB-180 and B[a]P (second priority) are considered within the computational experiments. Preliminary results of this stage are presented in the Intermediate Technical Report 4/2005 "POP Model Intercomparison Study. Stage II. Comparison of Mass Balance Estimates and Sensitivity Studies" [*Shatalov et al*., 2005].

The results of the comparison of model parameterizations of various POP models performed within the intercomparison study allow to evaluate possible uncertainties of pollutant-related parameters determined as scattering of values of these parameters between participating models. To do this, similar sets of pollutant-related properties of most of the participating models, in which the values of the particular parameters are relatively close to each other, are used. These estimates together with earlier evaluated sensitivities of MSCE-POP model output (air concentrations and depositions) with respect to these parameters are used for estimating the uncertainties of the model output caused by the uncertainties of pollutant-related parameters.

To evaluate the reliability of model description of main processes of POP fate in the environment, the comparison of calculation results obtained by the participating models in the course of the model intercomparison study is used. Here we concentrate at the comparison of model calculations of gas/particle partitioning and intermedia transport. We remark that MSCE-POP model describes atmospheric transport (advection and diffusion) and particulate deposition similar to the description of these processes in MSCE-HM model. Therefore, additional information on model description of these processes can be found in the report [*Travnikov and Iliyn*, 2005] concerning the description of MSCE-HM model.

The outline of the Chapter is as follows:

Section 1.1 is devoted to the comparison of pollutant-related parameters of PCB-153 (including degradation rates in various environmental compartments) included into the parameterizations of the participating models. Here the evaluation of the uncertainties of pollutant-related parameters and evaluation of the consequent uncertainties of MSCE-POP model output is made.

Section 1.2 comprises descriptions of main processes determining PCB behaviour in the environment: gas/particle partitioning, intermedia mass flows and concentrations at interfaces between the atmosphere and soil, seawater and vegetation.

Main conclusions are drawn in the end of this Chapter.

Additional information on the POP model intercomparison study can be found at the MSC-E website: www.msceast.org.

1.1. Comparison of physical-chemical properties and degradation rates between POP models

Physical-chemical properties and degradation rates of POPs in the main environmental media are one of the most important input data used for model calculations. Selection of model parameters is carried out on the basis of experimentally measured or theoretically estimated pollutant-specific properties available in the literature.

In this Section physical-chemical properties and degradation rates of PCB-153 used in the parameterization of MSCE-POP model are compared with those included in the description of other POP models, namely: CAM/POPs (Canada), DEHM-POP (Denmark), G-CIEMS (Japan), EVN-BETR and UK-MODEL (UK), CliMoChem (Switzerland). The comparison is done on the basis of the data on model parameterizations presented by modelers in the framework of the POP model intercomparison study (see [*Shatalov et al.,* 2004]).

Main pollutant-related parameters used in simulations of POP behaviour in the environment by the above models are:

- Henry's law constant (or air/water partition coefficient), K_{aw}
- Octanol/air partition coefficient, K_{oa}
- Subcooled liquid vapor pressure, p_{0L}
- Octanol/water partition coefficient, K_{ow}
- Organic carbon/water partition coefficient, K_{oc}
- Degradation rate constants in the environmental media, k_{air}, k_{soil}, k_{water}, k_{veg}, $k_{sediment}$

The above pollutant-related parameters are ordered here by sensitivities of the model output (air concentrations and deposition flux) with respect to the considered parameter. We recall that the sensitivity of, say, air concentrations with respect to a parameter is defined as the relative change of air concentrations (in per cent) caused by the change of the considered parameter by 1% (see sensitivity analysis in [*Gusev et al.,* 2005a]).

In the Chapter relative deviations of the above parameter values used in participating models is determined. Using these deviations as an estimate of the uncertainties of the considered parameters, possible uncertainties of the output of MSCE-POP model is calculated for each parameter on the basis of earlier calculated sensitivities. It should be taken into account that the sensitivities are defined at the distance of 1000 km from a source. So, the obtained uncertainties are typical for the most part of Europe. In the regions located far from emission sources the uncertainties due to pollutant-related properties are higher (see sensitivity analysis in [*Gusev et al.*, 2005a]).

The comparison of values of pollutant-related parameters for PCB-153 is made in the appropriate subsections. Most of these parameters are temperature-dependent. The dependence is described by base values (that is, values at some reference temperature) and coefficients describing the changes of a parameter with temperature. Here reference temperature T_0 is chosen to be 10 ºC or 283.15 ºK for all temperature-dependent parameters. The scattering of the values reported by the participants for each parameter can to some extent characterize its uncertainty. To evaluate the uncertainty, a number of statistical parameters (mean value, square deviation, maximum and minimum values and min/max ratio) the maximum, the minimum, the arithmetic mean, the median and the geometric mean) are calculated.

1.1.1. The Henry's law constant and the air/water partition coefficient

Relation between the air-water Henry's law constant, (H or K_H, Pa·m^3/mol) and the air/water partition coefficient (K_{aw}, dimensionless) is as follows:

$$K_{aw} = \frac{H}{RT}, \qquad (1.1)$$

where T - temperature, K;
R = 8.314 J/(mol·K) - universal gas constant.

Coefficient K_{aw} is mainly used in the description of the gaseous exchange process between the atmosphere and soil, and between the atmosphere and water, as well as of wet deposition of the POP gaseous phase. Besides, EVN-BETR and UK-MODEL and CliMoChem models use K_{aw} for the evaluation the octanol/air partition coefficient (K_{oa}) together with octanol/water partitioning coefficient K_{ow}:

$$K_{oa} = K_{ow} / K_{aw}. \qquad (1.2)$$

Temperature dependence of K_{aw} is included in all participating models. Some models (EVN-BETR and UK model, ClimoChem and DEHM-POP) use directly temperature dependence of K_{aw}, the others (CAM/POPs, G-CIEMS and MSCE-POP) use temperature dependence of H recalculating then K_{aw} by formula (1.1). The models G-CIEMS and SimpleBox use one and the same temperature dependence for K_{aw}. The same is true for ClimoChem and DEHM-POP models. The details of calculations and numerical values of the parameters are given in Annex B (Table B.1.). Comparison of temperature dependencies of K_{aw} for PCB-153 used by the considered models is given in Fig.1.1.

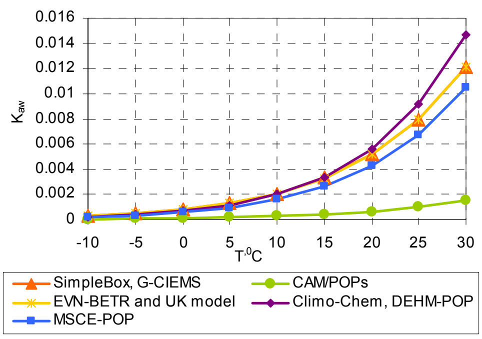


Fig. 1.1. *Comparison of temperature dependencies of air/water partition coefficient (K_{aw}, dimensionless) of PCB-153*

It is seen that most of the models (except for CAM/POPs) describe closely values of K_{aw} for various temperatures. The differences in K_{aw} description for this group of models are illustrated in Table 1.2, where K_{aw} numerical values for three arbitrary temperatures (-10°C, 10°C and 25°C) are given together with statistical parameters characterizing the scattering of these values.

Table 1.2. *Absolute values and statistical parameters of air/water partition coefficient (K_{aw}, dimensionless) of PCB-153 for three arbitrary temperatures (-10°C, 10°C and 25°C) and coefficients of temperature dependencies*

	T, ºC		
	– 10º	10º	25º
SimpleBox	$2.73{\cdot}10^{-4}$	$2.09{\cdot}10^{-3}$	$7.99{\cdot}10^{-3}$
G-CIEMS	$2.73{\cdot}10^{-4}$	$2.09{\cdot}10^{-3}$	$7.99{\cdot}10^{-3}$
EVN-BETR and UK model	$2.74{\cdot}10^{-4}$	$2.08{\cdot}10^{-3}$	$7.96{\cdot}10^{-3}$
Climo-Chem	$2.03{\cdot}10^{-4}$	$2.01{\cdot}10^{-3}$	$9.17{\cdot}10^{-3}$
DEHM-POP	$2.03{\cdot}10^{-4}$	$2.01{\cdot}10^{-3}$	$9.17{\cdot}10^{-3}$
MSCE-POP	$1.84{\cdot}10^{-4}$	$1.61{\cdot}10^{-3}$	$6.72{\cdot}10^{-3}$
Average	$2.35{\cdot}10^{-4}$	$1.98{\cdot}10^{-3}$	$8.17{\cdot}10^{-3}$
Square deviation	$3.88{\cdot}10^{-5}$	$1.70{\cdot}10^{-4}$	$8.36{\cdot}10^{-4}$
min	$1.84{\cdot}10^{-4}$	$1.61{\cdot}10^{-3}$	$6.72{\cdot}10^{-3}$
max	$2.74{\cdot}10^{-4}$	$2.09{\cdot}10^{-3}$	$9.17{\cdot}10^{-3}$
max/min	**1.5**	**1.3**	**1.4**

The ratio between maximum and minimum absolute values of K_{aw} of PCB-153 used for various values of ambient temperature is within a factor of 1.5.The values of K_{aw} used by MSCE-POP model differ from the average by about 20%.

Assuming that the uncertainty of air/water partitioning coefficient is about 50% (the maximum uncertainty between main group of models) and using sensitivities of model output for MSCE-POP model with respect to this parameter[1] it can be concluded that the obtained uncertainty leads to the uncertainty of model output about 3%.

1.1.2. The octanol/air partition coefficient

The octanol/air partition coefficient (K_{oa}, dimensionless) is used by EVN-BETR and UK-MODEL, G-CIEMS and DEHM-POP in the description of POP gas-particle partitioning in the atmosphere as absorption from air into an octanol-like film of particles according to [*Finizio et al.*,1997; *Falconer and Harner,* 2000]. Besides, this parameter is included into descriptions of the gaseous exchange between air and vegetation. It should be mentioned that EVN-BETR and UK-MODEL and CliMoChem models do not use K_{oa} parameter straight as input information for modelling but recalculate it from K_{ow} and K_{aw} (see formula (1.2) above).

All the participating models consider temperature dependence of this parameter. Coefficients of these dependencies are presented in Annex B (Table B.2.).

Following the data presented by modelers comparison of temperature dependencies of the octanol/air partition coefficient used by the models is presented in Fig. 1.2.

[1] Here and below we use sensitivities of calculated depositions for evaluation of model uncertainty. The uncertainties of air concentrations are slightly lower.

Most of the models (except for EVN-BETR and UK model) describe closely values of K_{oa} for various values of temperature. Describing equations of temperature dependence of K_{oa} in different ways, CAM/POPs and DEHM-POP nevertheless use very close values of this parameter for PCB-153. K_{oa} values used by MSCE-POP are somewhat higher and that used by SimpleBox and G-CIEMS are somewhat lower than previous ones.

In order to characterize the spread of octanol/air partition coefficient of PCB-153, the comparison of its absolute values at three particular temperatures (-10°C, 10°C and 25°C) between these models is made. Absolute values of K_{oa}, coefficients of temperature dependencies and their statistical parameters are presented in Table 1.3.

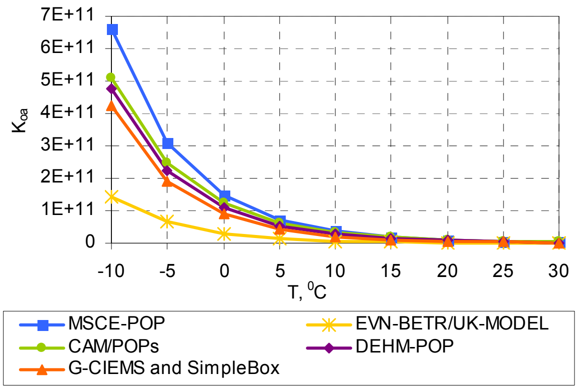


Fig. 1.2. *Comparison of temperature dependencies of octanol/air partition coefficient (K_{oa}, dimensionless) of PCB-153 used in the participating POP models*

Table 1.3. *Absolute values, coefficients of temperature dependencies and statistical parameters of octanol/air partition coefficient of PCB-153 for three selected temperatures (-10°C, 10°C and 25°C)*

	T, °C		
	-10°	10°	25°
CAM/POPs	$5.10 \cdot 10^{11}$	$3.29 \cdot 10^{10}$	$5.45 \cdot 10^{9}$
SimpleBox	$4.25 \cdot 10^{11}$	$2.05 \cdot 10^{10}$	$2.76 \cdot 10^{9}$
G-CIEMS	$4.25 \cdot 10^{11}$	$2.05 \cdot 10^{10}$	$2.76 \cdot 10^{9}$
DEHM-POP	$4.76 \cdot 10^{11}$	$2.74 \cdot 10^{10}$	$4.14 \cdot 10^{9}$
MSCE-POP	$6.63 \cdot 10^{11}$	$3.64 \cdot 10^{10}$	$5.33 \cdot 10^{9}$
Average	$5.00 \cdot 10^{11}$	$2.75 \cdot 10^{10}$	$4.09 \cdot 10^{9}$
Square deviation	$8.77 \cdot 10^{10}$	$6.43 \cdot 10^{9}$	$1.18 \cdot 10^{9}$
min	$4.25 \cdot 10^{11}$	$2.05 \cdot 10^{10}$	$2.76 \cdot 10^{9}$
max	$6.63 \cdot 10^{11}$	$3.64 \cdot 10^{10}$	$5.45 \cdot 10^{9}$
max/min	**2**	**2**	**2**

At all considered temperatures there is not a large difference in values of K_{oa} obtained with the use of existing temperature dependencies (max/min ratios equals 2).

So, for the majority of models differences in values of K_{oa} are about 100% at maximum. Such uncertainty leads to the uncertainty of output of MSCE-POP model about 5%. This figure is calculated with the use of the sensitivity of model output with respect to the considered parameter.

1.1.3. The subcooled liquid vapour pressure

The value of subcooled liquid vapour pressure (p_{0L}, Pa) is used in the modelling of the process of POP partitioning between its particulate and gaseous phase in the atmosphere in accordance with the Junge-Pankow adsorption model [*Junge*, 1977; *Pankow,* 1987]. Thus, in this cases the value of p_{0L} determining the particle-bound fraction of a pollutant in air strongly influences such subsequent important processes as dry and wet deposition and degradation in the atmosphere.

CliMoChem and DEHM-POP models do not use subcooled liquid vapour pressure for model calculations. EVN-BETR and UK-MODEL assumes this parameter temperature-independent. Other models (CAM/POPs, MSCE-POP, G-CIEMS and SimpleBox) use temperature dependences of this parameter. The coefficients of temperature dependencies for PCB-153 together with details of calculations are presented in Annex B (Table B.3).

As seen from the Table, the participating models use two sets of coefficients determining temperature dependence of p_{0L}, which do not differ from each other very much. The first set is used by G-CIEMS and SimpleBox. The second one is utilized by CAM/POPs and MSCE-POP. Comparison of these two temperature dependencies of p_{0L} is presented in Fig. 1.3. The temperature-independent value of the subcooled vapor pressure used in EVN-BETR and UK model agree with the values used by other models at 25 °C.

The dispersion of the subcooled liquid vapour pressure of PCB-153 can be characterized by the comparison of its absolute values at -10°C, 10°C and 25°C and coefficients of temperature dependence used by the participating models. Above mentioned values and corresponding statistical parameters are given in Table 1.4.

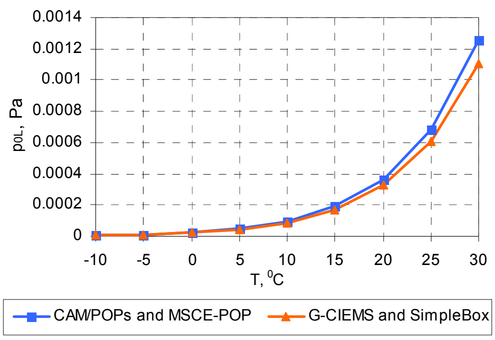


Fig. 1.3. *Comparison of temperature dependencies of subcooled liquid vapour pressure (p_{0L}, Pa) of PCB-153 used in data sets of the participating POP models*

Table 1.4. *Absolute values, coefficients of temperature dependence and statistical parameters of subcooled liquid vapour pressure (p_{0L}, Pa) of PCB-153 for three temperature values (-10 °C, 10 °C and 25 °C)*

	T, °C		
	-10°	10°	25°
CAM/POPs and MSCE-POP	$5.07{\cdot}10^{-6}$	$9.69{\cdot}10^{-5}$	$6.84{\cdot}10^{-4}$
G-CIEMS and SimpleBox	$4.80{\cdot}10^{-6}$	$8.82{\cdot}10^{-5}$	$6.06{\cdot}10^{-4}$
max/min	**1.1**	**1.1**	**1.1**

So, there is a high similarity between absolute values of subcooled liquid vapour pressure of PCB-153 presented by the models using temperature dependence of this parameter (max/min ratio is about 1.1). Its values used by models differ within the accuracy of 10% for all values of temperature. The uncertainty of p_{0L} evaluated on the basis of values used by models leads to minimum uncertainty of MSCE-POP model output (about 0.2%).

