Chapter 3

SENSITIVITY ANALYSIS OF MSCE-POP MODEL (REGIONAL VERSION)

This section devoted to the analysis of sensitivity of MSCE-POP model to physical-chemical properties of the pollutant in question and some environmental parameters. Since the atmosphere is main transport media for POPs, the emphasis in this investigation was put to atmospheric transport and deposition. As the output parameters for the analysis calculated atmospheric concentrations and deposition fluxes were chosen.

The module describing atmospheric transport in MSCE-POP model is the same as in HM model [*Travnikov and Ilyin*, 2005]. However, in addition to atmospheric transport, in model description of POP behavior in the environment additional processes are to be taken into account. These processes are concerned first of all with the ability of POPs to be present in the atmosphere both in gaseous and particulate phases. Depending on values of vapor pressure, fractions of particulate and gaseous phases of POP are changed. The process of gas/particle partitioning, gaseous exchange between the atmosphere and underlying surface and degradation should be taken into account in POP modelling. In doing so it should be taken into account that all these processes are highly temperature dependent. Here the influence of the processes dealing with POP gaseous phase to the final output (atmospheric concentrations and depositions) is investigated. In particular, the process of dry deposition of particulate phase is not included into consideration since its description is quite similar to that in heavy metal modelling.

For the analysis of model sensitivity to the input parameters we have chosen PCB-153 as a pollutant with essential fractions of both gaseous and particulate phases.

In this study gaseous exchange flux between the atmosphere and other environmental compartments is split into two components. The first is direct deposition flux that is the flux from the atmosphere to soil/sea/vegetation. This flux is calculated under the assumption that concentrations in media are equal to zero. The second is a re-emission flux calculated under the assumption that atmospheric concentrations equal zero. The re-emission is essential after long period of accumulation in media and/or under strong emission reductions. Thus, the processes affecting the final output values (atmospheric concentrations and depositions) included into the sensitivity study are:

- ***wet deposition*** of a pollutant in gaseous and particulate phases;
- ***direct gaseous deposition*** from the atmosphere to other environmental compartments (soil, seawater and vegetation);
- ***re-emission*** from the environmental compartments to the atmosphere;
- ***degradation*** in the atmosphere.

The process of ***gas/particle partitioning*** is not considered separately, but is included into the investigation of all above processes.

The set of input parameters used in the sensitivity analysis is shown in Table 3.1. These are pollutant-specific parameters used for model description of POP behavior in the environment and some environmental/atmospheric parameters.

To analyze the sensitivity "base" values and conventional ranges ("high" and "low" values) of all input parameters were selected. "Base" values are those selected in model parameterization. To choose the range of pollutant-specific parameters it was taken into account that the difference of an order of magnitude is close to the scattering of POP physical-chemical parameters found in the literature (see [*Shatalov et al.,* 2003]). So, for these parameters ranges ("high" and "low" values) are chosen in such a way that they differ by an order of magnitude. For each parameter "base" value is a geometrical mean between "high" and "low" ones. For environmental parameters mean values and characteristic ranges over Europe are used.

Table 3.1. *Input parameters used for evaluation of model sensitivity*

Parameter	Notation	Base value	Low value	High value
Pollutant-specific parameters of PCB-153				
Henry's law constant at 10 ºC, Pa·m^3/mol	K_H	3.78	1.20	12.0
Subcooled liquid vapor pressure at 10 ºC, Pa	p_{OL}	$9.69 \cdot 10^{-5}$	$3.06 \cdot 10^{-5}$	$3.06 \cdot 10^{-4}$
Octanol/air partitioning coefficient at 10 ºC, dimensionless	K_{OA}	$3.64 \cdot 10^{10}$	$1.15 \cdot 10^{10}$	$1.15 \cdot 10^{11}$
Octanol/water partitioning coefficient, dimensionless	K_{OW}	$7.94 \cdot 10^{6}$	$2.51 \cdot 10^{6}$	$2.51 \cdot 10^{7}$
Washout ratio for particulate phase, dimensionless	W_p	$1.5 \cdot 10^{5}$	$4.7 \cdot 10^{4}$	$4.7 \cdot 10^{5}$
Mass transfer coefficient to vegetation (deciduous forest), 1/s	$K_{avdecid}$	30	9.49	94.9
Mass transfer coefficient to vegetation (coniferous forest), 1/s	$K_{avconif}$	4.6	1.45	14.5
Degradation coefficient, 1/s	K_d	$1.2 \cdot 10^{-7}$	$3.7 \cdot 10^{-8}$	$3.7 \cdot 10^{-7}$
Environmental parameters				
Ambient air temperature	T	10 ˚C	0 ˚C	20 ˚C
Atmospheric aerosol specific surface, m^2/m^3	θ	$1.5 \cdot 10^{-4}$	$1.5 \cdot 10^{-5}$	$1.5 \cdot 10^{-3}$
Concentration of OH radicals in the atmosphere, molecules/cm^3	C_{OH}	$1.0 \cdot 10^{6}$	$1.0 \cdot 10^{5}$	$5.0 \cdot 10^{6}$
Precipitation amount, mm/hour	$Prec$	0.1	0.01	0.5
Organic carbon fraction in soil, dimensionless	f_{oc}	0.05	0.01	0.1

As it was mentioned above, some pollutant-specific properties of a pollutant are temperature-dependent. For example, temperature dependence of p_{OL} used in the model is given by:

$$p_{OL} = p_{OL}^0 \cdot e^{-a_P \cdot \left(1/T - 1/T_0 \right)}, \tag{3.1}$$

where T is an ambient temperature, K;

p_{OL}^0 is the value of p_{OL} at reference temperature T_0 = 283.15 K;

a_P is a constant determining the dependence of p_{OL} on temperature.

Thus, temperature dependence of p_{OL} can be described by two numerical parameters p_{OL}^0 and a_P. Preliminary estimation of model sensitivity has shown that the sensitivity of model output to the parameter a_P is rather week. So, only one numerical parameter p_{OL}^0 is included as an input parameter for sensitivity analysis of temperature dependence of p_{OL}.

Same approach is used for Henry's law constant H, octanol/air partitioning coefficient K_{OA} and degradation constant of the first order K_d.

The sensitivities of air concentrations and depositions to the considered parameter A are estimated as:

$$S_a = \Delta C_a / \Delta A \quad \text{and} \quad S_d = \Delta D / \Delta A \tag{3.2}$$

respectively, where:

$$\Delta C_a = \frac{C_a^{high} - C_a^{low}}{C_a^{base}} \cdot 100\% \quad \text{for air concentrations,} \tag{3.3}$$

$$\Delta D = \frac{D^{high} - D^{low}}{D^{base}} \cdot 100\% \quad \text{for depositions.} \tag{3.4}$$

and ΔA is defined by:

$$\Delta A = \frac{A^{high} - A^{low}}{A^{base}} \cdot 100\% \, . \tag{3.5}$$

Here C_a^{high}, C_a^{low} and C_a^{base} are values of air concentrations calculated for “high”, “low” and “base” values of the considered parameter A^{high}, A^{low} and A^{base}, and D^{high}, D^{low} and D^{base} are the corresponding values for depositions.

If there are several parameters affecting the process, the rest parameters were set to base values.

Sensitivity analysis is performed into two steps.

At the ***first step*** the sensitivity of particular deposition processes to values of selected input parameters is evaluated. Here only the processes of direct deposition (wet deposition and gaseous depositions from the atmosphere to the underlying surface) are considered

At the ***second step*** sensitivity of model output (air concentrations and depositions) with respect to the input parameters is performed. At this step degradation in the atmosphere and re-emission are also included into consideration. Since re-emission process is one of important processes in the description of POP behavior in the environment, special attention is paid to the analysis of its contribution to the atmospheric contamination.

3.1. Sensitivity of deposition processes with respect to selected parameters and ambient temperature

The evaluation of sensitivity of model description of direct deposition processes with respect to selected parameters is presented in this section. The analysis is carried out for total (gas + particles) concentration of the pollutant. The influence of gas/particle partitioning is taken into account in the course of investigation of deposition processes.

As output parameters for the analysis of deposition processes deposition velocities V_d of total (gas + particles) atmospheric concentrations are used:

$$V_d = f_d / C_{atm}^T \cdot 100 \ \text{cm/s,} \tag{3.6}$$

where f_d is the corresponding deposition flux, pg/m^2/s;

C_{atm}^T is total concentration of a pollutant in the atmosphere. Calculations were done using corresponding model blocks, pg/m^3.

The sensitivity of deposition velocity is analysed with respect to all parameters involved into model description of the considered process (see *Chapter 1*). To do this, values of deposition velocity are calculated for three values (low, base and high) of each parameter. Since, as it was mentioned above, the processes are strongly temperature-dependent we perform calculations for the range of temperatures from 0 ˚C to 30 ˚C (characteristic of surface atmospheric layer for the European region). So, in fact our "output parameter" is the whole temperature dependence of V_d within the specified temperature range.

