Chapter 4

# SENSITIVITY STUDY WITH RESPECT TO SUBSTANCE-SPECIFIC PROPERTIES USED IN THE DESCRIPTION OF BASIC PROCESSES FOR PCB-153

This chapter contains processed results of a sensitivity study with respect to physical-chemical parameter values used by the participating models for the calculations of parameters of model description of gas/particles partitioning, wet deposition and gaseous exchange between the atmosphere and soil, water and vegetation. Two sets of calculation results: obtained with "reference" data set of physical-chemical properties and with "own/alternative" data sets are presented.

For each data set used a presentation of modeling results is performed into two steps. At the first step we present the values of calculated parameters and characterize the spread in these values between models in each of the experiments. At the second step we show pairwise differences between participating models using the regression analysis.

The following statistical parameters for each experiment are used:

- the mean values $m$ of the considered parameters averaged between participating models;
- the values of square deviation $\sigma$ between results obtained by different 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:

$$A_T^2 = \alpha_{12} A_T^1 + \beta_{12} + \omega_{12}, \tag{4.1}$$

where $\alpha_{12}$ and $\beta_{12}$ are regression coefficients;

$\omega_{12}$ 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 $\alpha_{12}$ and $\beta_{12}$ (characterizing a non-random component of the regression relation), *the residual square deviation,* that is, square deviation $\sigma^{res}{}_{12}$ of $\omega_{12}$ (characterizing the magnitude of random component) and the correlation coefficient $r_{12}$.

Here numerical results for the first priority substance (PCB-153) only are presented. The corresponding results for substances of the second priority (PCB-28 and PCB-180) are presented in Annexes D and E.

## 4.1. Gas/particle partitioning

***Reference data set.*** Calculation results for PCB-153 together with $m_\varphi$ and $\sigma_\varphi$ are presented in Table 4.1. 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 4.1.*** *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) | EVN-BETR and UK-MODEL | DEHM-POP | G-CIEMS | | CAN/POPs | MSCE-POP | CliMoChem | SimpleBox* | $m_\varphi$ | $\sigma_\varphi$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | 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 $\varphi$ on *T* calculated by participating models is presented in Fig. 4.1. 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.

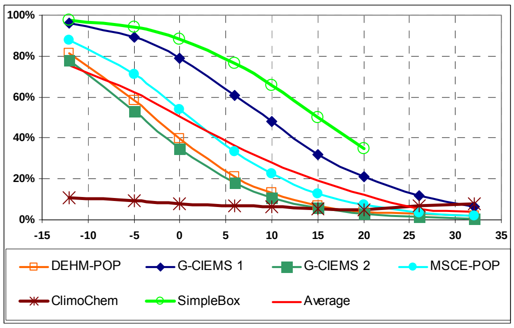



***Fig. 4.1.*** *Calculation results of the participating models (gas-particle partitioning) obtained with reference data set*

We recall that the experiments differ mainly by ambient air temperature *T* (and some other parameters, see [*Shatalov et al.*, 2004]). For each temperature within the considered interval of temperatures (-12°C - 32°C), square deviation $\sigma_\varphi$ between different model calculations (see last columns in Table 2.1) 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 4.2. It is seen that these coefficients are high enough and vary from 0.7 to 1.

***Table 4.2.*** *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 $\alpha$ and $\beta$ calculated for all pairs of models are shown in Table 4.3.

*__Table 4.3.__ Coefficients of regression dependence between the models ($\alpha$ / $\beta$)*

| | 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 $\alpha$ ranging from 0.05 to 10. For the most part of the models (not including CliMoChem results), $\alpha$ varies far less (from 0.72 to 1.14). Coefficients $\beta$ 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 $\varphi$ (Fig. 4.1) are similar for these models.

To assess the reliability of comparative analysis given above calculations of pairwise residual square deviation $\sigma$ were done (Table 4.4).

***Table 4.4.** Residual square deviation, $\sigma^{res}_{12}$*

| | 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 $\sigma$ 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 $\varphi$.

***Own/altenative data set.*** Calculation results for PCB-153 together with $m_\varphi$ and $\sigma_{.\varphi}$ are presented in Table 4.5. The data set used in calculations by each model is indicated in the first row.

***Table 4.5.** 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 | | CAN/POPs | MSCE-POP | CliMoChem | SimpleBox* | $m_\varphi$ | $\sigma_\varphi$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | 1 | 2 | | | | | | |
| 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 $\varphi$ on $T$ calculated by participating models with “own or alternative” data set is presented in Fig. 4.2. 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 4.6. It is seen that these coefficients are high and exceed 0.9.

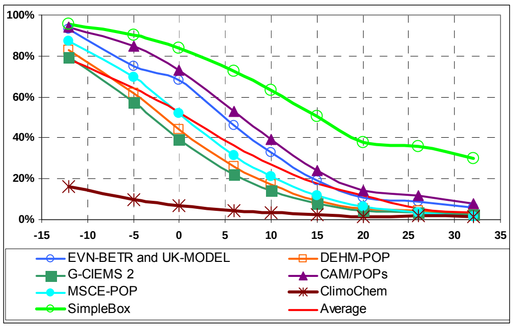



***Fig. 4.2.*** *Calculation results of the participating models (gas-particle partitioning) obtained with “own/alternative” data set*

***Table 4.6.*** *Correlation coefficients* $r_{12}$

| | DEHM-POP | G-CIEMS 2 | CAN/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 |
| CAN/POPs | – | – | – | 0.98 | 0.91 | 0.99 |
| MSCE-POP | – | – | – | – | 0.97 | 0.95 |
| CliMoChem | – | – | – | – | – | 0.86 |

The values of regression coefficients $\alpha$ and $\beta$ calculated for all pairs of models are shown in Table 4.7.

***Table 4.7.*** *Coefficients of regression dependence between the models ($\alpha$ / $\beta$)*

| | DEHM-POP | G-CIEMS 2 | CAN/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 |
| CAN/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 $\alpha$, 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 $\beta$ 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 $\sigma$ were done (Table 4.8).

***Table 4.8.*** *Residual square deviation,* $\sigma^{res}{}_{12}$

| | DEHM-POP | G-CIEMS 2 | CAN/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 |
| CAN/POPs | – | – | – | 0.161 | 0.058 | 0.100 |
| MSCE-POP | – | – | – | – | 0.036 | 0.214 |
| CliMoChem | – | – | – | – | – | 0.357 |

Values of $\sigma$ 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 4.9.

***Table 4.9.*** *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. 4.3.

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 4.9).

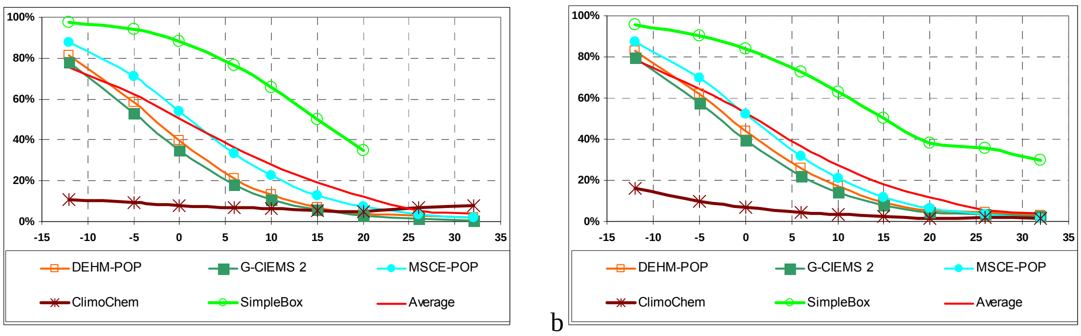



***Fig. 4.3.*** *Calculation results of the participating models obtained with "reference" (a) and "own/alternative" (b) data sets (for models presented both calculations)*

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. Two approaches based on adsorption and absorption schemes are mainly used by the participating models.

## 4.2. Wet deposition

***Reference data set.*** Calculation results for PCB-153 together with *m* and $\sigma$ are presented in Tables 4. 4.10 and 4.11.

***Table 4.10.*** *Calculation results: concentrations in precipitation (pg/L) ("reference" data set)*

| Exp. No | *T* (°C) | EVN-BETR and UK-MODEL | G-CIEMS | CAN/POPs | MSCE-POP | CliMoChem | SimpleBox | *m* | *σ* |
|---|---|---|---|---|---|---|---|---|---|
| 1 | -1 | | 1070 | | 805 | 320 | 1094 | 822 | 360 |
| 2 | 3 | | 967 | | 727 | 287 | 984 | 741 | 325 |
| 3 | 15 | | 310 | | 235 | 99 | 338 | 245 | 107 |
| 4 | -1 | | 1070 | | 805 | 32 | 1094 | 750 | 496 |
| 5 | 3 | | 967 | | 727 | 29 | 984 | 677 | 448 |
| 6 | 15 | | 310 | | 235 | 10 | 338 | 223 | 149 |

***Table 4.11.*** *Calculation results: wet deposition flux, ng/m²/hour ("reference" data set)*

| Exp. No | *T* (°C) | EVN-BETR and UK-MODEL | G-CIEMS | CAN/POPs | MSCE-POP | CliMoChem | SimpleBox | *m* | *σ* |
|---|---|---|---|---|---|---|---|---|---|
| 1 | -1 | | 1.07 | | 0.80 | 0.32 | 1.09 | 0.82 | 0.36 |
| 2 | 3 | | 0.97 | | 0.73 | 0.29 | 0.98 | 0.74 | 0.32 |
| 3 | 15 | | 0.31 | | 0.24 | 0.099 | 0.34 | 0.24 | 0.11 |
| 4 | -1 | | 10.7 | | 8.0 | 0.32 | 10.9 | 7.50 | 5.0 |
| 5 | 3 | | 9.7 | | 7.3 | 0.29 | 9.8 | 6.77 | 4.5 |
| 6 | 15 | | 3.1 | | 2.4 | 0.099 | 3.4 | 2.23 | 1.5 |

The comparison of calculated values of concentrations in precipitation is displayed in Fig. 4.4.

Pairwise regression analysis is performed only for calculated values of concentrations in precipitation since for wet deposition fluxes the results will be the same. Calculated correlation coefficients between the results of participating models are given in Table 4.12. It is seen that the correlation between models G-CIEMS, MSCE-POP and SimpleBox is very high.

***Table 4.12.*** *Correlation coefficients $r_{12}$*

| | MSCE-POP | CliMoChem | SimpleBox* |
|---|---|---|---|
| G-CIEMS | 1.00 | 0.42 | 1.00 |
| MSCE-POP | – | 0.42 | 1.00 |
| CliMoChem | – | – | 0.42 |

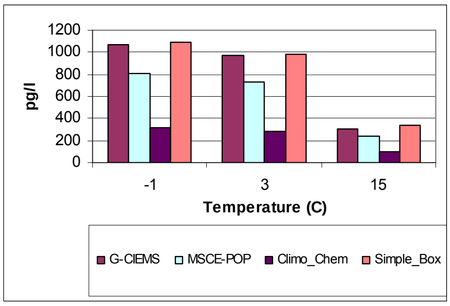



***Fig. 4.4.*** *Concentration in precipitation calculated by different models for different values of ambient temperatures, pg/L (reference data set)*

The values of regression coefficients $\alpha$ and $\beta$ calculated for all pairs of models are shown in Table 4.13.