1.1.4. The octanol/water partition coefficient

The octanol/water partition coefficient (K_{ow}, dimensionless) is used in the participating models for the estimation of the POP partitioning in the organic carbon/water system (K_{oc}) on the basis of regression dependencies and of the partition coefficient in the octanol/air system (K_{oa}). Thus, this parameter mainly affects the description of gas-particle partitioning in the atmosphere (for models using absorption approach), gaseous exchange between the atmosphere and soil (partitioning in soil compartment), and gaseous exchange between the atmosphere and vegetation (partitioning among vegetation compartment). K_{ow} is also included by CliMoChem model in the calculation of the water particle-bound fraction of a pollutant for modelling diffusion process from seawater to the atmosphere.

The most part of participating models (CAM/POPs, SimpleBox, G-CIEMS, EVN-BETR and UK-MODEL CliMoChem and DEHM-POP) involve the octanol/water partition coefficient of the considered PCBs in the form of the temperature dependence. As usual the temperature dependencies of this parameter are equated by downward exponents with different values of K_{ow} at reference temperature (10 °C) as the pre-exponential multiplier and with the values of the temperature coefficient of these dependencies defined with the help of the enthalpy or the internal energy of phase transfer. The exception is CAM/POPs model, in which the temperature dependence of K_{ow} is recalculated from temperature dependencies of the Henry's law constant and the octanol/air partition coefficient. MSCE-POP model uses temperature independent values of K_{ow}. The coefficients of K_{ow} temperature dependencies for PCB-153 together with the details of their evaluation and literature sources are presented in Annex B (Table B.4).

Temperature dependencies of the octanol/water partition coefficient of PCB-153 used in the calculations by the participating models are compared in Fig.1.4.

Comparison of the plots of temperature dependencies of the octanol/water partition coefficient of PCB-153 used in CAM/POPs, CliMoChem, DEHM-POP models and in SimpleBox, G-CIEMS, and EVN-BETR/UK-MODEL shows not substantial differences between values of log K_{ow} used by the models. To evaluate the scattering of K_{ow}, the variability of this parameter values used by the participating models is determined at three fixed values of temperature (-10°C, 10°C and 25°C). Absolute values, coefficients of temperature dependence and statistical parameters of octanol/water partition coefficient of PCB-153 for three arbitrary temperatures are given in Table 1.5.

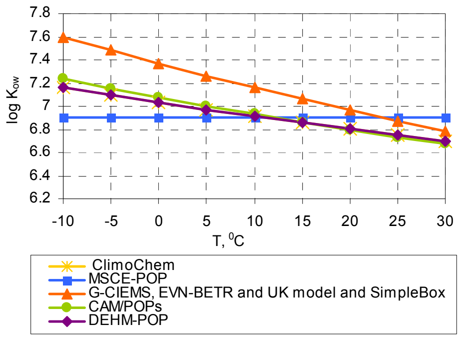


Fig.1.4. *Comparison of temperature dependencies of logK_{ow} of PCB-153 used in the models*

Table 1.5. *Absolute values, coefficients of temperature dependence and statistical parameters of octanol/water partition coefficient of PCB-153 for three arbitrary temperatures (-10 ℃, 10 ℃ and 25 ℃)*

	K_{ow}		
	-10°C	10°C	25°C
CAM/POPs	$1.72 \cdot 10^7$	$8.51 \cdot 10^6$	$5.42 \cdot 10^6$
SimpleBox	$3.96 \cdot 10^7$	$1.45 \cdot 10^7$	$7.46 \cdot 10^6$
G-CIEMS	$3.96 \cdot 10^7$	$1.45 \cdot 10^7$	$7.46 \cdot 10^6$
EVN-BETR/UK-MODEL	$3.96 \cdot 10^7$	$1.45 \cdot 10^7$	$7.46 \cdot 10^6$
CliMoChem	$1.44 \cdot 10^7$	$8.17 \cdot 10^6$	$5.62 \cdot 10^6$
DEHM-POP	$1.44 \cdot 10^7$	$8.17 \cdot 10^6$	$5.62 \cdot 10^6$
Average	$2.95 \cdot 10^7$	$1.20 \cdot 10^7$	$6.72 \cdot 10^6$
Square deviation	$1.22 \cdot 10^7$	$3.11 \cdot 10^6$	$9.55 \cdot 10^5$
min	$1.44 \cdot 10^7$	$8.17 \cdot 10^6$	$5.42 \cdot 10^6$
max	$3.96 \cdot 10^7$	$1.45 \cdot 10^7$	$7.46 \cdot 10^6$
max/min	**2.8**	**1.8**	**1.4**

The difference between all models using temperature dependencies in terms of absolute values of octanol/water partition coefficient of PCB-153 used for modelling is not large for all considered temperatures (max/min ratios of K_{ow} vary from 2.8 to 1.4). It is seen that the values of this parameter at all considered temperatures are the largest for SimpleBox, G-CIEMS and EVN-BETR/UK-MODEL. At the same time, CAM/POPs, CliMoChem, and DEHM-POP have lower values close to one another. The value of K_{ow} used by MSCE-POP model is close to those used by ClimoChem, DEHM-POP and CAM/POPs at 10 °C.

Using the obtained difference of K_{ow} values used in various models as an estimate of the uncertainty of this parameter and sensitivity of MSCE-POP model with respect to this parameter, the uncertainty of model output due to K_{ow} can be evaluated as 3.6%. Such relatively high value of the uncertainty shows that the considered parameter is important for the evaluation of PCB-153 long-range transport. In particular, it is planned to include temperature dependence of K_{ow} in MSCE-POP model in the nearest future.

1.1.5. The organic carbon/water partition coefficient

The organic carbon/water partition coefficient (K_{oc}, dm^3/kg) strongly influences the description of processes of POP sorption by soil and sediments. All models calculate K_{oc} via K_{ow} with the help of various regression relations. The form of regression dependencies and numerical values of their coefficients are presented in Annex B (Table B.5.).

It is seen that for determination of K_{oc}, regression coefficient equal to 0.41 [*Karikhoff*, 1981] is most frequently used. G-CIEMS uses regression equation different from other models. Hence, final value of K_{oc} is most substantially affected by the difference in K_{ow} values. Temperature dependencies of organic carbon/water partition coefficient of PCB-153 used in the calculations by the participating models are compared in Fig.1.5.

Values of K_{oc} used in EVN-BETR and UK-MODEL and SimpleBox are the highest among all models practically within the whole considered temperature interval. Values of this parameter used in G-CIEMS are lower than those used in other models. For most models (CAM/POPs, CliMoChem, DEHM-POP and temperature independent value of MSCE-POP) its values differ from each other not substantially. Table 1.6 presents the range of absolute values of organic carbon/water partition coefficient of PCB-153 recalculated from K_{ow} values taken at three particular temperatures (-10°C, 10°C and 25°C) for this latter group of models.

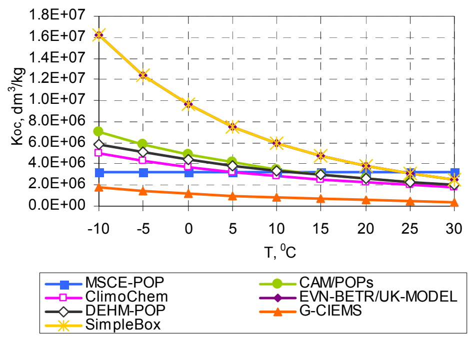


Fig. 1.5. *Comparison of temperature dependencies of organic carbon/water partition coefficient (K_{oc}, dm^3/kg) of PCB-153 used in the participating POP models*

Table 1.6. *Absolute values and statistical parameters of organic carbon/water partition coefficient (K_{oc}, dm^3/kg) of PCB-153 for three arbitrary temperatures (-10°C, 10°C and 25°C)*

	K_{oc}, dm^3/kg		
	-10°C	10°C	25°C
CAM/POPs	$7.06 \cdot 10^6$	$3.50 \cdot 10^6$	$2.23 \cdot 10^6$
CliMoChem	$5.03 \cdot 10^6$	$2.86 \cdot 10^6$	$1.97 \cdot 10^6$
DEHM-POP	$5.89 \cdot 10^6$	$3.35 \cdot 10^6$	$2.31 \cdot 10^6$
MSCE-POP	$3.26 \cdot 10^6$	$3.26 \cdot 10^6$	$3.26 \cdot 10^6$
Average	$5.31 \cdot 10^6$	$3.24 \cdot 10^6$	$2.44 \cdot 10^6$
Square deviation	$1.39 \cdot 10^6$	$2.37 \cdot 10^5$	$4.88 \cdot 10^5$
min	$3.26 \cdot 10^6$	$2.86 \cdot 10^6$	$1.97 \cdot 10^6$
max	$7.06 \cdot 10^6$	$3.50 \cdot 10^6$	$3.26 \cdot 10^6$
max/min	**2.2**	**1.2**	**1.7**

The difference between the highest and the lowest values of K_{oc} used by these models is not so large (max/min ratio varies from 2.2 to 1.2 for the considered temperatures). The values used by MSCE-POP models are in between the others.

Since the values of K_{oc} are in the direct dependence with values of K_{ow}, the uncertainty of model output due to the uncertainty of this parameter can be also evaluated as 3.6%.

1.1.6. Degradation rate constants of PCBs in the environmental media

The multi-compartment models contain a different number of the environmental media included in their descriptions. The degradation process of POPs in each medium is characterized by the values of its half-life ($t_{1/2}$) or degradation rate constant (k_d).

The degradation process in the atmosphere is mainly considered as the gas-phase reaction of a pollutant with hydroxyl radicals and all other reactions are neglected. The temperature-dependent second order rate constants of this reaction are used by CAM/POPs, CliMoChem and MSCE-POP models. No temperature dependence of degradation rate constants in air is used by EVN-BETR and UK-MODEL, SimpleBox and G-CIEMS.

In all models except for CliMoChem degradation processes in other media than air are temperature independent (for PCB-153). Degradation of POPs in soil, water, sediment and vegetation is described as a first-order process.

More detailed information on values of degradation rate constants including details of their calculations and literature sources is presented in Annex B (Table B.6).

The second-order rate constants of PCB-153 degradation process in the air in the form of temperature dependencies are compared in Fig. 1.6.

Following the data reported, CliMoChem and MSCE-POP models use one and the same values of temperature dependent rate constants of PCB-153 degradation in the atmosphere. CAM/POPs uses higher values.

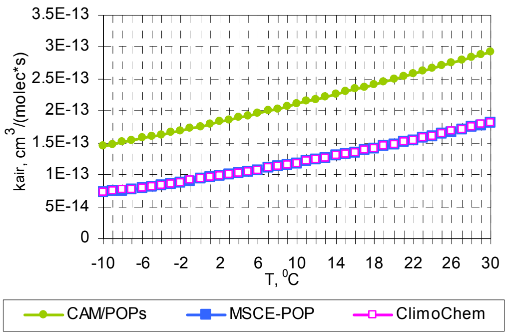


Fig. 1.6. *Comparison of temperature dependencies of degradation rate constant of PCB-153 in the atmosphere*

In order to have possibility to compare values of rate constant of PCB-153 degradation in the atmosphere used in all participating models, the rate constants of the second order were yearly averaged for the models, which keep this parameter temperature dependent. This calculation was made with the use of monthly averaged temperatures calculated on the basis of meteorological data for 1997, 1998 and 1999 in Europe. Then multiplying the second order rate constants by mean annual OH-radical concentration in the surface layer of 2 km depth at the latitude of 45^0N ($0.8 \cdot 10^6$ molec/cm^3) [*Yu Lu and Khall*, 1991], the first order degradation rate constants were calculated. The results for PCB-153 are presented in Table 1.7. However, the usage of the mean annual OH-radical concentration for all the models, which in reality include this parameter in different ways, is rather rough assumption. For an example, in CliMoChem it varies depending on the temperature and in MSCE-POP - depending on the season.

The rate constants of the first order degradation process in soil, sea and vegetation used in CliMoChem model, which keeps these parameters temperature dependent, were yearly averaged. This calculation was also made with the use of monthly averaged temperatures calculated on the basis of meteorological data for 1997, 1998 and 1999 in Europe.

To illustrate the dispersion of absolute values of the first-order degradation rate constants of PCB-153 in the atmosphere and in other media used in the participating models, statistical treatment of these parameters is made and some statistics are given in Table 1.8.

There is a considerable difference in absolute values of degradation rate constants of PCB-153 (s^{-1}) between the models, which are using and not using temperature dependencies of degradation rate constants. It is exemplified by the differences in highest and lowest values of these parameters for degradation processes in air, soil, and water and sediments. Max/min ratios for degradation processes in air, soil, and water vary within a factor of 4-5. The difference between temperature-dependent values of degradation rate constant of PCB-153 in air is within a factor of 2. EVN-BETR and UK-MODEL, SimpleBox, G-CIEMS use one and the same values of temperature independent rate constants taken from [*Mackay et al.* 1992]. The difference of degradation rate constant in vegetation between EVN-BETR and UK-MODEL and CliMoChem models (max/min ratio) is around 10. Degradation in sediments is considered in EVN-BETR and UK-MODEL only.

Table 1.7. *Monthly averaged temperatures calculated on the basis of meteorological data for 1997, 1998 and 1999 in Europe and the yearly average degradation rate constants of PCB-153 for the models which use temperature dependence of these parameters*

Month	Temperatures, °C			CAM/POPs	MSCE-POP	CLIMOCHEM			
	Over land	Over sea	Average	air, $cm^3 \cdot molec^{-1} \cdot s^{-1}$	air, $cm^3 \cdot molec^{-1} \cdot s^{-1}$	air, $cm^3 \cdot molec^{-1} \cdot s^{-1}$	soil, s^{-1} (for Over land temp)	sea, s^{-1} (for Over sea temp)	veg., s^{-1} (for aver. temp)
Jan	4	4	4	$1.90\cdot10^{-13}$	$1.02\cdot10^{-13}$	$1.03\cdot10^{-13}$	$4.67\cdot10^{-10}$	$6.43\cdot10^{-10}$	$9.89\cdot10^{-8}$
Feb	4	3	4	$1.90\cdot10^{-13}$	$1.02\cdot10^{-13}$	$1.03\cdot10^{-13}$	$4.67\cdot10^{-10}$	$6.13\cdot10^{-10}$	$9.89\cdot10^{-8}$
Mar	7	5	6	$1.97\cdot10^{-13}$	$1.07\cdot10^{-13}$	$1.08\cdot10^{-13}$	$5.37\cdot10^{-10}$	$6.74\cdot10^{-10}$	$1.04\cdot10^{-7}$
Apr	11	6	9	$2.07\cdot10^{-13}$	$1.15\cdot10^{-13}$	$1.16\cdot10^{-13}$	$6.44\cdot10^{-10}$	$7.06\cdot10^{-10}$	$1.11\cdot10^{-7}$
May	17	10	13	$2.22\cdot10^{-13}$	$1.26\cdot10^{-13}$	$1.27\cdot10^{-13}$	$8.37\cdot10^{-10}$	$8.47\cdot10^{-10}$	$1.22\cdot10^{-7}$
Jun	21	14	17	$2.38\cdot10^{-13}$	$1.38\cdot10^{-13}$	$1.38\cdot10^{-13}$	$9.92\cdot10^{-10}$	$1.01\cdot10^{-10}$	$1.33\cdot10^{-7}$
Jul	22	16	19	$2.46\cdot10^{-13}$	$1.44\cdot10^{-13}$	$1.45\cdot10^{-13}$	$1.03\cdot10^{-9}$	$1.10\cdot10^{-9}$	$1.39\cdot10^{-7}$
Aug	22	16	19	$2.46\cdot10^{-13}$	$1.44\cdot10^{-13}$	$1.45\cdot10^{-13}$	$1.03\cdot10^{-9}$	$1.10\cdot10^{-9}$	$1.39\cdot10^{-7}$
Sep	18	13	15	$2.30\cdot10^{-13}$	$1.32\cdot10^{-13}$	$1.32\cdot10^{-13}$	$8.74\cdot10^{-10}$	$9.68\cdot10^{-10}$	$1.28\cdot10^{-7}$
Oct	14	10	12	$2.18\cdot10^{-13}$	$1.24\cdot10^{-13}$	$1.24\cdot10^{-13}$	$7.35\cdot10^{-10}$	$8.47\cdot10^{-10}$	$1.19\cdot10^{-7}$
Nov	10	7	9	$2.07\cdot10^{-13}$	$1.15\cdot10^{-13}$	$1.16\cdot10^{-13}$	$6.16\cdot10^{-10}$	$7.39\cdot10^{-10}$	$1.11\cdot10^{-7}$
Dec	6	5	6	$1.97\cdot10^{-13}$	$1.07\cdot10^{-13}$	$1.08\cdot10^{-13}$	$5.13\cdot10^{-10}$	$6.74\cdot10^{-10}$	$1.04\cdot10^{-7}$
Averaged second-order rate constants, $cm^3 \cdot molec^{-1} \cdot s^{-1}$				$2.16\cdot10^{-13}$	$1.22\cdot10^{-13}$	$1.22\cdot10^{-13}$	-	-	-
Averaged first-order rate constants, s^{-1}				$1.72\cdot10^{-7}$	$9.73\cdot10^{-8}$	$9.78\cdot10^{-8}$	$7.29\cdot10^{-10}$	$8.27\cdot10^{-10}$	$1.18\cdot10^{-7}$

