

## Chapter 3

## SENSITIVITY ANALYSIS

The model sensitivity to uncertainty of different input parameters and model processes has been investigated. The aims of the analysis were definition of the most critical elements of the model formulation, assessment of the uncertainties introduced by individual parameters and estimation of the overall model uncertainty. Two heavy metals (lead and mercury) were included into the analysis. Lead exemplifies characteristics of particle-bound heavy metals, whereas mercury is characterized by long-lived gaseous form, chemical transformations and principally differs from other metals. The main model output variables considered in the analysis are heavy metal concentration in the ambient air (TGM for mercury), concentration in precipitation and total deposition flux. To reduce the influence of the boundary effects on the analysis the output variables were analysed within the target area, which is somewhat smaller than the model domain (Fig 3.1). Besides, influence of the Mercury Depletion Events (MDE) on the model results was analysed in the Arctic region only (within the Arctic Circle).

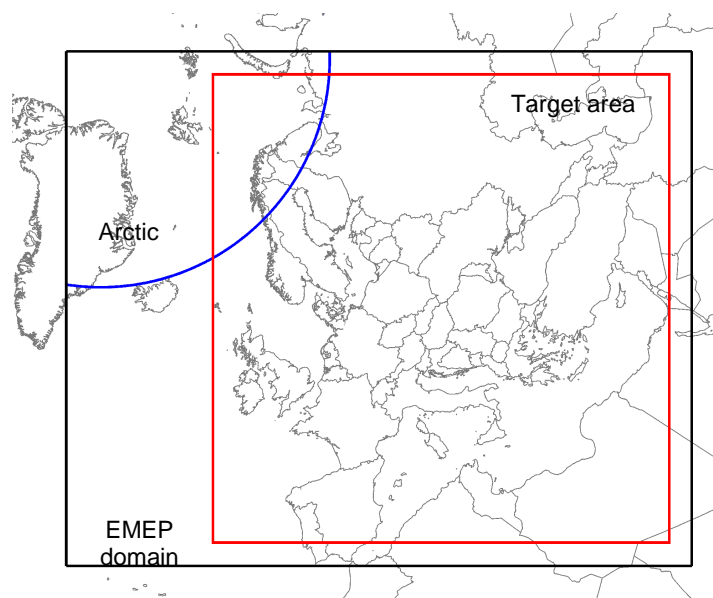


Fig. 3.1. Target areas of the sensitivity analysis

### 3.1. Meteorological variability

The model sensitivity to the variability of meteorological parameters (wind speed, surface pressure, cloudiness, precipitation etc.) was analyzed as a separate case since these parameters are adjusted by the meteorological pre-processor and cannot be considered independently. To assess the model uncertainty due to the variability of meteorological parameters a multi-year (1990-2002) calculation was performed with the same emissions data, initial and boundary concentrations. The obtained mean annual fields of the output parameters were compared between each other and with the average value. To evaluate the inter-annual variation of the model results distribution of the relative deviation was calculated:

$$\varepsilon_{ij}^{met} = \frac{Y_{ij}^{\max} - Y_{ij}^{\min}}{2\bar{Y}_{ij}} 100\%, \quad (3.1)$$

