

Executive summary

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 late 90th is comparable with anthropogenic emissions and became in some countries a main source of air contamination together with transboundary transport.

The description of behavior 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. The present Note is aimed at refinement of model description of some processes governing the behavior of POPs in soils.

Among processes having essential influence on POP fate in soil we mention here vertical transport with dissolved organic carbon and redistribution of POPs between different phases in soil.

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 adsorbed phase requires considerable time (usually from one to six months). POP desorption in the inverse direction is also non-uniform and delayed.

Proposals for 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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Introduction

Recently issues of environmental pollution by persistent organic pollutants attract an increasing attention of the world community. Problems of their long-range transport and accumulation in the environment and impact of these chemicals on human health are being studied within the framework of a great number of international organizations and programs such as EMEP, AMAP, HELCOM, OSPAR, WMO, UNEP and others.

Due to semivolatility of many POPs and their persistence in natural compartments (seawater, soil) these chemicals are accumulated in the compartments with further volatilization to air. It enhances the capability of such POPs to the long-range transport and makes natural media be their "accumulators" and potential pollution sources in the case of their anthropogenic emission reduction. It was demonstrated [Shatalov *et al.*, 2001] that as a result of PCB long-term accumulation by 1998 their volatilization from soil was about 50% of the total emission to the atmosphere. Thus the investigation of POP accumulation, transformation and transport is an important part of studies of their spreading in the environment.

On the other hand, high cost of measurements of POP concentrations in the environmental compartments necessitates using an integrated measurement-model approach for the assessment of the environmental pollution with these substances. From this viewpoint further development and improvement of the description of natural processes affecting POP long-range transport and accumulation in the environment are needed.

The object of the work is the analysis of literature data on POP transformation and migration in soil and making recommendations for model modification and more accurate description of these processes within

European region and the Northern hemisphere. The first part of the review is aimed primarily to evaluate the input of POP adsorption processes on accumulation and migration of these chemicals in soil.

For this purpose:

- Literature data on POP partitioning between different phases in soil (gaseous, dissolved, adsorbed by dissolved and particulate organic matter) are analyzed;
- Computational experiments were carried out, that demonstrated the effect of POP transport with of dissolved organic matter as well as redistribution with two fractions of sorbed POPs (equilibrium and non-equilibrium) on migration and accumulation of the chemicals in soil;
- Recommendations are suggested for integration of the last two processes to the MSCE-POP transport model.

This work has been done in accordance with the EMEP/MSCE work-plan approved by the Executive Body for the Convention on Long-Range Transboundary Air Pollution [ECE/EB.AIR/75, Annex VI, item 2.7 (b)].

1. Brief description of soil structure and properties

Soil is a product of complex interactions between soil-producing rock, topography, climate and living organisms. Soils are subdivided into mineral and organic ones depending on the parent bed (weathered rocks or peat). The soil profile has several layers (horizons) and it is formed during hundreds of years. The upper layer (horizon A, it is usually the domain of roots of weeds, the depth is 10-100 cm) is most rich in humus and microorganisms. In deeper layer (horizon B) their content is considerably less. The lowest horizon (C) is the underlying bed. The soil consists of aggregates resistant to water erosion. In their turn aggregates consist of a mineral part (quartz particles, clay minerals, metal oxides) and an organic part (mainly polymeric humic substances or humus), interstitial water with dissolved salts (soil solution) and soil air.

At present there are following approaches to the classification of soils:

1. According to granulometric composition (texture) of melkozem fraction (particle sizes less than 2 mm). Depending on the ratio of sand (2 - 0.06 mm), silt (0.06-0.002 mm) and clay (< 0.002 mm) particles the soils are divided on sand, clay sand, silt, loam, sandy clay loam, clay loam, sandy clay, silt clay, clay [Роуэлл, 1998].
2. According to soil types, which are characterized by a certain set of physical, physical-chemical and biological properties. They are tundra, gleyey-podzol, sod-podzol, sod, boggy, flood, grey forest, chernozem, chesnut, sierozem, brown, desert, oxisalts, groomsalts etc.
3. Every soil type is formed in a certain natural zone (tundra, taiga etc.) or landscape (marshes, bogs etc.) characterized by its hydrothermal regime and vegetation. Therefore vegetation type (or land use) is often indicated instead of soil type or land surface is divided into natural zones or landscapes as it is done in Tables 2 and 3. Soil cultivation as a result of agricultural activity drastically changes its properties, for this reason cultivated soils are set out to a separate group.

Table 1 demonstrates some main soil types and their characteristics.

There are many soil classifications with a different number of gradations. One of the problems of information collection for modelling is a determination of consistency between different classifications. Data on land use spatial distribution used in MCS-E can be found in MSC-E web-site: www.msceast.org.