Table 1.8. *Absolute values and statistical parameters of degradation rate constants of first order (PCB-153)*

	k_{air}, s^{-1}	k_{soil}, s^{-1}	k_{water}, s^{-1}	$k_{sediment}$, s^{-1}	k_{veg}, s^{-1}
CAM/POPs*	$1.72\cdot10^{-7}$	-	-	-	-
CliMoChem*	$9.78\cdot10^{-8}$	$7.29\cdot10^{-10}$	$8.27\cdot10^{-10}$	-	$1.18\cdot10^{-7}$
MSCE-POP*	$9.73\cdot10^{-8}$	$1.17\cdot10^{-9}$	$1.60\cdot10^{-9}$	-	-
SimpleBox**	$3.50\cdot10^{-8}$	$3.50\cdot10^{-9}$	$3.50\cdot10^{-9}$	-	-
G-CIEMS**	$3.50\cdot10^{-8}$	$3.50\cdot10^{-9}$	$3.50\cdot10^{-9}$	-	-
EVN-BETR/UK-MODEL**	$3.50\cdot10^{-8}$	$3.50\cdot10^{-9}$	$3.50\cdot10^{-9}$	$3.50\cdot10^{-9}$	$1.13\cdot10^{-8}$
Average	$7.87\cdot10^{-8}$	$2.48\cdot10^{-9}$	$2.59\cdot10^{-9}$	-	-
Square deviation	$5.02\cdot10^{-8}$	$1.26\cdot10^{-9}$	$1.15\cdot10^{-9}$	-	-
min	$3.50\cdot10^{-8}$	$7.29\cdot10^{-10}$	$8.27\cdot10^{-10}$	-	-
max	$1.72\cdot10^{-7}$	$3.50\cdot10^{-9}$	$3.50\cdot10^{-9}$	-	-
max/min	**4.9**	**4.8**	**4.2**	**-**	**10.4**

* - the model uses temperature dependence of the degradation rate in the atmosphere
** - the model does not use temperature dependence of the degradation rate in the atmosphere

Using the obtained relative deviations of degradation rate values between models as an estimate of the uncertainty of this parameter, the uncertainty of model output of MSCE-POP model due to the description of degradation process can be evaluated as 6%.

Thus, the analysis of parameterizations of models participating in the POP model intercomparison study can be used for evaluating possible uncertainties of pollutant-related parameters. Most of the models use similar sets of pollutant-related properties as MSCE-POP does and the difference in values of these parameters for such models are not so high. The uncertainties of MSCE-POP model output can be evaluated on the basis of scattering of these parameters with the help of earlier calculated values of model sensitivity (see [*Gusev et al.,* 2005a]). Relatively high uncertainty of the output is due to degradation rates in environmental media (about 6%). The uncertainties due to air/water, octanol/air and octanol/water partitioning coefficients are still essential (from 2 to 5%). It was found that inclusion of temperature dependence of octanol/water partitioning coefficient into the MSCE-POP model parameterisation is necessary. Since all models use very close values of the subcooled liquid vapour pressure, the above estimated uncertainty due to this parameter is rather low (less than 1%). The overall uncertainty due to the uncertainties of pollutant-related parameters can be evaluated as 20% at maximum.

1.2. Comparison of process description between POP models

To reveal similarities and distinction of MSCE-POP model's main output in comparison with that of other well-known models, some results of the POP Model Intercomparison Study are presented in this Section. Predicted concentrations in the main environmental media (atmosphere, soil, water and vegetation) together with intermedia mass flows are compared between different models.

The main emphasis in the Intercomparison Study [*Shatalov et al*., 2004; *Shatalov et al*., 2005] was put on the comparison of the description and parameterization of basis processes affecting PCB fate in the environment. Three PCB congeners - low chlorinated PCB-28, medium PCB-153 and high chlorinated PCB-180 – are considered within the study. Up to the present time a sensitivity study with respect to physical-chemical parameter values used by the participating models in the description of gas/particle partitioning, deposition and gaseous exchange processes was performed. Besides, mass balance estimates (masses in different environmental compartments; masses degraded in these compartments; mass flows transported in/out of the specified domain; intermedia mass flows; and concentrations at each media interface) and calculated deposition and concentration fields of PCBs in different environmental compartments were obtained. A sensitivity study with respect to physical-chemical parameter values used for mass balance estimates was also carried out. Additionally, POP depositions and concentrations in various environmental compartments as predicted by different models were compared with monitoring data. The final analysis of comparison of these results is under preparation.

The computational experiments on calculation of gas/particle partitioning and intermedia exchange flows are performed with the use of physical-chemical data set of the individual model ("own data set") on the basis of agreed input data (POP emission data scenario with zero initial concentrations and with initial concentrations in media of the specified calculation domain) and a number of geophysical parameters of the calculation domain (e.g. land cover data, leaf area index, organic matter content in soil, etc).

The POP Model Intercomparison Study involves models that are different in terms of overall modelling approach and objectives. This includes differences in process descriptions as well as variability in their spatial and temporal resolutions. Besides, parameterizations of models participating in the intercomparison study include the basic physical-chemical properties and degradation rates of PCBs, which in general can be characterized by considerable scattering of absolute values (see section 1.1 above). Therefore, in order to make the comparison of model results more transparent and easy for interpretation, it was reasonable to harmonise such important input parameters as physical-chemical properties and degradation rates of PCBs for all models. To do this, input data set common for all models was selected for each of the considered PCB congeners. A use of "reference" data sets in the model intercomparison study allows clearing up the influence of difference in input parameters such as physical-chemical properties and degradation rates on model output and comparing model approaches as they are. As "reference" sets for the calculation experiments with PCBs the internally consistent data on vapour pressure, Henry's law constant, water solubility, octanol/water and octanol/air partition coefficients presented by *Li et al.* [2003] was taken. For the recalculation of organic carbon/water partition coefficient from octanol/water coefficient, the values of coefficients of regression relation from [*Karikhoff*, 1981] are proposed. For the sake of simplicity, degradation rate constants in various environmental media are assumed seasonally independent. These values were taken from [*Mackay et al*., 1992]. Annex B of this report contains information on "reference" data set of PCB-153 physical-chemical properties selected for the model calculations within this intercomparison study. The results obtained with "own" data set are compared with those based on "reference" data set also in order to evaluate sensitivity of mass balance estimates to variation of physical-chemical parameter values.

Since some models use "reference" data set as a set of own physical-chemical properties, an "alternative" data set was elaborated to perform sensitivity study for such models. The "alternative" data set (see also Annex B) is in general agreement with the individual physical-chemical data sets of CliMoChem and DEHM-POP models based mainly on data taken from [*Beyer et al*., 2002]. Values of subcooled liquid vapour pressure and water solubility that are not used as parameters in the models mentioned above are added from the same paper. Coefficients of regression relation of the organic carbon/water partition coefficient with the temperature dependent octanol-water coefficient are taken from [*Seth et al*., 1999] as they used in CliMoChem model. Degradation rate constants in various environmental media used in CliMoChem model in the form of temperature dependencies are transferred into seasonally independent values.

PCBs being typical POPs are characterized by the presence in the environment not only in the particulate phase but also in the gaseous phase in different proportions depending on degree of chlorination of a congener. The processes of advective transport, dry and wet depositions of particulate phase are described in MSCE-POP model similarly as they are in MSCE-HM model. Therefore, here we concentrate at such POP-specific processes as gas-particle partitioning, and intermedia transport.

The exposition in subsequent subsections goes as follows.

First, the comparison of description of gas-particle partitioning process and model results of calculation experiments devoted to this process are presented. The latter includes results of the sensitivity study with respect to physical-chemical parameter values used by the participating models in the description of the considered process.

Second, the comparison of calculated values of PCB-153 air concentrations and concentrations formed in the interfaces of main environmental media (soil, ocean and vegetation) is discussed. Mass flows between main media interfaces obtained by different models are also compared.

Main output of the POP model intercomparison study in terms of verification of MSCE-POP model's results will be discussed in the framework of EMEP/TFMM Workshop on the review of the MSC-E models on HM and POPs (Moscow, 13-14 October 2005). Here numerical results for the first priority substance (PCB-153) are given. The corresponding results for substances of the second priority (PCB-28 and PCB-180) will be presented at the Workshop.

1.2.1. Gas/particle partitioning

Model approaches

In *Shatalov et al*. [2004] descriptions of the considered process are available for seven participating models: EVN-BETR and UK-MODEL, CliMoChem, G-CIEMS, DEHM-POP, SimpleBox, CAM/POPs and MSCE-POP. Basically, there exist two approaches to model evaluation of the fraction of particulate phase of a pollutant in the atmosphere. The first is based on the Junge-Pankow adsorption model [*Junge*, 1977; *Pankow*, 1987]. In this case POP fraction φ adsorbed on the atmospheric aerosol particles is calculated using vapor pressure of the subcooled liquid p_{0L}:

$$\varphi = \frac{c \cdot \theta}{p_{0L} + c \cdot \theta} \tag{1.3}$$

where c is the constant depending on thermodynamic parameters of adsorption process and on properties of aerosol particle surface;

θ is the specific surface of aerosol particles, m^2/m^3.

This approach is used in SimpleBox, CAM/POPs and MSCE-POP models. In all these models the temperature dependence of p_{0L} is taken into account. Besides, CAM/POPs model additionally uses 12-bin structure of sulphate aerosol size for calculations of gas/aerosol partitioning.

The second is based on absorption model of gas/aerosol partitioning [*Finizio et al.*, 1997; *Falconer and Harner*, 2000]. Under this approach the fraction of POPs absorbed by organic matter of aerosol particles is calculated with the use of particle/gas partition coefficient K_{PA} defined via octanol/air partition coefficient K_{oa}:

$$\varphi = \frac{K_{PA} \cdot TSP}{(K_{PA} \cdot TSP + 1)} \tag{1.4}$$

Here φ is the fraction of compound sorbed to particles, K_{PA} is the gas-particle partition coefficient, and TSP is the total suspended particle concentration. K_{PA} is calculated using different regression relations via K_{oa}, in particular [*Falconer and Harner*, 2000]:

$$\log K_{PA} = m_r \log K_{oa} + \log f_{om} - 11.91, \tag{1.5}$$

where m_r - constant expected to have a value close to +1 for equilibrium partitioning;
K_{oa} - octanol-air partition coefficient;
f_{om} - fraction of organic matter in the particles.

This approach is used in DEHM-POP.

To calculate gas-particle partitioning coefficient CliMoChem uses another equation taken from [*Finizio et al*. 1997]:

$$K_{PA} = K_{oa}^{0.55} \cdot 10^{-8.23} \tag{1.6}$$

EVN-BETR and UK-MODEL and G-CIEMS calculated this coefficient with the help of Eq.(1.7) and (1.8), respectively:

$$K_{PA} = 3.5 \cdot K_{oa} \tag{1.7}$$

$$K_{PA} = f_{om}\, K_{oa} / (\tilde{\rho} \cdot 1000), \tag{1.8}$$

where f_{om} is the organic matter mass fraction, and $\tilde{\rho}$ is the density of aerosol particles.

Below the results of calculations of φ for different environmental conditions carried out by the participating models are analyzed. The following models took part in this comparison: CAM/POPs, CliMoChem, DEHM-POP, EVN-BETR and UK-MODEL, G-CIEMS, SimpleBox, and MSCE-POP.

Input data

Nine sets of input data (different ambient temperatures in the range from − 12ºC to 32ºC) are proposed for modelling experiments with PCB-153.

Table 1.9. *Input data for computation experiments with PCB-153 describing gas/particle partitioning*

N	Experi-ment 1	Experi-ment 2	Experi-ment 3	Experi-ment 4	Experi-ment 5	Experi-ment 6	Experi-ment 7	Experi-ment 8	Experi-ment 9
Averaged ambient temperature, C	-12	-5	0	6	10	15	20	26	32
Total Suspended Matter, TSP, $\mu g/m^3$	30	30	30	30	30	30	30	49	66
Organic content in the aerosol, %	20	20	20	20	20	20	20	20	20

Output of computation experiments describing gas/particle partitioning process is PCB particulate fraction in the atmosphere.

Results

This section contains the analysis of the results of experiments on the calculations of particulate fraction φ of the considered pollutants obtained by the participating models. Two sets of calculation results: obtained with “reference” data set of physical-chemical properties common for all models and with “own/alternative” data sets are used. Here numerical results for the first priority substance - PCB-153 are presented.

Analysis of the experiments. The analysis is performed into two stages. At the first stage we present an analysis of the values of calculated fractions of particulate phase and characterize the spread in these values between models in each of the experiments. At the second stage we analyze pairwise differences between participating models using the regression analysis.

Here we use the following statistical parameters for each experiment:

- the value m_φ of fractions of particulate phase averaged between participating models;
- the value of square deviation σ_φ between results obtained by different models;

First of the above parameters illustrates the level of particulate phase fraction calculated by all considered models. The second parameter characterizes the dispersion of this fraction between the models.

The analysis of pairwise differences between calculation results obtained by different models is based on the regression relation between calculated values of parameters A_T^1 and A_T^2 obtained by each two models for different experiments:

$$A_T^2 = \alpha_{12} A_T^1 + \beta_{12} + \omega_{12}, \tag{1.9}$$

where α_{12} and β_{12} are regression coefficients;

ω_{12} is the random component of the regression relation (“white noise”).

For evaluation of closeness of calculated results obtained by models, we shall use regression coefficients α_{12} and β_{12} (characterizing a non-random component of the regression relation), *the residual square deviation,* that is, square deviation $\sigma^{res}{}_{12}$ of ω_{12} (characterizing the magnitude of random component) and the correlation coefficient r_{12}.

Reference data set. Calculation results for PCB-153 together with m_φ and σ_φ are presented in Table 1.10. For G-CIEMS calculations of gas-particle partitioning using molecular weight only (G-CIEMS 1) and using absorption scheme (G-CIEMS 2) were carried out.

Table 1.10. *Calculation results: fractions of particulate phase of PCB-153 calculated by models and statistical parameters used for evaluation (reference data set)*

Exp. No	T (°C)	DEHM-POP	G-CIEMS		MSCE-POP	CliMoChem	SimpleBox*	m_φ	σ_φ
			1	2					
1	-12	0.81	0.96	0.78	0.88	0.11	0.98	0.75	0.32
2	-5	0.58	0.89	0.53	0.71	0.09	0.94	0.62	0.31
3	0	0.40	0.79	0.35	0.54	0.08	0.88	0.51	0.30
4	6	0.21	0.61	0.18	0.33	0.07	0.76	0.36	0.27
5	10	0.13	0.48	0.11	0.22	0.06	0.66	0.28	0.24
6	15	0.07	0.32	0.06	0.13	0.06	0.50	0.19	0.18
7	20	0.04	0.21	0.03	0.07	0.05	0.35	0.12	0.13
8	26	0.03	0.12	0.01	0.04	0.07		0.05	0.04
9	32	0.02	0.06	0.01	0.02	0.08		0.04	0.03

* - only 7 experiments for Simple Box

The plot of dependence of φ on T calculated by participating models is presented in Fig. 1.7. In addition, at the same plot the graph of average (between models) particulate fraction is given (red line). It is seen that practically all models (except CliMoChem) closely describe temperature dependence of particulate fraction. For the lower temperatures, values of fraction of particulate phase of PCB-153 calculated by CliMoChem are much lower than ones calculated by other participating models. Considering results of the first seven experiments, the highest results of this parameter are obtained by SimpleBox model.