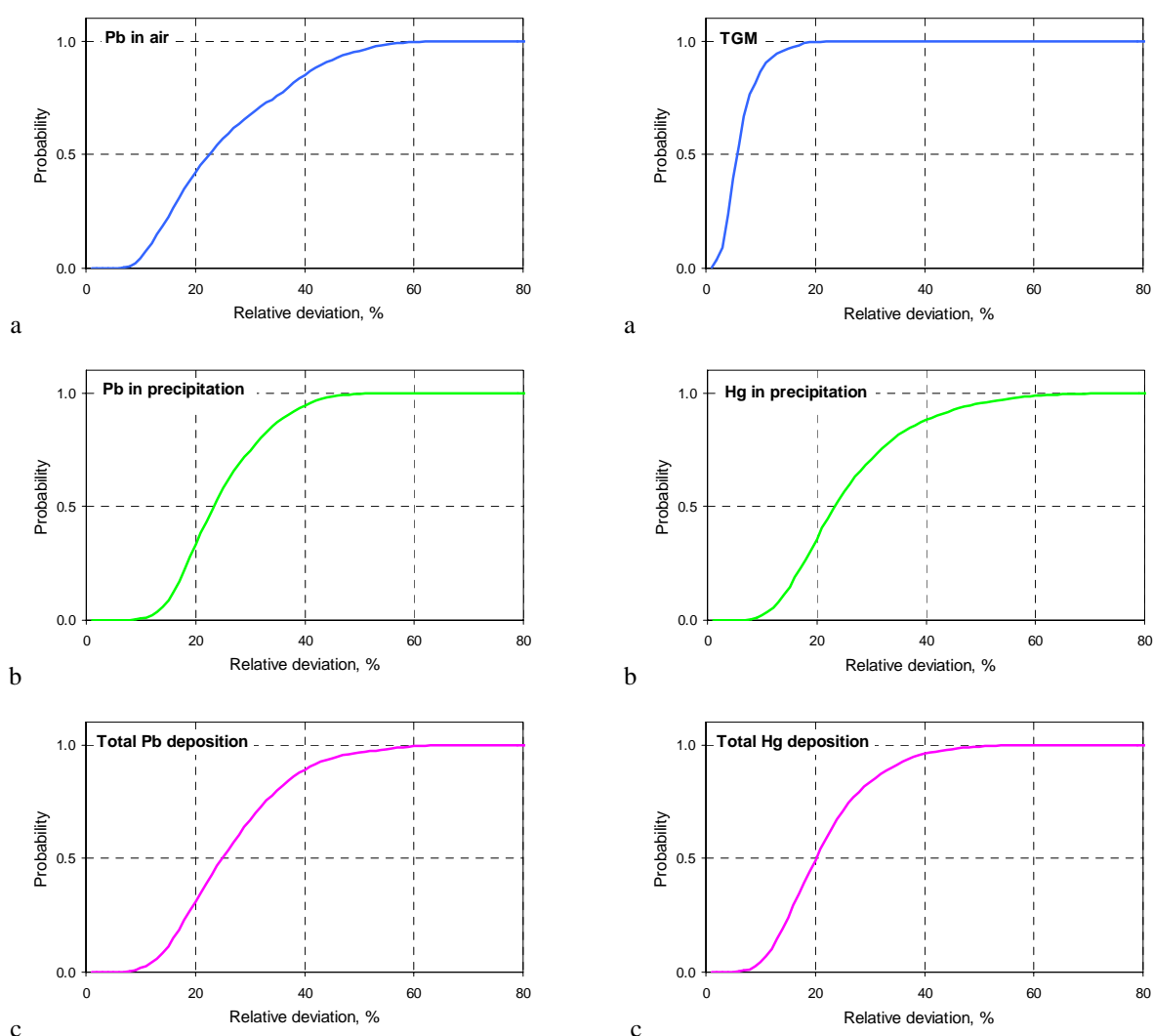
where  $Y_{ij}$  is a mean annual value of one of the model output parameters in a gridcell (i,j);

$\bar{Y}_{ij}$  is the parameter average over the whole calculation period.

Probability distributions of the relative deviation over the target area are presented in Figs. 3.2 and 3.3 for lead and mercury respectively. As seen from the figure the relative deviation of lead output parameters varies from 10% to 60% in different parts of the model domain. The same range of variation characterizes mercury concentration in precipitation and total deposition. However, variability of total gaseous mercury is noticeably lower and does not exceed 20%. To quantify the average uncertainty of the model outputs due to meteorological variability the Mean-Square Relative Error (MSRE) was calculated:

$$\varepsilon^{met} = \sqrt{\frac{1}{N} \sum_{i,j} (\varepsilon_{ij}^{met})^2}, \quad (3.2)$$

where  $N$  is the number of gridcells and summing is performed over all cells of the target area.



**Fig. 3.2.** Cumulative distribution functions of relative deviation of **Pb** concentration in air (a), in precipitation (b), and total deposition (c) due to the inter-annual variability of meteorological parameters

**Fig. 3.3.** Cumulative distribution functions of relative deviation of **Hg** concentration in air (a), in precipitation (b), and total deposition (c) due to the inter-annual variability of meteorological parameters

The MSRE the main model output variables is presented in Table 3.1 along with the range of the relative deviation variation corresponding to 90% confidence interval.

