Annex D

SENSITIVITY ANALYSIS OF THE SOIL MODULE

The behaviour of persistent organic pollutants in such environmental compartments as soil, vegetation and seawater strongly influence on their long-range transport. However, POP behaviour in these media is determined by a number of processes of different importance. For the development of POP transport multicompartment models the investigation of the influence of processes affecting POP behaviour in environmental compartments (that is, ***sensitivity study with respect to processes***) is of major importance. In this Annex we perform sensitivity study with respect to some processes governing POP behaviour in soil. The behaviour of POPs in seawater compartment will be considered in the Annex E.

The processes of accumulation in and volatilization from soil are of importance for some POPs such as PCBs, PCDD/Fs and others. In particular, according to model calculations [*Shatalov et al*., 2001], re-emission PCB flux from soil in Europe in the late 1990s is comparable with anthropogenic emissions and became in some countries a main source of air contamination together with transboundary transport.

The description of behaviour of POPs in soil and of atmosphere/soil exchange process used in MSCE-POP model is rather simplified and does not take into account some processes having considerable influence on POP fate in soil (transport with the dissolved organic carbon, dynamic redistribution between different soil phases, convection fluxes along macropores, leaching to rivers, bioturbation and others). At present the work aimed at refinement of model description of some processes governing the behaviour of POPs in soils is ongoing (see [*Vassilyeva and Shatalov*, 2002]). Here we consider the results of numerical experiments evaluating possible influence of vertical transport with dissolved organic carbon and dynamic redistribution of POPs between different phases in soil. More detailed analysis of these processes and choice of parameters used for such evaluation are considered in the above cited report.

***Transport with dissolved organic carbon*.** Dissolved organic carbon (DOC) is a component of soil solute for almost all soil types. The most interesting fraction of DOC is mobile dissolved organic carbon, which can be readily transported along soil micro- and macropores. DOC concentration in soil solute depends on soil type and, in particular, on fraction of organic content in soil of given type. As a first approximation the quantity of mobile organic carbon is about 1% of total organic carbon content in soil.

***Redistribution between different soil phases*.** In the context of high storage capacity of the soil solid phase for some POPs, the processes of their sorption and desorption to soil solution are of a particular importance. At present in the model a concept of instantaneous equilibrium between dissolved POP fraction and that sorbed on solid soil organics is used. However, recently more and more evidences appear that real sorption-desorption exchange between POPs and soil differ drastically from equilibrium ones. It is connected with soil organics heterogeneity and low availability of POPs located in micropores. Due to a high volume of POP molecule and its continuous interaction with the hydrophobic surface while moving inside the soil organics micropores, the establishment of thermodynamic equilibrium between the dissolved and sorbed phase requires considerable time (usually from one to six months). POP desorption in the inverse direction is also non-uniform and delayed.

D.1. Model assumptions

To evaluate the influence of the above processes on soil concentrations of POPs (and, as a consequence, on the process of atmosphere/soil gaseous exchange) numerical experiments simulating processes of POP accumulation in soil and their re-volatilization from soil were performed. Calculations were carried out for the simplified environmental configuration consisting of one atmospheric layer (representing surface atmospheric layer in the real environment) and five soil layers of different thickness (Figure D.1).