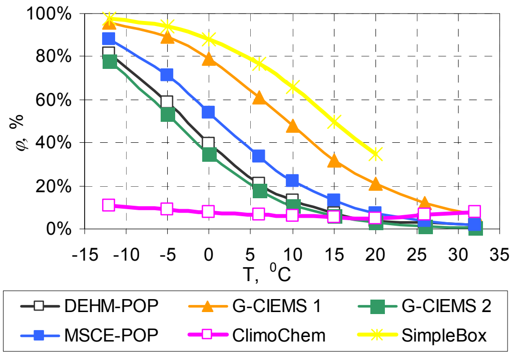


Fig. 1.7. *Temperature dependence of fraction of particulate phase (φ, %) obtained by participating models on the basis of "reference" data set*

We recall that the experiments differ mainly by ambient air temperature T (and some other parameters, see Section 1.2.1. "Model approaches"). For each temperature within the considered interval of temperatures (-12°C - 32°C), square deviation σ_φ between different model calculations (see last columns in Table 1.10) do not exceed the averaged value of particulate phase fractions. Since square deviation of particulate fraction is about 60% of the mean value, it can be concluded that most models closely describe the gas/particle partitioning process.

Calculated correlation coefficients between the results of participating models are given in Table 1.11. It is seen that these coefficients are high enough and vary from 0.7 to 1.

Table 1.11. *Correlation coefficients* r_{12}

	G-CIEMS 1	G-CIEMS 2	MSCE-POP	CliMoChem	SimpleBox*
DEHM-POP	0.92	1.00	0.99	0.88	0.89
G-CIEMS 1	–	0.91	0.97	0.70	0.99
G-CIEMS 2	–	–	0.98	0.88	0.87
MSCE-POP	–	–	–	0.83	0.93
CliMoChem	–	–	–	–	0.92

* - by 7 experiments only

The values of regression coefficients α and β (see relation (1.9)) calculated for all pairs of models are shown in Table 1.12.

Table 1.12. *Coefficients of regression dependence between the models (α / β)*

	G-CIEMS 1	G-CIEMS 2	MSCE-POP	CliMoChem	SimpleBox*
DEHM-POP	1.1 / 0.21	0.95 / –0.01	1.1 / 0.05	0.06 / 0.06	0.72 / 0.49
G-CIEMS 1	–	0.73 / –0.13	0.90 / –0.12	0.04 /0.05	0.81 / 0.23
G-CIEMS 2	–	–	1.14 / 0.07	0.06 / 0.06	0.73 / 0.51
MSCE-POP	–	–	–	0.05 / 0.06	0.72 / 0.43
CliMoChem	–	–	–	–	10 / - 0.02

* - by 7 experiments only

The differences between the models are explained mainly by scaling coefficients α ranging from 0.04 to 10. For the most part of the models, α varies far less (from 0.72 to 1.14). Coefficients β are not very large for all pairs of models (lying in the range from –0.13 to 0.51). This is a numerical expression of the fact that shapes of curves expressing temperature dependencies of φ (Fig. 1.7) are similar for these models.

To assess the reliability of comparative analysis given above calculations of pairwise residual square deviation σ were done (Table 1.13).

Table 1.13. *Residual square deviation, σ^{res}_{12}*

	G-CIEMS 1	G-CIEMS 2	MSCE-POP	CliMoChem	SimpleBox*
DEHM-POP	0.36	0.03	0.13	0.03	0.27
G-CIEMS 1	–	0.31	0.22	0.04	0.08
G-CIEMS 2	–	–	0.16	0.03	0.29
MSCE-POP	–	–	–	0.03	0.21
CliMoChem	–	–	–	–	0.23

* - by 7 experiments only

It is seen that the values of σ range from 0.03 to 0.36. This testifies the possibility of usage regression analysis for evaluation of the difference between model calculations.

Thus, all models describe temperature dependence of the fraction of particulate phase of PCB-153 in the atmosphere similarly. The difference of model results can be explained by difference in base values of K_{oa} or p_{ol} since the change of these values leads to scaling of calculated values of φ.

Own/alternative data set. Calculation results for PCB-153 obtained up to the moment together with m_φ and σ_φ are presented in Table 1.14. The data set used in calculations by each model is indicated in the first row.

Table 1.14. *Calculation results: fractions of particulate phase of PCB-153 calculated by models and statistical parameters used for evaluation "own/alternative" data set)*

Exp. No	T (°C)	EVN-BETR and UK-MODEL	DEHM-POP	G-CIEMS 1	G-CIEMS 2	CAM/POPs	MSCE-POP	CliMoChem	SimpleBox	m_φ	σ_φ
Data set		own	own		alt	own	own	own	alt		
1	-12	0.93	0.83		0.80	0.94	0.87	0.16	0.96	0.78	0.28
2	-5	0.75	0.62		0.57	0.85	0.70	0.10	0.90	0.64	0.27
3	0	0.68	0.44		0.39	0.73	0.52	0.07	0.84	0.52	0.26
4	6	0.46	0.26		0.22	0.53	0.32	0.04	0.72	0.36	0.22
5	10	0.33	0.17		0.14	0.39	0.21	0.03	0.63	0.27	0.20
6	15	0.19	0.095		0.08	0.24	0.12	0.023	0.50	0.18	0.16
7	20	0.11	0.053		0.04	0.14	0.065	0.017	0.38	0.12	0.12
8	26	0.086	0.042		0.03	0.12	0.032	0.018	0.36	0.06	0.04
9	32	0.057	0.029		0.02	0.078	0.016	0.017	0.30	0.04	0.03

The plot of dependence of φ on T calculated by participating models with "own / alternative" data set is presented in Fig. 1.8. In addition, at the same plot the graph of average (between models) particulate fraction is given (red line).

Calculated correlation coefficients between the results of participating models are given in Table 1.15. It is seen that these coefficients are high and exceed 0.9.

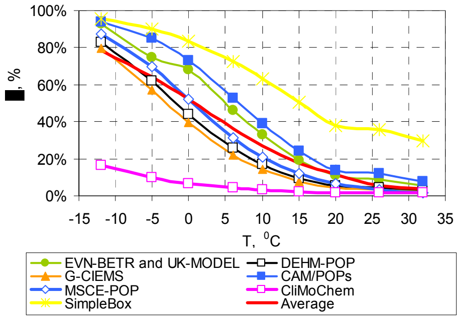


Fig. 1.8. *Temperature dependence of fraction of particulate phase (φ, %) obtained by participating models on the basis of "own/alternative" data set*

Table 1.15. *Correlation coefficients* r_{12}

	DEHM-POP	G-CIEMS 2	CAM/POPs	MSCE-POP	CliMoChem	SimpleBox
EVN-BETR and UK MODEL	0.98	0.97	1.00	0.99	0.93	0.98
DEHM-POP	–	1.00	0.97	1.00	0.98	0.93
G-CIEMS 2	–	–	0.96	0.99	0.99	0.91
CAM/POPs	–	–	–	0.98	0.91	0.99
MSCE-POP	–	–	–	–	0.97	0.95
CliMoChem	–	–	–	–	–	0.86

The values of regression coefficients α and β calculated for all pairs of models are shown in Table 1.16.

Table 1.16. *Coefficients of regression dependence between the models (α / β)*

	DEHM-POP	G-CIEMS 2	CAM/POPs	MSCE-POP	CliMoChem	SimpleBox
EVN-BETR and UK MODEL	0.87/ –0.07	0.83/ –0.07	1.02/0.04	0.96/ –0.07	0.14/ –0.004	0.76/0.32
DEHM-POP	–	0.96/ –0.01	1.11/0.13	1.09/0.01	0.17/0.006	0.80/0.40
G-CIEMS 2	–	–	1.15/0.15	1.13/0.03	0.18/0.008	0.83/0.41
CAM/POPs	–	–	–	0.93/ –0.10	0.14/ –0.007	0.74/0.29
MSCE-POP	–	–	–	–	0.15/0.005	0.76/0.38
CliMoChem	–	–	–	–	–	4.34/0.39

The difference between the models' results is determined by scaling coefficient α, which varies within not very wide range (from 0.14 to 4.34). However, it is seen that this coefficients are very close to 1 for the most part of considered pairs of models (range from 0.8 to 1.3). Coefficients β are small enough compared with mean values of the considered parameter for the most part of model pairs also (lying in the range from –0.10 to 0.41).

To assess the reliability of comparative analysis given above calculations of pairwise residual square deviation σ were done (Table 1.17).

Table 1.17. *Residual square deviation,* σ^{res}_{12}

	DEHM-POP	G-CIEMS 2	CAM/POPs	MSCE-POP	CliMoChem	SimpleBox
EVN-BETR and UK MODEL	0.167	0.188	0.075	0.125	0.050	0.137
DEHM-POP	–	0.031	0.237	0.069	0.027	0.260
G-CIEMS 2	–	–	0.272	0.102	0.022	0.284
CAM/POPs	–	–	–	0.161	0.058	0.100
MSCE-POP	–	–	–	–	0.036	0.214
CliMoChem	–	–	–	–	–	0.357

Values of σ vary within not very wide range also from 0.022 to 0.357.

Comparison between two data sets. The difference between calculation results obtained with two data sets of pollutant properties (for those models who provided calculations for both these sets) is shown in Table 1.18.

Table 1.18. *Difference between calculations with two data sets*

Exp.No	*T* (°C)	DEHM-POP	G-CIEMS 2	MSCE-POP	CliMoChem	SimpleBox
1	-12	2%	2%	-1%	48%	-2%
2	-5	6%	8%	-2%	7%	-4%
3	0	11%	13%	-3%	-16%	-5%
4	6	23%	22%	-6%	-36%	-5%
5	10	29%	28%	-7%	-47%	-4%
6	15	35%	36%	-9%	-58%	1%
7	20	42%	41%	-10%	-66%	9%
8	26	47%	148%	-11%	-73%	
9	32	57%	236%	-12%	-79%	

This difference is visualized in Fig. 1.9.

It is seen that the difference in calculation of gas/particle partitioning caused by usage of "reference " and "own or alternative" data sets of pollutant properties is moderate. Large differences are characteristic of high temperatures where values of fractions of particulate phase are small (see Table 1.18).

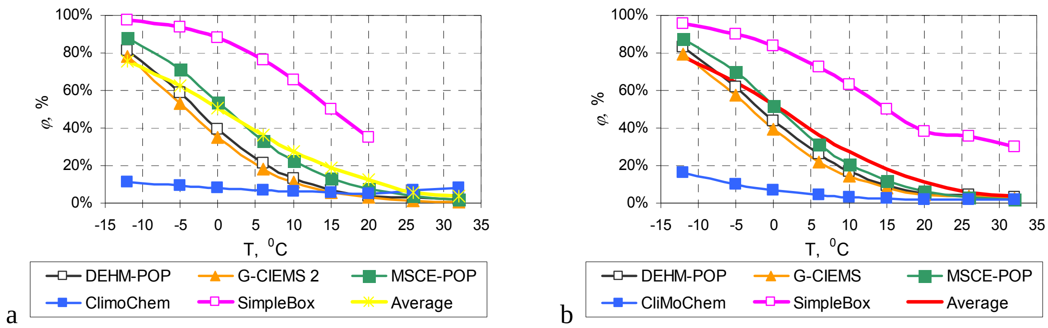


Fig. 1.9. *Temperature dependence of fraction of particulate phase (φ, %) obtained by participating models on the basis of "reference" (a) and "own/alternative" (b) data sets (for models presented both calculations)*

Thus, for the considered interval of temperatures, most models' results on particulate fractions of PCB-153 in the atmosphere obtained using different approaches to the description of gas/particle partitioning process are rather close to each other. The participating models mainly use two approaches based on adsorption and absorption schemes.

1.2.2. Concentrations in main environmental media and intermedia mass flows

This subsection contains a preliminary analysis of mass balance estimates and results of the sensitivity study with respect to physical-chemical parameter values used for these estimates. A comparison of model results on PCB-153 concentrations formed in the main environmental media (atmosphere, soil, ocean) is discussed. Calculated values of PCB-153 mass flows between the atmosphere and soil, water and vegetation are also considered.

Parameterizations of the considered processes (dry and wet depositions and gaseous exchange between the atmosphere and different underlying surfaces) implemented in the participating models are presented in detail in [*Shatalov et al*., 2004].

Eight models participated in calculations of mass balance, spatial distribution of depositions and concentrations, and in the sensitivity study as well as in the comparison of model results with monitoring data: ADEPT, CAM/POPs, CliMoChem, DEHM-POP, EVN-BETR and UK-MODEL, G-CIEMS, SimpleBox, and MSCE-POP. The calculations of SimpleBox model are performed with two versions: SimpleBox 3.0 and SimpleBox 3.12. The latter version does not assume that the soil compartment has homogeneous concentrations, but it assumes an exponentially decline of soil concentration with depth. Results of this model include calculations done on the basis of initial concentrations given as input data, zero initial concentrations for one-year period (2000) and with historical emissions for 20-year period (from 1981 to 2000). Initial concentrations in CliMoChem simulation for 2000 are based on a historical emission scenario run from 1981 to 1999. DEHM-POP and MSCE-POP models performed calculations both with initial concentrations given as input data and with zero initial concentrations. Results of CAM/POPs, EVN-BETR and UK-MODEL, and G-CIEMS were calculated with the use of initial concentrations. Results of ADEPT model were calculated with zero initial concentrations in the main environmental media for the beginning of 2000.

CliMoChem model calculates masses and mass fluxes per season (each three months, starting in January, April, July and October) and monthly values are not available. For comparison with these results, seasonal values of all output parameters were calculated on the basis of monthly values given by all other models. For the sake of comparison with EVN-BETR and UK-MODEL results on net intermedia mass flows from the atmosphere to different underlying surfaces (soil, water, vegetation), values of net mass flows are calculated for all other models as sum of dry and wet deposition and gaseous exchange mass flows.

As it was agreed at the third EMEP expert meeting on intercomparison of POP models, for comparison of intermedia mass flows results obtained with non-zero initial concentrations are used. All results of this type submitted up to the moment of this report preparation are included in the comparison. The considered estimates of PCB-153 mass flows transported from one compartment to another and concentrations in these media include results of one-year calculation with initial concentrations in media given as input data calculated by CAM/POPs, EVN-BETR and UK-MODEL, G-CIEMS, MSCE-POP, and SimpleBox 3.0 (this version will be presented below as SimpleBox 3.0_1) models as well as results of long-term calculations for 20-year period with zero initial data and historical emissions carried out by CliMoChem, SimpleBox 3.0 and SimpleBox 3.12 (these versions will be presented below as SimpleBox 3.0_3 and SimpleBox 3.12_3) models. Results of CliMoChem, G-CIEMS, MSCE-POP, and SimpleBox models obtained on the basis of two different physical-chemical data sets allow us to reveal sensitivity of the estimates on intermedia mass flows and concentrations in these media to the variations in the input data.

Input data

Following the programme of the intercomparison study, a base year for the calculation is 2000. To perform calculation experiments, the European calculation domain (35° N – 70° N; 10° W – 30° E) is used. Description of the specified calculation domain proposed for the experiments includes several environmental characteristics commonly used by all models: land cover data, leaf area index, organic matter content in the soil, and total percentage of land, water and vegetation areas.

In calculations such input parameters as volume of each environmental compartment including also air height, soil depth, water depth and meteorological data in 2000 for the specified calculation domain are used by the participants in accordance with their modelling approaches. Particular parameters of environmental compartments such as properties of atmospheric aerosol, soil properties, etc are also chosen for each model individually.

G-CIEMS and SimpleBox carried out these calculations with the use of “reference” and “alternative” data sets. Results of EVN-BETR and UK-MODEL were obtained only on the basis of “reference” data set; results of CAM/POPs – on the basis of “own” data set. All other models performed the calculations on the basis of “reference” and “own” data sets.

In all model results emissions are based on the expert estimates of 2000 and historical emissions presented by [*Breivik et al.*, 2002] (see also www.nilu.no/projects/globalpcb/). Emissions are equally distributed around the year.

Results

The comparison of results on each computation experiment consists of two parts. In the first part the results of calculation experiments are compared between the models. The comparison of absolute values obtained by the models on the basis of ‘reference” data set as well as on the basis of “own or alternative” data sets is made. The following statistical parameters for each experiment are used:

m - the mean values of the considered parameters averaged between participating models;

σ - the values of square deviation between results obtained by different models.

The second part is devoted to the comparison of the calculation results obtained by each model on the basis of two different data sets of physical-chemical properties. The percentage difference in the results calculated on the basis of “own or alternative” data sets of pollutant-specific properties in comparison with those obtained with the use of “reference” data set and normalized to the “reference” results is shown. In the case of computational experiments on mass flows between media, the absolute values of the calculation results are compared.

Model results on PCB intermedia mass flows and concentrations in the main media are presented in this section for three following interfaces: atmosphere-soil; atmosphere - seawater; and atmosphere – vegetation.