**Table 3.1.** Characteristics of the model output uncertainty due to the variability of meteorological parameters

Output parameter	MSRE, %	Range, %
<b>Lead</b>		
Air concentration	28	12 - 44
Concentration in precipitation	26	15 - 37
Total deposition	29	15 - 41
<b>Mercury</b>		
TGM concentration	7	3 - 11
Concentration in precipitation	28	14 - 42
Total deposition	23	12 - 34

### 3.2. Model sensitivity to parameters and processes

The model sensitivity to different input parameters and to the model processes formulation was estimated by variation of the parameter or switching off the appropriate process. The obtained mean annual fields of the pollutant concentration in air and in precipitation as well as total deposition flux were compared with the base case. The main model parameters included into the sensitivity analysis are listed in Table 3.2. The table also includes expert estimates of the parameters uncertainty (half interval of the relative error) used in Section 3.3 for evaluation of the model uncertainty due to individual parameters. It should be noted that these estimates have rather qualitative character.

**Table 3.2.** Parameters and processes considered in the sensitivity analysis

Parameter and processes	Notation	Uncertainty
<b>Lead</b>		
Anthropogenic emissions	$E_{ant}$	50% *
Natural emissions and re-emission	$E_{nat}$	90%
Wet deposition coefficient	$L_{wet}$	75%
Dry deposition velocity	$V_d$	75%
Boundary concentration	$C_{bound}$	90%
Eddy diffusion coefficient	$K_z$	50%
Liquid water content	$LWC$	50%
Aerosol mass median diameter	$MMD$	50%
<b>Mercury</b>		
Anthropogenic emissions	$E_{ant}$	50% *
Speciation of anthropogenic emission **	$E_{spec}$	40%
Natural emissions and re-emission	$E_{nat}$	90%
Wet deposition coefficient	$L_{wet}$	75%
Dry deposition velocity (all species)	$V_d$	75%
Dry deposition of GEM	$V_d (GEM)$	90%
Dry deposition of fog	$V_d (fog)$	90%
Lateral boundary concentration of GEM	$C_{bound} (GEM)$	20%
Lateral boundary concentration of TPM	$C_{bound} (TPM)$	90%
Upper boundary concentration	$C_{upp}$	50%
Oxidation by $O_3$ in gas phase	$k_{O_3(gas)}$	50%
Oxidation by $O_3$ in aqueous phase	$k_{O_3(aq)}$	50%
Oxidation by OH in gas phase	$k_{OH(gas)}$	75%
Oxidation by OH in aqueous phase	$k_{OH(aq)}$	75%
Oxidation by $Cl_2$ in gas phase	$k_{Cl_2(gas)}$	90%
Oxidation by $Cl_2$ in aqueous phase	$k_{Cl_2(aq)}$	90%
Reduction through sulphite complexes	$k_{red(ag)}$	50%
Hg ion-chloride equilibrium constant	$K_{Hg^{2+}}$	50%
Solution-adsorption equilibrium constant	$K_{sorb}$	50%
pH of cloud water	$pH$	20%
Chloride ion concentration	$[Cl^-]$	90%
Aerosol solubility	$K_{part}$	50%
Liquid water content	$LWC$	50%
Henry's constant for $Hg^0$	$H_{Hg^0}$	20%
Henry's constant for $HgCl_2$	$H_{HgCl_2}$	75%

\* - only stochastic component of anthropogenic emissions uncertainty is considered. The systematic component (underestimation) is behind the scope of the current research.

\*\* - fraction of oxidized Hg forms (TPM and RGM) in anthropogenic emissions

The change of a model output variable is quantified in each gridcell of the target area by the relative deviation:

$$\varepsilon_{ij}^Y = \frac{Y_{ij} - Y_{ij}^{base}}{Y_{ij}^{base}} \quad (3.3)$$

An example of the model response to variation one of the input parameters is shown in Fig. 3.5. The figure illustrates probability distribution of the relative deviation of the model outputs due to twofold increasing and decreasing of the dry deposition velocity of lead. As seen the most significant effect is on air concentration, which changes can reach 50%. On the contrary, variation of total deposition flux is weaker because of the opposite effects of wet and dry deposition contributions.

