

Annex F

ADDITIONAL COMPUTATION EXPERIMENTS

F.1. Gas/aerosol partitioning

Here we present an evaluation of influence of variation of specific surface area of POP particles-carriers in the atmosphere on calculation results. This parameter is used for evaluation of POP fraction associated with particles in the atmosphere. As it was mentioned in Section 2.2, particle-bound POP fraction ϕ is calculated in the MSCE-POP model using Junge-Pankow equation [Junge, 1977; Pankow, 1987]

$$\phi = \frac{c\theta}{p_L^0 + c\theta},$$

where c is the constant dependent on thermodynamic parameters of the adsorption process and on properties of aerosol particle surface ($c = 0.17 \text{ Pa}\cdot\text{m}$ [Junge, 1977]);
 θ is the specific surface of aerosol particles, m^2/m^3 ($\theta = 1.5\cdot 10^{-4}$ for background aerosol [Whitby, 1978]);
 p_L^0 is the subcooled liquid-vapour pressure (Pa).

Value of p_L^0 is supposed to be temperature-dependent:

$$\log p_L^0 = -\frac{A}{T} + B$$

where A and B are some constants depending on a POP in question;
 T is the ambient temperature (K).

At present, as a rough approximation, the value of specific surface of aerosol particles θ in the model is chosen one and the same ($1.5\cdot 10^{-4} \text{ m}^2/\text{m}^3$) for the whole Northern Hemisphere. Below we analyze the uncertainty due to application of this approximation since the observation data show that this value can vary essentially in different regions [Lohmann *et al.*, 2000]. The analysis is done on the example of PCB-153.

There are two types of changes caused by variation of the parameter θ . First, lower values of θ in clean regions (compared with those applied in the model) lead to the decrease of deposition velocities and, consequently, to the increase of air concentrations. Second, higher values of θ lead to the increase of deposition velocities in contaminated regions, which results in decrease of air concentrations of the pollutant transported from these regions to clean regions (in particular, the Arctic).

Calculation experiments for transport of PCB-153 for one year under the assumption of zero initial concentrations in all the media are carried out. We compare two possible scenarios of calculations. The first scenario uses one and the same value $\theta = 1.5\cdot 10^{-4} \text{ m}^2/\text{m}^3$ for all Northern Hemisphere. The second scenario assumes $\theta = 0.42\cdot 10^{-4} \text{ m}^2/\text{m}^3$, $\theta = 1.5\cdot 10^{-4} \text{ m}^2/\text{m}^3$ and $\theta = 3.5\cdot 10^{-4} \text{ m}^2/\text{m}^3$ for clean, intermediate and contaminated regions, respectively. The corresponding spatial distribution of θ is constructed on the base of emission fields for PCB-153. Namely, regions with PCB-153 emission flux less than $0.005 \text{ g}/\text{km}^2/\text{y}$ are considered as clean with $\theta = 0.42\cdot 10^{-4} \text{ m}^2/\text{m}^3$, in regions where emission

flux ranges between 0.005 and 0.5 g/km²/y the value $\theta = 1.5 \cdot 10^{-4} \text{ m}^2/\text{m}^3$ is used (intermediate regions), and the regions with high emission density (more than 0.5 g/km²/y) are considered as contaminated with $\theta = 3.5 \cdot 10^{-4} \text{ m}^2/\text{m}^3$.

The results of calculations using these two scenarios are displayed in Figure F.1.