Atmosphere-soil. Model results on concentrations of PCB-153 in the atmosphere at its interface with soil and in the surface soil layer, which are conditioned by intermedia transport, are considered below.

Comparison of annual values of PCB-153 concentration in the atmosphere at its interface with soil calculated by the models on the basis of “**reference**” and “**own or alternative**” data sets is presented in Fig. 1.10. The blue line in the plots shows the value of the corresponding parameter averaged between models. Different color of columns corresponds to the different types of calculations (one-year calculations on the basis of initial data; and then long-tem calculations with historical emissions).

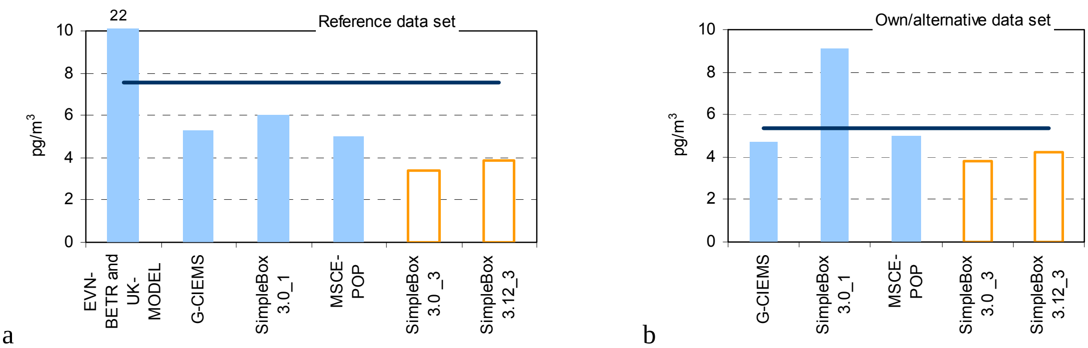
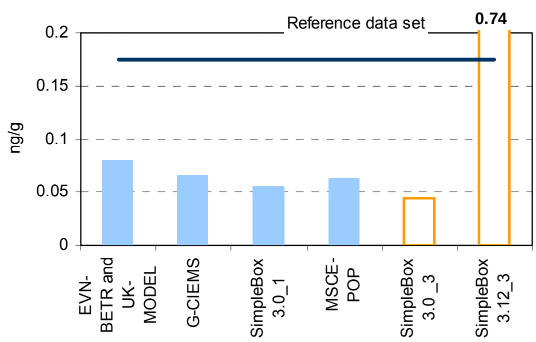


Fig. 1.10. *Comparison of annual values of PCB-153 concentration in the atmosphere at its interface with soil (pg/m^3) calculated by different models on the basis of “reference”(a) and “own or alternative” (b) data sets*

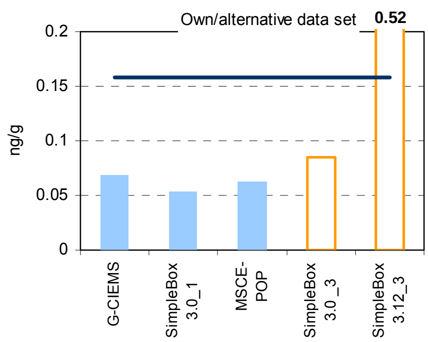
It can be seen that air concentrations values obtained on “reference” and “own/alternative” data sets are very close practically for all models except for EVN-BETR and UK-MODEL. Therefore, in the results obtained by the participating models on the basis of “reference” data set the scattering of absolute values of PCB-153 concentrations in the atmosphere is somewhat higher than that for results based on “own/alternative” data set (in “reference” set of results m = 7.59 pg/m^3, σ = 7.12 pg/m^3; in “own/alternative” set of results m = 5.37 pg/m^3, σ = 2.13 pg/m^3). Nevertheless, square deviation of annual values presented by different participating models does not exceed the averaged value in both cases. The difference between results obtained with two different data sets of physical-chemical properties is rather small. For the calculation results of G-CIEMS, the values of PCB-153 concentration in the atmosphere at its interface with soil obtained with the use of “own or alternative” data sets are smaller than those obtained with “reference” data set; and vice versa for SimpleBox and MSCE-POP models’ results. The largest difference in the results obtained with two data sets is characteristic of SimpleBox 3.0 calculations performed on the basis of initial conditions.

Comparison of annual values of PCB-153 concentration in surface soil layer calculated by the models on the basis of “**reference**” and “**own/alternative**” data sets is presented in Fig. 1.11. The black line in the plot shows the value of the corresponding parameter averaged between models. Different color of columns corresponds to the different types of calculations (one-year calculations on the basis of initial data; and then long-term calculations with historical emissions).

According to the data presented, most models similarly describe soil concentrations. Results on PCB-153 concentration in surface soil layer calculated on the basis of “reference” and “own or alternative” data sets demonstrate reasonable agreement between most models’ calculations except for results of version 3.12 of SimpleBox model. Due to that, for annual values of PCB-153 concentration in surface soil layer (in “reference” set of results m = 0.17 ng/g, σ = 0.28 ng/g; in “own/alternative” set of results m = 0.16 ng/g, σ = 0.20 ng/g), square deviation is higher than the averaged value. Difference between different models’ results obtained on the basis of two data sets of physical-chemical properties varies from 0.2 to 92%. For the calculation results of all models except G-CIEMS and SimpleBox 3.0 (based on historical emissions), the values of PCB-153 concentration in surface soil layer obtained with the use of “own or alternative” data sets are less than those obtained with “reference” data set. The largest difference in the results obtained with two data sets is characteristic of SimpleBox 3.12 results obtained on the basis of historical emissions. MSCE-POP results are characterized by the lowest sensitivity to the variations in physical-chemical data used.



a



b

Fig. 1.11. *Comparison of annual values of PCB-153 concentration in surface soil layer (ng/g) calculated by different models on the basis of “reference” (a) and “own or alternative” (b) data sets*

Thus, the most of participating models predicted close values of PCB-153 concentrations in the atmosphere at its interface with soil and in the surface soil layer. The difference between the maximum and minimum values of soil concentrations is higher than that for air concentrations. The difference between results obtained on the basis of “reference” and “own/alternative” physical-chemical data sets is rather small for air concentrations (50% in maximum). For soil concentrations it is about 90%.

Annual values of net exchange flow between atmosphere and soil calculated on the basis of two data sets of physical-chemical properties are compared between different models in Fig. 1.12. Different color of columns corresponds to the different types of calculations (one-year calculations on the basis of initial data; and then long-tem calculations with historical emissions).

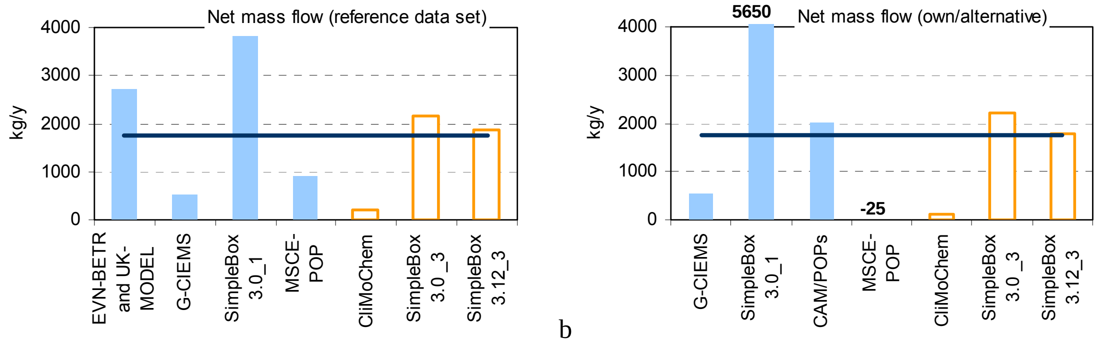


Fig. 1.12. *Comparison of PCB-153 annual values of net exchange flow between atmosphere and soil calculated by different models on the basis of “reference”(a) and “own or alternative” (b) data sets*

The blue line in the plots shows the value of the corresponding parameter averaged between models. For calculations performed on the basis of “reference” data set, the scattering of absolute annual values between models is not large (m = 1744 kg/y; σ = 1303 kg/y). Square deviation σ does not exceed the mean value of this parameter averaged between the participating models. In the case of results obtained with the use of “own/alternative” data sets, the difference in absolute annual values between different models’ calculations is more considerable (m = 1760 kg/y; σ = 1946 kg/y). According to the data presented, for all models’ results this flow is directed from the atmosphere to soil and only in the case of MSCE-POP calculations made on the basis of initial conditions with the use of “own/alternative” data sets it is practically compensated. The highest values in both sets of calculations are characteristic of SimpleBox 3.0 results based on initial concentrations given as input data. Two groups of the participating models in terms of close results can be distinguished further: with relatively low absolute values (CliMoChem, G-CIEMS and MSCE-POP results based on initial conditions) and with medium values, which are close to the averaged value (EVN-BETR and UK-MODEL, CAM/POPs, and all of the rest results of SimpleBox).

Since the net exchange flow is a sum of different types of exchange flows, below the latter are considered separately. Comparison of annual values of dry and wet deposition and gaseous exchange flows between atmosphere and soil calculated by models on the basis of two physical-chemical data sets is presented in Fig. 1.13.

The absolute values of dry deposition flows between the atmosphere and soil are the most close for all models among other flows. More noticeable difference between model results is observed in absolute values of wet deposition and gaseous exchange. The maximum value of dry deposition flow among all others is obtained in CAM/POPs calculations based on initial conditions and “own/alternative” data set. The highest values of wet deposition in both sets of results are characteristic of SimpleBox 3.0 calculations performed with the use of initial conditions. G-CIEMS model provided the lowest values of gaseous exchange flows. In the case of MSCE-POP results obtained on the basis of initial conditions and SimpleBox 3.12 results based on historical emissions the gaseous flow is a re-emission flow whereas in calculations of all other models it is directed from the atmosphere to soil. The relatively low values of all considered flows are characteristic of CliMoChem model in calculations performed with "reference" and "own/alternative" data sets. Difference between results of calculations with both physical-chemical data sets is not very large for most models.

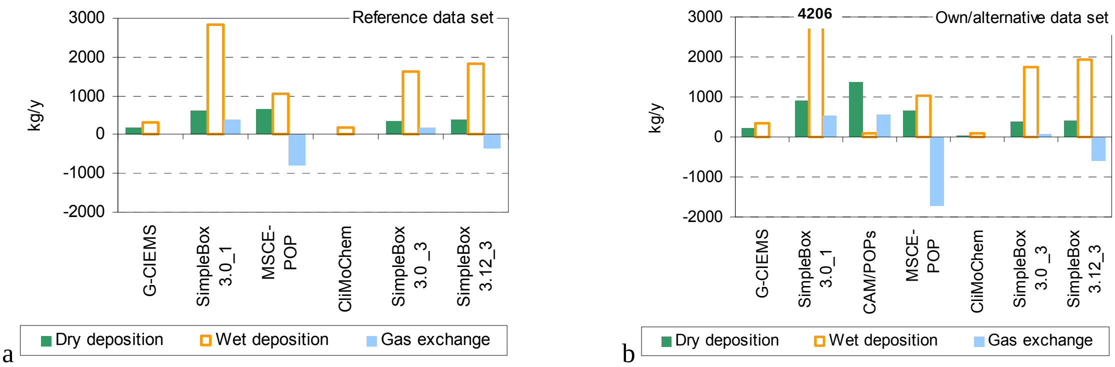


Fig.1.13. *Comparison of PCB-153 annual values of dry and wet deposition and gaseous exchange flows between atmosphere and soil calculated by different models on the basis of "reference"(a) and "own or alternative" (b) data sets*

To reveal differences in calculated values obtained on "reference" and "own/alternative" data sets, model results on dry and wet depositions and gaseous exchange between the atmosphere and soil are considered below in more detail.

According to the results on dry deposition of PCB-153 from the atmosphere to soil calculated on the basis of "reference" and "own/alternative" data sets (in "reference" set of results m = 372 kg/y, σ = 241 kg/y; in "own/alternative" set of results m = 565 kg/y, σ = 458 kg/y), most models give relatively close values in terms of annual and monthly absolute values. Square deviation σ does not exceed the mean values of this parameter averaged between the participating models. Comparison of annual values of PCB-153 dry deposition from the atmosphere to soil calculated by the models on the basis of "**reference**" and "**own or alternative**" data sets is presented in Fig. 1.14. The blue line in the plots shows the value of the corresponding parameter averaged between models. Different color of columns corresponds to the different types of calculations (one-year calculations on the basis of initial data; and then long-tem calculations with historical emissions).

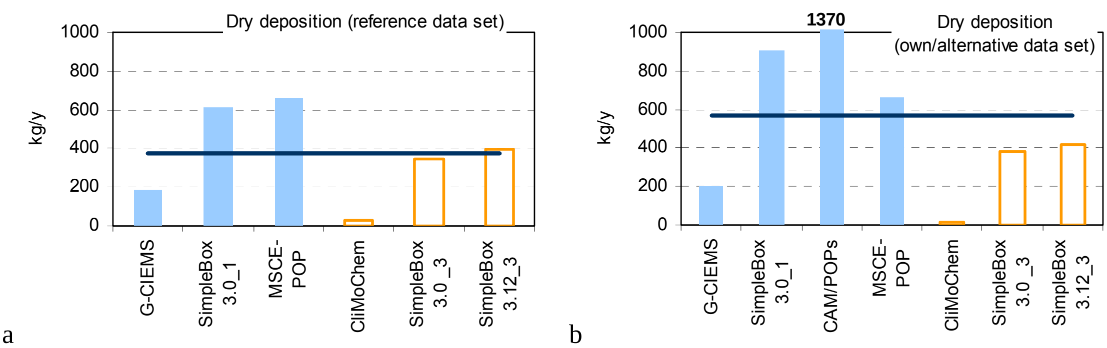


Fig. 1.14. *Comparison of annual values of PCB-153 mass flows transported from the atmosphere to soil: dry deposition (kg/y) calculated by different models on the basis of "reference"(a) and "own or alternative" (b) data sets*

According to the data presented, the difference between two sets of model results varies from 0.3 to 48% depending on a model. The largest difference in the values obtained with “reference” and “own/alternative” data sets is characteristic of SimpleBox 3.0 results based on initial conditions. There is a negligible difference between values obtained on both data sets and presented in the results of MSCE-POP obtained with the use of initial conditions. For G-CIEMS, SimpleBox 3.0 (initial conditions) and SimpleBox 3.0 and 3.12 results based on historical emissions, the annual values of PCB-153 dry deposition mass flows between the atmosphere and soil obtained with the use of “own or alternative” data sets are higher than those obtained with “reference” data set; and vice versa for the rest of model results.

The scattering between different models’ results on PCB-153 wet deposition mass flows from the atmosphere to soil is more considerable than that on dry depositions. However, according to the results presented (in “reference” set of results m = 1303 kg/y, σ = 1006 kg/y; in “own/alternative” set of results m = 1356 kg/y, σ = 1468 kg/y), for annual values obtained on the basis of “reference” data set square deviation is less than the averaged value. Comparison of annual values of PCB-153 wet deposition mass flows from the atmosphere to soil calculated by the models on the basis of “**reference**” and “**own or alternative**” data sets is presented in Fig. 1.15. The blue line in the plots shows the value of the corresponding parameter averaged between models. Different color of columns corresponds to the different types of calculations (one-year calculations on the basis of initial data; and then long-tem calculations with historical emissions).

The difference between calculated annual values of PCB-153 wet deposition mass flows obtained by participating models with two data sets of physical-chemical properties lies in the range from 0.2 to 48%. In results of G-CIEMS, SimpleBox 3.0 (initial conditions); SimpleBox (historical emissions) and MSCE-POP (initial conditions), the annual values of calculation results obtained with the use of “own or alternative” data sets exceed those obtained with “reference” data set; and vice versa for CliMoChem results. The results of MSCE-POP model based on initial conditions show rather weak sensitivity of calculated values with respect to variations of pollutant-related parameters. Considerable difference in the results obtained with two data sets (48%) is characteristic of SimpleBox 3.0 results (initial conditions).