***Table 4.13.*** *Coefficients of regression dependence between the models ($\alpha$ / $\beta$)*

| | MSCE-POP | CliMoChem | SimpleBox* |
|---|---|---|---|
| G-CIEMS | 0.75/2.7 | 0.16/4.8 | 0.99/29.4 |
| MSCE-POP | – | 0.21/4.2 | 1.32/25.8 |
| CliMoChem | – | – | 1.12/660 |

Finally, pairwise residual square deviation $\sigma$ are shown in Table 4.14. Again, these results confirm the closeness between the three above mentioned models.

***Table 4.14.*** *Residual square deviation, $\sigma^{res}_{12}$*

| | MSCE-POP | CliMoChem | SimpleBox* |
|---|---|---|---|
| G-CIEMS | 1 | 281 | 8 |
| MSCE-POP | – | 281 | 7 |
| CliMoChem | – | – | 741 |

***Own/alternative data set.*** Calculation results for PCB-153 together with *m* and $\sigma$ are presented in Tables 4. 4.15 and 4.16.

***Table 4.15.*** *Calculation results: concentrations in precipitation (pg/L) (own/alternative data set)*

| Exp. No | *T* (°C) | EVN-BETR and UK-MODEL | G-CIEMS | CAN/POPs | MSCE-POP | CliMoChem | SimpleBox | *m* | $\sigma$ |
|---|---|---|---|---|---|---|---|---|---|
| 1 | -1 | 1870 | 1073 | 3042 | 808 | 312 | 1084 | 1365 | 964 |
| 2 | 3 | 1510 | 969 | 2130 | 729 | 282 | 978 | 1100 | 643 |
| 3 | 15 | 1480 | 311 | 3262 | 237 | 90 | 334 | 952 | 1238 |
| 4 | -1 | – | 1073 | – | 808 | 31 | 1084 | 749 | 495 |
| 5 | 3 | – | 969 | – | 729 | 28 | 978 | 676 | 447 |
| 6 | 15 | – | 311 | – | 237 | 9 | 334 | 223 | 148 |

***Table 4.16.*** *Calculation results: wet deposition flux, ng/m²/hour (own/alternative data set)*

| Exp. No | *T* (°C) | EVN-BETR and UK-MODEL | G-CIEMS | CAN/POPs | MSCE-POP | CliMoChem | SimpleBox | *m* | $\sigma$ |
|---|---|---|---|---|---|---|---|---|---|
| 1 | -1 | 1.870 | 1.073 | 3.042 | 0.808 | 0.312 | 1.084 | 1.365 | 0.964 |
| 2 | 3 | 1.510 | 0.969 | 2.130 | 0.729 | 0.282 | 0.978 | 1.100 | 0.643 |
| 3 | 15 | 1.480 | 0.311 | 3.262 | 0.237 | 0.090 | 0.334 | 0.952 | 1.238 |
| 4 | -1 | – | 10.728 | – | 8.080 | 0.312 | 10.845 | 7.491 | 4.953 |
| 5 | 3 | – | 9.686 | – | 7.290 | 0.282 | 9.784 | 6.761 | 4.470 |
| 6 | 15 | – | 3.115 | – | 2.370 | 0.090 | 3.340 | 2.229 | 1.485 |

The comparison of calculated values of concentrations in precipitation is displayed in Fig. 4.5.

Pairwise regression analysis is performed only for calculated values of concentrations in precipitation since for wet deposition fluxes the results will be the same. Calculated correlation coefficients between the results of participating models are given in Table 4.17. The correlation between results obtained by models G-CIEMS, Climo-Chem, MSCE-POP and SimpleBox is very high.

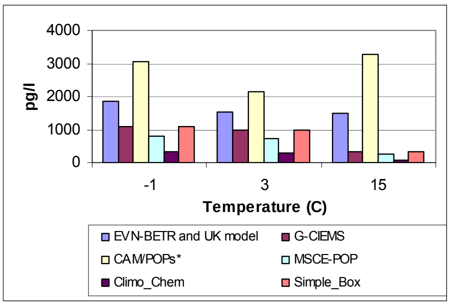



***Fig. 4.5.*** *Concentration in precipitation calculated by different models for different values of ambient temperatures, pg/L (own/alternative data set)*

***Table 4.17.*** *Correlation coefficients* $r_{12}$

| | G-CIEMS | CAN/POPs | MSCE-POP | CliMoChem | SimpleBox |
|---|---|---|---|---|---|
| EVN-BETR and UK model | 0.66 | 0.27 | 0.66 | 0.66 | 0.66 |
| G-CIEMS | – | -0.55 | 1.00 | 1.00 | 1.00 |
| CAN/POPs | – | – | -0.55 | -0.55 | -0.55 |
| MSCE-POP | – | – | – | 1.00 | 1.00 |
| CliMoChem | – | – | – | – | 1.00 |

The values of regression coefficients $\alpha$ and $\beta$ calculated for all pairs of models are shown in Table 4.18.

***Table 4.18.*** *Coefficients of regression dependence between the models* ($\alpha$ / $\beta$)

| | G-CIEMS | CAN/POPs | MSCE-POP | CliMoChem | SimpleBox |
|---|---|---|---|---|---|
| EVN-BETR and UK model | 1.25/-1246 | 0.74/1616 | 0.94/-933 | 0.37/-363 | 1.24/-1208 |
| G-CIEMS | – | -0.80/3438 | 0.75/3.5 | 0.29/-0.51 | 0.98/-1208 |
| CAN/POPs | – | – | -0.28/1385 | -0.11/538 | -0.37/1837 |
| MSCE-POP | – | – | – | 0.39/-1.87 | 1.31/22.6 |
| CliMoChem | – | – | – | – | 3.38/29.0 |

Finally, pairwise residual square deviation σ are shown in Table 4.19.

***Table 4.19.*** *Residual square deviation,* $\sigma^{res}_{12}$

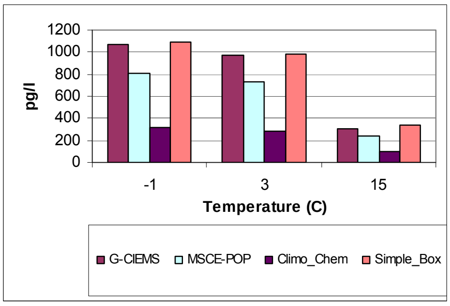
| | G-CIEMS | CAN/POPs | MSCE-POP | CliMoChem | SimpleBox |
|---|---|---|---|---|---|
| EVN-BETR and UK model | 439 | 818 | 329 | 128 | 430 |
| G-CIEMS | – | 709 | 0.64 | 0.07 | 2.5 |
| CAN/POPs | – | – | 366 | 142 | 481 |
| MSCE-POP | – | – | – | 0.31 | 1.6 |
| CliMoChem | – | – | – | – | 2.7 |

***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 4.20.

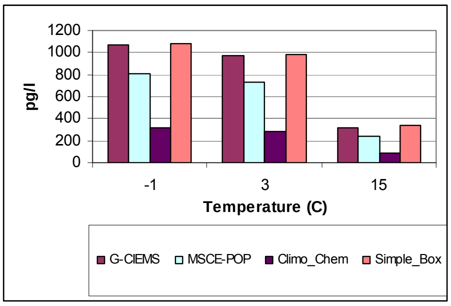
***Table 4.20.*** *Difference between calculations with two data sets*

| Exp. No | *T* (°C) | G-CIEMS | MSCE-POP | CliMoChem | SimpleBox |
|---|---|---|---|---|---|
| 1 | -1 | 0.3% | 0.4% | -2.4% | -0.9% |
| 2 | 3 | 0.2% | 0.3% | -1.9% | -0.6% |
| 3 | 15 | 0.5% | 0.8% | -8.5% | -1.1% |

These results are visualized in Fig. 4.6.




a




b

***Fig. 4.6.*** *Calculation results of the participating models obtained with " reference" (a) and "own/alternative" (b) data sets (for models presented both calculations)*

Thus, the differences in wet deposition flux and concentrations in precipitation calculated by models are essential. However, square deviation does not exceed the mean value of these parameters averaged between the participating models both in the results obtained on the basis of "reference" and "own/alternative" data sets. The difference in calculation results on wet deposition caused by the usage of "reference" and "own /alternative" data sets of pollutant properties is negligible. This process needs further investigation.

## 4.3. Gaseous exchange between atmosphere and soil

Here we present numerical results of calculations of soil concentrations and net gaseous flux to soil obtained by the participating models and their analysis for PCB-153 with “reference” and “own/alternative” data sets.

EVN-BETR and UK model, SimpleBox, and DEHM-POP models have made calculations on these experiments using steady-state approach. CliMoChem and CAN/POPs models have obtained results under equilibrium assumption. For G-CIEMS model two versions of calculations are presented: for steady-state (G-CIEMS 1) and at equilibrium using interim calculation parameters of the model (G-CIEMS 2). For MSCE-POP model two calculation versions are presented as well: steady-state calculations (MSCE-POP 1) and calculations from dynamic model (MSCE-POP 2). In the latter case calculations for 60-year period with air concentration roughly simulating the trend of PCB air concentrations and additional two years with constant air concentrations equal to that specified in the input data. In this case soil concentrations in the end of calculation period were used for comparison. Fig. 4.7 illustrates air concentration trend used in calculations for Experiment 1.

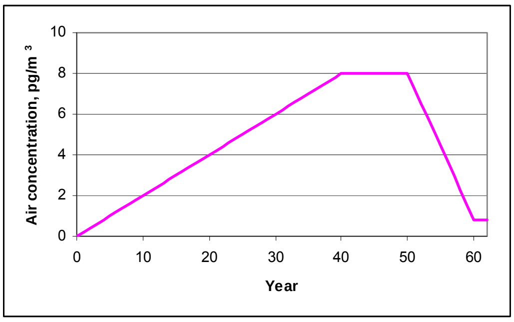



*Fig. 4.7. Air concentration trend used for calculations for MSCE-POP model (MSCE-POP 2) for Experiment 1*

In addition, the analysis of accumulation and clearance processes calculated by five models (CAN/POPs, ClimoChem, EVN-BETR and UK model, SimpleBox and MSCE-POP) is performed.

***Reference data set.*** Calculation results for soil concentrations together with $m$ and $\sigma$ calculated with “reference” data set of PCB-153 properties are presented in Table 4.21. Net gaseous fluxes to soil of PCB-153 calculated by the models and statistical parameters used for its evaluation are given in Table 4.22.