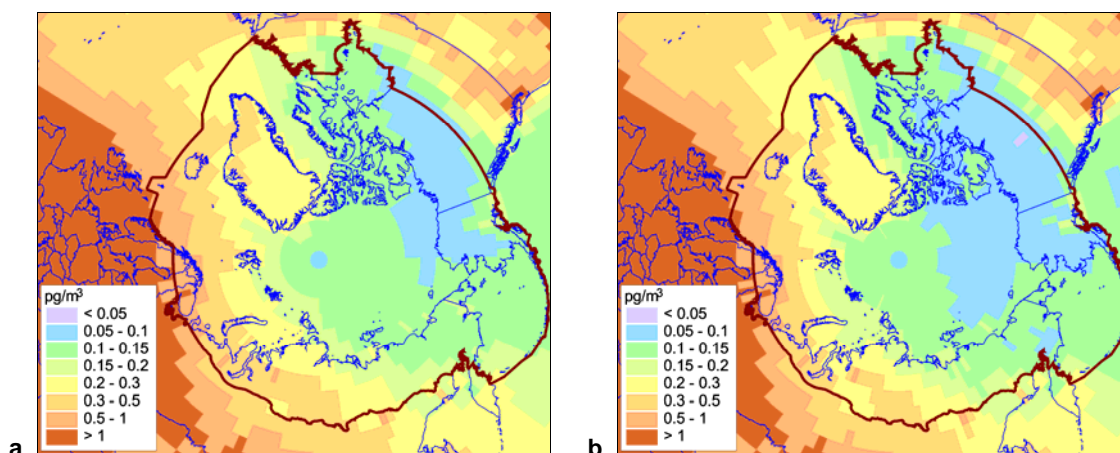


Figure F.1. Air concentrations of PCB-153 (gas + particles) obtained under first (a) and second (b) scenario in the Arctic, pg/m³

As seen from these maps there are certain differences in air concentration fields obtained under the above scenarios. Namely, the difference of the results of these two simulations over the whole Northern Hemisphere ($\Delta = (C_2 - C_1)/C_1$) ranges from –20% to about 15% (depending on location, see Figure F.2).

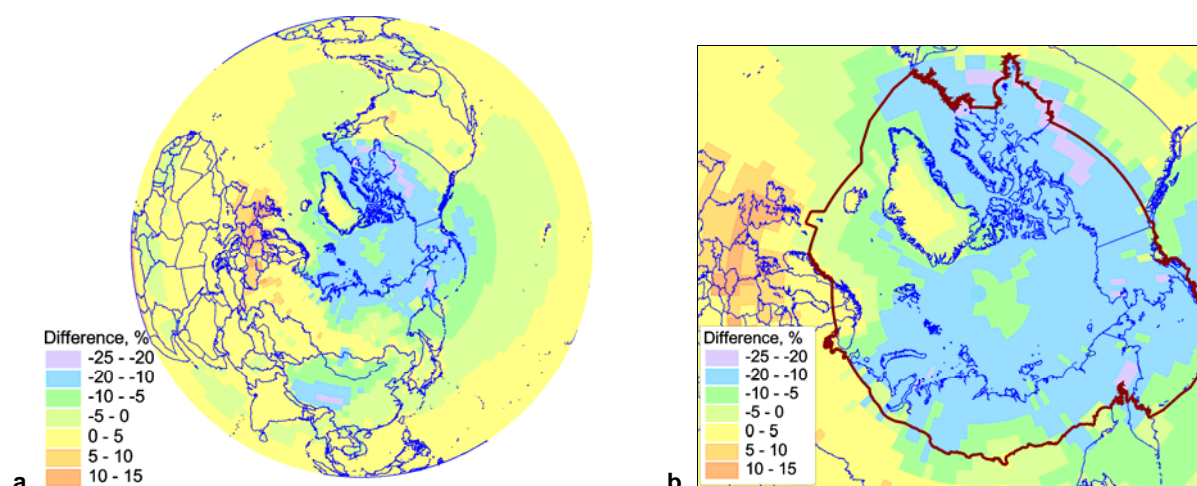


Figure F.2. Differences between values of air concentrations of PCB-153 obtained under first and second scenario, % for the whole hemisphere (a) and the Arctic (b)

Annual depositions obtained for two considered scenarios differ from –60% to 50% in different parts of the Northern Hemisphere (Figure F3).