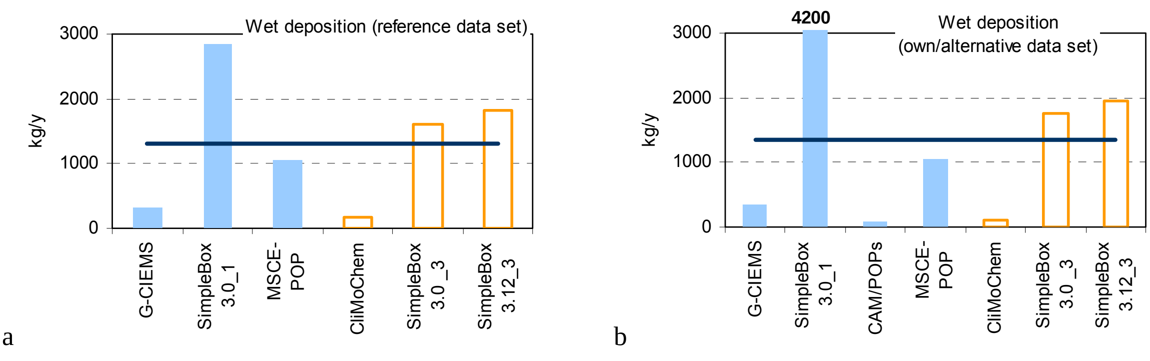


Fig. 1.15. *Comparison of annual values of PCB-153 mass flows transported from the atmosphere to soil: wet deposition (kg/y) calculated by different models on the basis of “reference”(a) and “own or alternative” (b) data sets*

For two sets of results obtained, the differences in annual values of PCB-153 gaseous exchange flows between the atmosphere and soil calculated by the participating models are large (in “reference” set of results m = –93 kg/y, σ = 428 kg/y; in “own/alternative” set of results m = –162 kg/y, σ = 794 kg/y). Square deviation of these values is considerably higher than mean values averaged between all models results. Comparison of annual values of PCB-153 gaseous exchange between the atmosphere and soil calculated by the models on the basis of "**reference**" and "**own or alternative**" data sets is presented in Fig. 1.16. The blue line in the plots shows the value of the corresponding parameter averaged between models. Different colour of columns corresponds to the different types of calculations (one-year calculations on the basis of initial data; and then long-tem calculations with historical emissions).

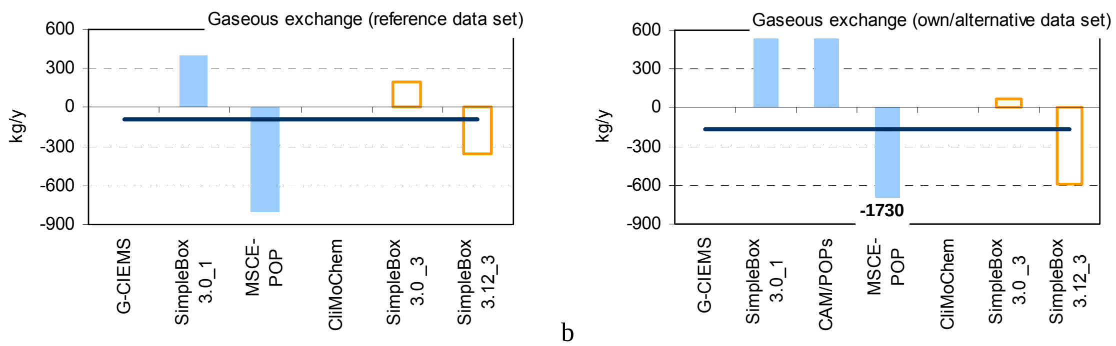


Fig. 1.16. *Comparison of annual values of PCB-153 mass flows transported from the atmosphere to soil: gaseous exchange (kg/y) calculated by different models on the basis of "reference"(a) and "own or alternative" (b) data sets*

Considerable difference between absolute values obtained on the basis of two different data sets is characteristic of MSCE-POP calculations made on the basis of initial concentrations (more than 115%) and of SimpleBox 3.0 and 3.12 calculations performed with the use of initial conditions and historical emissions (36 – 65%). At that in all these results, the calculated absolute values based on "own/alternative" data set are higher than those based on "reference" data set.

Thus, according to the results presented above, most participating models provide reasonable agreement in description of net intermedia mass flows directed from the atmosphere to soil. The results obtained on the basis of "reference" data set of pollutant-related parameters are somewhat closer than those obtained with "own or alternative" data set. The absolute values of dry deposition flows directed from the atmosphere to soil agree better between all models than those calculated for other types of exchange flows contributing to the net flow considered above. More noticeable difference between model results is observed in absolute values of wet deposition; the highest dispersion is characteristic of values of gaseous exchange flows. Two models calculate considerable re-emission gaseous flux from soil. Difference between results of calculations performed with the use of "reference" and "own/alternative" data sets is not very large for most models. For dry and wet depositions it does not exceed 50%, in calculations of gaseous exchange it totals approximately to 100%.

Atmosphere - seawater. Model results on concentrations of PCB-153 in the atmosphere at its interface with ocean and in the surface water layer, which are conditioned by intermedia transport, are considered below.

Comparison of annual values of PCB-153 concentration in the atmosphere at its interface with ocean calculated by the models on the basis of "**reference**" and "**own/alternative**" data sets is presented in Fig. 1.17. The blue line in the plots shows the value of the corresponding parameter averaged between models. Different color of columns corresponds to the different types of calculations (one-year calculations on the basis of initial data; and then long-tem calculations with historical emissions).

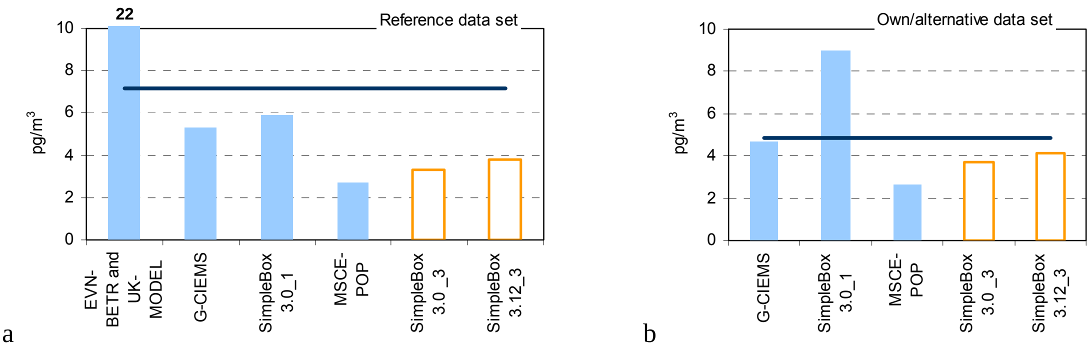


Fig. 1.17. *Comparison of annual values of PCB-153 concentration in the atmosphere at its interface with ocean (pg/m^3) calculated by different models on the basis of "reference"(a) and "own or alternative" (b) data sets*

Similar to the case with PCB-153 air concentrations formed at its interface with soil, in both sets of results obtained most models (except for EVN-BETR and UK-MODEL) predicted rather close values of air concentrations formed at its interface with ocean. For the results calculated on the basis of "reference" data set square deviation of annual values exceeds the mean value averaged between different models (in "reference" set of results m = 7.17 pg/m^3, σ = 7.36 pg/m^3; in "own/alternative" set of results m = 4.83 pg/m^3, σ = 2.43 pg/m^3). Difference between two sets of results obtained on the basis of "reference" and "own/alternative" data sets is in the range from 3 to 52 % (results of MSCE-POP and SimpleBox 3.0 obtained on the basis of initial conditions, respectively). For the calculation results of G-CIEMS and MSCE-POP models, the values of PCB-153 concentration in the atmosphere at its interface with ocean obtained with the use of "own or alternative" data sets are smaller than those obtained with "reference" data set, and vice versa for all SimpleBox results.

Comparison of annual values of PCB-153 concentration in surface ocean layer calculated by the models on the basis of "**reference**" and "**own/alternative**" data sets is presented in Fig. 1.18. The blue line in the plots shows the value of the corresponding parameter averaged between models. Different colour of columns corresponds to the different types of calculations (one-year calculations on the basis of initial data; and then long-tem calculations with historical emissions).

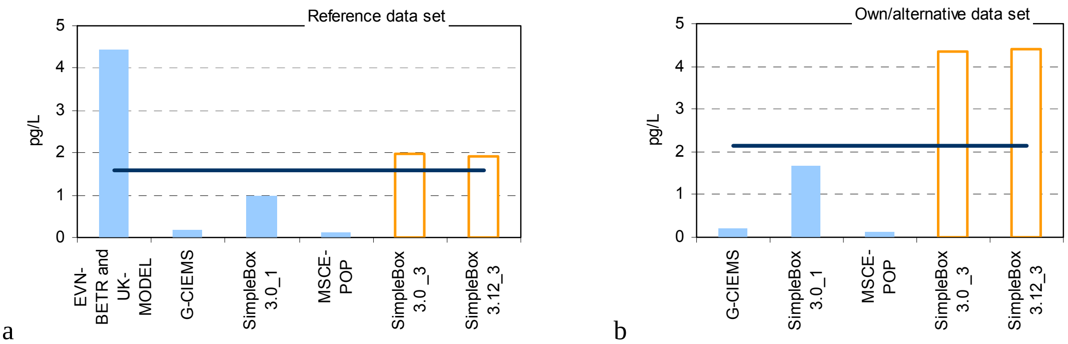


Fig. 1.18. *Comparison of annual values of PCB-153 concentration in surface ocean layer (pg/L) calculated by different models on the basis of "reference"(a) and "own or alternative" (b) data sets*

The variability of water concentrations for most models is not very large but it is higher than that for air concentrations. The maximum values are obtained by EVN-BETR and UK-MODEL on the basis of "reference" data set and by SimpleBox 3.12 model on the basis of "own/alternative" data set. MSCE-POP model's results are characterized by the lowest values of water concentrations in both cases. Square deviation σ between different model results is practically equal to the mean averaged value in the both cases (in "reference" set of results m = 1.60 pg/L, σ = 1.60 pg/L; in "own/alternative" set of results m = 2.16 pg/L, σ = 2.13 pg/L). Results of all models obtained on the basis of "reference" data set differ from those based on "own/alternative" data set in the range from 3 to 130%. The maximum difference is characteristic of SimpleBox 3.12 results based on historical emissions), and the minimum difference – of MSCE-POP results. For the calculation results of all models, the values of PCB-153 concentration in surface ocean layer obtained with the use of "own or alternative" data sets exceed those obtained with "reference" data set.

The values of PCB-153 concentrations in the atmosphere at its interface with ocean are close for most participating models. The scattering in calculated values of water concentrations is more considerable. However, square deviation between different models' results is practically equal to the mean averaged value in the both cases. The difference between absolute values of air and water concentrations obtained with both physical-chemical data sets totals to 50 and 130 %, respectively.

The scattering of absolute annual values of net exchange flow between the atmosphere and seawater obtained on the basis of "reference" data set (m = 3087 kg/y; σ = 3527 kg/y) is higher than that of annual values calculated with the use of "own/alternative" data set (m = 2298 kg/y; σ = 1922 kg/y). In the first case, square deviation σ exceeds the mean value of this parameter averaged between the participating models.

Annual values of net exchange flow between atmosphere and seawater calculated on the basis of two data sets are compared between different models in Fig. 1.19. The blue line in the plots shows the value of the corresponding parameter averaged between models. Different colour of columns corresponds to the different types of calculations (one-year calculations on the basis of initial data; and then long-tem calculations with historical emissions).

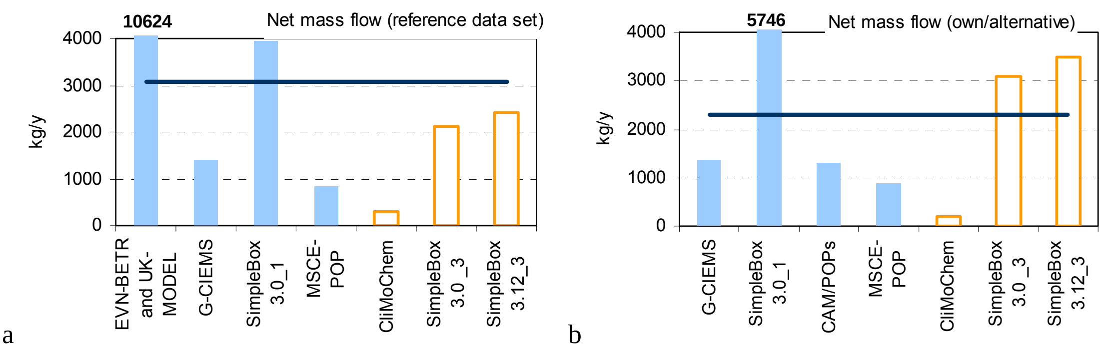


Fig. 1.19. *Comparison of PCB-153 annual values of net exchange flow between atmosphere and seawater calculated by different models on the basis of "reference"(a) and "own or alternative" (b) data sets*

According to the results presented, all models obtained net flows directed from the atmosphere to water. There are three groups of close models' results, which can be isolated depending on magnitude of absolute values. First group of models with relatively low values includes CliMoChem, CAM/POPs, G-CIEMS and MSCE-POP models. Higher flows are calculated by SimpleBox 3.0 and 3.12 on the basis of historical emissions. Third group of results obtained on the basis of initial conditions by EVN-BETR and UK-MODEL and SimpleBox 3.0 models is characterized by the highest absolute values among others. Difference between results based on both physical-chemical data sets is rather small for all models except for SimpleBox.

Annual absolute values of dry and wet deposition and gaseous exchange flows, which formed the considered net exchange flows between the atmosphere and seawater, are compared below. Comparison of annual values of dry and wet deposition and gaseous exchange flows between the atmosphere and seawater calculated by models on the basis of two physical-chemical data sets is presented in Fig. 1.20.

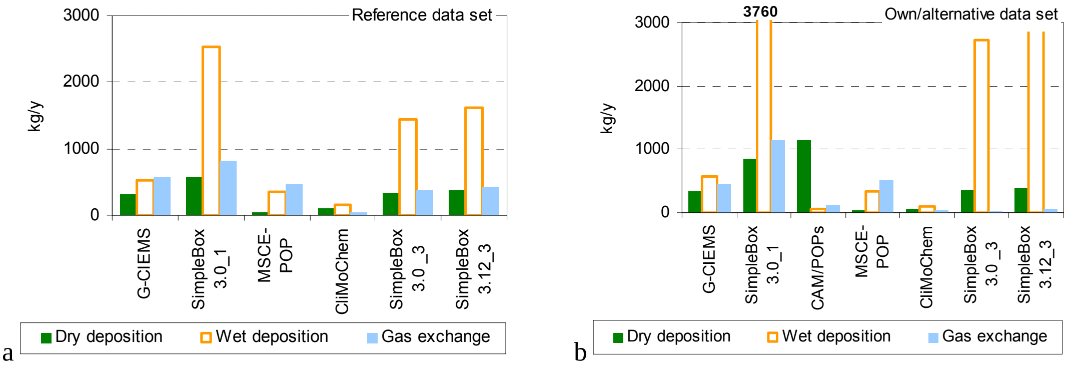


Fig. 1.20. *Comparison of PCB-153 annual values of dry and wet deposition and gaseous exchange flows between atmosphere and seawater calculated by different models on the basis of "reference"(a) and "own or alternative" (b) data sets*

The results on dry and wet deposition and gaseous exchange flows between these media obtained on both data sets ("reference" and "own/alternative") show that scattering of absolute values of wet deposition flows is the most noticeable in comparison with other flows. Similar to the results for atmosphere-soil interface, CAM/POPs calculations based on initial conditions and "own/alternative" data set predicted the maximum value of dry deposition flow among all others. The lowest values of dry depositions from the atmosphere to water are obtained by MSCE-POP model. The highest values of wet deposition in both sets of results are characteristic of Simple Box 3.0 calculations based on initial conditions. This model provided also the maximum values of gaseous exchange flows. Of note, most models show noticeable gaseous flows directed from the atmosphere to water. Difference between results of calculations with "reference" and "own/alternative" data sets is the most considerable for SimpleBox model.

Model results on dry and wet depositions and gaseous exchange between the atmosphere and soil are considered below in more detail.

The annual and monthly values of dry deposition of PCB-153 from the atmosphere to water calculated on the basis of "reference" and "own/alternative" data sets (in "reference" set of results m = 281 kg/y, σ = 193 kg/y; in "own/alternative" set of results m = 449 kg/y, σ = 405 kg/y) are in reasonable agreement for most models. Square deviation σ in both cases does not exceed the mean values of this parameter averaged between the participating models. Comparison of annual values of PCB-153 dry deposition mass flows from the atmosphere to water calculated by the models on the basis of "**reference**" and "**own or alternative**" data sets is presented in Fig. 1.21. The blue line in the plots shows the value of the corresponding parameter averaged between models. Different color of columns corresponds to the different types of calculations (one-year calculations on the basis of initial data; and then long-tem calculations with historical emissions).

According to the data presented, the difference in absolute values obtained on the basis of both data sets ("reference" and "own/alternative") between models' results varies from 4 to 48%. For the calculation results obtained by CliMoChem and MSCE-POP, the annual values of PCB-153 dry deposition mass flows from the atmosphere to water calculated with "own or alternative data sets" are less than those obtained with "reference data set"; and vice versa for G-CIEMS and SimpleBox model results. The largest difference in the results obtained with two data sets is characteristic of SimpleBox 3.0 calculations based on initial conditions.