***Table 4.21.*** *Calculation results: soil concentrations of PCB-153 (ng/g) calculated by models and statistical parameters used for evaluation (“reference” data set)*

| No | Air conc, pg/m$^3$ | EVN-BETR and UK-MODEL | DEHM-POP | G-CIEMS | | CAM/ POPs | MSCE-POP | | CliMoChem | SimpleBox | $m$ | $\sigma$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | 1 | 2 | | 1 | 2 | | | | |
| 1 | 0.8 | – | 0.85 | 0.007 | 0.083 | 0.38 | 0.011 | 0.074 | 0.0004 | 0.0001 | 0.18 | 0.30 |
| 2 | 5.5 | – | 0.40 | 0.065 | 1.3 | 5.66 | 0.079 | 0.58 | 0.003 | 0.001 | 1.01 | 1.93 |
| 3 | 6.8 | – | 0.31 | 0.065 | 0.93 | 3.91 | 0.094 | 0.83 | 0.005 | 0.001 | 0.77 | 1.32 |
| 4 | 2.8 | – | 0.067 | 0.012 | 0.11 | 0.48 | 0.038 | 0.22 | 0.001 | 0.000 | 0.12 | 0.16 |

***Table 4.22.*** *Calculation results: net gaseous flux to soil, of PCB-153 (ng/m$^2$/d) calculated by models and statistical parameters used for evaluation (“reference” data set)*

| No | Air conc, pg/m$^3$ | EVN-BETR and UK-MODEL | DEHM-POP | G-CIEMS | | CAN/POPs | MSCE-POP | | CliMoChem | SimpleBox | $m$ | $\sigma$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | 1 | 2 | | 1 | 2 | | | | |
| 1 | 0.8 | | | 0.0004 | 0 | $1.75 \cdot 10^{-13}$ | 0.03 | 0.02 | 0.01 | 0.07 | 0.03 | 0.03 |
| 2 | 5.5 | | | 0.002 | 0 | $2.5 \cdot 10^{-12}$ | 0.24 | 0.21 | 0.10 | 0.49 | 0.21 | 0.19 |
| 3 | 6.8 | | | 0.003 | 0 | $1.92 \cdot 10^{-12}$ | 0.28 | 0.20 | 0.12 | 0.61 | 0.24 | 0.23 |
| 4 | 2.8 | | | 0.001 | 0 | $3.67 \cdot 10^{-13}$ | 0.10 | 0.03 | 0.05 | 0.25 | 0.09 | 0.10 |

* - statistical parameters are calculated for models using steady-state and dynamic approaches.

Pairwise regression analysis is performed only for values of soil concentrations and deposition fluxes calculated by models using steady state and dynamic approaches. In spite of the fact that numerical values of soil concentrations are highly different, the variations of the corresponding numerical values caused by change of environmental conditions between different experiments are similarly described by most of models. This can be seen from values of pairwise correlation coefficients (Table 4.23).

***Table 4.23.*** *Correlation coefficients for soil concentrations of PCB-153 ("reference" data set)*

| | | G-CIEMS | | CAN/POPs | MSCE-POP | | CliMoChem | SimpleBox |
|---|---|---|---|---|---|---|---|---|
| | | 1 | 2 | | 1 | 2 | | |
| DEHM-POP | | -0.25 | -0.17 | -0.16 | -0.47 | -0.37 | -0.38 | -0.29 |
| G-CIEMS | 1 | | 0.97 | 0.96 | 0.96 | 0.95 | 0.94 | 0.99 |
| | 2 | | | 1.00 | 0.88 | 0.83 | 0.82 | 0.93 |
| CAN/POPs | | | | | 0.87 | 0.82 | 0.80 | 0.92 |
| MSCE-POP | 1 | | | | | 0.98 | 0.98 | 0.98 |
| | 2 | | | | | | 1.00 | 0.98 |
| ClimoChem | | | | | | | | 0.97 |

Correlation coefficients for net gaseous flux are presented in Table 4.24.

***Table 4.24.*** *Correlation coefficients for net gaseous flux to soil of PCB-153 ("reference" data set)*

| | | MSCE-POP | | CliMoChem | SimpleBox |
|---|---|---|---|---|---|
| | | 1 | 2 | | |
| G-CIEMS | | 0.91 | 0.76 | 0.94 | 0.94 |
| MSCE-POP | 1 | – | 0.96 | 1.00 | 1.00 |
| | 2 | – | – | 0.94 | 0.94 |
| CliMoChem | | – | – | – | 1.00 |

Calculated regression coefficients $\alpha$ and $\beta$ for soil concentrations and deposition fluxes are given in Tables 4.25 and 4.26, respectively.

***Table 4.25.*** *Coefficients of regression dependence between the models ($\alpha$ / $\beta$) for soil concentrations of PCB-153 ("reference" data set)*

| | | G-CIEMS | | CAN/POPs | MSCE-POP | | ClimoChem | SimpleBox |
|---|---|---|---|---|---|---|---|---|
| | | 1 | 2 | | 1 | 2 | | |
| DEHM-POP | | -0.024/0.005 | -0.316/0.74 | -1.281/3.13 | -0.054/0.08 | -0.389/0.58 | -0.002/0.003 | -0.001/0.001 |
| G-CIEMS | 1 | – | 18.380/-0.08 | 78.239/-0.33 | 1.136/0.01 | 10.103/0.05 | 0.054/0.0003 | 0.021/0.00001 |
| | 2 | – | – | 4.283/-0.01 | 0.055/0.02 | 0.469/0.14 | 0.002/0.001 | 0.001/0.0002 |
| CAN/POPs | | – | – | – | 0.013/0.02 | 0.108/0.14 | 0.001/0.001 | 0.0002/0.0002 |
| MSCE-POP | 1 | – | – | – | – | 8.882/-0.07 | 0.048/-0.0004 | 0.018/-0.0002 |
| | 2 | – | – | – | – | – | 0.005/-0.000001 | 0.002/-0.00003 |
| ClimoChem | | – | – | – | – | – | – | 0.359/-0.00002 |

***Table 4.26.*** *Coefficients of regression dependence between the models ($\alpha$ / $\beta$) for net gaseous flux to soil of PCB-153 ("reference" data set)*

| | | MSCE-POP | | CliMoChem | SimpleBox |
|---|---|---|---|---|---|
| | | 1 | 2 | | |
| G-CIEMS | | 118/-0.02 | 88/-0.02 | 51/-0.01 | 253/-0.03 |
| MSCE-POP | 1 | – | 0.85/-0.02 | 0.41/0.004 | 2.06/0.02 |
| | 2 | – | – | 0.44/0.02 | 2.19/0.10 |
| CliMoChem | | – | – | – | 4.99/-0.001 |

Residual square deviation for soil concentrations and net gaseous flux are shown in Tables 4.27 and 4.28, respectively.

**Table 4.27.** *Residual square deviation, $\sigma^{res}_{12}$ for soil concentrations of PCB-153 ("reference" data set)*

| | | G-CIEMS | | CAN/POPs | MSCE-POP | | ClimoChem | SimpleBox |
|---|---|---|---|---|---|---|---|---|
| | | 1 | 2 | | 1 | 2 | | |
| DEHM-POP | | 0.05 | 1.04 | 4.47 | 0.06 | 0.55 | 0.003 | 0.001 |
| G-CIEMS | 1 | – | 0.27 | 1.25 | 0.02 | 0.19 | 0.001 | 0.0001 |
| | 2 | – | – | 0.10 | 0.03 | 0.33 | 0.002 | 0.0004 |
| CAN/POPs | | – | – | – | 0.03 | 0.34 | 0.002 | 0.0005 |
| MSCE-POP | 1 | – | – | – | – | 0.11 | 0.001 | 0.0002 |
| | 2 | – | – | – | – | – | 0.0001 | 0.0003 |
| ClimoChem | | – | – | – | – | – | – | 0.0003 |

**Table 4.28.** *Residual square deviation, $\sigma^{res}_{12}$ for net gaseous flux to soil of PCB-153 ("reference" data set)*

| | | MSCE-POP | | CliMoChem | SimpleBox |
|---|---|---|---|---|---|
| | | 1 | 2 | | |
| G-CIEMS | | 0.08 | 0.12 | 0.03 | 0.14 |
| MSCE-POP | 1 | – | 0.05 | 0.01 | 0.03 |
| | 2 | – | – | 0.03 | 0.14 |
| CliMoChem | | – | – | – | 0.003 |

***Own/alternative data set.*** Calculation results soil concentrations together with *m* and $\sigma$ calculated with "own/alternative" data set of PCB-153 properties are presented in Table 4.29. Net gaseous fluxes to soil of PCB-153 calculated by the models and statistical parameters used for its evaluation are given in Table 4.30. Table 4.29 contains also the information of the data set used for calculations for each model.

**Table 4.29.** *Calculation results: soil concentrations of PCB-153 (ng/g) calculated by models and statistical parameters used for evaluation ("own/alternative" data set)*

| No | Air conc, pg/m$^3$ | EVN-BETR and UK-MODEL | DEHM-POP | G-CIEMS | | CAM/POPs | MSCE-POP | | CliMoChem | SimpleBox | *m* | $\sigma$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | 1 | 2 | | 1 | 2 | | | | |
| | | own | own | alt | | own | own | | own | alt | | |
| 1 | 0.8 | 0.002 | 0.46 | 0.01 | 0.09 | 0.57 | 0.02 | 0.10 | 0.002 | 0.23 | 0.17 | 0.21 |
| 2 | 5.5 | 0.01 | 7.62 | 0.07 | 1.41 | 8.70 | 0.15 | 0.83 | 0.02 | 2.23 | 2.34 | 3.40 |
| 3 | 6.8 | 0.02 | 6.32 | 0.07 | 0.93 | 6.42 | 0.20 | 1.17 | 0.02 | 2.37 | 1.95 | 2.62 |
| 4 | 2.8 | 0.004 | 1.40 | 0.01 | 0.11 | 0.79 | 0.05 | 0.30 | 0.01 | 0.44 | 0.35 | 0.48 |

**Table 4.30.** *Calculation results: net gaseous flux to soil, of PCB-153 (ng/m$^2$/d) calculated by models and statistical parameters used for evaluation ("own/alternative" data set)**

| No | Air conc, pg/m$^3$ | EVN-BETR and UK-MODEL | DEHM-POP | G-CIEMS | | CAN/POPs | MSCE-POP | | CliMoChem | SimpleBox | *m* | $\sigma$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | 1 | 2 | | 1 | 2 | | | | |
| 1 | 0.8 | 0.001 | – | 0.0004 | 0 | $3.51 \cdot 10^{-13}$ | 0.030 | 0.009 | 0.014 | 0.003 | 0.010 | 0.011 |
| 2 | 5.5 | 0.006 | – | 0.002 | 0 | $5.01 \cdot 10^{-12}$ | 0.229 | 0.157 | 0.097 | 0.202 | 0.115 | 0.097 |
| 3 | 6.8 | 0.008 | – | 0.003 | 0 | $2.06 \cdot 10^{-12}$ | 0.254 | 0.082 | 0.120 | 0.094 | 0.093 | 0.092 |
| 4 | 2.8 | 0.003 | – | 0.001 | 0 | $3.94 \cdot 10^{-13}$ | 0.077 | -0.071 | 0.047 | -0.061 | -0.001 | 0.058 |

* - statistical parameters are calculated for models using steady-state and dynamic approaches.