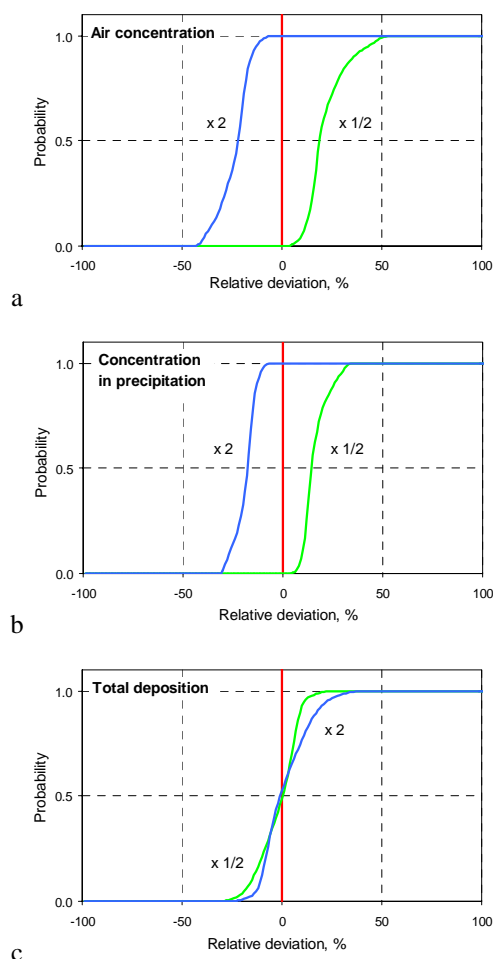
To characterize sensitivity of the model output variable  $Y$  to variation of input parameter  $X$  the sensitivity coefficient is calculated as follows

$$\frac{\delta Y}{\delta X} = \frac{\sqrt{\frac{1}{N} \sum_{i,j} (\varepsilon_{ij}^Y)^2}}{X / X_{base} - 1} \quad (3.4)$$

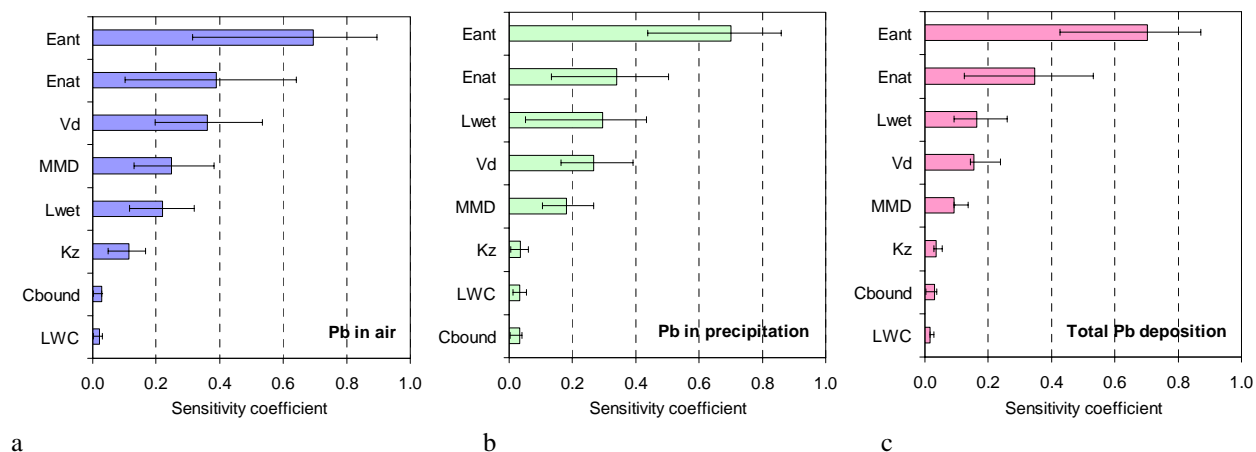
The presented below analysis of the model sensitivity does not include consideration of separate meteorological parameters by reasons discussed above. Instead, the contribution of these parameters to the model uncertainty is considered in aggregate in Section 1.3.

### Lead

The sensitivity coefficients of the main model outputs to uncertainty of input parameters are illustrated for lead in Fig. 3.6. The error bars in the figure show the 90% confidence interval of the sensitivity coefficient variation over the target area. As seen from the figure the model is the most sensitive to anthropogenic, natural emissions along with re-emission (at current calculations natural emission and re-emission make up roughly a half of anthropogenic ones). Among other important parameters are the wet deposition coefficient and the dry deposition velocity, which in its turn is influenced by the aerosol mass median diameter. On the other hand, the model is only weakly sensitive to such parameters as boundary concentrations and the liquid water content.