For each value of temperature the sensitivity of a deposition process to a given input parameter *A* was calculated as

$$S = \Delta V_d / \Delta A \,. \tag{3.7}$$

Here ΔV_d is the relative variation of deposition velocity due to the change of the considered parameter *A* within its specified range:

$$\Delta V_d = \frac{V_d^{high} - V_d^{low}}{V_d^{base}} \cdot 100\% \,, \tag{3.8}$$

and V_d^{high}, V_d^{low} and V_d^{base} being V_d values calculated for the process with high, low and base value of the parameter, respectively. The value of relative variation ΔA of the parameter *A* is calculated by formula (5) above.

Wet deposition

Here the evaluation of sensitivity of wet deposition process with respect to the following pollutant-specific and environmental parameters used in the model description of the process is presented:

- Henry's law constant K_H at reference temperature (10 ºC),
- Washout ratio for particulate phase W_p,
- Subcooled liquid vapor pressure p_{OL} at reference temperature.
- Precipitation amount *Prec*,
- Atmospheric aerosol specific surface θ.

The process of wet deposition of POPs is a result of two simultaneous processes: deposition of gaseous phase and deposition of particulate phase. The washout ratio of gaseous phase calculated on the basis of Henry's law constant ranges from 100 to 2000 for different temperatures. On the contrary, washout ratio for particulate phase accepted in the model equals to $1.5 \cdot 10^5$ which is by about two orders of magnitude higher than that for gaseous phase. Thus, wet deposition velocity strongly depends on temperature. Due to this fact, sensitivity of the whole temperature dependence of wet deposition velocity with respect to the above parameters should be analyzed. Taking into account numerical values of washout coefficients for particulate and gaseous phases and temperature dependence of their fractions, it can be concluded that wet deposition velocity is high at low values of temperature (when the fraction of particulate phase is high, see Fig. 3.1b and vice versa. Temperature dependence of wet deposition velocity V_d^{wet} at base values of the parameters is shown in Fig. 3.1a. The sensitivity of wet deposition velocity with respect to temperature is very high and equals to about 1.1.

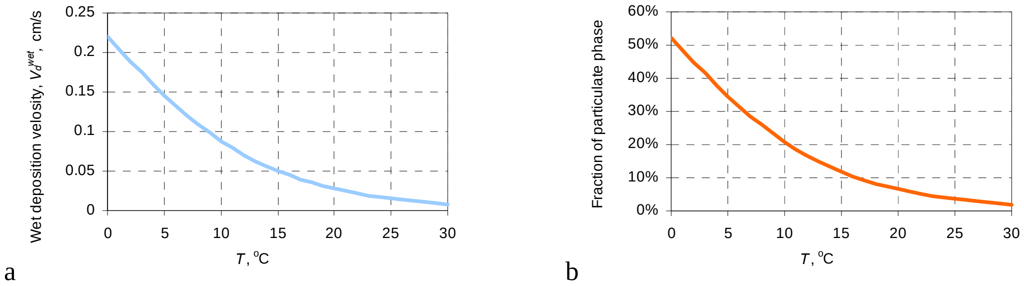

Fig.3.1. *Temperature dependence of wet deposition velocity V_d^{wet} at base values of the parameters (a) and temperature dependence of the fraction of the particulate phase (b)*

The sensitivity of wet deposition velocity with respect to each of the selected parameters is analyzed below.

Henry's law constant **(K_H)**. The plot of temperature dependence of wet deposition velocity for high, base and low values of K_H (see Table 3.1 above) is shown in Fig. 3.2a.

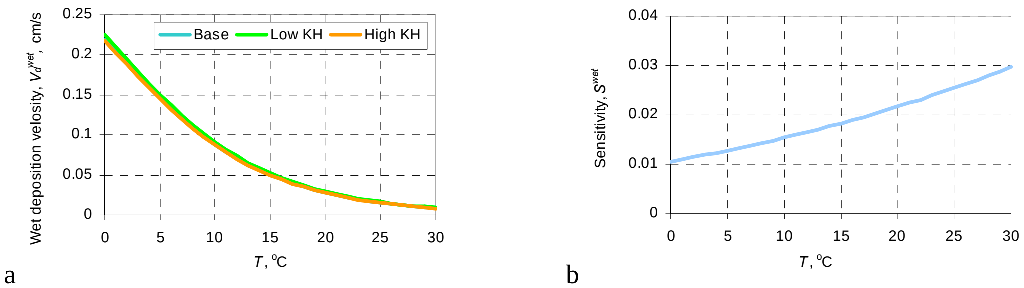

Fig. 3.2. *Temperature dependence of V_d^{wet} for base, high and low values of K_H (a) and of sensitivity with respect to this parameter (b)*

The sensitivity of wet deposition velocity to the values of K_H is weak. This is conditioned by the fact that main contribution to the value of wet deposition velocity for PCB-153 is made by scavenging of particulate phase. The values of sensitivity S^{wet} of wet deposition velocity with respect to K_H range from 0.01 for 0 ºC to 0.03 for 30 ºC (Fig. 3.2b).

Washout ratio of particulate phase (W_p). The plot of temperature dependence of V_d^{wet} for three selected values of W_p is shown in Fig. 3.3a.

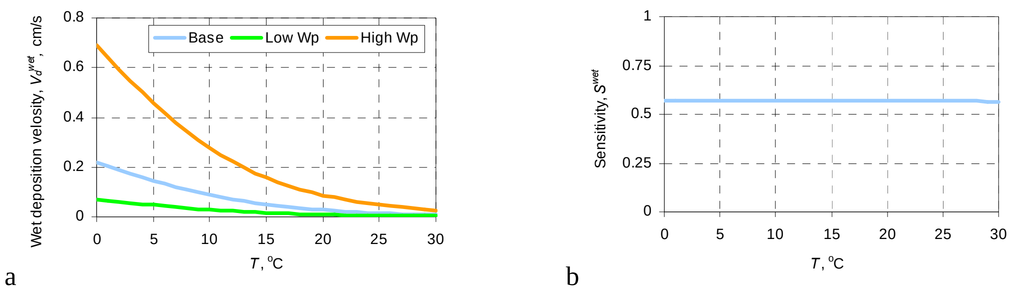

Fig 3.3. *Temperature dependence of V_d^{wet} for base, high and low values of W_p (a) and of sensitivity with respect to this parameter (b)*

Since wet deposition velocity mainly determined by scavenging of particulate phase, values of this velocity strongly depend on W_p. The value of sensitivity S^{wet} with respect to this parameter is about 0.57 and is almost independent on temperature (Fig. 3.3b).

Subcooled liquid vapor pressure (p_{OL}). The difference between calculations of wet deposition velocity for three selected values of p_{OL} is shown in Fig.3.4a.

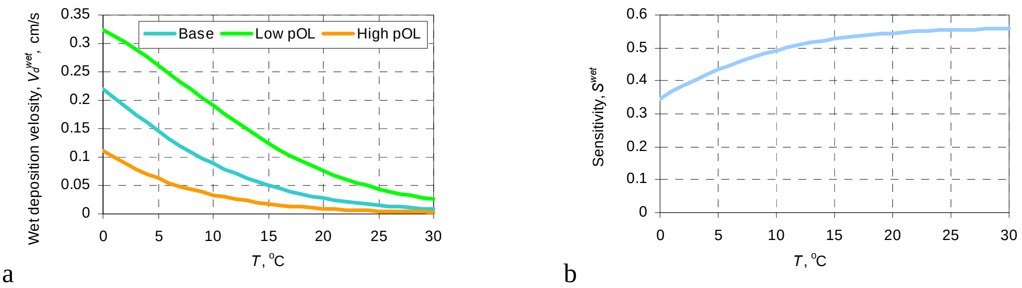

Fig. 3.4. *Temperature dependence of* V_d^{wet} *for base, high and low values of* p_{OL} *(a) and of sensitivity with respect to this parameter (b)*

Wet deposition velocity considerably depends on the value of p_{OL}. The sensitivity S^{wet} of wet deposition velocity ranges from 0.35 to 0.55 for temperature range 0 – 30 ºC (Fig. 3.4b).

***Precipitation amount* (*Prec*).** The plot of temperature dependence of V_d^{wet} for three selected values of *Prec* is shown in Fig 3.4a.