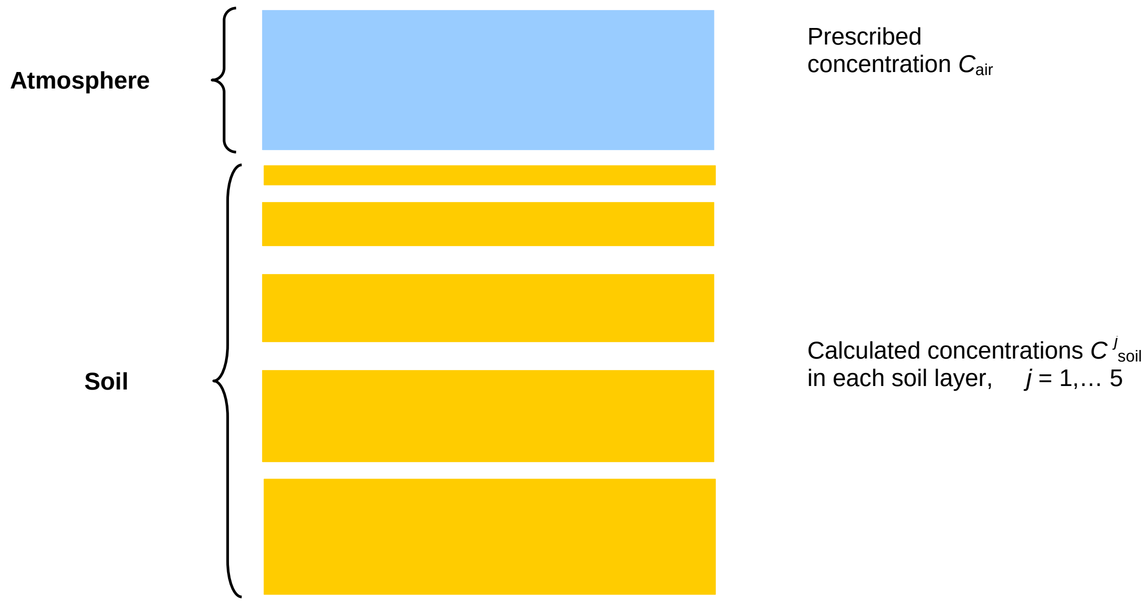

Figure D.1. *Simplified model of the environment used in sensitivity study of selected soil processes*

In simulations concentration (C_{air}) in the atmosphere was prescribed at some conventional level and then soil concentrations in all five soil layers (C^{j}_{soil}) were computed (more detailed description of numerical experiments is given below).

Modeling was carried out with the use of the soil module of the MSCE-POP model (the description can be found on http://www.msceast.org/pops/media.html). Initially it was taken from [*Jacobs and van Pul*, 1996] and based on the theory of [*Jury et al.*, 1983].

According to this scheme, a pollutant entering soil from the atmosphere is distributed between the gaseous (f_{air}), liquid (f_{liquid}) and solid (f_{solid}) soil phases in accordance with equilibrium coefficients K_{AW} and $f_{OC}K_{OC}$, hereby the equilibrium is set up immediately. At present the scheme is complemented with the fraction of dissolved organic matter (f_{DOC}) and with the fraction of the chemical non-equilibrium sorbed by solid phase ($f_{non\text{-}equil}$) or low available with individual degradation rate (Fig. D.5).

The share of a substance sorbed by DOC is calculated by the partition coefficient of equilibrium partitioning between DOC and the dissolved phase $f_{DOC}K_{DOC}$. In this context it is assumed that the DOC fraction is 1% of total organic matter in soil $f_{DOC} = 0.01 f_{SOM}$. K_{DOC} is assessed through the linear correlation between logarithmic K_{DOC} and K_{OW} has been determined for the majority of POPs. These dependences obtained by *J.Poershman and F.D.Kopinke* [2001] for PAHs and PCBs are respectively:

$$\log K_{DOC} = 0.98 \log K_{OW} – 0.39$$

$$\log K_{DOC} = 0.93 \log K_{OW} – 0.54.$$

Note that the pollutant associated with DOC is transported with the soil solution.

According to model assumptions the solid non-equilibrium sorbed fraction is sorbed by 70% of soil organic matter. The rest organic chemical is equilibrium sorbed by the remaining 30% of soil organic matter. The exchange between these phases takes place according to the first order kinetic equation with characteristic time $T_{non\text{-}equil,50}$ = 1 year. It is also assumed that the non-equilibrium sorbed fraction degrades "slowly". Its degradation is practically coincides with the degradation rate of humus itself with half-life 25 years. A pollutant equilibrium sorbed by SOM is "rapidly" degraded with the rate constant depending on an individual pollutant.

The scheme of a pollutant distribution between different soil components is shown in Figure D.2.