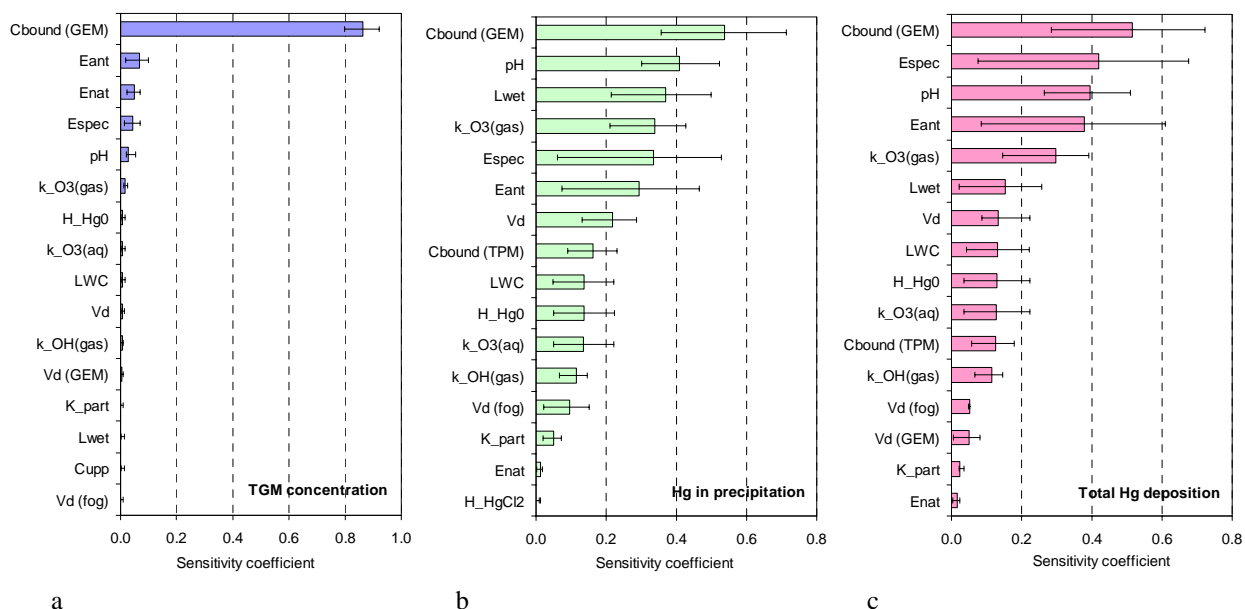
**Fig. 3.5.** Cumulative distribution functions of the relative deviation of Pb concentration in air (a), in precipitation (b), and total deposition (c) due to variation of the dry deposition velocity. The curves correspond to twofold increasing and decreasing of the parameter



**Fig. 3.6.** Coefficients of the model sensitivity to the main input parameters for Pb concentration in air (a), in precipitation (b) and for total Pb deposition flux (c). The error bars show 90% confidence interval

### Mercury

The character of the mercury model sensitivity is principally different from that described above. The main reason for that is long residence time of the bulk mercury form in the atmosphere – gaseous elemental mercury (GEM) – and chemical transformations in gaseous and aqueous phases governing mercury removal from the atmosphere. The mercury model sensitivity coefficients to uncertainty of the main input parameters are shown in Fig. 3.7.



**Fig. 3.7.** Coefficients of the model sensitivity to the main input parameters for TGM concentration (a), Hg concentration in precipitation (b) and for total Hg deposition flux (c). The error bars show 90% confidence interval

The sensitivity of TGM concentration is dominated by boundary concentration of GEM. The contribution of GEM in total gaseous mercury makes up to 99%. Taking into account very long residence time of GEM in the free troposphere (an order of year) it is obvious that this bulk mercury form can easily reach the centre of Europe or even cross the model domain. Sensitivity of TGM concentration to other parameters is significantly lower. The GEM concentration is the most important parameter for Hg concentration in precipitation and total deposition flux as well. However, since these output variables are mostly defined by oxidized mercury forms, they are also quite sensitive to other parameters responsible for emissions, oxidation and removal processes. Among them are anthropogenic emissions and their speciation characteristics, oxidation by ozone in gaseous phase, wet deposition coefficient etc. Besides, as seen a very important parameter is *pH* of cloud water. It should be noted that at the base values of the model parameters the sulphite channel of Hg reduction in aqueous phase is practically inactive due to suppressing reaction with chloride ion available in excess leading to formation of stable chloride complexes. But situation changes considerably if *pH* increased because of activation of the reduction channel. It leads to significant decrease of Hg concentration in precipitation. Another specific feature of mercury removal is very low sensitivity to natural emission along with re-emission within the model domain. It is expected that mercury is emitted from natural sources as well as re-emitted in elemental form. As a result the most part of these emissions flow out the model domain not being oxidized and removed.