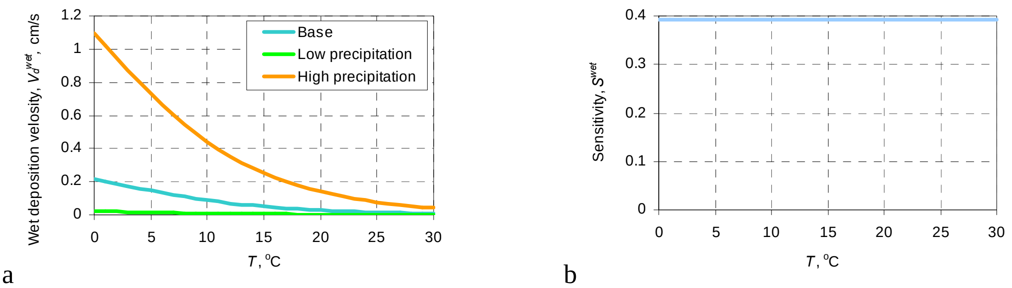

Fig. 3.5. *Temperature dependence of* V_d^{wet} *for base, high and low values of* Prec *(a) and of sensitivity with respect to this parameter (b)*

Values of wet deposition velocity considerably depend on *P*. The value of sensitivity S^{wet} with respect to this parameter is about 0.4 and is independent on temperature (Fig. 3.4b).

Atmospheric aerosol specific surface (θ). The comparison of the results obtained with three selected values of θ is given in Fig. 3.6a. Temperature dependence of sensitivity S^{wet} of wet deposition velocity with respect to the parameter is demonstrated in Fig. 3.6b.

Wet deposition velocity considerably depends on the value of atmospheric aerosol specific surface. Temperature dependence of sensitivity S^{wet} is moderate and its value ranges from 0.15 to 0.2 for temperature range 0 – 30 ºC (Fig. 3.6b).

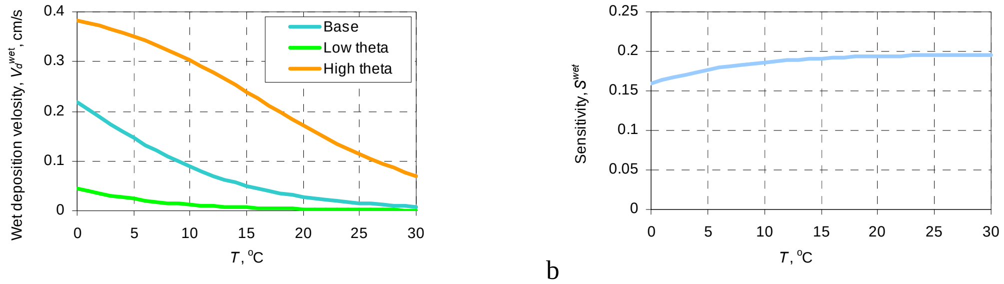

***Fig. 3.6**. Temperature dependence of values of V_d^{wet} for base, low and high values of θ (a) and of sensitivity with respect to this parameter (b)*

Resume. The plot of sensitivities of wet deposition velocity with respect to selected parameters at 10 ºC is shown in Fig. 3.7.

The sensitivity of wet deposition velocity with respect to temperature is very high (about 1.1). Among pollutant-specific parameters maximum sensitivity is characteristic of washout ratio of particulate phase and subcooled liquid vapor pressure (over 0.5). Moderate sensitivity is calculated with respect to atmospheric aerosol specific surface (about 0.2). The dependence of wet deposition velocity on Henry's law constant is weak.

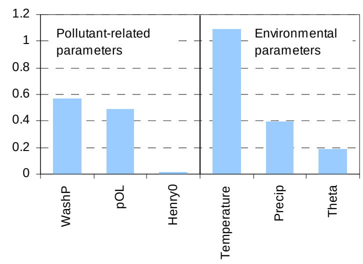

***Fig.3.7.** Sensitivities of V_d^{wet} with respect to selected parameters*

Direct gaseous flux from the atmosphere to soil

Here sensitivity of air/soil gaseous deposition velocity V_d^{gsoil} is analyzed with respect to the following pollutant-related and environmental parameters used in the model for the description of gaseous dry deposition to soil:

- Henry's law constant K_H at reference temperature (10 ºC),
- Octanol/water partitioning coefficient K_{OW},
- Vapor pressure over subcooled liquid p_{OL} at reference temperature.
- Atmospheric aerosol specific surface θ.
- Organic carbon fraction in soil f_{oc}.

The temperature dependence of V_d^{gsoil} at base values of the parameters is governed by two opposite-directed factors. First, Henry's law constant is increasing with temperature, which leads to the increase of atmospheric resistance to gaseous exchange (see *Chapter 1*) and, as a consequence, to the decrease of gaseous flux from the atmosphere to soil. On the opposite, the fraction of gaseous phase of PCB-153 grows with the increase of temperature, which leads to the increase of gaseous flux. As a

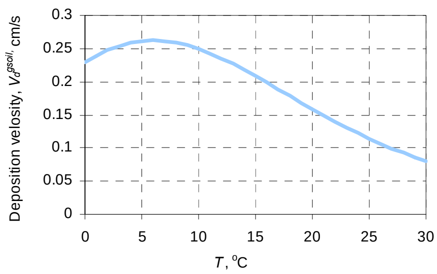

***Fig. 3.8.** Temperature dependence of deposition velocity V_d^{gsoil} for gaseous exchange between atmosphere and soil*

result, deposition velocity of gaseous exchange with soil increases up to the maximum at 6 ºC and then decreases with further temperature increase. Temperature dependence of deposition velocity V_d^{gsoil} for air/soil gaseous exchange is displayed in Fig. 3.8. The sensitivity of V_d^{gsoil} with respect to temperature is about 0.25.

Henry's law constant (K_H). The comparison of the results obtained with three selected values of K_H is given in Fig. 3.9a. Temperature dependence of sensitivity S^{gsoil} of deposition velocity of gaseous exchange with soil to the value of Henry's law constant is demonstrated in Fig. 3.9b.

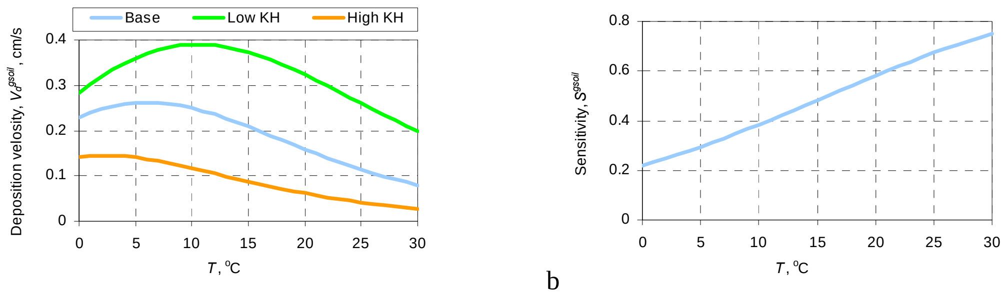

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Fig.3.9. *Temperature dependence of values of V_d^{gsoil} for base, low and high values of Henry coefficient K_H (a) and of sensitivity with respect to this parameter (b)*

Since the fraction of PCB-153 gaseous phase in the atmosphere increases with temperature, the influence of Henry's law constant to deposition velocity of gaseous exchange with soil is also increasing. The corresponding sensitivity S^{gsoil} ranges from about 0.2 at 0 ºC up to more than 0.7 at 30 ºC (Fig. 3.9b).

Octanol/water partitioning coefficient (K_{OW}). The plot of temperature dependence of V_d^{gsoil} calculated for three selected values of K_{OW} is displayed in Fig. 3.10a.

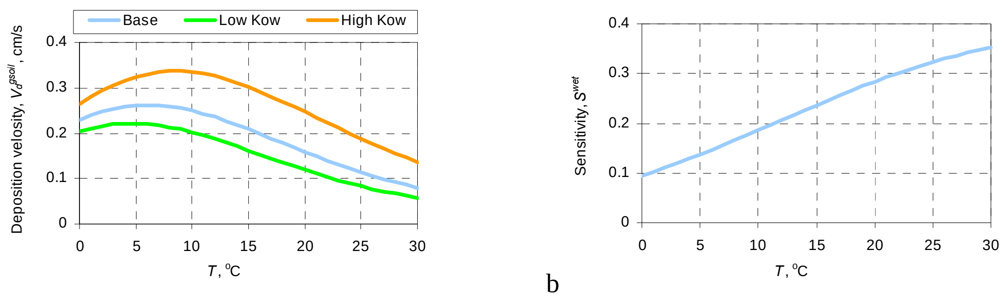

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Fig.3.10. *Temperature dependence of values of V_d^{gsoil} for base, low and high values of octanol/water partitioning coefficient K_{OW} (a) and of sensitivity with respect to this parameter (b)*

Calculations show moderate dependence of deposition velocity of gaseous exchange with soil with respect to the parameter. Values of sensitivity S^{gsoil} for different values of temperature vary from 0.1 to 0.35. The increase of influence of K_{OW} to the process of gaseous exchange with soil is conditioned by the same reasons as for Henry's law constant.

Vapor pressure over subcooled liquid (p_{OL}). This parameter affects the process of gaseous exchange with soil via the process of gas/aerosol partitioning. The plot of temperature dependence of V_d^{gsoil} for three selected values of the parameter is shown in Fig. 3.11a.