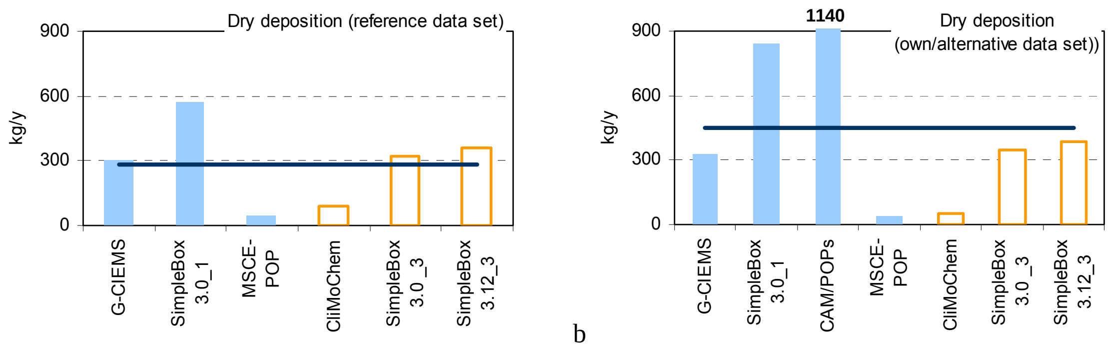


Fig. 1.21. *Comparison of annual values of PCB-153 mass flows transported from the atmosphere to water: dry deposition (kg/y) calculated by different models on the basis of "reference"(a) and "own or alternative" (b) data sets*

According to the presented results on PCB-153 wet deposition mass flows from the atmosphere to water (in "reference" set of results m = 1105 kg/y, σ = 919 kg/y; in "own/alternative" set of results m = 1511 kg/y, σ = 1595 kg/y), the difference in results obtained on the basis of "own/alternative" data set is larger than that in results based on "reference" data set. Square deviation between participating models' results based on "reference" data set is less than the averaged value. Comparison of annual values of PCB-153 wet deposition mass flows between the atmosphere to water calculated by the models on the basis of "**reference**" and "**own or alternative**" data sets is presented in Fig. 1.22. The blue line in the plots shows the value of the corresponding parameter averaged between models. Different colour of columns corresponds to the different types of calculations (one-year calculations on the basis of initial data; and then long-tem calculations with historical emissions).

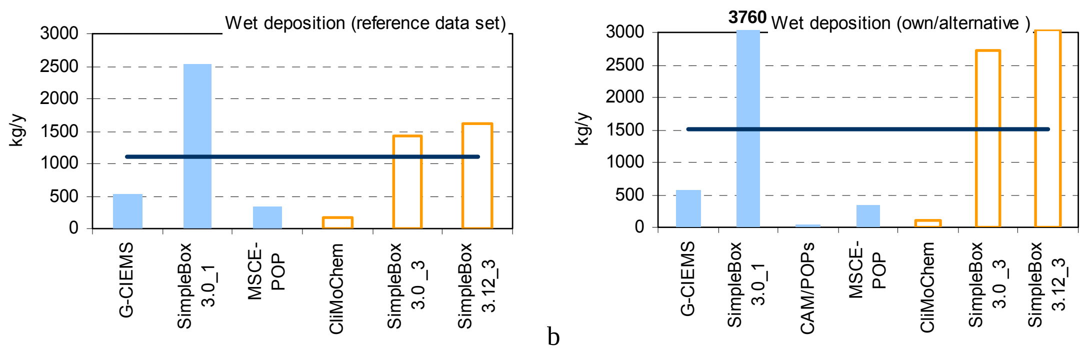


Fig. 1.22. *Comparison of annual values of PCB-153 mass flows transported from the atmosphere to water: wet deposition (kg/y) calculated by different models on the basis of "reference"(a) and "own or alternative" (b) data sets*

The difference between the presented results obtained on the basis of both physical-chemical data sets varies from 4 to 90%. The largest difference in the results obtained with two data sets is characteristic of SimpleBox 3.0 and 3.12 calculations performed on the basis of historical emissions. The lowest sensitivity to variations of pollutant-related parameters is observed in calculation results of MSCE-POP model obtained on the basis of initial conditions. Annual values of PCB-153 wet deposition mass flows from the atmosphere to water calculated by CliMoChem and MSCE-POP models with the use of "reference" data set exceed those based on "own or alternative" data sets; and vice versa for G-SIEMS and SimpleBox model results.

In comparison with the results on gaseous exchange flow obtained for the atmosphere-soil interface, the difference in values on gaseous exchange mass flows between the atmosphere and water calculated on the basis of "reference" data set is essentially lower since square deviation of these calculated values does not exceed the mean value averaged between all models (m = 444 kg/y, σ = 256 kg/y). The scattering of "own/alternative" set of results for the atmosphere-water interface (m = 338 kg/y, σ = 409 kg/y) is noticeably higher than that for results based on "reference" data set. Comparison of annual values of PCB-153 gaseous exchange mass flows between the atmosphere and water calculated by the models on the basis of "**reference**" and "**own or alternative**" data sets is presented in Fig. 1.23. The blue line in the plots shows the value of the corresponding parameter averaged between models. Different color of columns corresponds to the different types of calculations (one-year calculations on the basis of initial data; and then long-tem calculations with historical emissions).

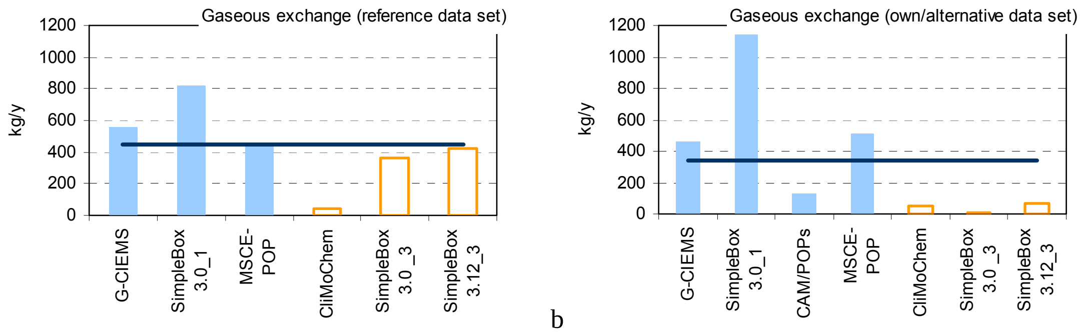


Fig. 1.23. *Comparison of annual values of PCB-153 mass flows transported from the atmosphere to water: gaseous exchange (kg/y) calculated by different models on the basis of "reference"(a) and "own or alternative" (b) data sets*

According to the data presented, results of CliMoChem, SimpleBox 3.0 (initial conditions) and MSCE-POP models obtained on the basis of "own/alternative" data set are higher than those calculated with the use of "reference" data set; and vice versa for the rest of other models' results. The most considerable difference in absolute values calculated with the use of "reference" and "own/alternative" data sets is characteristic of SimpleBox 3.0 and 3.12 calculations carried out on the basis of initial conditions and historical emissions.

Thus, in the results obtained most participating models provided rather close values of net intermedia mass flows between the atmosphere and water. All models obtained net flows directed from the atmosphere to water. The scattering in results calculated by different models on the basis of "reference" data set is higher than that in the results obtained with "own or alternative" data set. The difference in absolute values of wet deposition and gaseous exchange flows is more noticeable in comparison with dry deposition flows. Maximum difference between results on all flows calculated with the use of "reference" and "own or alternative" data sets does not exceed 90%.

Atmosphere – vegetation. Model results on concentrations of PCB-153 in the atmosphere at its interface with vegetation and in vegetation, which are conditioned by intermedia transport, are considered below.

Comparison of annual values of PCB-153 concentration in the atmosphere at its interface with vegetation calculated by the models on the basis of "**reference**" and '**own/alternative**" data sets is presented in Fig. 1.24. The blue line in the plots shows the value of the corresponding parameter averaged between models. Different color of columns corresponds to the different types of calculations (one-year calculations on the basis of initial data; and then long-tem calculations with historical emissions).

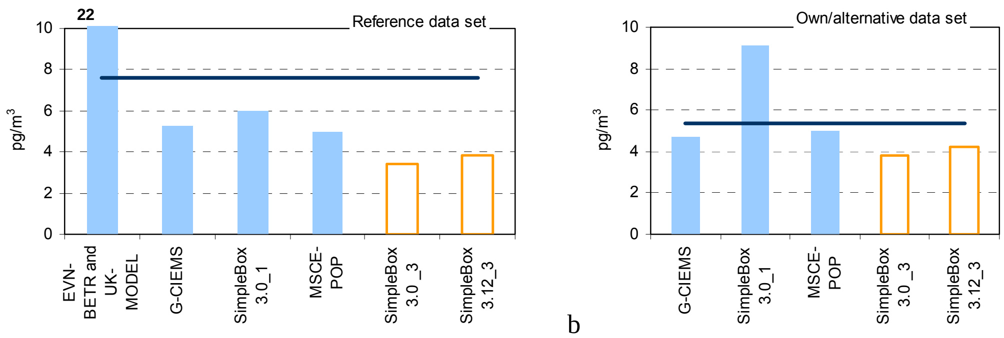


Fig. 1.24. *Comparison of annual values of PCB-153 concentration in the atmosphere at its interface with vegetation (pg/m*^{3}*) calculated by different models on the basis of "reference"(a) and "own or alternative" (b) data sets*

According to the results presented, PCB-153 concentrations in the atmosphere at its interface with vegetation are close to each other for most participating models. The results of EVN-BETR and UK-MODEL ("reference" data set) and SimpleBox 3.0 ("own/alternative" data set) models based on initial conditions that are exceeding all other models' results lead to significant bias of averaged values of air concentrations to the maximum values. However, for two sets of results obtained the differences in annual values of PCB-153 concentration in the atmosphere at its interface with vegetation are not considerable (in "reference" set of results m = 7.58 pg/m^3, σ = 7.12 pg/m^3; in "own/alternative" set of results m = 5.37 pg/m^3, σ = 2.13 pg/m^3). Square deviation of these values in all cases is lower than the mean values averaged between all models results. For the calculation results of G-CIEMS, the values of PCB-153 concentration in the atmosphere at its interface with vegetation obtained with the use of "own or alternative" data sets are smaller than those obtained with "reference" data set; and vice versa for MSCE-POP and all SimpleBox results. The largest difference in the results obtained with two physical-chemical data sets (52%) is characteristic of SimpleBox 3.0 calculations performed on the basis of initial conditions. For MSCE-POP this difference is minimum among all others and totals to 1%.

Comparison of annual values of PCB-153 concentration in vegetation calculated by the models on the basis of "**reference**" and '**own/alternative**" data sets is presented in Fig. 1.25. The green line in the plot shows the value of the corresponding parameter averaged between models. Different color of columns corresponds to the different types of calculations (one-year calculations on the basis of initial data; and then long-tem calculations with historical emissions).

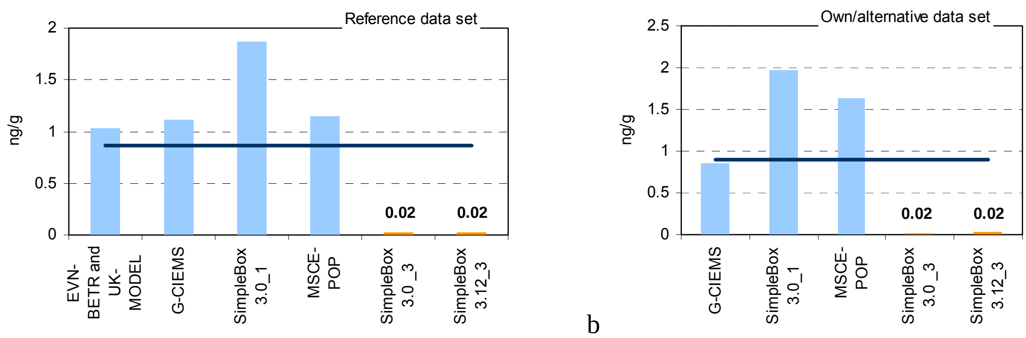


Fig. 1.25. *Comparison of annual values of PCB-153 concentration in vegetation (ng/g) calculated by different models on the basis of "reference"(a) and "own or alternative" (b) data sets*

The differences between annual values of PCB-153 concentration in vegetation calculated by the participating models are rather considerable for two sets of results obtained (in "reference" set of results m = 0.87 ng/g, σ = 0.72 ng/g; in "own/alternative" set of results m = 0.90 ng/g, σ = 0.90 ng/g).

The highest and the lowest values of the considered parameter are obtained by different versions of SimpleBox model (3.0 and 3.12). Square deviation of these values is not higher than the mean values averaged between all models results. For the calculation results of all models except G-CIEMS and SimpleBox 3.0 (historical emissions), the values of PCB-153 concentration in vegetation obtained with the use of “own or alternative data sets” exceed those obtained with “reference data set”. The largest difference in the results obtained with two data sets equal to 42% is characteristic of MSCE-POP results. Results of SimpleBox 3.0 are the less sensitive to the changes in pollutant-related parameters.

Results on PCB-153 concentrations in the atmosphere at its interface with vegetation are in good agreement for most models. The variation in values of concentrations in vegetation is higher than that in the air concentrations. The difference between absolute values of air and vegetation concentrations obtained with “reference” and “own or alternative” physical-chemical data sets totals to 50 and 42 %, respectively.

According to the comparison of results on net exchange flow between the atmosphere and vegetation, the difference in annual values obtained by the participating models both on the basis of “reference” (m = 1190 kg/y; σ = 3742 kg/y) and “own/alternative” (m = -779 kg/y; σ = 3598 kg/y) data sets is very large. Square deviation σ of absolute annual values obtained by the participating models is much higher than the mean value of this parameter averaged between the models. That testifies a considerable discrepancy in simulation of intermedia transport between these compartments by different models.

Annual values of net exchange flow between atmosphere and vegetation calculated on the basis of two data sets (‘reference” and “own/alternative”) are compared between different models in Fig. 1.26. The blue line in the plots shows the value of the corresponding parameter averaged between models. Different color of columns corresponds to the different types of calculations (one-year calculations on the basis of initial data; and then long-tem calculations with historical emissions).

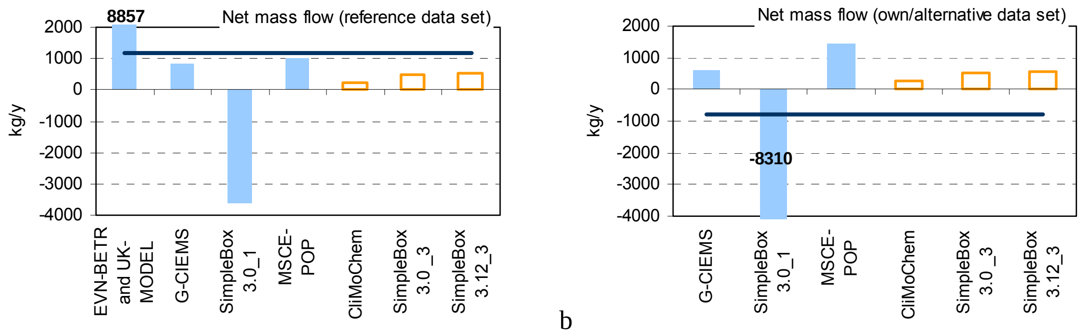


Fig. 1.26. *Comparison of PCB-153 annual values of net exchange flow between atmosphere and vegetation calculated by different models on the basis of “reference”(a) and “own or alternative” (b) data sets*

A comparison of model results on net exchange flow of PCB-153 for the atmosphere and vegetation interface demonstrates that for most models this flow is transported from the atmosphere to vegetation. However, calculations made by SimpleBox 3.0 model on the basis of initial conditions show high re-emission flux from vegetation. The maximum values in results obtained on the basis of “reference” and “own or alternative” data sets is characteristic of EVN-BETR and UK–MODEL and SimpleBox 3.0 model (initial conditions), respectively. In spite of the fact that the scattering of absolute values is very large, the most models - CliMoChem, G-CIEMS, MSCE-POP and SimpleBox 3.0 and 3.12 (historical emissions) models demonstrate relatively close results. The difference in net exchange values obtained on the basis of two data sets is noticeable for G-CIEMS, MSCE-POP, and Simple Box 3.0 (initial conditions).

Comparison of annual values of dry and wet deposition and gaseous exchange flows between the atmosphere and vegetation calculated by models on the basis of two physical-chemical data sets is presented in Fig. 1.27.