### 3.3. Uncertainty due to individual parameters

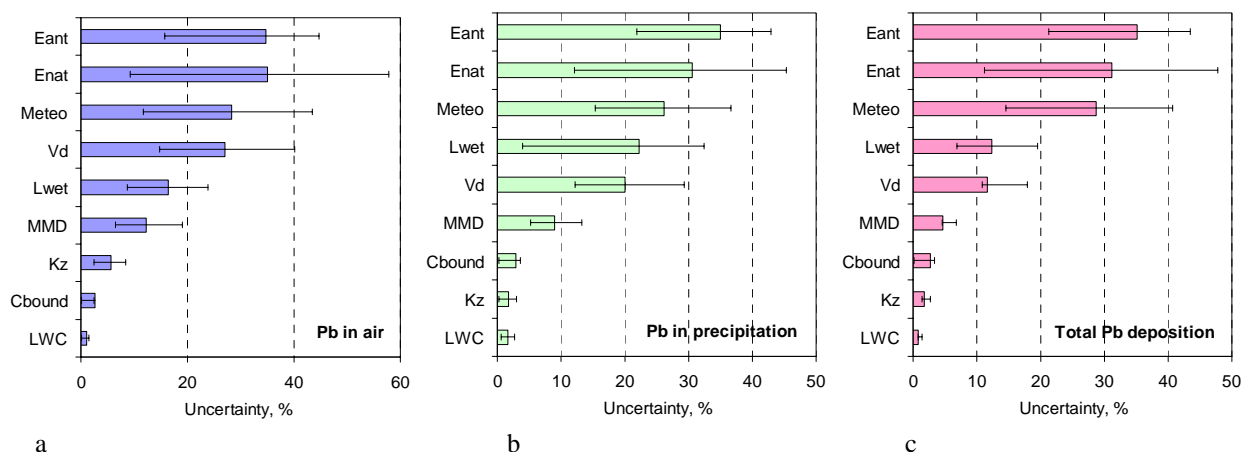
Uncertainty of different input parameters can differ significantly. Therefore contribution of an input parameter to the overall model uncertainty depends not only on the model sensitivity but also on inaccuracy of the parameter itself. To evaluate the uncertainty of a model output *Y* due to contribution of an input parameter *X* we multiplies the appropriate sensitivity coefficient by the uncertainty of the parameter  $\varepsilon_X$ :

$$E_X^Y = \frac{\delta Y}{\delta X} \varepsilon_X. \quad (3.5)$$

Estimates of the input parameters uncertainties are presented in Table 3.2. The aggregate contribution of meteorological parameters is based on the results presented in Section 3.1. It should be noted that the following analysis results to significant extent depend on the uncertainties of input parameters and should be considered as tentative because of rough character of the input uncertainties estimates.