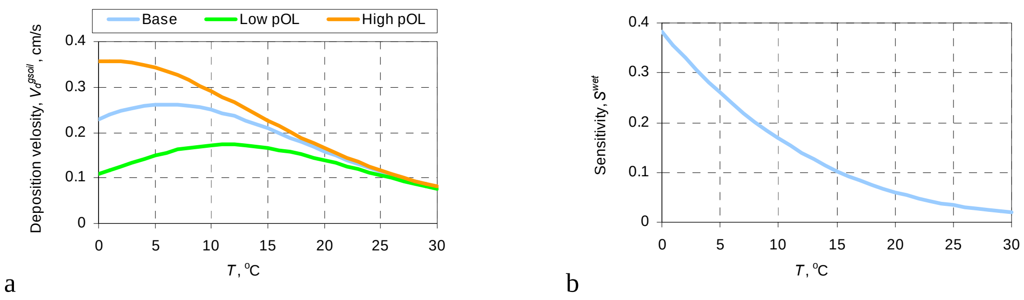

Fig. 3.11. *Temperature dependence of values of V_d^{gsoil} for base, low and high values of vapor pressure over subcooled liquid (a) and of sensitivity with respect to this parameter (b)*

Since for high values of p_{OL} PCB-153 is present in the atmosphere mainly in gaseous phase at all temperatures considered, the influence of temperature dependence of vapor pressure is rather low and deposition velocity decreases with temperature increase due to growth of Henry coefficient for all temperatures. Inversely, for low values of p_{OL} the influence of gas/particle partitioning process is prevailing and the increase of deposition velocity takes place up to 18 ºC. The sensitivity S^{gsoil} of deposition velocity of gaseous exchange with soil is decreasing from 0.4 at 0 ºC up to about 0.02 at 30 ºC (Fig. 3.11b). The decrease of sensitivity with temperature is explained by the fact that the influence of gas/particle partitioning process to the deposition velocity at high temperatures is much weaker than the influence of values of Henry coefficient.

Atmospheric aerosol specific surface (θ). The results of calculations of V_d^{gsoil} for for three selected values of θ are presented in Fig. 3.12a.

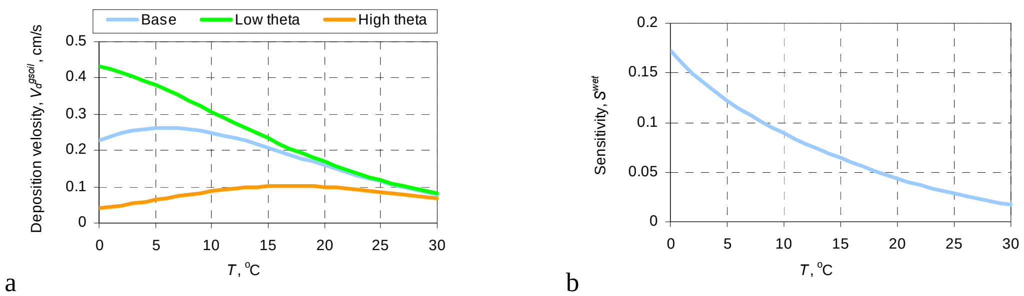

Fig. 3.12. *Temperature dependence of values of V_d^{gsoil} for base, low and high values of θ (a) and of sensitivity with respect to this parameter (b)*

The sensitivity of deposition velocity of air/soil gaseous exchange with respect to atmospheric aerosol specific surface is moderate. As in the case of vapor pressure, sensitivity of V_d^{gsoil} to the considered parameter decreases with temperature. The reasons for such decrease are explained above.

Fraction of organic carbon content in soil (f$_{oc}$). The plots of temperature dependence of V_d^{gsoil} for three selected values of f_{oc} and of sensitivity with respect to this parameter are shown in Fig. 3.13a and b, respectively.

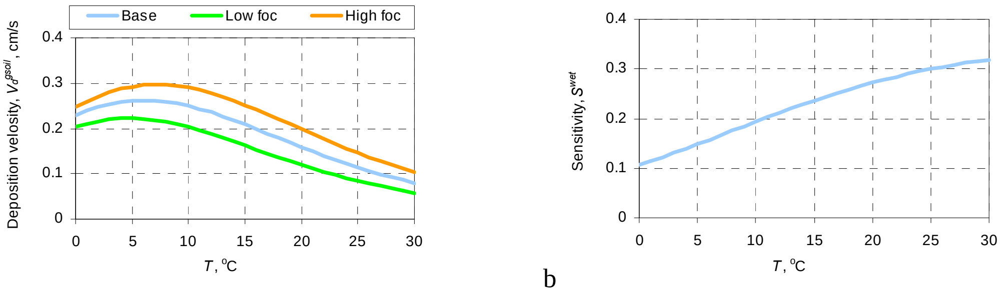

Fig.3.13. *Temperature dependence of values of V_d^{gsoil} for base, low and high values of f_{oc} (a) and of sensitivity with respect to this parameter (b)*

Calculations show moderate sensitivity of V_d^{gsoil} with respect to f_{oc}. The increase of sensitivity with temperature is conditioned by the increase of gaseous fraction of PCB-153 in the atmosphere.

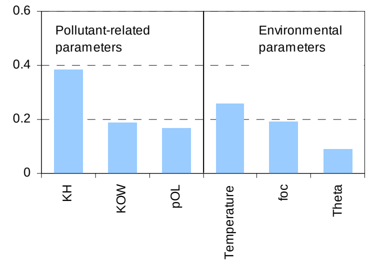

Fig. 3.14. *Sensitivities of V_d^{gsoil} with respect to selected parameters*

Resume. The plot of sensitivities of deposition velocity of direct gaseous flux to soil with respect to selected parameters at 10 ºC is shown in Fig. 3.14.

Calculations show high sensitivity of deposition velocity of direct gaseous flux to soil with respect to Henry's law constant (about 0.4). The sensitivities of V_d^{gsoil} with respect to temperature (about 0.25), fraction of organic carbon in soil (0.2), K_{OW} and p_{OL} (about 0.2 for both parameters) are moderate. The sensitivity with respect to atmospheric aerosol specific surface is somewhat lower (less than 0.1).

Direct gaseous flux from the atmosphere to vegetation

Here sensitivity of dry gaseous deposition velocity is examined with respect to the following parameters used in the model for the description of air/vegetation gaseous exchange:

- Octanol/air partitioning coefficient K_{OA} at reference temperature (10 ºC),
- Mass transfer coefficient for deciduous forest $K_{avdecid}$,
- Mass transfer coefficient for coniferous forest $K_{avconif}$,
- Subcooled liquid vapor pressure p_{OL} at reference temperature,

In addition, the process is affected by specific aerosol surface θ.

As in case of air/soil exchange, temperature dependence of V_d^{gveg} at reference values of the parameters is governed by two opposite-directed factors. The decrease of octanol/air partitioning coefficient with temperature increase leads to the decrease of gaseous flux from the atmosphere to vegetation. Inversely, the fraction of gaseous phase of PCB-153 grows with the increase of temperature, which leads to the increase of gaseous flux. As a result, deposition velocity of gaseous exchange with vegetation slightly increases up to the maximum at 2 ºC and then decreases with further temperature increase.

Temperature dependence of deposition velocity V_d^{gveg} for air/vegetation gaseous exchange at base values of the parameters is displayed in Fig. 3.15.

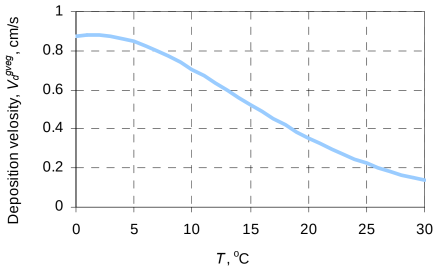

Fig. 3.15. *Temperature dependence of deposition velocity V_d^{gveg} for gaseous exchange between atmosphere and vegetation at base values of the parameters*

Subcooled liquid vapor pressure p_{OL}. The sensitivity of air/vegetation gaseous exchange with respect to p_{OL} behaves quite similarly to that of air/soil exchange (Figs. 3.16a and b).

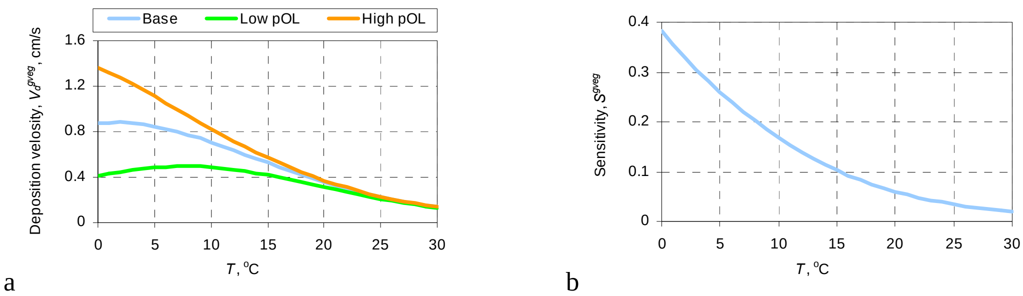

Fig. 3.16. *Temperature dependence of values of V_d^{gveg} for base, low and high values of p_{OL} (a) and of sensitivity with respect to this parameter (b)*

Mass transfer coefficient for coniferous forest ($K_{avconif}$) and atmospheric aerosol specific surface (θ). The sensitivities with respect to $K_{avconif}$ and θ are low enough (see Figs. 3.17 and 3.18).