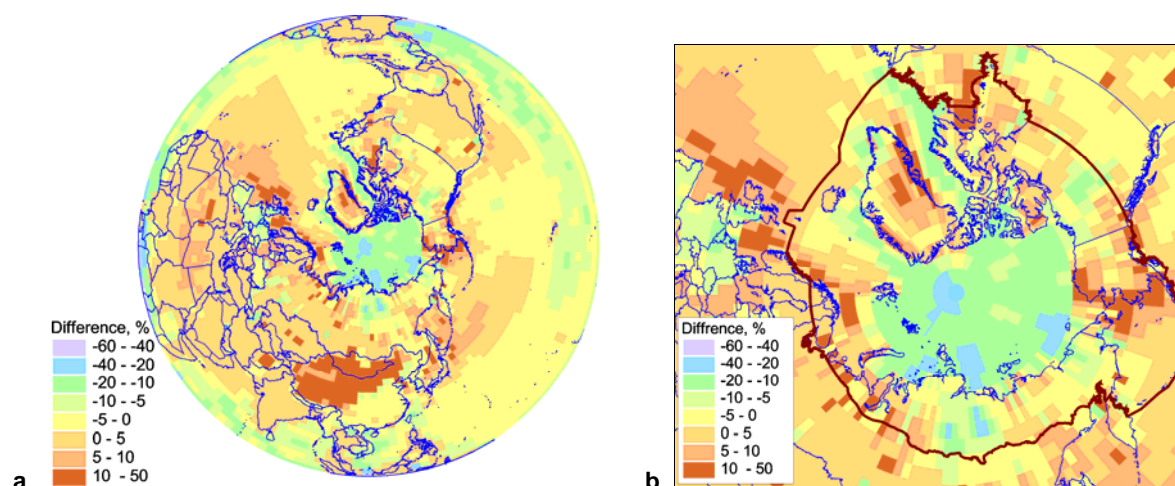


Figure F.3. Differences between values of depositions of PCB-153 obtained under first and second scenario, % for the whole hemisphere (a) and the Arctic (b)

It is reasonable to examine the sensitivity of seasonal variations of PCB-153 air concentrations and total depositions to five regions-receptors of the Russian North and to the Arctic as a whole with respect to variations of the parameter θ . Table F1 displays the values of relative differences of these quantities obtained under the two described scenarios.

Table F.1. Relative differences (%) between calculations under first and second scenarios (monthly averaged air concentrations (gas + particles) and total monthly wet + dry particulate depositions) for five regions-receptors of the Russian North and annual averages

Region	Surface air concentrations		Total depositions	
	Max monthly	Annual	Max monthly	Annual
Murmansk Oblast	- 3	- 1	9	5
Nenets AO	- 17	- 10	17	7
Yamalo-Nenets AO and Taimyr AO	- 23	- 12	10	1
Republic of Saha	- 26	- 9	- 9	- 2
Chukotka AO	- 24	- 16	- 23	- 5
Arctic region	- 13	- 9	- 13	- 2

From these data it is seen that the values of PCB-153 monthly averaged air concentrations are changed up to - 26% (decrease) for different months and regions. On the average the second scenario gives lower surface atmospheric concentrations. The deposition values vary from - 23% to 10% depending on month and region. Application of more detailed description of θ spatial distribution leads to increase of both monthly and annual deposition values in Murmansk oblast, Nenets AO and Yamalo-Nenets and Taimyr AO, and shows the decreased values in Republic of Sakha and Chukotka AO as well as for the Arctic as a whole.

The differences in seasonal variations of concentrations and depositions for Chukotka AO (where the differences for deposition are the largest, see Table F.1) are exemplified by plots of Figure F.4. Total increase of concentrations and depositions is explained by the fact that simulations were performed under the assumption that initial concentrations in all the media are zero and for one year only.

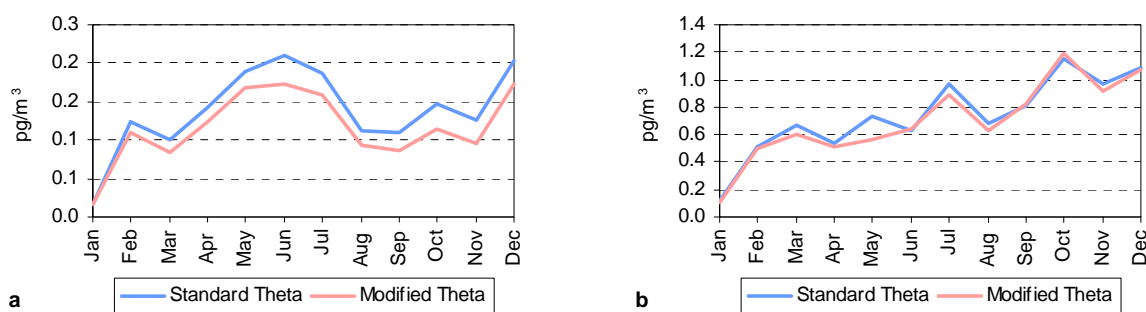


Figure F.4. Seasonal variations of monthly averages of air concentrations (a) and total monthly deposition (b) obtained under first and second scenario in Chukotka AO

It is seen that seasonal variations for both deposition and air concentrations for the two considered scenarios have similar characters.