Pairwise regression analysis is performed only for values of soil concentrations and deposition fluxes calculated by models using steady-state and dynamic approaches. In spite of the fact that numerical values of soil concentrations are highly different, the variations of the corresponding numerical values caused by change of environmental conditions between different experiments are similarly described by models. This can be seen from values of pairwise correlation coefficients (Table 4.31).

***Table 4.31.*** *Correlation coefficients for soil concentrations of PCB-153 (“own/alternative” data set)*

| | | DEHM-POP | G-CIEMS | | CAN/POPs | MSCE-POP | | ClimoChem | SimpleBox |
|---|---|---|---|---|---|---|---|---|---|
| | | | 1 | 2 | | 1 | 2 | | |
| EVN-BETR and UK MODEL | | 0.93 | 0.98 | 0.86 | 0.90 | 1.00 | 1.00 | 1.00 | 0.99 |
| DEHM-POP | | – | 0.99 | 0.98 | 0.99 | 0.90 | 0.90 | 0.91 | 0.98 |
| G-CIEMS | 1 | – | – | 0.95 | 0.97 | 0.95 | 0.95 | 0.96 | 1.00 |
| | 2 | – | – | – | 1.00 | 0.82 | 0.82 | 0.83 | 0.93 |
| CAN/POPs | | – | – | – | – | 0.86 | 0.86 | 0.87 | 0.96 |
| MSCE-POP | 1 | – | – | – | – | – | 1.00 | 1.00 | 0.97 |
| | 2 | – | – | – | – | – | – | 1.00 | 0.97 |
| ClimoChem | | – | – | – | – | – | – | – | 0.97 |

Correlation coefficients for net gaseous flux are presented in Table 4.32.

***Table 4.32.*** *Correlation coefficients for net gaseous flux to soil of PCB-153 (“own/alternative” data set)*

| | | G-CIEMS 1 | MSCE-POP | | CliMoChem | SimpleBox |
|---|---|---|---|---|---|---|
| | | | 1 | 2 | | |
| EVN-BETR and UK MODEL | | 0.96 | 0.97 | 0.63 | 1.00 | 0.64 |
| G-CIEMS 1 | | – | 0.87 | 0.38 | 0.94 | 0.41 |
| MSCE-POP | 1 | – | – | 0.79 | 0.99 | 0.80 |
| | 2 | – | – | – | 0.68 | 0.99 |
| CliMoChem | | – | – | – | – | 0.70 |

Calculated regression coefficients $\alpha$ and $\beta$ for soil concentrations and deposition fluxes are given in Table 4.33 and 34, respectively.

***Table 4.33.*** *Coefficients of regression dependence between the models ($\alpha$ / $\beta$) for soil concentrations of PCB-153 (“own/alternative” data set)*

| | | DEHM-POP | G-CIEMS | | CAN/POPs | MSCE-POP | | ClimoChem | SimpleBox |
|---|---|---|---|---|---|---|---|---|---|
| | | | 1 | 2 | | 1 | 2 | | |
| EVN-BETR and UK MODEL | | 440/ -0.19 | 4.15/ -0.002 | 74.1/ -0.06 | 486/ -0.46 | 11.3/ -0.001 | 64.4/ -0.01 | 1.23/ -0.0001 | 149/ -0.09 |
| DEHM-POP | | – | 0.01/ 0.002 | 0.18/ -0.07 | 1.14/ -0.39 | 0.02/ 0.02 | 0.12/ 0.11 | 0.002/ 0.002 | 0.31/ 0.07 |
| G-CIEMS | 1 | – | – | 19.2/ -0.08 | 124/ -0.51 | 2.54/ 0.01 | 14.5/ 0.06 | 0.28/ 0.001 | 35.4/ -0.01 |
| | 2 | – | – | – | 6.26/0.14 | 0.11/ 0.04 | 0.61/ 0.21 | 0.01/ 0.004 | 1.64/0.27 |
| CAN/POPs | | – | – | – | – | 0.02/ 0.03 | 0.10/ 0.18 | 0.002/0.003 | 0.27/ 0.21 |
| MSCE-POP | 1 | – | – | – | – | – | 5.71/ -0.0004 | 0.11/0.0001 | 12.9/ -0.04 |
| | 2 | – | – | – | – | – | – | 0.02/0.0001 | 2.26/ -0.04 |
| ClimoChem | | – | – | – | – | – | – | – | 119/ -0.06 |

***Table 4.34.*** *Coefficients of regression dependence between the models ($\alpha$ / $\beta$) for net gaseous flux to soil of PCB-153 (“own/alternative” data set)*

| | | G-CIEMS 1 | MSCE-POP | | CliMoChem | SimpleBox |
|---|---|---|---|---|---|---|
| | | | 1 | 2 | | |
| EVN-BETR and UK MODEL | | 0.29/0.0003 | 36.0/ -0.01 | 20.5/ -0.05 | 15.9/0.0001 | 24.6/ -0.05 |
| G-CIEMS 1 | | – | 108/ -0.02 | 41.9/ -0.02 | 50.0/ -0.01 | 52.1/ -0.02 |
| MSCE-POP | 1 | – | – | 0.69/ -0.06 | 0.43/0.01 | 0.83/ -0.06 |
| | 2 | – | – | – | 0.33/0.05 | 1.16/0.01 |
| CliMoChem | | – | – | – | – | 1.67/ -0.06 |

Residual square deviation for soil concentrations and net gaseous flux are shown in Tables 4.27 and 4.28, respectively.

***Table 4.27.*** *Residual square deviation, $\sigma^{res}_{12}$ for soil concentrations of PCB-153 ("own/alternative" data set)*

| | | DEHM-POP | G-CIEMS | | CAN/POPs | MSCE-POP | | ClimoChem | SimpleBox |
|---|---|---|---|---|---|---|---|---|---|
| | | | 1 | 2 | | 1 | 2 | | |
| EVN-BETR and UK MODEL | | 2.18 | 0.01 | 0.57 | 3.10 | 0.01 | 0.07 | 0.001 | 0.33 |
| DEHM-POP | | – | 0.01 | 0.21 | 0.82 | 0.06 | 0.36 | 0.01 | 0.40 |
| G-CIEMS | 1 | – | – | 0.35 | 1.63 | 0.04 | 0.25 | 0.004 | 0.10 |
| | 2 | – | – | – | 0.57 | 0.09 | 0.49 | 0.01 | 0.70 |
| CAN/POPs | | – | – | – | – | 0.08 | 0.43 | 0.01 | 0.55 |
| MSCE-POP | 1 | – | – | – | – | – | 0.001 | 0.0004 | 0.49 |
| | 2 | – | – | – | – | – | – | 0.0005 | 0.50 |
| ClimoChem | | – | – | – | – | – | – | – | 0.44 |

***Table 4.28.*** *Residual square deviation, $\sigma^{res}_{12}$ for net gaseous flux to soil of PCB-153 ("own/alternative" data set)*

| | | G-CIEMS 1 | MSCE-POP | | CliMoChem | SimpleBox |
|---|---|---|---|---|---|---|
| | | | 1 | 2 | | |
| EVN-BETR and UK MODEL | | 0.0004 | 0.04 | 0.13 | 0.01 | 0.15 |
| G-CIEMS 1 | | – | 0.09 | 0.16 | 0.03 | 0.18 |
| MSCE-POP | 1 | – | – | 0.10 | 0.01 | 0.12 |
| | 2 | – | – | – | 0.06 | 0.03 |
| CliMoChem | | – | – | – | – | 0.14 |

***Comparison between two data sets.*** The difference between calculated values of soil concentrations obtained with two data sets of pollutant properties (for those models who provided calculations for both these sets) is shown in Table 4.29. The corresponding differences between calculated values of net flux to soil were not calculated since near the equilibrium small changes in pollutant properties can lead to essential changes of fluxes (in relative values).

***Table 4.29.*** *Difference between calculations with two data sets*

| No | Air conc, pg/m$^3$ | EVN-BETR and UK-MODEL | DEHM-POP | G-CIEMS | | CAM/ POPs | MSCE-POP | | CliMoChem | SimpleBox |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | 1 | 2 | | 1 | 2 | | |
| 1 | 0.8 | | -45.6% | 0.0030% | 10.2% | 50.1% | 61.5% | 42.0% | 453.8% | 169141.1% |
| 2 | 5.5 | | 1807.1% | 0.0010% | 8.1% | 53.8% | 84.0% | 44.2% | 437.1% | 170552.4% |
| 3 | 6.8 | | 1933.5% | -0.0001% | -0.4% | 64.3% | 116.8% | 40.8% | 389.0% | 159125.2% |
| 4 | 2.8 | | 1999.1% | -0.0032% | -3.7% | 66.3% | 36.8% | 35.8% | 349.4% | 148384.2% |

Models describe gaseous flux between atmosphere and soil more closely than soil concentrations. The differences in concentrations are lower with "reference" data set than those with "own/alternative" data. The difference between calculated values of soil concentrations obtained with two data sets of pollutant properties ("reference" and "own/alternative") is considerable for most models. Model descriptions of air/soil exchange and their parameterizations need further consideration.

***Accumulation/clearance dynamics of PCBs in soil.*** The aim of this subsection is to analyze model descriptions of long-term processes of accumulation of selected PCB congeners in soil and clearance of soil compartment at emission termination. To do this, modelling of air/soil exchange with constant air concentration for a sufficiently long period were carried out by CAN/POPs, CliMoChem, EVN-BETR and UK model, MSCE-POP, and SimpleBox models both using "reference" and "own or alternative" data sets of PCB properties.

The period under simulation was split into two periods. During the first period (accumulation) air concentrations are kept at the level defined in the corresponding input data set and initial data are assumed to be zero. Soil concentrations obtained in the end of the first period were used as initial data for the second period (clearance). During this period air concentrations are set to zero.

Fig. 4.8 shows the results of the experiment obtained by CAN/POPs, MSCE-POP, EVN-BETR and UK model, and SimpleBox models, respectively with “reference” data set. Maximum values presented on the plots correspond to the soil concentrations achieved at steady state after rather long period of accumulation.