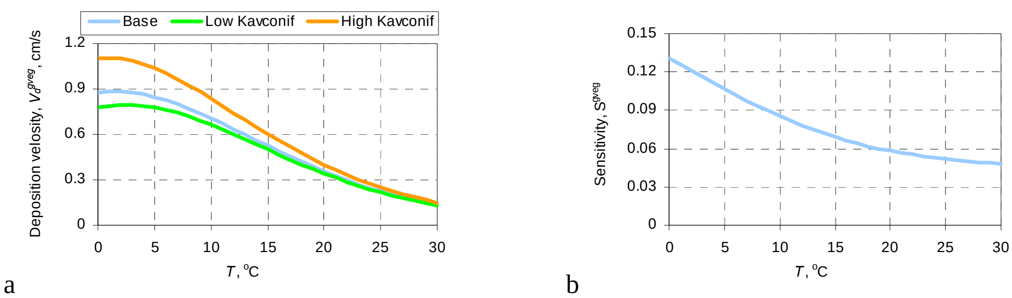

Fig. 3.17. *Temperature dependence of values of V_d^{gveg} for base, low and high values of $K_{avconif}$ (a) and of sensitivity with respect to this parameter (b)*

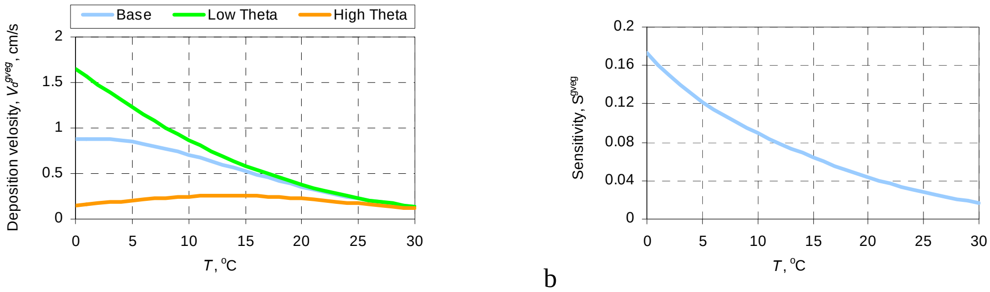

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Fig.3.18. *Temperature dependence of values of* V_d^{gveg} *for base, low and high values of* θ *(a) and of sensitivity with respect to this parameter (b)*

***Octanol/air partitioning coefficient* (K_{OA}).** Temperature dependence of deposition velocity of air/vegetation exchange for three selected values of K_{OA} are presented in Fig. 3.19a.

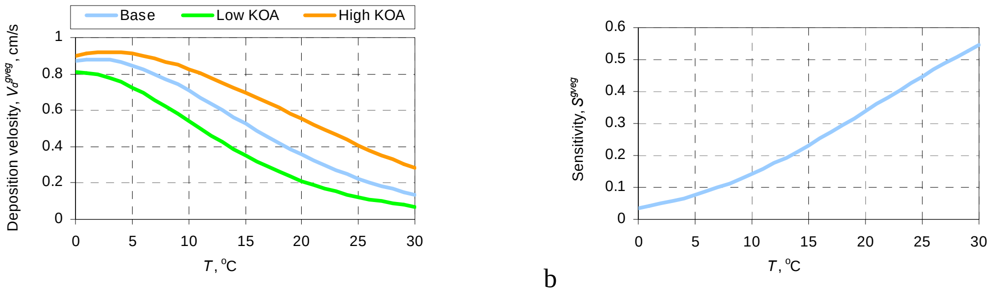

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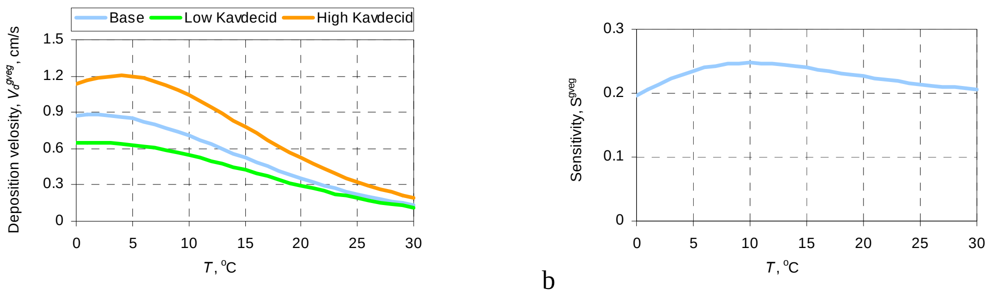
Fig. 3.19. *Temperature dependence of values of* V_d^{gveg} *for base, low and high values of* K_{OA} *(a) and of sensitivity with respect to this parameter (b)*

The sensitivity of V_d^{gveg} with respect to K_{OA} is highly temperature dependent and is high for high values of temperature. Such dependence is conditioned by the increase of fraction of PCB-153 gaseous phase in the atmosphere with temperature. (Fig. 3.19b).

***Mass tansfer coefficient for deciduous forest* ($K_{avdecid}$).** Temperature dependence of deposition velocity V_d^{gveg} for gaseous exchange with vegetation for three selected values of $K_{avdecid}$ is displayed in Fig. 3.20a. The effect of two opposite-directed factors is more pronounced for high value of $K_{avdecid}$.

The value of sensitivity S^{gveg} with respect to this parameter is in the range 0.2 – 0.25 and is almost independent on temperature (Fig. 3.20b).



a b

Fig. 3.20. *Temperature dependence of* V_d^{gveg} *for base, high and low values of* $K_{avdecid}$ *(a) and of sensitivity with respect to this parameter (b)*

Resume. The plot of sensitivities of deposition velocity of direct gaseous flux to vegetation with respect to selected parameters at 10 ºC is shown in Fig. 3.21.

Calculations show high sensitivity of deposition velocity of direct gaseous flux to soil with respect to temperature (about 0.35). The sensitivity with respect to mass transfer coefficient for gaseous exchange with deciduous forest is somewhat lower (about 0.25) and sensitivities with respect to p_{OL} and K_{OA} are moderate (about 0.15). The sensitivity with respect to atmospheric aerosol specific surface is low (less than 0.1). Calculated value of sensitivity with respect to $K_{avdecid}$ (about 0.25) is high. However, the comparison of gaseous fluxes to vegetation for other POP models makes it reasonable to perform further refinement of the description of air/vegetation exchange.

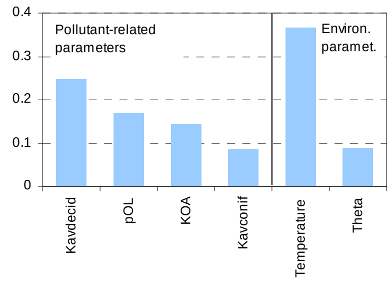


Fig.3.21. *Sensitivities of* V_d^{gveg} *with respect to selected parameters*

Direct gaseous flux from the atmosphere to seawater

In this section the analysis of sensitivity of dry gaseous deposition velocity V_d^{gsea} with respect to the following parameters used in the model for the description of air/seawater exchange is made:

- Henry coefficient H at reference temperature (10 ºC),
- Vapor pressure over subcooled liquid p_{OL} at reference temperature.

Temperature dependence of V_d^{gsea} at base values of the parameters is shown in Fig. 3.22.

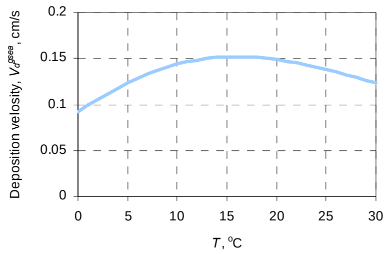
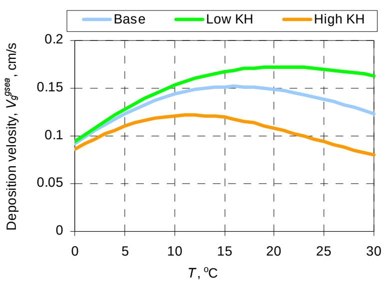


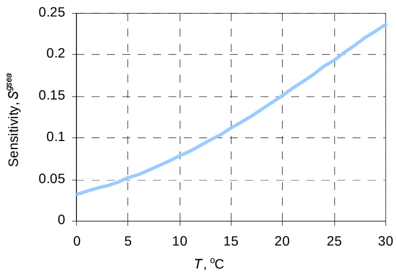
Fig. 3.22. *Temperature dependence of deposition velocity* V_d^{gsea} *for gaseous flux from atmosphere to seawater*

The explanation of the type of temperature dependence of V_d^{gsea} is quite similar to the case of gaseous exchange between the atmosphere and soil.