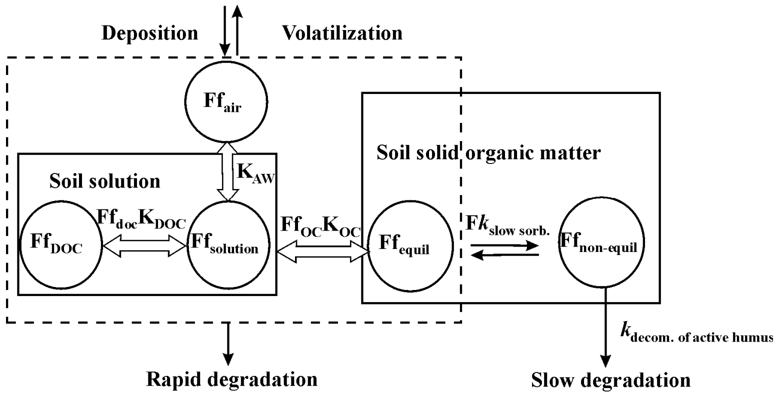

Figure D.2. *Model realization of POP partitioning between soil components and its degradation*

Following the scheme used, the pollutant migration over the soil horizon is conditioned by diffusion processes in the liquid and gaseous phase and by the transport of the real dissolved and sorbed to DOC fractions of a pollutant together with the liquid flow J_w. The vertical soil profile is represented by 5 calculation layers with boundary on (from top to bottom) 1) - 0.01, 2) - 0.05, 3) - 0.2, 4) - 0.8 and 5) - 3 cm.

The general formulation of the numerical problem was as follows. PCB-153 was selected as a characteristic POP, which physical-chemical properties were used in the experiment. This is due to the fact that the properties of this indicator congener are often used for calculations of the long-range transport of PCB mixture [*Pekar et al.*, 1998].

Besides it was demonstrated [*Shatalov et al.*, 2001] that soil is the most important accumulating compartment in calculations of PCB transport. Physical-chemical properties of PCB-153 at temperature 25^0C can be found in [*Shatalov et al.*, 2001]. Modeling was performed at soil organic carbon content f_{OC} = 5% typical of usual chernozem. The wet precipitation flux was assumed equal to J_w=10 cm/year.

In calculations two periods were considered – the accumulation time (5 years), during which PCB atmospheric concentration was 1 ng/m^3 and the clearance interval with air concentration assumed equal to zero. It was considered that pollutant input to soil takes place only due to gas exchange with the atmosphere. The calculations resulted in the profile of pollutant vertical distribution. This profile allows drawing conclusions about the penetration depth variation and about the dependence on the involvement to the model of the considered processes.

D.2. Evaluation of the effect of POP fraction sorbed by dissolved organic matter

To assess the DOC effect on POP transport, the calculation results with and without consideration of DOC sorbed fraction are considered below (Fig. D.3).

The comparison of the curves depicted in Figure D.3 indicates that the consideration of DOC phase increases the pollutant concentration in soil as much as 1.75 times during the accumulation period (5 years). It is explained by more intensive transport of a pollutant sorbed on DOC together with the water flow.

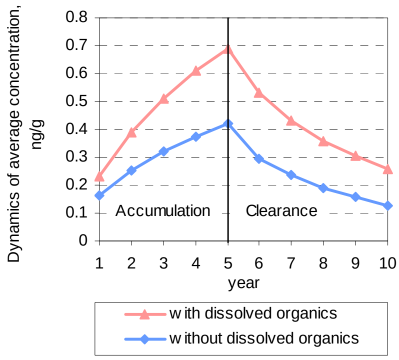

Figure D.3. *The comparison of calculation results of POP accumulation in soil and soil clearance with and without DOC consideration*

This process also significantly affects pollutant distribution down to soil profile. As evident from Figures D.4.a and b, the consideration of DOC phase slightly increases the depth of POP penetration. For example, by the end of 5^{th} year the concentration in the third layer (Fig. D.4.a) is 5 times higher than that obtained without DOC phase (Fig. D.4.b).

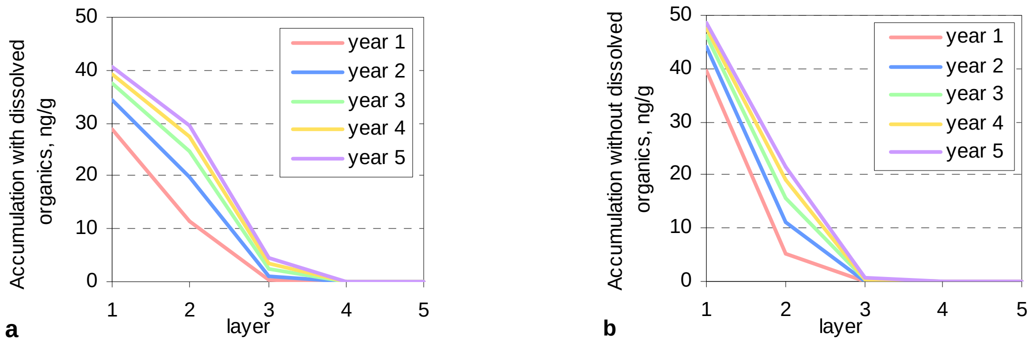

Figure D.4. *POP concentrations in the soil layers (1-5) during the accumulation period (5 years). Calculations with (a) and without (b) DOC consideration*