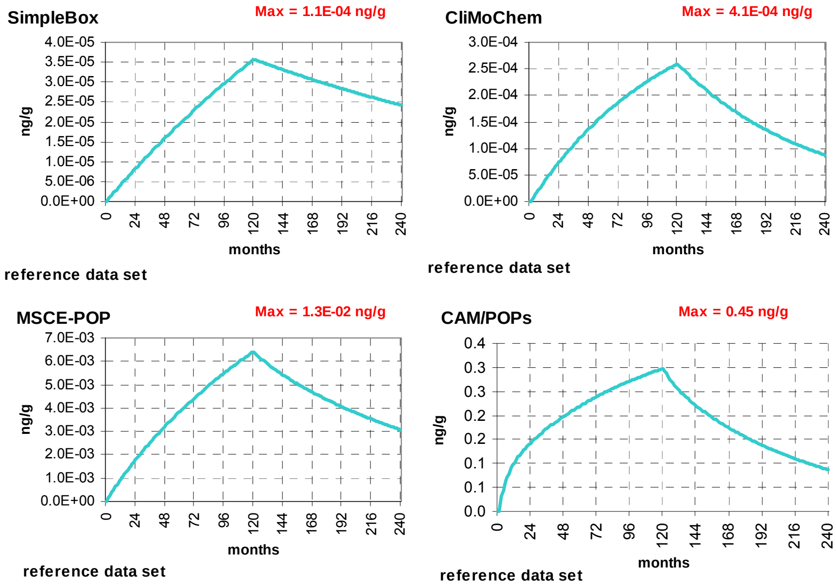



*Fig. 4.8.* *Long-term trends of accumulation and clearance obtained by participating models (“reference” data set)*

The results obtained with the use of “own/alternative” data sets are presented in Fig. 4.9.

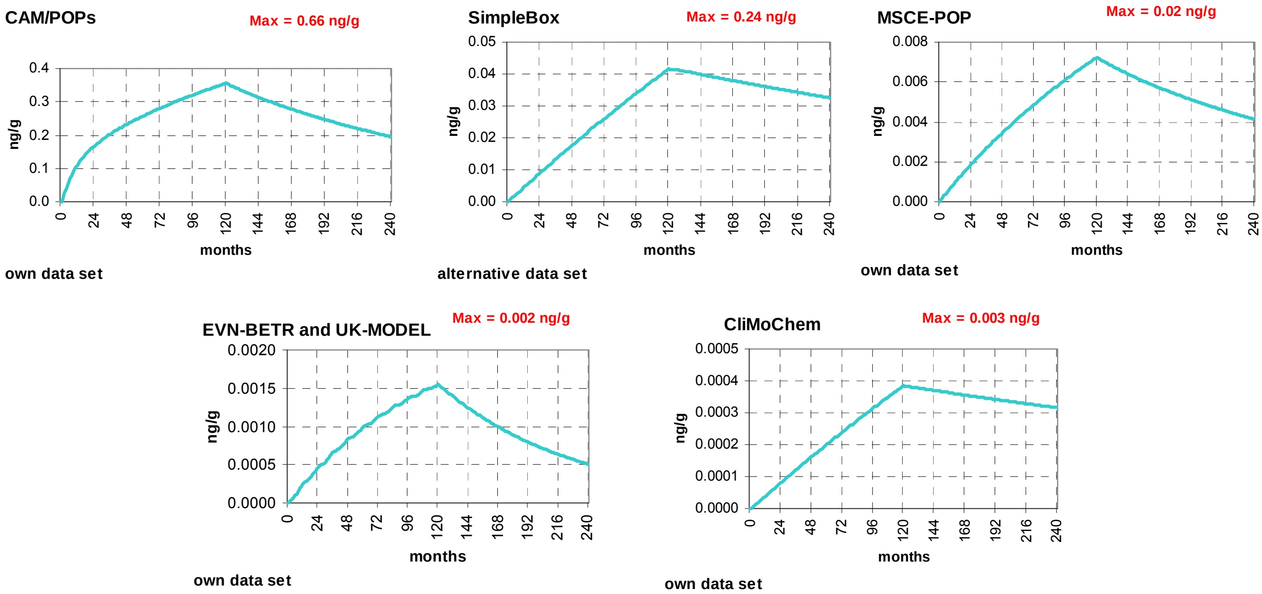



*Fig. 4.9.* *Long-term trends of accumulation and clearance obtained by participating models (“own/alternative” data set)*

For the analysis of calculated trends of soil concentrations at both accumulation and clearance stages bi-exponential approximation of accumulation and clearance is performed. This approximation has the form:

$$C_{soil} = C_1(1-e^{-\lambda_1 t}) + C_2(1-e^{-\lambda_2 t}), \quad \lambda_1 > \lambda_2 \qquad \text{(accumulation stage)}$$

$$C_{soil} = C_1 e^{-\lambda_1 t} + C_2 e^{-\lambda_2 t}, \quad \lambda_1 > \lambda_2 \qquad \text{(clearance stage)}$$

where $t$ is the time, months;

$\lambda_1$ and $\lambda_2$ are exchange rate constants, month$^{-1}$;

$C_1$ and $C_2$ are constants determining shares of concentrations involved in fast/slow process.

Such form of the dependence of soil concentrations on time is characteristic of a process with two characteristic times of exchange: fast exchange characteristic time $T_{1/2}^1$ = ln(2)/$\lambda_1$ and slow exchange characteristic time $T_{1/2}^2$ = ln(2)/$\lambda_2$. Calculations show that bi-exponential approximation well explains the trends of soil concentrations both at accumulation and clearance phases.

The values of characteristic times obtained by the approximation are shown in Table 4.30.

***Table 4.30.*** *Parameters of multi-exponential approximation*

| | CAN/POPs | | ClimoChem | | EVN-BETR and UK model | | MSCE-POP | | SimpleBox | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Slow | Fast | Slow | Fast | Slow | Fast | Slow | Fast | Slow | Fast |
| "Reference" data set | | | | | | | | | | |
| Accumulation phase | 8.3 | 0.58 | 6.9 | 6.9 | – | – | 11 | 1.5 | 18 | 18 |
| Clearance phase | 7.1 | 2.3 | 6.3 | 6.3 | – | – | 11 | 2.9 | 18 | 18 |
| "Own/alternative" data set | | | | | | | | | | |
| Accumulation phase | 13 | 0.75 | 51 | 51 | 6.6 | 6.6 | 18 | 2.9 | 36 | 36 |
| Clearance phase | 14 | 5.8 | 35 | 35 | 6.2 | 6.0 | 18 | 5.8 | 28 | 28 |

As a result of this analysis all models can be split into two groups. The first group form models for which values of $T_{1/2}$ for two exponentials are close to each other (single-exponential models): Climo-Chem, EVN-BETR and UK MODEL, and SimpleBox. The second group contains models for which values of $T_{1/2}$ for slow and fast exponentials differ considerably (two-exponential models): CAN/POPs and MSCE-POP. The values of $T_{1/2}$ (for slow exponent) vary from 7 to 50 years.

The difference between results obtained with "reference" and "own/alternative" data sets (for those models which have performed both calculations) is illustrated by Fig. 4.10.

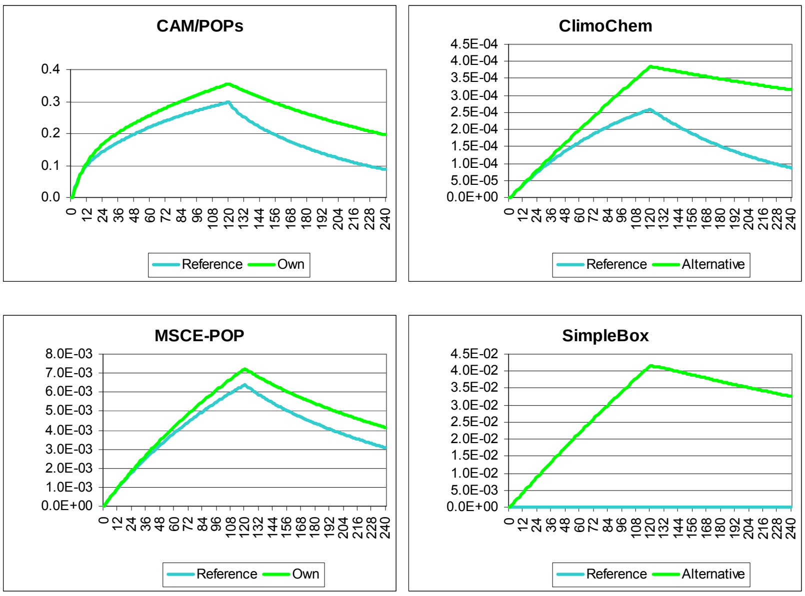



***Fig. 4.10.*** *Difference in long-term trends due to usage of different sets of PCB properties*

## 4.4. Gaseous exchange between atmosphere and water

***Reference data set.*** Calculation results for water concentrations together with *m* and $\sigma$ calculated with "reference" data set of PCB-153 properties are presented in Table 4.31.

***Table 4.31***. *Calculation results: water concentrations of PCB-153 (pg/L) calculated by all participating models and statistical parameters used for evaluation ("reference" data set)*

| N | EVN-BETR and UK-MODEL | CAN/POPs | DEHM-POP | CliMoChem | G-CIEMS | SimpleBox | MSCE-POP | *m* | $\sigma$ |
|---|---|---|---|---|---|---|---|---|---|
| 1 | – | 8.40 | 6.86 | 11.01 | 30.15 | 20.30 | 6.70 | 13.90 | 9.44 |
| 2 | – | 2.40 | 1.27 | 2.62 | 7.44 | 3.09 | 1.24 | 3.01 | 2.30 |
| 3 | – | 4.80 | 3.19 | 2.39 | 5.92 | 5.88 | 3.02 | 4.20 | 1.54 |
| 4 | – | 3.00 | 2.88 | 10.78 | 32.47 | 6.14 | 2.85 | 9.69 | 11.58 |

Fig. 4.11 displays the result on water concentrations of PCB-153 calculated by the participating models with the use of "reference" data set.

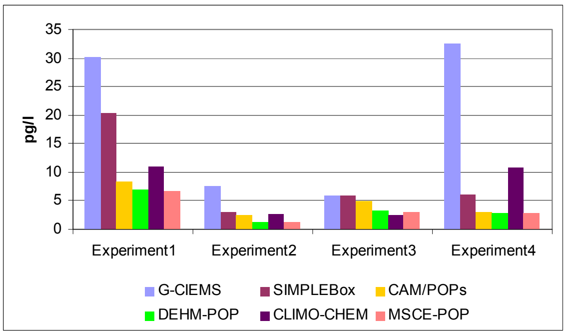



***Fig. 4.11.*** *Calculation results of the participating models (water concentrations) obtained with "reference" data set*

Gaseous fluxes to water, from water and net gaseous flux of PCB-153 calculated by the participating models are given in Table 4.32.