Henry's law constant (K_H). The comparison of the results obtained with three selected values of K_H is given in Fig. 3.23a. Temperature dependence of sensitivity S^{gsea} of deposition velocity of gaseous exchange with seawater to the value of K_H is demonstrated in Fig. 3.23b.



a



b

Fig. 3.23. *Temperature dependence of values of* V_d^{gsea} *for base, low and high values of Henry's law constant (a) and of sensitivity with respect to this parameter (b)*

Since the fraction of PCB-153 gaseous phase in the atmosphere increases with temperature, the influence of Henry coefficient value to deposition velocity of gaseous exchange with seawater is also increasing. The corresponding sensitivity S^{gsoil} increases from about 0.03 at 0 ºC up to about 0.25 at 30 ºC (Fig. 3.20b).

***Vapor pressure over subcooled liquid* (p_{OL}).** This parameter affects the process of gaseous exchange with seawater via the process of gas/aerosol partitioning. The plot of temperature dependence of V_d^{gsea} for three selected values of the parameter is shown in Fig. 3.24a.

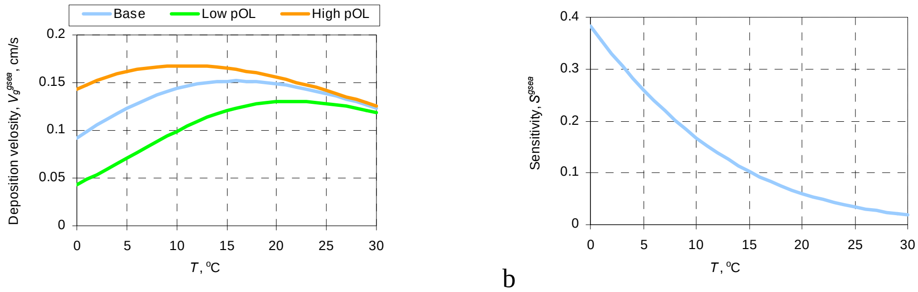


Fig. 3.24. *Temperature dependence of values of V_d^{gsea} for base, low and high values of vapor pressure over subcooled liquid (a) and of sensitivity with respect to this parameter (b)*

Similarly to the case of atmosphere/soil exchange, for high values of p_{OL} PCB-153 is present in the atmosphere mainly in gaseous phase at all temperatures considered, the influence of temperature dependence of vapor pressure is rather low and deposition velocity decreases with temperature increase due to growth of Henry coefficient for temperatures exceeding 10 ºC. Inversely, for low values of p_{OL} the influence of gas/particle partitioning process is prevailing and the increase of deposition velocity takes place up to 22 ºC. The sensitivity S^{gsea} of deposition velocity of gaseous exchange with seawater is decreasing from 0.4 at 0 ºC up to about 0.02 at 30 ºC (Fig. 3.21b). The decrease of sensitivity with temperature is explained by the fact that the influence of gas/particle partitioning process to the deposition velocity at high temperatures is much weaker than the influence of values of Henry coefficient.

Resume. The plot of sensitivities of deposition velocity of direct gaseous flux to seawater with respect to selected parameters at 10 ºC is shown in Fig. 3.25.

The process of gaseous exchange with seawater is mostly sensitive with respect to temperature (the value of sensitivity is about 0.2). The sensitivities of dry deposition velocity for direct gaseous deposition to seawater with respect to p_{OL} and K_H are moderate (0.17 and 0.08, respectively).

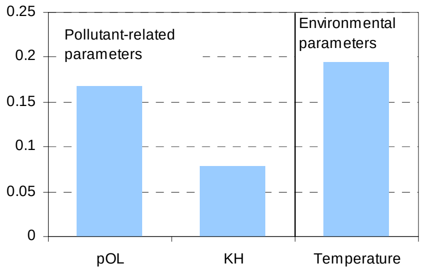


***Fig. 3.25**. Sensitivities of V_d^{gsea} with respect to selected parameters*

3.2. Sensitivity of model output with respect to selected parameters

The sensitivity of model output (spatial distributions of air concentrations and depositions) with respect to pollutant-dependent parameters will be considered by the example of Henry coefficient K_H. The sensitivity to the rest parameters will be evaluated further.

To evaluate the sensitivity of air concentration and deposition spatial distribution three model runs of MSCE-POP model for one-year period were performed for low, base and high values of K_H. All these runs use the meteorology of 2000 and one and the same emission data: conventional point source located in France (Paris) of the power 2.8 t/y.

For all cells of the calculation grid the values of sensitivity of air concentrations and depositions were calculated using the above described approach (see formulas (3.2) above).

Spatial distributions of sensitivities of air concentrations and depositions with respect to Henry coefficient are presented in Fig. 3.26. The location of the point source is shown by arrows.

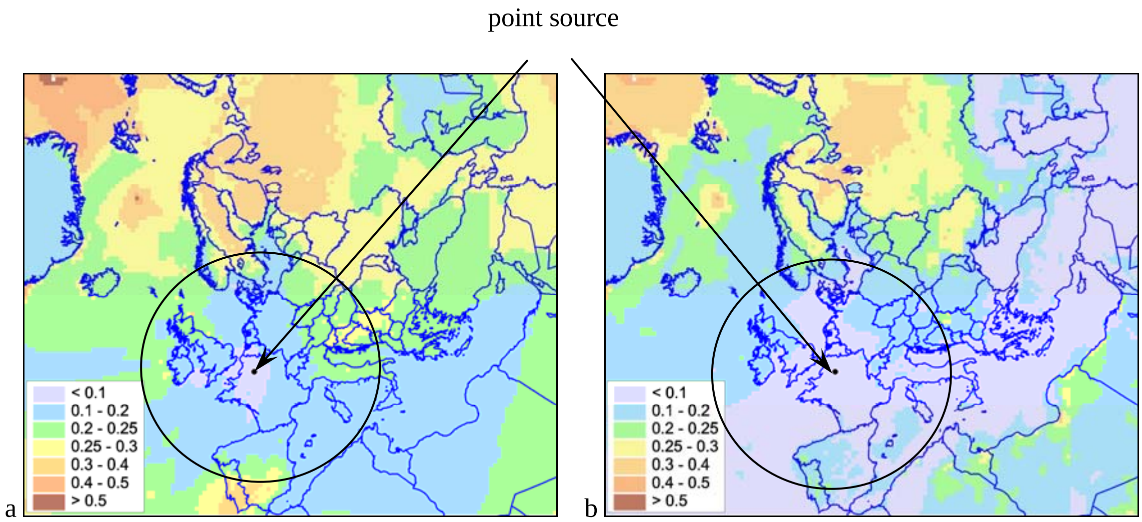


Fig. 3.26. *Spatial distributions of sensitivity of air concentrations (a) and depositions (b) with respect to Henry coefficient. Arrows show the location of the point source (1000 km – zone is marked)*

Calculations show that the sensitivity with respect to Henry coefficient is low near the point source (less than 0.1) and is growing from the source in the directions of prevailing winds. In Northern Europe and some regions of the Arctic sensitivity can reach 0.5. Below the sensitivities of air concentrations and depositions will be analyzed for two characteristic distances: about 1000 km and about 5000 km from the point source.

The sensitivities of model output near the point source (about 1000 km) are characteristic of regions close to main emission sources. In these regions the influence of re-emission processes to air concentrations and depositions are much lower than the influence of sources. The sensitivity of model output with respect to the input parameters listed in Table 3.1 close to emission sources will be performed without taking re-emission into account.

The sensitivities of air concentrations and depositions at greater distances from the source (about 5000 km) are characteristic of remote regions (e.g. northern part of Europe, the Arctic, etc). Here the influence of re-emission process occurs to be essential. Below the evaluation of the influence of re-emission process to air concentrations and depositions and sensitivity with respect to main parameters affecting this process is analyzed.

Sensitivity analysis near sources

In this section the sensitivity of model output (air concentrations and depositions) with respect to the input parameters listed in Table 3.1 without taking into account re-emission process is performed. For evaluation of this sensitivity MSCE-POP model with changed model domain under the assumption of zero concentrations in soil, seawater and vegetation is used (Fig. 3.27). Wind speed, temperature and precipitation amount were chosen to be fixed in the calculations (4 m/s and 10 ˚C, respectively).