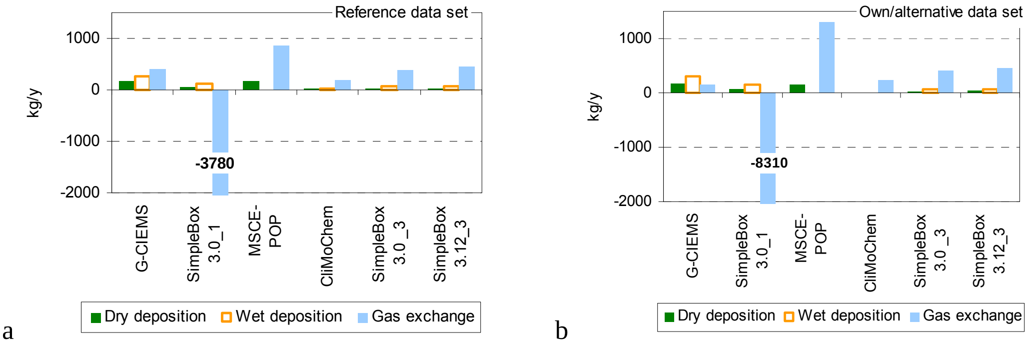


Fig. 1.27. *Comparison of PCB-153 annual values of dry and wet deposition and gaseous exchange flows between atmosphere and vegetation calculated by different models on the basis of "reference"(a) and "own or alternative" (b) data sets*

For model results calculated by the participating models on the basis of both physical-chemical data sets ("reference" and "own/alternative"), the absolute values of dry and wet deposition between the atmosphere and vegetation are closer to each other than those of gaseous exchange flows. The difference between results of both calculations on dry depositions is rather small for all models. Higher variability of absolute values of wet deposition is observed. The maximum value of wet deposition flow is characteristic of G-CIEMS. It should be noted that wet deposition on vegetation is not taken into account in MSCE-POP model. For most models PCB-153 gaseous exchange flows are directed from the atmosphere to vegetation. MSCE-POP in "reference" results and G-CIEMS in "own/alternative" results presented the highest value of this gaseous flow among them. At that, calculations performed by SimpleBox 3.0 model on the basis of initial conditions show high re-emission flow from vegetation. For G-CIEMS, MSCE-POP and SimpleBox 3.0 (initial conditions) models noticeable difference in gaseous exchange flux between calculations on "reference" and "own/alternative" data sets can be seen.

To reveal differences in calculated values obtained on "reference" and "own/alternative" data sets, model results on dry and wet depositions and gaseous exchange between the atmosphere and soil are considered below in more detail.

According to the results on dry deposition of PCB-153 from the atmosphere to vegetation calculated on the basis of both data sets (in "reference" set of results m = 74 kg/y, σ = 66 kg/y; in "own/alternative" set of results m = 79 kg/y, σ = 70 kg/y), most models predicted rather close absolute annual values. Square deviation σ does not exceed the mean values of this parameter averaged between the participating models in both cases. Comparison of annual values of PCB-153 dry deposition mass flows from the atmosphere to vegetation calculated by the models on the basis of "**reference**" and "**own or alternative**" data sets is presented in Fig.1.28. The blue line in the plots shows the value of the corresponding parameter averaged between models. Different color of columns corresponds to the different types of calculations (one-year calculations on the basis of initial data; and then long-tem calculations with historical emissions).

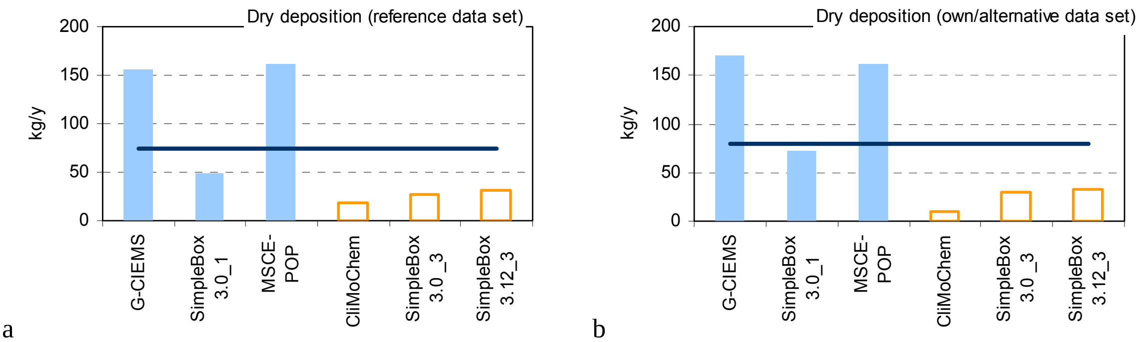


Fig. 1.28. *Comparison of annual values of PCB-153 mass flows transported from the atmosphere to vegetation: dry deposition (kg/y) calculated by different models on the basis of "reference"(a) and "own or alternative" (b) data sets*

According to the data presented, the difference between two sets of model results varies from 0.3 to 50% depending on a model. The largest difference in the values obtained with two data sets is characteristic of CliMoChem results based on historical emissions. Negligible difference between values obtained on "reference" and "own/alternative" data sets is characteristic of MSCE-POP results based on initial conditions. For CliMoChem results, the annual values of PCB-153 dry deposition mass flows from the atmosphere to vegetation calculated with "own or alternative" data sets are smaller than those obtained with "reference" data set; and vice versa for G-CIEMS, MSCE-POP and all SimpleBox results.

The scattering between different models' results on PCB-153 wet deposition mass flows from the atmosphere to vegetation is higher than that on dry depositions. However, according to the results presented (in "reference" set of results m = 106 kg/y, σ = 97 kg/y; in "own/alternative" set of results m = 121 kg/y, σ = 110 kg/y), square deviation of this parameter values is less than the averaged value in both sets of obtained results. Comparison of annual values of PCB-153 wet deposition mass flows from the atmosphere to vegetation calculated by the models on the basis of "**reference**" and "**own or alternative**" data sets is presented in Fig.1.29. The blue line in the plots shows the value of the corresponding parameter averaged between models. Different color of columns corresponds to the different types of calculations (one-year calculations on the basis of initial data; and then long-tem calculations with historical emissions).

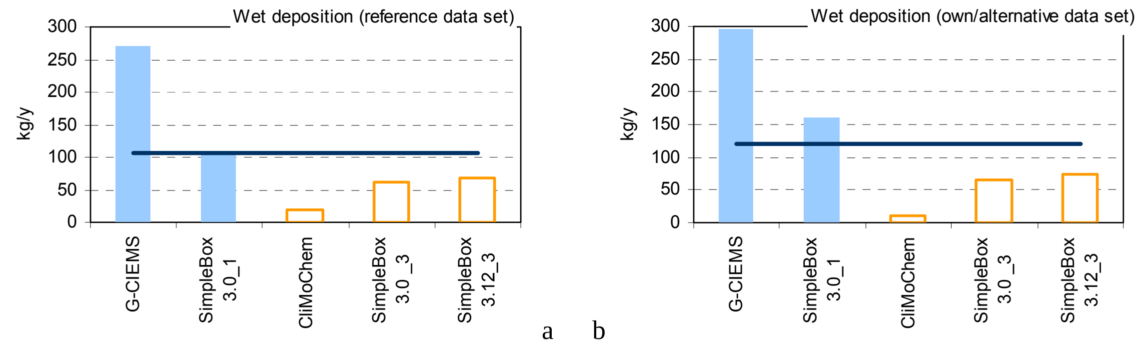


Fig. 1.29. *Comparison of annual values of PCB-153 mass flows transported from the atmosphere to vegetation: wet deposition (kg/y) calculated by different models on the basis of "reference"(a) and "own or alternative" (b) data sets*

For the calculation results of G-CIEMS and SimpleBox 3.0 and 3.12 models (initial conditions and historical emissions), the values of PCB-153 wet deposition mass flows from the atmosphere to vegetation obtained with the use of "own or alternative" data sets exceed those obtained with "reference" data set; and vice versa for CliMoChem model. The largest difference in the results obtained with two data sets making up approximately 50% is characteristic of SimpleBox 3.0 results based on initial conditions; the lowest difference equal to 9% is observed in results of MSCE-POP model.

According to the results on PCB-153 gaseous exchange flows for the atmosphere - vegetation interface calculated by the participating models on the basis of two physical-chemical data set (in "reference" set of results m = -250 kg/y, σ = 1745 kg/y; in "own/alternative" set of results m = -960 kg/y, σ = 3624 kg/y), the differences in both annual and monthly absolute values are very large. Square deviation of these values is higher than mean values averaged between all models results. Comparison of annual values of PCB-153 gaseous exchange mass flows from the atmosphere to vegetation calculated by the models on the basis of "**reference**" and "**own or alternative**" data sets is presented in Fig.1.30. The blue line in the plots shows the value of the corresponding parameter averaged between models. Different color of columns corresponds to the different types of calculations (one-year calculations on the basis of initial data; and then long-tem calculations with historical emissions).

According to the results presented, the most considerable difference in the values obtained on "reference" and "own/alternative" data sets is characteristic of SimpleBox 3.0 model results calculated on the basis of initial conditions. The less noticeable difference among different models is obtained in the rest of this model's results. Results of MSCE-POP and CliMoChem models obtained with the use of "own/alternative" data set exceed those based on "reference" data set; and vice versa for G-CIEMS.

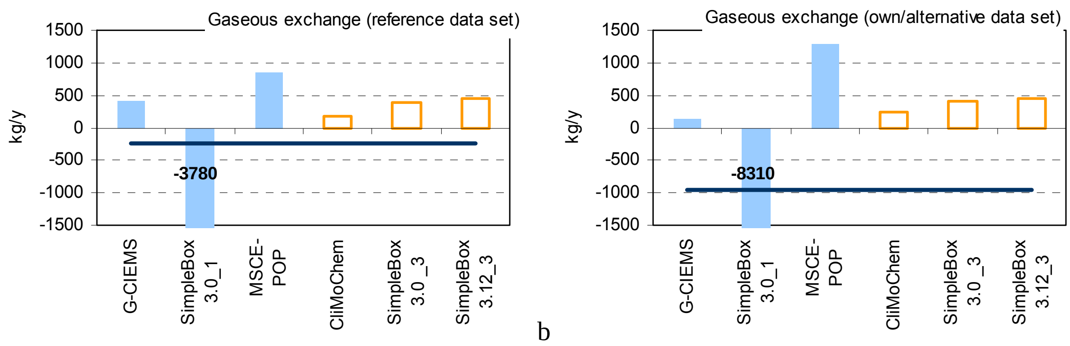


Fig. 1.30. *Comparison of annual values of PCB-153 mass flows transported from the atmosphere to vegetation: gaseous exchange (kg/y) calculated by different models on the basis of "reference"(a) and "own or alternative" (b) data sets*

Thus, it can be noted that considerable scattering of net exchange flows for the atmosphere - vegetation interface obtained by different models is conditioned by the difference in gaseous exchange flows. The most participating models provided reasonable agreement in description of dry and wet mass flows from the atmosphere to vegetation. One model predicted high re-emission flux from vegetation to the atmosphere in the case of values obtained on the basis of initial conditions. The difference between results of calculations carried out with the use of "reference" and "own/alternative" data sets is about 120%.

1.2.3. Conclusions

In this Chapter some extracts of the main outcome of the POP model intercomparison study are considered. Physical-chemical properties and degradation rates of PCB-153 included into the parameterizations of the participating models are compared and uncertainties in model results caused by their scattering are evaluated. A comparison of model results on description of such important processes of PCB-153 behaviour in the environment as gas-particle partitioning, dry and wet depositions, gaseous exchange between the atmosphere and different underlying surfaces is presented. The important output of POP models - predicted air concentrations and concentrations formed at the interfaces of other environmental media due to the intermedia mass flows are also compared. This report provides information on the comparison of results for PCB-153.

Physical-chemical properties of POPs

Values of physical-chemical properties and degradation rates used for the model calculations strongly affect the results of calculation experiments. The analysis of parameterizations of models participating in the POP model intercomparison study is made for evaluating possible uncertainties of pollutant-related parameters. To do this, similar sets of pollutant-related properties of most of the participating models, in which the values of the parameters are relatively close to those of MSCE-POP, are used. Then, the uncertainties of MSCE-POP model output are evaluated on the basis of the approach described in [*Gusev et al.,* 2005a].

- Assuming that the uncertainty of each particular parameter is characterized by the scattering of its values between the models, the uncertainty of MSCE-POP model output can be evaluated as 20% at maximum. This value is composed of the uncertainties of the model output caused by scattering of the particular parameters:

  - Most models use temperature dependent air-water partition coefficient. The ratio between maximum and minimum absolute values of this coefficient for PCB-153 used by these models is within a factor of 1.5. The estimated uncertainty of this parameter leads to the uncertainty of MSCE-POP model output of approximately 3%.
  - All models use temperature dependent values of octanol/air partition coefficient. The ratio between maximum and minimum absolute values of this parameter for PCB-153 used by most models is within a factor of 2. The estimated uncertainty of MSCE-POP model output due to the above uncertainty of this parameter is about 5%.
  - Most models use temperature dependent values of subcooled liquid vapour pressure. There is a high similarity between its absolute values for PCB-153 presented by the models using temperature dependence of this parameter (max/min ratio is about 1.1). The estimated uncertainty of MSCE-POP model due to this parameter is less than 1%.
  - Most models use temperature dependent octanol-water partition coefficient. The ratio between its maximum and minimum absolute values for PCB-153 used by these models lies within a factor of 2.8. MSCE-POP model used this parameter as temperature-independent value close to those of CliMoChem, DEHM-POP and CAM/POPs at 10 °C. Since the uncertainty of MSCE-POP model output due to the estimated uncertainty of this parameter is found to be about 4%, there is a necessity to include the temperature dependence of octanol/water partition coefficient into the MSCE-POP model parameterisation.
  - All models recalculate values of the organic carbon-water partition coefficient on the basis of the octanol-water partition coefficient. The ratio between its maximum and minimum absolute

values for PCB-153 for most models is within a factor of 2.2. The uncertainty of model output due to the uncertainty of this parameter is the same as that due to octanol-water partition coefficient (approximately 4%).

- Degradation rate constants of PCB-153 in air, soil and water considered in all models are characterised by max/min ratio varying from 4 to 5. The ratio between maximum and minimum absolute values of degradation rate constant in air obtained for models using temperature dependencies is within a factor of 2. The obtained uncertainty of degradation rates leads to relatively high uncertainty of MSCE-POP model output (about 6%). This shows that the evaluation of degradation rates is one of the important tasks in modelling.

Description of POP gas-particle partitioning and intermedia exchange

As the next step, the model description of gas-particle partitioning and intermedia transport of PCB-153 used in MSCE-POP model is compared with that of other models. The main emphasis is put on the comparison of model approaches. Thus, it was found that:

- Gas/particle partitioning process is described mainly with the help of two different approaches (adsorption and absorption). Most models calculate rather close values of particulate fractions of PCB-153 in the atmosphere for the considered interval of temperatures. All models describe rather closely a tendency in variability of calculated particulate fraction of PCB-153 with temperature. Correlation coefficients are high for all pairs of models (0.83 – 1.0). Since square deviation of particulate fraction is about 60% of the mean value, it can be concluded that most models closely describe the gas/particle partitioning process.
- Air concentrations as the most important output of the participating models are in good agreement between all models' results. Most models, including MSCE-POP, predict close annual concentrations of PCB-153 in the atmosphere at its interfaces with soil and vegetation lying in the range from 3.4 to 6.0 pg/m^3 and at its interface with water – in the range from 2.7 to 5.9 pg/m^3. The maximum calculated value of annual air concentration in the atmosphere at its interfaces with the considered types of underlying surfaces is equal to 22 pg/m^3.
- The most part of participating models predict relatively close values of PCB-153 concentrations in soil, water and vegetation. However, variability of calculated concentrations in these environmental media is higher than that for the atmosphere. Very close absolute values of surface soil concentrations (0.04 - 0.08 ng/g) are characteristic of most models' results including that of MSCE-POP. Being considerably higher than those given above, the maximum calculated soil concentration is equal to 0.7 ng/g. The range of annual water concentrations calculated by all models changes from 0.12 to 4.42 pg/L. The minimum value of water concentrations is obtained by MSCE-POP. The difference between all models results on annual concentrations in vegetation (0.02 –1.9 ng/g) is within a factor of 2. This parameter calculated by MSCE-POP model amounts to 1.2 ng/g.

A preliminary analysis of the considered results of the POP model intercomparison study shows that in spite of the differences existing in the model parameterisations and descriptions of the basic processes, the reasonable agreement in simulation of gas-particle partitioning and air concentrations of PCB-153 is observed for most models including MSCE-POP.