***Table 4.32***. *Calculation results: fluxes of PCB-153 to/from water (ng/m$^2$/day) calculated by all participating models and statistical parameters used for evaluation ("reference" data set)*

| N | EVN-BETR and UK-MODEL | CAN/POPs | DEHM-POP | CliMoChem | G-CIEMS | SimpleBox | MSCE-POP | *m* | $\sigma$ |
|---|---|---|---|---|---|---|---|---|---|
| Gaseous flux to water | | | | | | | | | |
| 1 | – | – | – | 0.98 | 1.02 | 4.59 | 2.21 | 2.20 | 1.69 |
| 2 | – | – | – | 0.25 | 0.25 | 0.74 | 0.53 | 0.44 | 0.24 |
| 3 | – | – | – | 0.18 | 0.20 | 1.12 | 0.42 | 0.48 | 0.44 |
| 4 | – | – | – | 1.37 | 1.10 | 1.95 | 2.17 | 1.65 | 0.50 |
| Gaseous flux from water | | | | | | | | | |
| 1 | – | 0.39 | – | 0.31 | 0.0019 | 0.35 | 2.16 | 0.64 | 0.86 |
| 2 | – | 5.31 | – | 0.10 | 0.0006 | 0.05 | 0.52 | 1.20 | 2.31 |
| 3 | – | 0.21 | – | 0.03 | 0.0002 | 0.06 | 0.39 | 0.14 | 0.16 |
| 4 | – | 0.03 | – | 0.72 | 0.0053 | 0.10 | 2.15 | 0.60 | 0.91 |
| Net gaseous flux | | | | | | | | | |
| 1 | – | 0.39 | – | 0.67 | 1.02 | 4.24 | 0.05 | 1.27 | 1.69 |
| 2 | – | 5.31 | – | 0.16 | 0.25 | 0.69 | 0.01 | 1.29 | 2.27 |
| 3 | – | 0.21 | – | 0.14 | 0.20 | 1.07 | 0.02 | 0.33 | 0.42 |
| 4 | – | 0.03 | – | 0.65 | 1.10 | 1.85 | 0.02 | 0.73 | 0.77 |

Below we present parwise comparison of modelling results for water concentrations and net gaseous flux to water. Correlation coefficients for water concentrations are shown in Table 4.32.

***Table 4.32.*** *Correlation coefficients for water concentrations ("reference" data set)*

| | DEHM-POP | CliMoChem | G-CIEMS | SimpleBox | MSCE-POP |
|---|---|---|---|---|---|
| CAN/POPs | 0.97 | 0.46 | 0.38 | 0.95 | 0.97 |
| DEHM-POP | – | 0.65 | 0.58 | 0.98 | 1.00 |
| CliMoChem | – | – | 1.00 | 0.66 | 0.67 |
| G-CIEMS | – | – | – | 0.59 | 0.60 |
| SimpleBox | – | – | – | – | 0.98 |

Correlation coefficients for net gaseous flux are demonstrated in Table 4.33.

***Table 4.33.*** *Correlation coefficients for net gaseous flux ("reference" data set)*

| | CliMoChem | G-CIEMS | SimpleBox | MSCE-POP |
|---|---|---|---|---|
| CAN/POPs | -0.56 | -0.54 | -0.49 | -0.60 |
| CliMoChem | – | 1.00 | 0.79 | 0.67 |
| G-CIEMS | – | – | 0.74 | 0.60 |
| SimpleBox | – | – | – | 0.97 |

Values of regression coefficients $\alpha$ and $\beta$ for water concentrations and net gaseous flux calculated for all pairs of models are given in Tables 4.34 and s.35, respectively.

***Table 4.34.*** *Coefficients of regression dependence between the models ($\alpha$ / $\beta$) for water concentrations ("reference" data set)*

| | DEHM-POP | CliMoChem | G-CIEMS | SimpleBox | MSCE-POP |
|---|---|---|---|---|---|
| CAN/POPs | 0.85/ -0.40 | 0.82/2.88 | 2.00/9.72 | 2.74/-3.89 | 0.83/-0.39 |
| DEHM-POP | – | 1.34/1.95 | 3.52/6.50 | 1.06/-2.59 | 0.98/ -0.01 |
| CliMoChem | – | – | 2.93/ -0.64 | 1.06/1.76 | 0.32/1.32 |
| G-CIEMS | – | – | – | 0.32/2.73 | 0.10/1.61 |
| SimpleBox | – | – | – | – | 0.29/0.86 |

***Table 4.35.*** *Coefficients of regression dependence between the models ($\alpha$ / $\beta$) for net gaseous flux ("reference" data set)*

| | CliMoChem | G-CIEMS | SimpleBox | MSCE-POP |
|---|---|---|---|---|
| CAN/POPs | -0.06/0.50 | -0.10/0.80 | -0.31/2.42 | -0.004/0.03 |
| CliMoChem | – | 1.64/ -0.02 | 4.31/0.22 | 0.04/0.01 |
| G-CIEMS | – | – | 2.43/0.40 | 0.02/0.01 |
| SimpleBox | – | – | – | 0.01/0.01 |

Finally, values of residual square deviation for water concentrations and net gaseous flux are collected in Tables 4.36 and 4.37.

***Table 4.36.*** *Residual square deviation, $\sigma$ for water concentrations ("reference" data set)*

| | DEHM-POP | CliMoChem | G-CIEMS | SimpleBox | MSCE-POP |
|---|---|---|---|---|---|
| CAN/POPs | 0.96 | 7.47 | 22.88 | 4.03 | 1.02 |
| DEHM-POP | – | 6.37 | 20.08 | 2.60 | 0.10 |
| CliMoChem | – | – | 2.19 | 10.08 | 2.97 |
| G-CIEMS | – | – | – | 10.83 | 3.20 |
| SimpleBox | – | – | – | | 0.71 |

***Table 4.37.*** *Residual square deviation, $\sigma$ for net gaseous flux ("reference" data set)*

| | CliMoChem | G-CIEMS | SimpleBox | MSCE-POP |
|---|---|---|---|---|
| CAN/POPs | 0.42 | 0.70 | 2.39 | 0.02 |
| CliMoChem | – | 0.07 | 1.67 | 0.02 |
| G-CIEMS | – | – | 1.86 | 0.02 |
| SimpleBox | – | – | – | 0.01 |

***Own/alternative data set.*** Calculation results for water concentrations together with $m$ and $\sigma$ calculated with "own/alternative" data set of PCB-153 properties are presented in Table 4.38. Here data set of PCB-153 properties used for calculations by each model is indicated (second row).

***Table 4.38***. *Calculation results: water concentrations of PCB-153 (pg/L) calculated by all participating models and statistical parameters used for evaluation ("own/alternative" data set)*

| N | EVN-BETR and UK-MODEL | CAN/POPs | DEHM-POP | CliMoChem | G-CIEMS | SimpleBox | MSCE-POP | $m$ | $\sigma$ |
|---|---|---|---|---|---|---|---|---|---|
| Set | own | own | own | own | alt | alt | own | | |
| 1 | 5.56 | 8.40 | 7.10 | 8.50 | 30.39 | 73.83 | 8.78 | 20.37 | 25.07 |
| 2 | 0.98 | 2.40 | 1.25 | 1.51 | 7.81 | 13.20 | 1.59 | 4.11 | 4.66 |
| 3 | 3.11 | 4.80 | 3.74 | 4.10 | 6.13 | 35.94 | 4.26 | 8.87 | 11.97 |
| 4 | 2.10 | 3.00 | 2.51 | 3.00 | 33.69 | 29.31 | 3.40 | 11.00 | 14.07 |

Fig. 4.12 displays the result on water concentrations of PCB-153 calculated by the participating models with the use of "own / alternative" data set.

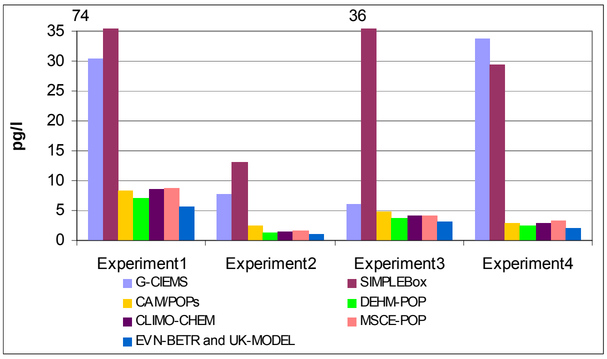



***Fig. 4.12.*** *Calculation results of the participating models (water concentrations) obtained with "own/alternative" data set*

Gaseous fluxes to water, from water and net gaseous flux of PCB-153 calculated by the models are given in Table 4.39.

***Table 4.39***. *Calculation results: fluxes of PCB-153 to/from water (ng/m²/day) calculated by all participating models and statistical parameters used for evaluation ("own/alternative" data set)*

| N | EVN-BETR and UK-MODEL | CAN/POPs | DEHM-POP | CliMoChem | G-CIEMS | SimpleBox | MSCE-POP | $m$ | $\sigma$ |
|---|---|---|---|---|---|---|---|---|---|
| Gaseous flux to water | | | | | | | | | |
| 1 | 2.60 | 2.08 | – | 0.86 | 1.02 | 4.37 | 2.27 | 2.20 | 1.27 |
| 2 | 0.56 | 0.61 | – | 0.21 | 0.26 | 0.71 | 0.55 | 0.48 | 0.20 |
| 3 | 0.66 | 0.40 | – | 0.17 | 0.02 | 1.08 | 0.42 | 0.46 | 0.37 |
| 4 | 1.71 | 1.49 | – | 0.86 | 1.12 | 1.99 | 2.33 | 1.59 | 0.54 |
| Gaseous flux from water | | | | | | | | | |
| 1 | 0.13 | – | – | 0.73 | 0.0017 | 2.71 | 2.24 | 1.16 | 1.24 |
| 2 | 0.03 | – | – | 0.18 | 0.0007 | 0.39 | 0.55 | 0.23 | 0.24 |
| 3 | 0.03 | – | – | 0.13 | 0.0000 | 0.84 | 0.41 | 0.28 | 0.35 |
| 4 | 0.14 | – | – | 0.78 | 0.0061 | 0.90 | 2.32 | 0.83 | 0.92 |
| Net gaseous flux | | | | | | | | | |
| 1 | 2.47 | 2.08 | – | 0.12 | 1.02 | 1.66 | 0.03 | 1.23 | 1.01 |
| 2 | 0.53 | 0.61 | – | 0.03 | 0.26 | 0.31 | 0.01 | 0.29 | 0.25 |
| 3 | 0.64 | 0.40 | – | 0.04 | 0.02 | 0.23 | 0.01 | 0.22 | 0.25 |
| 4 | 1.57 | 1.49 | – | 0.08 | 1.12 | 1.10 | 0.01 | 0.90 | 0.68 |

The parwise comparison of modelling results is done for water concentrations and net gaseous flux to water. Correlation coefficients for water concentrations are shown in Table 4.40.