#### *Lead*

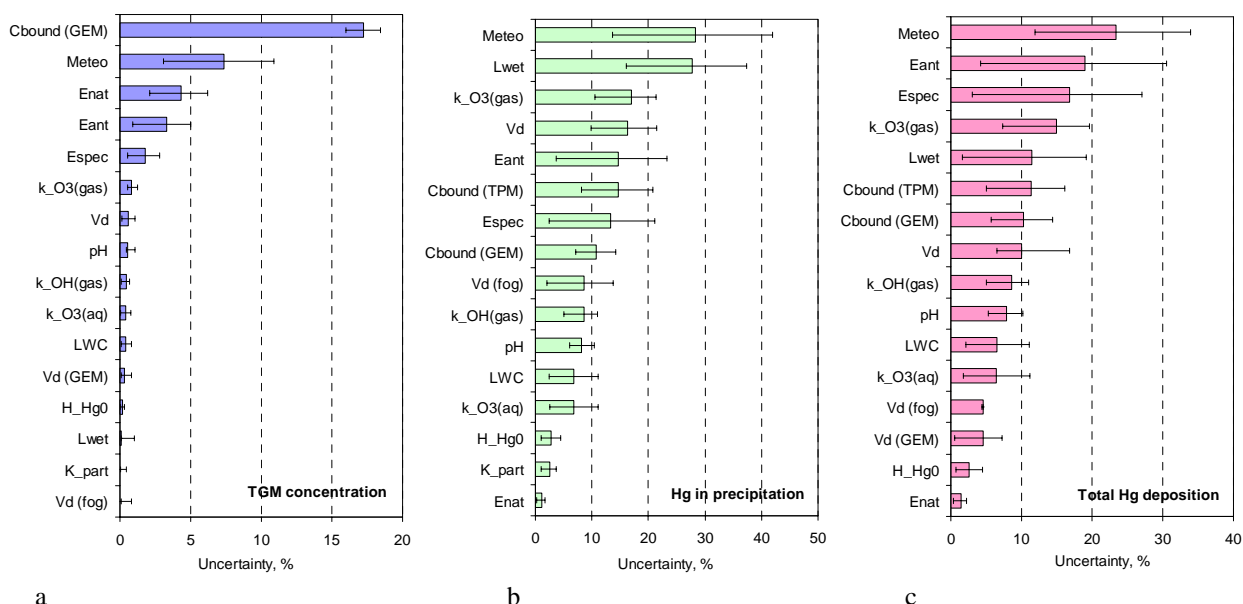
Uncertainties of the main output variables for lead caused by inaccuracies of input parameters are illustrated in Fig. 3.8. The most significant uncertainties are introduced by anthropogenic and natural emissions along with re-emission and exceed 30% on average. High uncertainty of natural emission and re-emission leads to their contribution to the overall uncertainty at least comparable with the anthropogenic one. Meteorological parameters and characteristics of removal processes also cause considerable model uncertainty.



**Fig. 3.8.** Uncertainty of Pb concentration in air (a), in precipitation (b) and of total Pb deposition flux (c) due to inaccuracy of main input parameters. The error bars show 90% confidence interval

### Mercury

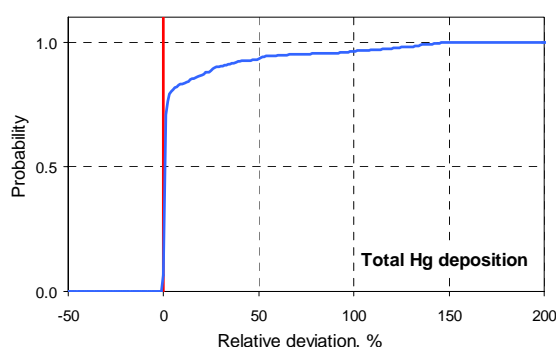
The most important parameters determined uncertainties of mercury concentration in air, in precipitation as well as total deposition flux are ranged in Fig. 3.9. The highest uncertainty of TGM concentration is due to the boundary concentration of GEM and do not exceed 20%. On the other hand, this parameter is not so important for two other output variables. The uncertainty of Hg concentration in precipitation is mostly determined by uncertainty of meteorological parameters, removal characteristics and oxidation by ozone in gas phase. Besides, anthropogenic emissions and boundary conditions for TPM are also important. Meteorological variability and anthropogenic emission along with its speciation introduced the most significant uncertainty to total Hg deposition flux.



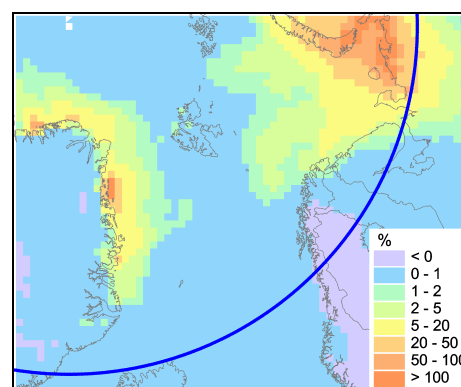
**Fig. 3.9.** Uncertainty of TGM concentration (a), Hg concentration in precipitation (b) and of total Hg deposition flux (c) due to inaccuracy of main input parameters. The error bars show 90% confidence interval

## MDE

The effect of Mercury Depletion Events on total annual Hg deposition in the Arctic was investigated using the tentative parameterization of the phenomenon (see Section 1.3). Fig. 3.10 shows probability distribution of the relative deviation of total annual Hg deposition due to effect of MDE within the Arctic Circle. In some areas of the Arctic total annual deposition of mercury can increase up to 100% and more. As seen from the spatial distribution of the relative deviation (Fig. 3.11) the most significant increase takes place over the coastal areas of the Arctic Ocean. It could be concluded that this short-term phenomenon (occurring during several weeks in the springtime) can have significant effect on the long-term pollution of the Arctic with mercury. However, further research of MDE kinetics is required to develop reliable parameterization of the phenomenon for the model.