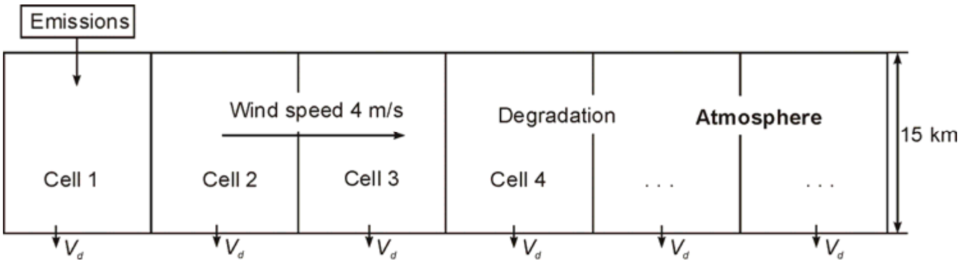


Fig. 3.27. *Model domain used and processes taken into account for evaluation of model sensitivity near the point source*

The height of the atmosphere equals 15 km. The whole model domain consists of 20 cells 50×50 km located at a straight line. A conventional emission source of a fixed power is permanently acting in cell 1. Later on the pollutant is transported with wind speed 4 m/s (average value for Europe). Besides, the substance is degraded and deposited to the underlying surface. Deposition velocity V_d is calculated taking into account wet deposition, dry deposition of particles and direct dry gaseous deposition to various types of underlying surface:

$$V_d = V_d^{wet} + V_d^{part} + V_d^{sea} \cdot \varphi_{sea} + V_d^{soil} \cdot \varphi_{soil} + V_d^{decid} \cdot \varphi_{decid} + V_d^{conif} \cdot \varphi_{conif} + V_d^{grass} \cdot \varphi_{grass} . \qquad (3.9)$$

Here V_d^{wet} is wet deposition velocity of total (gas + particles) air concentrations;

V_d^{part} is dry deposition velocity of particulate deposition;

V_d^{sea}, V_d^{soil}, V_d^{decid}, V_d^{conif} and V_d^{grass} are earlier calculated deposition velocities to sea, soil and three types of vegetation (deciduous forest, coniferous forest and grass);

φ_{sea}, φ_{soil}, φ_{decid}, φ_{conif} and φ_{grass} are fractions of cell area covered by corresponding type of underlying surface.

The fractions of cell area covered by different types of underlying surface as it is accepted for modelling are shown in Table 3.2. Since main emission sources are land-based, we assume that land fraction in each cell is 80%. The values of fractions of land covered by bare soil and different types of vegetation are average for Europe.

Table 3.2. *Fractions φ of cell area covered by various types of underlying surface accepted for sensitivity evaluation*

Type of underlying surface			Fraction φ
Land	Bare soil		18%
	Vegetation-covered soil	Deciduous forest	6%
		Coniferous forest	9%
		Grass	47%
Seawater			20%

To evaluate the sensitivity of air concentrations and depositions with respect to all parameters listed in Table 3.1 in the region near the point source model runs with three values of each parameter (low, base and high) were performed. Then sensitivities of air concentrations and depositions were calculated in each grid cell using formula (3.2) above.

It should be mentioned that the sensitivity of model output with respect to the considered parameters strongly depend on the distance from the point source. As an example, the plot of the dependence of sensitivity of air concentrations to a number of input parameters is presented in Fig. 3.28.

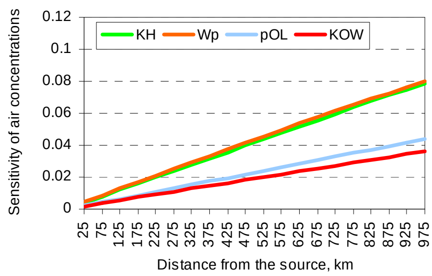


Fig. 3.28. *The dependence of sensitivities of air concentrations with respect to a number of input parameters on the distance from the point source*

From the plot it is seen that the values of sensitivity are growing with the distance from a point source. This is conditioned by the fact that uncertainties due to the change of parameters are accumulated during the transport of a pollutant over long distances.

For evaluation of sensitivities of air concentrations and depositions with respect to the selected pollutant-specific and environmental parameters in regions close to emission sources the values of average sensitivities over the calculation domain may be used. These sensitivities are demonstrated in Fig. 3.29.

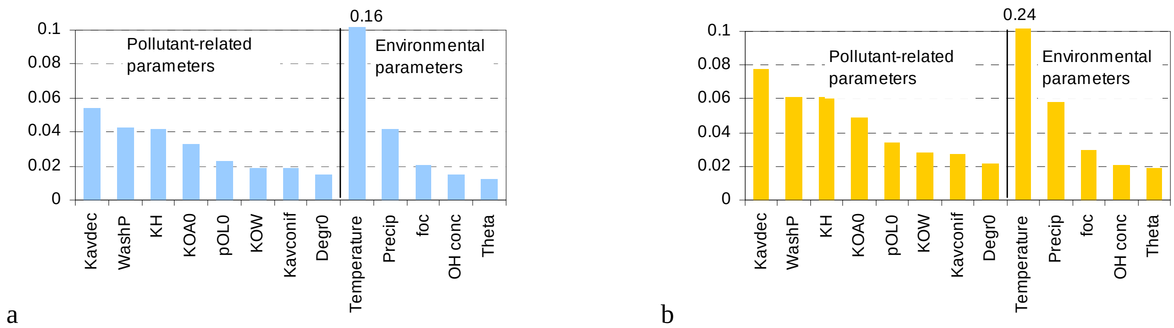


Fig. 3.29. *Sensitivity of air concentrations (a) and depositions (b) with respect to PCB-153 pollutant-related and environmental parameters*

Both air concentrations and depositions are mostly sensitive to the values of ambient temperature. The values of sensitivities with respect to washout ratio, Henry's law constant, precipitation rate and octanol/water partitioning coefficient are about 0.03 – 0.04 for air concentrations and 0.05 – 0.06 for depositions. The sensitivities with respect to the rest parameters are lower (up to 0.02 for air concentrations and 0.03 for depositions). Low sensitivity of output parameters with respect to degradation process is explained by relatively high persistence of PCB-153 in the atmosphere. Due to this fact the rate of removal of PCB-153 from the atmosphere due to degradation is essentially lower than removal rate due to deposition processes.

The values of calculated sensitivities allow estimating uncertainties of model output if the uncertainties of the input parameters are known. For example, uncertainties of air concentrations and depositions with respect to the considered parameters under the assumption that the uncertainties of all input parameters amounts to an order of magnitude are presented in Fig. 3.30.

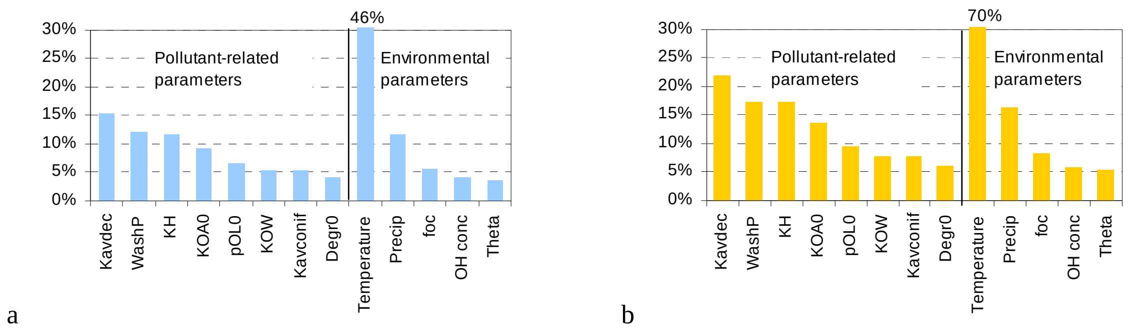


Fig. 3.30. *Scattering of air concentrations (a) and depositions (b) corresponding to the change of the input parameters by an order of magnitude*

With the help of the above estimates of sensitivity with respect to particular parameters overall uncertainty due to uncertainties of pollutant-related parameters can be evaluated via the uncertainties of the input parameters. To do that we suppose that variations of these parameters are independent and that the uncertainty of each parameter is chosen in accordance to Table 3.1. Under the above assumptions the uncertainty of output values caused by uncertainties in pollutant-specific data is estimated as 30% for air concentrations and 40% for depositions. The uncertainties calculated taking into account both pollutant-specific and environmental parameters can reach 50% for air concentrations and 70% for depositions. Of course, refinement of uncertainty ranges of these input parameters can essentially change model uncertainties. We emphasize that the discrepancies in environmental parameters used for evaluation of overall model uncertainty are different from that used in calculation of the results presented in Fig. 3.30.

Sensitivity analysis far from sources

In the evaluation of sensitivities of air concentrations and depositions near emission sources the influence of re-emission process was neglected. However, for evaluation of contamination in remote regions especially during long time periods the influence of re-emission is essential. Here the analysis of sensitivity of air concentrations to re-emission process (that is, contributions of re-emission process to air concentrations) and to main input parameters affecting this process is made. Since for PCB-153 soil is the main reservoir at the present state of investigation re-emission from soil only will be considered.