***Table 4.40.*** *Correlation coefficients for water concentrations ("own/alternative" data set)*

| | CAN/POPs | DEHM-POP | CliMoChem | G-CIEMS | SimpleBox | MSCE-POP |
|---|---|---|---|---|---|---|
| EVN-BETR and UK MODEL | 0.99 | 1.00 | 0.99 | 0.44 | 0.99 | 0.99 |
| CAN/POPs | – | 0.99 | 0.99 | 0.35 | 0.98 | 0.98 |
| DEHM-POP | – | – | 1.00 | 0.44 | 1.00 | 1.00 |
| CliMoChem | – | – | – | 0.48 | 1.00 | 1.00 |
| G-CIEMS | – | – | – | – | 0.52 | 0.51 |
| SimpleBox | – | – | – | – | – | 1.00 |

Correlation coefficients for net gaseous flux are demonstrated in Table 4.41.

***Table 4.41.*** *Correlation coefficients for net gaseous flux ("own/alternative" data set)*

| | CAN/POPs | CliMoChem | G-CIEMS | SimpleBox | MSCE-POP |
|---|---|---|---|---|---|
| EVN-BETR and UK MODEL | 0.98 | 1.00 | 0.86 | 0.99 | 0.85 |
| CAN/POPs | – | 0.97 | 0.93 | 1.00 | 0.75 |
| CliMoChem | – | – | 0.86 | 0.99 | 0.86 |
| G-CIEMS | – | – | – | 0.91 | 0.47 |
| SimpleBox | – | – | – | – | 0.79 |

Values of regression coefficients $\alpha$ and $\beta$ for water concentrations and net gaseous flux calculated for all pairs of models are given in Tables 4. 4.42 and 4.43, respectively.

***Table 4.42.*** *Coefficients of regression dependence between the models ($\alpha$ / $\beta$) for water concentrations ("own/alternative" data set)*

| | CAN/POPs | DEHM-POP | CliMoChem | G-CIEMS | SimpleBox | MSCE-POP |
|---|---|---|---|---|---|---|
| EVN-BETR and UK MODEL | 1.37/0.63 | 1.29/ -0.13 | 1.53/ -0.22 | 3.25/9.94 | 13.1/ -0.30 | 1.56/ -0.06 |
| CAN/POPs | – | 0.93/-0.65 | 1.10/-0.85 | 1.91/10.64 | 9.34/-5.34 | 1.11/-0.67 |
| DEHM-POP | – | – | 1.19/ -0.08 | 2.54/10.2 | 10.2/0.96 | 1.21/0.09 |
| CliMoChem | – | – | – | 2. 30/ 9.67 | 8.53/1.59 | 1.02/0.16 |
| G-CIEMS | – | – | – | – | 0.92/20.1 | 0.11/2.41 |
| SimpleBox | – | – | – | – | – | 0.12/ -0.02 |

***Table 4.43.*** *Coefficients of regression dependence between the models ($\alpha$ / $\beta$) for net gaseous flux ("own/alternative" data set)*

| | CAN/POPs | CliMoChem | G-CIEMS | SimpleBox | MSCE-POP |
|---|---|---|---|---|---|
| EVN-BETR and UK MODEL | 0.84/0.05 | 0.05/0.004 | 0.52/ -0.07 | 0.74/ -0.14 | 0.01/0.003 |
| CAN/POPs | – | 0.06/0.003 | 0.65/ -0.14 | 0.87/ -0.17 | 0.01/0.004 |
| CliMoChem | – | – | 10.4/ -0.10 | 14.9/ -0.19 | 0.2/0.002 |
| G-CIEMS | – | – | – | 1.13/0.14 | 0.01/0.01 |
| SimpleBox | – | – | – | – | 0.01/0.01 |

Finally, values of residual square deviation for water concentrations and net gaseous flux are collected in Tables 4.44 and 4.45.

***Table 4.44.*** *Residual square deviation, $\sigma$ for water concentrations ("own/alternative" data set)*

| | CAN/POPs | DEHM-POP | CliMoChem | G-CIEMS | SimpleBox | MSCE-POP |
|---|---|---|---|---|---|---|
| EVN-BETR and UK MODEL | 0.69 | 0.20 | 0.54 | 22.67 | 5.17 | 0.60 |
| CAN/POPs | – | 0.50 | 0.70 | 23.57 | 8.49 | 0.94 |
| DEHM-POP | – | – | 0.33 | 22.65 | 4.29 | 0.47 |
| CliMoChem | – | – | – | 22.17 | 2.63 | 0.24 |
| G-CIEMS | – | – | – | – | 37.96 | 4.55 |
| SimpleBox | – | – | – | – | – | 0.08 |

*Table 4.45.* *Residual square deviation, $\sigma$ for net gaseous flux ("own/alternative" data set)*

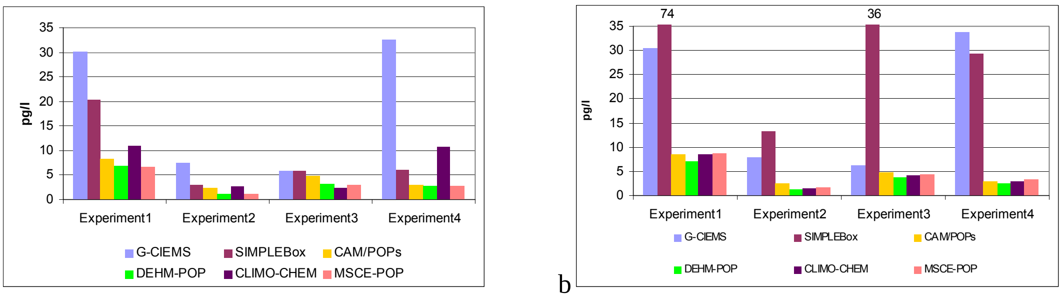
| | CAN/POPs | CliMoChem | G-CIEMS | SimpleBox | MSCE-POP |
|---|---|---|---|---|---|
| EVN-BETR and UK MODEL | 0.26 | 0.005 | 0.48 | 0.14 | 0.01 |
| CAN/POPs | – | 0.02 | 0.36 | 0.08 | 0.01 |
| CliMoChem | – | – | 0.48 | 0.18 | 0.01 |
| G-CIEMS | – | – | – | 0.50 | 0.02 |
| SimpleBox | – | – | – | – | 0.01 |

***Comparison between two data sets.*** The difference between calculated values of concentrations in water and gaseous fluxes to/from water obtained with two data sets of pollutant properties (for those models who provided calculations for both these sets) is shown in Tables 4.46 and 4.47, respectively.

*Table 4.46.* *Difference between calculations with two data sets (water concentrations)*

| N | EVN-BETR and UK-MODEL | CAN/POPs | DEHM-POP | CliMoChem | G-CIEMS | SimpleBox | MSCE-POP |
|---|---|---|---|---|---|---|---|
| 1 | – | 0.00% | 3.5% | -23% | 0.78% | 263% | 31% |
| 2 | – | 0.00% | -1.2% | -42% | 4.9% | 328% | 28% |
| 3 | – | 0.00% | 17% | 72% | 3.7% | 511% | 41% |
| 4 | – | 0.00% | -13% | -72% | 3.8% | 378% | 20% |

This difference is visualized in Fig. 4.13.




a b

*Fig. 4.13.* *Calculation results of the participating models obtained with " reference" (a) and "own/alternative" (b) data sets (for models presented both calculations)*

*Table 4.47.* *Difference between calculations with two data sets (net gaseous flux)*

| N | EVN-BETR and UK-MODEL | CAN/POPs | DEHM-POP | CliMoChem | G-CIEMS | SimpleBox | MSCE-POP |
|---|---|---|---|---|---|---|---|
| 1 | – | 430% | – | -81% | 0.01% | -61% | -40% |
| 2 | – | -88% | – | -83% | 2.8% | -55% | -42% |
| 3 | – | 90% | – | -74% | -89% | -78% | -35% |
| 4 | – | 5110% | – | -87% | 1.66% | -41% | -45% |

## 4.5. Gaseous exchange between atmosphere and vegetation

***Reference data set.*** Calculation results for concentrations in vegetation together with $m$ and $\sigma$ calculated with "reference" data set of PCB-153 properties are presented in Table 4.48. Gaseous fluxes to vegetation, from vegetation and net gaseous flux of PCB-153 calculated by the models are given in Table 4.49.

***Table 4.48***. *Calculation results: concentrations of PCB-153 in vegetation (ng/g) calculated by all participating models and statistical parameters used for evaluation ("reference" data set)*

| N | EVN-BETR and UK-MODEL | CliMoChem | SimpleBox | MSCE-POP | *m* | $\sigma$ |
|---|---|---|---|---|---|---|
| 1 | – | 6.4 | 0.40 | 0.10 | 2.31 | 2.91 |
| 2 | – | 8.7 | 0.48 | 0.23 | 3.15 | 3.95 |
| 3 | – | 2.5 | 0.16 | 0.05 | 0.89 | 1.12 |
| 4 | – | 8.6 | 0.53 | 0.21 | 3.10 | 3.87 |

***Table 4.49***. *Calculation results: fluxes of PCB-153 to/from vegetation (ng/m$^2$/day) calculated by all participating models and statistical parameters used for evaluation ("reference" data set)*

| N | EVN-BETR and UK-MODEL | CliMoChem | SimpleBox | MSCE-POP | *m* | $\sigma$ |
|---|---|---|---|---|---|---|
| Gaseous flux to vegetation | | | | | | |
| 1 | – | 0.35 | 0.52 | 0.33 | 0.40 | 0.08 |
| 2 | – | 1.12 | 1.64 | 0.75 | 1.17 | 0.37 |
| 3 | – | 0.18 | 0.26 | 0.16 | 0.20 | 0.04 |
| 4 | – | 0.83 | 1.21 | 0.68 | 0.90 | 0.22 |
| Gaseous flux from vegetation | | | | | | |
| 1 | – | 0.35 | 0.12 | 0.0009 | 0.16 | 0.15 |
| 2 | – | 1.12 | 0.82 | 0.012 | 0.65 | 0.47 |
| 3 | – | 0.18 | 0.08 | 0.0008 | 0.09 | 0.07 |
| 4 | – | 0.83 | 0.50 | 0.0064 | 0.45 | 0.34 |
| Net gaseous flux | | | | | | |
| 1 | – | 0 | 0.40 | 0.33 | 0.24 | 0.17 |
| 2 | – | 0 | 0.82 | 0.74 | 0.52 | 0.37 |
| 3 | – | 0 | 0.18 | 0.16 | 0.11 | 0.08 |
| 4 | – | 0 | 0.71 | 0.67 | 0.46 | 0.32 |

Below we present pairwise comparison of modelling results for concentrations in vegetation and net gaseous flux. Correlation coefficients for concentrations in vegetation are shown in Table 4.50.