**Fig. 3.10.** Cumulative distribution function of the relative deviation of total annual Hg deposition due to effect of MDE



**Fig. 3.11.** Spatial distribution of the relative deviation of total annual Hg deposition due to effect of MDE. Solid line depicts the Arctic Circle

## 3.4. Overall uncertainty

The overall model uncertainty can be roughly estimated from the uncertainties due to individual parameters using the following equation

$$E^Y = \sqrt{\sum_X (E_X^Y)^2}. \quad (3.6)$$

Estimated uncertainties of the main model parameters for lead and mercury are presented in Table 3.3. As it was mentioned above results of this analysis to significant extent depend on the uncertainties of input parameters and should be considered as tentative.

The intrinsic model uncertainty includes contributions of all model parameters except anthropogenic, natural emissions and re-emission. The overall model uncertainty along with other parameters includes uncertainty due to anthropogenic, natural emissions and re-emission. However, only the stochastic component of anthropogenic emissions uncertainty is considered. A possible influence of the systematic error (underestimation) is not included. The range indicates 90% confidence interval of the uncertainty variation over the model domain. The intrinsic model uncertainty of lead concentration in air, concentration in precipitation and total deposition varies from 20% to 65% over the domain with average values 43%, 40% and 33% respectively. The overall uncertainties reach 60% on average

(the range 30-97%). The intrinsic model uncertainty of mercury differs for different outputs. It does not exceed 20% on average for TGM concentration (the range 16-22%) but reaches 40% for total deposition and 50% for concentration in precipitation (the ranges 20-57% and 29-74% respectively). The overall uncertainty for mercury only slightly exceeds the intrinsic one indicating limited effect of emissions uncertainty on the model results.

**Table 3.3.** Model intrinsic and the overall uncertainties of the main model output parameters

Output parameter	Intrinsic		Overall *	
	Uncertainty, %	Range, %	Uncertainty, %	Range, %
<b>Lead</b>				
Air concentration	43	22 - 64	65	39 - 97
Concentration in precipitation	40	20 - 57	61	32 - 85
Total deposition	33	19 - 49	58	31 - 81
<b>Mercury</b>				
TGM concentration	19	16 - 22	20	16 - 23
Concentration in precipitation	53	29 - 74	56	29 - 80
Total deposition	39	20 - 57	46	20 - 70

\* - only stochastic component of anthropogenic emissions uncertainty is considered. The systematic component (underestimation) is not included

### 3.5. Conclusions of the sensitivity analysis

The main conclusions of the sensitivity analysis are:

- Uncertainty of modelling results due to inter-annual variability of meteorological parameters amounts to 20-30% on average except that of TGM concentration, which does not exceed 10%.
- The model outputs for lead are the most sensitive to anthropogenic emissions, natural emission and re-emission and to removal parameters. Sensitivity of the mercury model outputs is highest to boundary concentration of gaseous elemental mercury and to lower extent to anthropogenic emissions (along with speciation), cloud water *pH* and wet deposition characteristics as well as to oxidation by ozone in gaseous phase.
- Total annual deposition of mercury over the coastal areas of the Arctic Ocean can increase by 100% and more due to the effect of Mercury Depletion Events.
- The most significant contribution to the model uncertainty for lead is made by emissions, meteorological parameters and removal characteristics. Beside these parameters, the mercury model uncertainty is also determined by boundary concentration of gaseous elemental mercury (it is dominating for TGM concentration) and oxidation by ozone in gaseous phase.
- The intrinsic model uncertainty of lead concentration in air, concentration in precipitation and total deposition are estimated as 43%, 40% and 33% respectively; the appropriate uncertainties for mercury are 19%, 53% and 39%. The overall uncertainty of these main model outputs can be assessed as 65%, 61%, 58% respectively for lead and 20%, 56%, 46% for mercury. However, it should be noted that the final values of the uncertainty to significant extent depend on estimates of inaccuracy of input parameters.