The dynamics of vertical profile within the clearance period is demonstrated by Figure D.5. Calculations show that at the stage of clearance the concentration of DOC phase considerably slows down soil clearance (Fig. D.5.a and b). With the consideration of DOC phase (Fig. D.5.a) as before the concentration in the 3^{rd} layer is 5 times higher than that obtained without DOC consideration (Fig. D.5.b).

Thus the numerical experiment demonstrated that the consideration of POP sorption by dissolved organics enhances POP migration down to soil profile and influences their accumulation in soil.

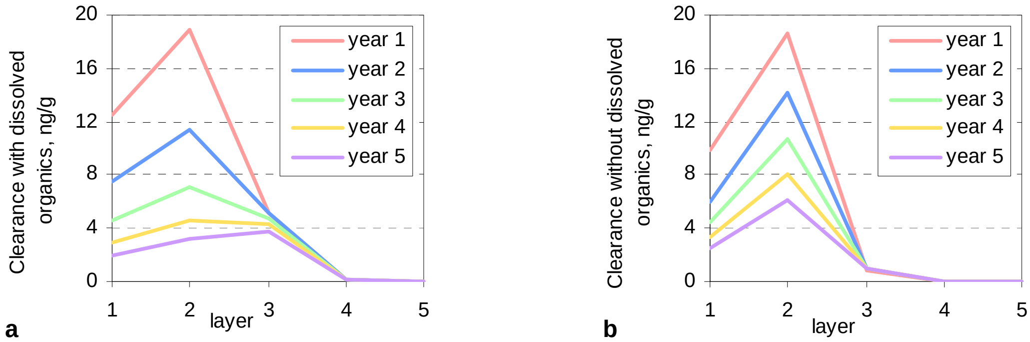

Figure D.5. *Pollutant concentrations in soil layers (1-5) during clearance period (5 years). Calculations performed with (a) and without (b) DOC consideration*

D.3. Evaluation of the effect of non-equilibrium sorbed POP fraction

To evaluate the influence of non-equilibrium sorbed POP fraction the description of a kinetic process of redistribution between equilibrium and non-equilibrium soil fractions was added to the model. Calculation results with and without consideration of this fraction are presented by plots in Figure D.6. During 5-year accumulation period with the consideration of this fraction at first the process proceeds slower but by the end of the period it is slightly more rapid than without the consideration of this fraction.

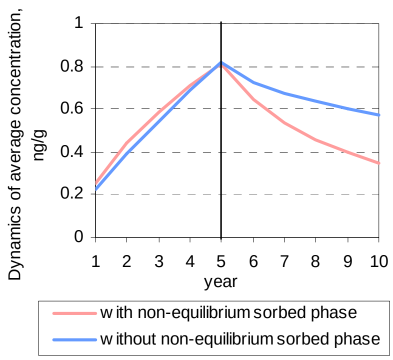

Figure D.6. *The comparison of calculation results with and without consideration of non-equilibrium sorbed POP fraction*

An additional calculation run of PCB accumulation during 20-year's period shows that the consideration of the low available fraction leads to a tangible increase of soil capacity resulted from the low intensity of degradation processes in this phase. As to the clearance period the consideration of the non-equilibrium sorption leads to slower decline of the pollutant concentration. In particular, by the end of the period the difference reaches 1.7 times.

The consideration of this fraction also influences the pollutant vertical distribution in soil (Fig. D.7). As follows from Figures D.7.a and b the consideration of the non-equilibrium fraction slightly increases the penetration depth of the pollutant. For instance, by the end of accumulation period (5th year), the POP concentration in the 3rd layer with the consideration of the non-equilibrium sorbed fraction (Fig. D.7.a) is somewhat higher than those obtained without its consideration (Fig. D.7.b). As to the 1st layer the pattern is reverse.