***Table 4.50.*** *Correlation coefficients for concentrations in vegetation ("reference" data set)*

| | SimpleBox | MSCE-POP |
|---|---|---|
| CliMoChem | 0.99 | 0.94 |
| SimpleBox | – | 0.90 |

The results show that differences between concentrations are described similarly by all three models. Calculated absolute values of concentrations in vegetation differ essentially.

Correlation coefficients for net gaseous flux between SimpleBox and MSCE-POP models equals 0.997. Correlations with ClimoChem models have not been calculated since gaseous flux calculated by this model equals zero.

Values of regression coefficients $\alpha$ and $\beta$ for concentrations in vegetation calculated for all pairs of models are given in Table 4.51.

***Table 4.51.*** *Coefficients of regression dependence between the models ($\alpha$ / $\beta$) for concentrations in vegetation ("reference" data set)*

| | SimpleBox | MSCE-POP |
|---|---|---|
| CliMoChem | 17/ -0.33 | 32/1.80 |
| SimpleBox | – | 0.47/ -0.04 |

Regression coefficients $\alpha$ and $\beta$ between SimpleBox and MSCE-POP models equal 0.94 and –0.02, respectively. This testifies good agreement of net flux calculated by these two models.

Finally, values of residual square deviation for concentrations in vegetation are collected in Table 4.52.

***Table 4.52.*** *Residual square deviation, $\sigma$ for concentrations in vegetation ("reference" data set)*

| | SimpleBox | MSCE-POP |
|---|---|---|
| CliMoChem | 0.75 | 1.66 |
| SimpleBox | – | 0.06 |

Residual square deviation for regression dependence between net gaseous flux calculated by SimpleBox MSCE-POP models equals 0.04.

***Own/alternative data set.*** Calculation results for concentrations in vegetation together with *m* and $\sigma$ calculated with "own/alternative" data set of PCB-153 properties are presented in Table 4.53. Here data set of PCB-153 properties used for calculations by each model is indicated (second row). Gaseous fluxes to vegetation, from vegetation and net gaseous flux of PCB-153 calculated by the models are given in Table 4.54.

***Table 4.53***. *Calculation results: concentrations of PCB-153 in vegetation (ng/g) calculated by all participating models and statistical parameters used for evaluation ("own/alternative" data set)*

| N | EVN-BETR and UK-MODEL | CliMoChem | SimpleBox | MSCE-POP | *m* | $\sigma$ |
|---|---|---|---|---|---|---|
| Set | own | own | alt | own | | |
| 1 | 0.22 | 0.42 | 0.40 | 0.10 | 0.29 | 0.13 |
| 2 | 0.05 | 0.54 | 0.45 | 0.27 | 0.33 | 0.19 |
| 3 | 0.05 | 0.17 | 0.15 | 0.05 | 0.11 | 0.05 |
| 4 | 0.09 | 0.60 | 0.48 | 0.22 | 0.35 | 0.20 |

***Table 4.54***. *Calculation results: fluxes of PCB-153 to/from vegetation (ng/m$^2$/day) calculated by all participating models and statistical parameters used for evaluation ("own/alternative" data set)*

| N | EVN-BETR and UK-MODEL | CliMoChem | SimpleBox | MSCE-POP | *m* | $\sigma$ |
|---|---|---|---|---|---|---|
| Gaseous flux to vegetation | | | | | | |
| 1 | 4.8 | 0.35 | 0.52 | 0.34 | 1.51 | 1.93 |
| 2 | 16.5 | 1.12 | 1.64 | 0.88 | 5.04 | 6.62 |
| 3 | 2.7 | 0.18 | 0.26 | 0.16 | 0.83 | 1.08 |
| 4 | 0.12 | 0.83 | 1.21 | 0.72 | 0.72 | 0.39 |
| Gaseous flux from vegetation | | | | | | |
| 1 | 4.92 | 0.05 | 0.26 | 0.0006 | 1.31 | 2.09 |
| 2 | 16.5 | 0.72 | 1.26 | 0.0097 | 4.63 | 6.88 |
| 3 | 2.72 | 0.04 | 0.15 | 0.0006 | 0.73 | 1.15 |
| 4 | 0.12 | 0.35 | 0.83 | 0.0047 | 0.32 | 0.32 |
| Net gaseous flux | | | | | | |
| 1 | -0.07 | 0.31 | 0.26 | 0.33 | 0.21 | 0.16 |
| 2 | -0.03 | 0.40 | 0.38 | 0.87 | 0.40 | 0.32 |
| 3 | -0.02 | 0.14 | 0.11 | 0.16 | 0.10 | 0.07 |
| 4 | -0.0004 | 0.48 | 0.38 | 0.72 | 0.40 | 0.26 |

The parwise comparison of modelling results is done for concentrations in vegetation and net gaseous flux to vegetation. Correlation coefficients for concentrations in vegetation are shown in Table 4.55.

***Table 4.55.*** *Correlation coefficients for water concentrations ("own/alternative" data set)*

| | CliMoChem | SimpleBox | MSCE-POP |
|---|---|---|---|
| EVN-BETR and UK MODEL | 0.08 | 0.25 | -0.32 |
| CliMoChem | – | 0.98 | 0.89 |
| SimpleBox | – | – | 0.82 |

Correlation coefficients for net gaseous flux are demonstrated in Table 4.56.

*__Table 4.56.__ Correlation coefficients for net gaseous flux ("own/alternative" data set)*

| | CliMoChem | SimpleBox | MSCE-POP |
|---|---|---|---|
| EVN-BETR and UK MODEL | 0.26 | 0.19 | 0.34 |
| CliMoChem | – | 0.98 | 0.88 |
| SimpleBox | – | – | 0.94 |

Values of regression coefficients $\alpha$ and $\beta$ for concentrations in vegetation and net gaseous flux calculated for all pairs of models are given in Tables 4.57 and 4.58, respectively.

*__Table 4.57.__ Coefficients of regression dependence between the models ($\alpha / \beta$) for concentrations in vegetation ("own/alternative" data set)*

| | CliMoChem | SimpleBox | MSCE-POP |
|---|---|---|---|
| EVN-BETR and UK MODEL | 0.19/ 0.42 | 0.48/ 0.32 | -0.41/ 0.20 |
| CliMoChem | – | 1.23/ -0.02 | 1.65/0.17 |
| SimpleBox | – | – | 0.56/ -0.04 |

*__Table 4.58.__ Coefficients of regression dependence between the models ($\alpha / \beta$) for net gaseous flux ("own/alternative" data set)*

| | CliMoChem | SimpleBox | MSCE-POP |
|---|---|---|---|
| EVN-BETR and UK MODEL | 1.32/0.37 | 0.86/ 0.31 | 3.81/0.64 |
| CliMoChem | – | 1.13/ 0.01 | 0.40/0.12 |
| SimpleBox | – | – | 2.39/ -0.15 |

Finally, values of residual square deviation for concentrations in vegetation and net gaseous flux are collected in Tables 4.59 and 4.60.

*__Table 4.59.__ Residual square deviation, $\sigma$ for concentrations in vegetation ("own/alternative" data set)*

| | CliMoChem | SimpleBox | MSCE-POP |
|---|---|---|---|
| EVN-BETR and UK MODEL | 0.33 | 0.25 | 0.17 |
| CliMoChem | – | 0.06 | 0.15 |
| SimpleBox | – | – | 0.10 |

*__Table 4.60.__ Residual square deviation, $\sigma$ for net gaseous flux ("own/alternative" data set)*

| | CliMoChem | SimpleBox | MSCE-POP |
|---|---|---|---|
| EVN-BETR and UK MODEL | 0.25 | 0.22 | 0.53 |
| CliMoChem | – | 0.05 | 0.12 |
| SimpleBox | – | – | 0.19 |

***Comparison between two data sets.*** The difference between calculated values of water concentrations and net gaseous flux obtained with two data sets of pollutant properties (for those models who provided calculations for both these sets) is shown in Tables 4.61 – 4.64.

*__Table 4.61.__ Difference between calculations with two data sets (concentrations in vegetation)*

| N | CliMoChem | SimpleBox | MSCE-POP |
|---|---|---|---|
| 1 | -93% | -0.24% | 1.30% |
| 2 | -94% | -7.6% | 18.06% |
| 3 | -93% | -7.9% | 3.11% |
| 4 | -93% | -9.9% | 7.92% |

***Table 4.62.*** *Difference between calculations with two data sets (gaseous flux to vegetation)*

| N | CliMoChem | SimpleBox | MSCE-POP |
|---|---|---|---|
| 1 | 0% | 0% | 1.2% |
| 2 | 0% | 0% | 18% |
| 3 | 0% | 0% | 2.9% |
| 4 | 0% | 0% | 6.9% |

***Table 4.63.*** *Difference between calculations with two data sets (gaseous flux from vegetation)*

| N | CliMoChem | SimpleBox | MSCE-POP |
|---|---|---|---|
| 1 | -87% | 120% | -32% |
| 2 | -36% | 54% | -16% |
| 3 | -76% | 86% | -32% |
| 4 | -58% | 65% | -28% |

***Table 4.64.*** *Difference between calculations with two data sets (net gaseous flux)**

| N | SimpleBox | MSCE-POP |
|---|---|---|
| 1 | -36% | 1.3% |
| 2 | -54% | 18% |
| 3 | -39% | 3.1% |
| 4 | -46% | 7.9% |

* The difference between values of net gaseous flux calculated by ClimoChem model is not calculated because for "reference" data set this flux is reported to be zero

Thus, according to the comparison of the results presented above, it can be concluded that:

- -Most models describe similarly gas/particle partitioning. The results obtained with "own" set of pollutant-related data agree better between models than those based on "reference" data set. The difference in calculation of gas/particle partitioning caused by usage of "reference" and "own or alternative" data set of pollutant properties is moderate. Large differences are characteristic of high temperatures where values of fractions of particulate phase are small. The results obtained with "own or alternative" set of pollutant-related data agree better between models.
- The differences in absolute values of wet deposition flux and concentrations in precipitation calculated by models are essential. However, square deviation does not exceed the mean value of these parameters averaged between the participating models both in the results obtained on the basis of "reference" and "own/alternative" data sets. The difference in calculation results on wet deposition caused by the usage of "reference" and "own /alternative" data sets of pollutant properties is negligible. This process needs further investigation.
- Models describe gaseous flux between atmosphere and soil more closely than soil concentrations. The differences in concentrations are lower with "reference" data set than those with "own/alternative" data. The difference between calculated values of soil concentrations obtained with two data sets of pollutant properties ("reference" and "own/alternative") is considerable for most models. Model descriptions of air/soil exchange and their parameterizations need further consideration.
- In general, most models closely describe processes of gaseous exchange between the atmosphere and water. The difference between calculated values of water concentrations and net gaseous flux from/to water obtained with two data sets of pollutant properties ("reference" and "own/alternative") is essential for some models. The same applies to the description of gaseous exchange between atmosphere and vegetation.