In view of large enough uncertainties in emission data, the simplified approach (first scenario) seems to be reasonable at the first step of the assessment of contamination levels of the Arctic as a whole and of the Russian North. Moreover usage of second scenario needs detailed spatial distribution of aerosol particles, which in turn is rather uncertain. However, for modeling of POP long-range transport the application of detailed spatial distribution of specific aerosol surface is a priority task. These distributions are expected to be obtained as an output of aerosol dynamics and transport models.

F.2. Diurnal variations of OH radical concentrations

According to observational data [Lee *et al.*, 1998, Mandalakis *et al.*, 2003], PCB atmospheric concentrations undergo substantial diurnal variations. Daily PCB concentrations for different congeners vary as much as 2-4 times. This phenomenon can be conditioned by atmospheric transport, deposition, gas exchange with the underlying surface and degradation, etc. One of the most important processes of PCB destruction in the atmosphere is reaction with OH radical. In the model this process is described by the following equation (see Section 2.2):

$$\frac{dC}{dt} = -k \cdot C \cdot [\text{OH}], \quad (\text{F.1})$$

where C is the pollutant concentration in the gas phase of the atmosphere, ng/m^3 ;
 $[\text{OH}]$ is the concentration of OH radical, molecules/cm^3 ;
 k is the degradation rate constant for air, $\text{cm}^3/\text{s/molecules}$,

where the temperature dependence of the parameter k is provided by the equation:

$$k = A \cdot \exp(-E_a / RT), \quad (\text{F.2})$$

where A is the exponential multiplier;
 E_a is the activation energy;
 R is the universal gas constant;
 T is the ambient air temperature.

Thus, as seen from the Eqs. (F.1, F.2) PCB degradation in the atmosphere is affected by temperature and OH radical concentration variations. In general, OH radical concentrations are subject to temporal and spatial variations. At present in the model as a first approximation OH radical concentrations have no diurnal variations and depend only on a season. Below the uncertainty caused by this assumption is roughly evaluated.

As a measure of uncertainty the relative deviation between pollutant concentrations obtained under two following scenarios is used: 1) with mean value of OH radical concentration round the clock within each season (\overline{OH}) and 2) with diurnal variations of OH radical concentration. These scenarios are considered separately for three seasons: winter, spring/fall and summer. Spatial distribution of OH radical is uniform for each season. Mean values of OH radical concentrations over the Northern Hemisphere for each season used in scenario 1 are given in Table F.2.

Table F.2. Mean values of accepted OH radical concentrations (\overline{OH}) used in scenario 1

Season	Mean daily OH radical concentration, molecules/cm ³ , [Yu Lu and Khall, 1991]
Winter	$0.09 \cdot 10^6$
Spring/Fall	$0.8 \cdot 10^6$
Summer	$2 \cdot 10^6$

For scenario 2, diurnal variation profile of OH radical concentrations is based on the data from paper [Mandalakis et al., 2003]. According to meteorological data used in the model, the day is divided into 4 periods 6 hours each. In the night concentrations of OH radical are taken to be zero, in the daytime concentrations are taken two times higher than averaged values (Table F3). Experimental diurnal temperature variations with amplitude of 10 degrees are assumed the same for both scenarios (Table F.3).

Table F.3. Diurnal variations of OH radical concentrations accepted in the scenario 2 and ambient temperature variation used in both scenarios

Season	OH radical concentration, molecules/cm ³		Temperature, C	
	Day	Night	Day	Night
Winter	$0.18 \cdot 10^6$	0	-5	-15
Spring/Fall	$1.6 \cdot 10^6$	0	10	0
Summer	$4 \cdot 10^6$	0	25	15

According to Eq. (F.1), under the assumption of equal initial air concentration, the relative deviation Δ of air concentrations, between the first and the second scenario is evaluated as:

$$\Delta = \frac{C_2 - C_1}{C_1} = \exp \left[\frac{Time}{4} \left(\sum_{i=1}^4 OH_i \cdot k_i - \overline{OH} \sum_{i=1}^4 k_i \right) \right] - 1, \quad (F.3)$$

where $Time$ is the time period;

OH_i and $k_i = k(T_i)$ is OH radical concentrations and degradation rate constants for each day period respectively;

\overline{OH} is the mean value of OH radical concentration.