The dynamics of vertical profile of soil contamination during the clearance period is presented by plots in Figure D.8. The comparison of these plots indicated that the consideration of the discussed phase substantially decelerates soil self-clearance. It can be mentioned that with the consideration of this fraction the concentration in the 1st layer calculated with allowance of non-equilibrium sorption (Fig. D.8.a) is 5 times higher than without the fraction consideration (Fig. D.8.b).

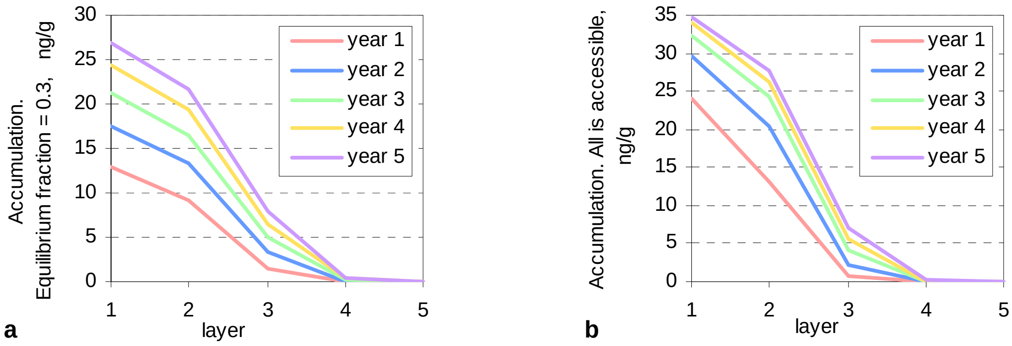

Figure D.7. *POP concentration in the soil layers (1-5) during the accumulation period (5 years). Calculations with (a) and without (b) consideration of the non-equilibrium sorbed POP fraction*

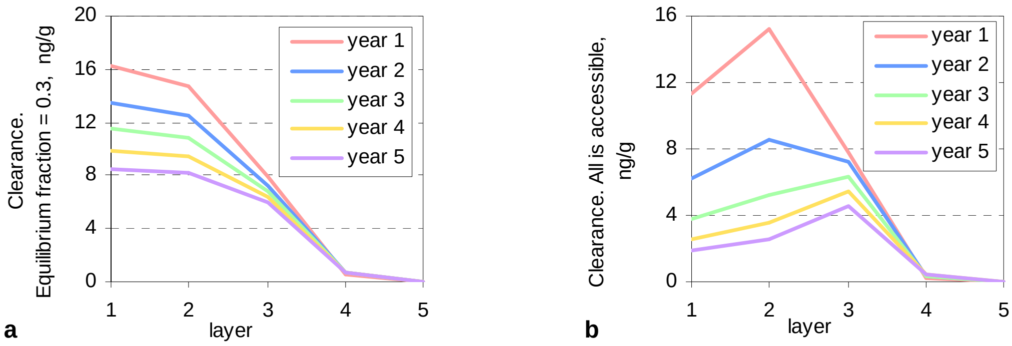

Figure D.8. *POP concentrations in the soil layers (1-5) at the stage of clearance (5 years). Calculations with (a) and without (b) consideration of the low available fraction*

These results are in agreement with the literature data concerning the delayed self-purification of soil contaminated with POPs and with long preservation of the aged POP residues [*Alexander*, 1994], as well as with the results of durated revolatilization of POPs from soil [*Duyzer, van Oss*, 1997].

Thus the consideration of kinetics of POP sorption by particulate soil organic matter appreciably changes the pollutant vertical distribution, particularly during the clearance period, what increases this period substantially.

D.4. Model refinement

On the basis of the above described investigations a scheme describing POP redistribution between different phases in soil and vertical transport with dissolved organics was included into MSCE-POP model description. This scheme includes the following POP phases in soil:

- gaseous (POP in the intercellular air);
- dissolved:
- sorbed on dissolved organic carbon;
- sorbed on readily accessible soil organics fraction;
- sorbed on potentially accessible soil organics fraction.

The model assumes the concept of instantaneous equilibrium between all phases but the last. The exchange between two last phases is described by a kinetic equation of first order.

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