For evaluation of contribution made by re-emission from soil to air concentrations and depositions the calculation domain in MSCE-POP model consisting of 100 cells 50×50 km located in the horizontal direction. It is supposed that under each atmospheric cell a soil cell of depth 20 cm is present. In addition to dry deposition flux of particles, wet deposition flux and gaseous flux from the atmosphere to soil re-emission flux from soil to the atmosphere is considered.

Below we evaluate contribution of re-emission process to atmospheric concentrations and the influence of long-term accumulation to evaluation of long-range transport of PCB-153.

Sensitivity to re-emission process. For evaluation of the contribution of re-emission to air concentrations two different runs of the model for 50-year period were performed: with zero re-emission flux and taking into account re-emission. Then the contribution of re-emission process to air concentrations was calculated as relative difference between air concentrations calculated by these two runs in the end of each year:

$$\Delta C_a = \frac{C_a^m - C_a^0}{C_a^m} \cdot 100\% \,, \tag{3.10}$$

where C_a^0 are air concentrations calculated without re-emission;

C_a^m are air concentrations taking into account the re-emission process.

The plot of dependence of ΔC_a on the distance from the source after 1, 10, 20, 30, 40 and 50 years after the beginning of simulations is presented in Fig. 3.31.

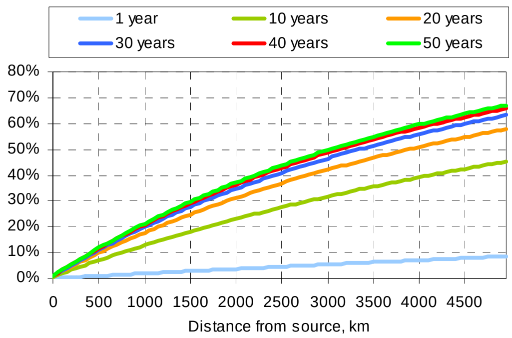


Fig. 3.31. *The influence of re-emissions ΔC_a for various calculation periods*

Calculations show that the contribution from re-emission process is increasing with the distance from emission source. Even for one-year period the contribution from re-emissions at 5000 km from the considered point source equals about 9% and for 50-year period reaches over 65%. The 50-year temporal trends of re-emission contribution in cells 1 (near the point source), 50 (2500 km from the source) and 100 (5000 km from the source) are presented in Fig. 3.32.

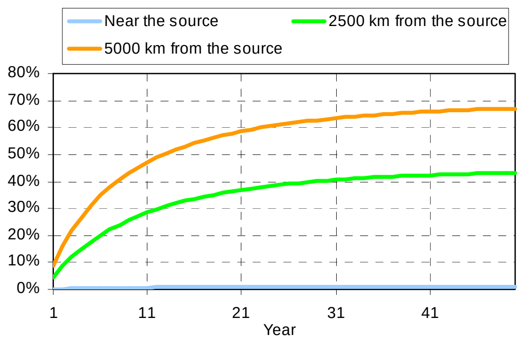


Fig. 3.32. *Temporal trends of re-emission contribution near the point source, at 2500 km from the source and at 5000 km from the source)*

Calculations show that within 50-year period contributions of re-emissions for all three considered distances from the source are growing with time reaching equilibrium to the end of the period.

The calculations made show that for PCB-153 the influence of re-emissions from soil can be considerable especially for regions located far from main emission sources.

Sensitivity to selected parameters. Here the evaluation of sensitivity of air concentration and depositions calculated taking into account re-emission flux with respect to parameters used in the model for the description of re-emission process is made. These parameters are Henry's law constant K_{H}, octanol/water partitioning coefficient K_{OW} and subcooled liquid vapor pressure p_{OL}. For the sensitivity of air concentrations with respect to these parameters model runs with their low, base and high values were performed. Average values of sensitivity over the model domain are presented in Fig. 3.33.

These values are much higher than sensitivities at 1000 km distance (see above). So, sensitivity of model results to pollutant-specific parameters is very high in the remote regions where absolute values of air concentrations are low.

Temporal trends of sensitivities calculated in the middle of the calculation domain (at the distance of 2500 km from the point source) are illustrated in Fig. 3.34.

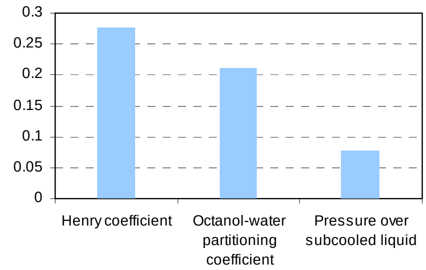


Fig. 3.33. *Sensitivity of air concentrations with respect to pollutant-related parameters averaged over 5000 km from the point source*

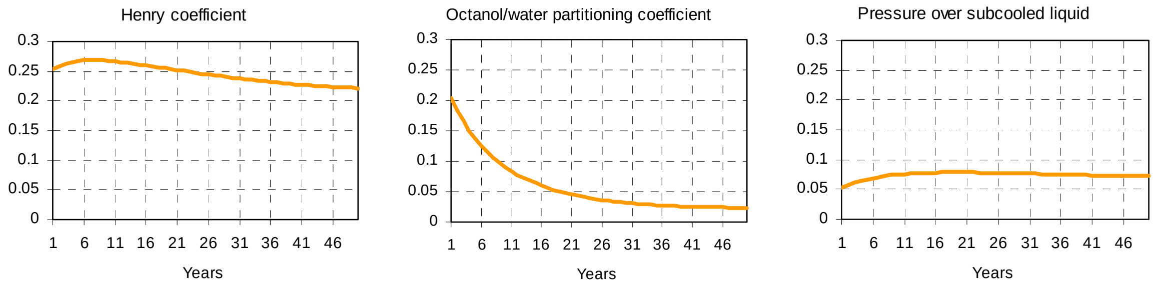


Fig.3.34. *Temporal trends of sensitivity with respect to selected pollutant-related parameters at the distance of 2500 km from the source*

Calculations show that sensitivities become stable during 10-20 years.

So, for regions with high emission levels the estimates obtained in the previous subsection (see Fig. 3.29) are typical. For regions located far from emission sources re-emission processes play essential role. The uncertainties due to pollutant-specific and environmental parameters are greater for the remote regions.

3.3. Conclusions

The sensitivity analysis of particular deposition processes and of main model output (air concentrations and depositions) with respect to pollutant-specific and environmental parameters was made. Since POPs are present in the atmosphere both in particulate and gaseous phases, the processes of gas/particle partitioning in the atmosphere and of gaseous exchange with underlying surface play an essential role in the description of POP behavior in the environment. The process of dry particulate deposition and the influence of emission uncertainty and meteorological variability at the model output were not included into consideration since their investigation is similar to MSCE-HM model. For the analysis PCB-153 was chosen as a representative POP with considerable values of both gaseous and particulate fractions in the atmosphere.

Due to strong temperature dependence of these processes the analysis was carried out for temperature range from 0 ºC to 30 ºC (typical for surface atmospheric layer in Europe). The ranges of pollutant specific parameters were chosen to be an order of magnitude whereas the ranges of environmental parameters were calculated on the basis of model input data (see Table 3.1).

From the above analysis the following conclusions can be made:

- Model output (air concentrations and depositions) is mostly sensitive to the ambient temperature. In particular, for PCB-153 the change of ambient temperature within an order of magnitude around 10 ºC leads to the change of air concentrations by 50% and depositions by 70%. The same seems to be true for the majority of POPs. So, taking into account temperature dependence of pollutant-specific parameters is of great importance for POP modelling.
- High spatial and temporal variability is characteristic of sensitivity of model output with respect to all considered parameters for all POPs. In particular, sensitivity of PCB-153 air concentration with respect to a number of input parameters changes about 20 times at 1000 km distance away from the point source (Fig. 3.28 above).
- The influence of re-emission process is significant after long-term period of POP application especially in the remote regions. For 50-year period at 5000 km from a source the contribution of PCB-153 re-emission to the values of air concentrations can reach 60%. POP emission reduction can also lead to the increase of re-emission contribution to air concentrations and depositions.
- The pollutant-related parameters for with high enough sensitivity to PCB-153 air concentrations and depositions are: Henry's law constant, washout ratio for aerosol phase and octanol/water partitioning coefficient. The change of these parameters by an order of magnitude causes the change in air concentrations and depositions of about 5% – 15% in regions close to emission sources. The sensitivity to these parameters in remote regions can be essentially higher reaching 50% – 70% under the change of the parameters within an order of magnitude.
- The sensitivity of air concentrations and depositions with respect to precipitation amount, fraction of organic carbon in soil and specific surface of the aerosol is essential. In particular, change of precipitation amount by an order of magnitude leads to the change of air concentrations over 10% and of depositions over 15% in regions close to emission sources.

Further work on the refinement of model parameterization will be carried out taking into account the results of the present study and the peculiarities of other POPs.