The degradation process is more important for low chlorinated PCBs, which are present in the atmosphere mainly in the gas phase, than for high chlorinated PCBs, associated with the atmospheric particles in more extent. For this reason the uncertainty evaluation is carried out on the example of the PCB-28 degradation parameters ($A = 1.7 \cdot 10^{-10} \text{ cm}^3/\text{s/molecules}$, $E_a = 13700 \text{ J/mol}$ [Beyer and Matthies, 2001]). Temporal dependence of relative deviations between air concentrations calculated by two scenarios for each season is depicted in Figure F5.

The deviation gradually increases with time, the slope of the curves depends on the season. Maximum OH radical concentrations are estimated for summer, therefore the deviation curve has the steepest slope. From the figure it is seen that the deviation over a season (90 days) can reach values of 70-80%.

Degradation half-lives for the considered seasons, taking into account corresponding OH radical concentrations (Table F.2), equal to 4, 14 and 175 days for summer, spring/fall and winter respectively. These periods for summer and spring/fall are marked by vertical dotted lines in Figure F5. By the end of the respective half-lives the deviation Δ is less than 10% for each season.

These calculations give lower estimates of the uncertainty. In reality the uncertainty is likely to be higher. This may be conditioned by a number of factors, for instance, by the diurnal variations of a pollutant concentrations caused by re-emissions or some other processes. This phenomenon seems to be rather important and should be properly studied in future.

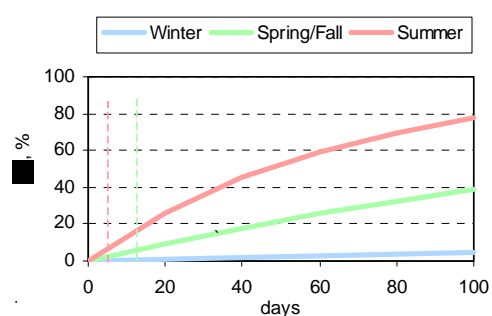


Figure F.5. Relative deviation (Eq. F.3) of calculation results obtained under two scenario for PCB-28, Δ , %. The dotted vertical lines denote degradation half-life in the atmosphere for corresponding season.

References

- Beyer A and M. Matthies [2001] Criteria for Atmospheric Long-range Transport Potential and Persistence of Pesticides and Industrial Chemicals. Umweltforschungsplan des Bundesministerium für Umwelt, Naturschutz und Reaktorsicherheit. Stoffbewertung, Gentechnik, Forderkennzeichen (UFOPLAN) 299 65 402.
- Junge C.E. [1977] Basic considerations about trace constituent in the atmosphere is related to the fate of global pollutant. In: Fate of pollutants in the air and water environment. Part I, I.H. Suffet (ed.) (Advanced in *Environ. Sci. Technol.*, v.8), Wiley-Interscience, New York.
- Lee R.G.M., H. Hang, D. Makey and K.C. Jones [1998] Measurement and modelling of the diurnal cycling of atmospheric PCBs and PAHs, *Environ. Sci. Technol.*, v.32, pp.2172-2179.
- Lohmann R, T. Harner, O. Thomas and K.C. Jones [2000] A comparative study of the gas-particle partitioning of PCDD/Fs, PCBs and PAHs. *Environ. Sci. Technol.*, v.34, pp.4943-4951.
- Mandalakis M., Berresheim H. and Stephanou E.G. [2003] Direct Evidence for Destruction of Polychlorobiphenyls by OH Radicals in the Subtropical Troposphere. ARTICLE IN PRESS: *Environmental Science and Technology*.
- Pankow J.F. [1987] Review and comparative analysis of the theories on partitioning between the gas and aerosol particulate phases in the atmosphere. *Atmos. Environ.*, v.21, pp.2275-2283.
- Whitby K.T. [1978] The Physical Characteristics of Sulphur Aerosols. *Atmos. Environ.*, v.12, pp.135 – 159
- Yu Lu and M.A.K. Khall [1991] Tropospheric OH: model calculation of spacial, temporal and secular variations. *Chemosphere*, v. 23, pp.397-444.