Table 1. Some characteristics of main soil types of the former USSR

| Soil | pH _{KCl} | Humus in the upper horizon, % of total mass | Humus type, C _{gr} :C _{fk} |
|-------------------|-------------------|---|--|
| Tundra | 4 – 6 | 2.5 – 4 | 0.3 – 0.7 |
| Sod-podzol | 5 – 6 | 3 – 4 | 0.6 – 1.7 |
| Grey forest | 5 – 7 | 4 – 6 | 0.8 – 1.7 |
| Rich chernozem | 5 – 7 | 9 – 10 | 1.9 – 2.3 |
| Usual chernozem | 5 – 7 | 7 – 8 | 2.7 – 3.1 |
| Light chesnut | 5 – 7 | 2 – 5 | 1 – 1.4 |
| Brown semi-desert | 6 - 7 | 1 – 1.2 | 0.4 – 0.8 |

Note. More detailed characteristics can be found in [Орлов; 1996; Справочник агрохимика; 1990]

Table 2. Soil respiration and estimated half-life (T_{50}) of soil organic matter decomposition in comparison with its total stock in different natural zones or landscapes (according to [Paul, Clark, 1996])

| Natural zones and landscapes | Soil organic matter, t/ha | Soil respiration, t/ha | T_{50} , y |
|------------------------------|---------------------------|------------------------|--------------|
| Tundra | 204 | 0.6 | 345 |
| Boreal forests | 206 | 3.2 | 63 |
| Temperate grasslands | 189 | 4.4 | 43 |
| Temperate forests | 134 | 6.6 | 20 |
| Woodlands | 69 | 7.1 | 10 |
| Cultivated lands | 79 | 5.4 | 15 |
| Desert scrub | 58 | 2.2 | 26 |
| Tropical grasslands | 42 | 6.3 | 7 |
| Tropical lowland forests | 287 | 10.9 | 27 |
| Swamps and marshes | 723 | 2 | 365 |

Table 3. Values of phytomass decomposition intensity in the main natural zones [according to Родин & Базилевич, 1965 cited from Орлов & Безуглова, 2000]

| Natural zones | PDI |
|--------------------------|------|
| Arctic tundra | 3.5 |
| Shrubby tundra | 34.8 |
| Northern taiga | 8.6 |
| Southern taiga | 6.4 |
| Oak woods | 2.3 |
| Meadow steppe | 0.87 |
| Dry steppe | 0.36 |
| Desert scrub | - |
| Savannahs | 0.11 |
| Tropical lowland forests | 0.08 |

The solid phase of soil has high sorptive capacity in relation to many inorganic substances (especially to cations) and organic molecules. Specific soil organic matter (SOM, or soil humus) plays the key role in sorption of non-polar organic chemicals. The major part of SOM is particulate and consists mainly of humic substances – products of incomplete decomposition of vegetable and animal litter. Humic substances are specific polymer molecules of a complex molecular composition, containing different functional groups (mainly oxygen containing) imparting humic substance properties of weak acids. Soil organic matter is present as highly

dispersed particles (partially organic-mineral) with a developed network of micropores. As a result of dissociation of acid groups, the surface of polymer humic molecules is negatively charged. The humus surface has also non-polar regions (structurally similar to lipids, wax and resins) with aromatic structures and aliphatic lateral chains, which provide its high hydrophobicity. Soil humus has a large specific surface of 800 - 900 m²/g. Mineral soils in the upper layer contain 1-10% of SOM (recalculated to soil organic carbon about 0.5 - 5% respectively) by weight and organic soils – up to 100%. Approximately 1% of total organic matter is present as a dissolved organic matter (or dissolved organic carbon - DOC). About 20% of DOC is in the soil solution and represents the bulk of organic matter migrating along the soil profile. As it will be demonstrated below due to high sorption capacity and mobility, this small fraction of soil organic matter can essentially affect POP leaching (migration down to soil profile).

On the surface of solid particles soil microorganisms (microcolonies of bacteria and actinomycetes and hyphae of micromycetes) are located. Cell diameters of the majority of microorganisms (0.5 - 2 µm) enable them to penetrate only into meso- and macro-pores (0.2 - 100 µm). For this reason, substances

inside micro-pores ($< 0.2 \mu\text{m}$) are less accessible than those sorbed on particle surfaces. Under normal ambient conditions, the soil pores are equally occupied by soil solution and air, and soil air is similar to atmospheric one. When soil is flooded, microorganisms rapidly consume oxygen, and anaerobic conditions are set up. Any groups of microorganisms find their niche in each micro-aggregate. Therefore different species of microorganisms (aerobes and anaerobes, autotrophs and heterotrophs using as a growth substrate carbon dioxide or organic compounds respectively) are simultaneously present there. Bottom sediments in water reservoirs differ from the surface soil by low content of oxygen which is consumed by microorganisms while utilizing dead organic matter as well as by the availability of fermentation products (hydrogen, hydrogen sulfide, carbon dioxide) and by predomination of reduction processes.

Soil organic matter both of natural and anthropogenic origin is subjected to a continuous transformation under the action of biotic or abiotic factors. Microbial processes are the most important, and their intensity depends upon the quantity of accessible organic matter, nutrition elements (nitrogen, phosphorus, potassium, microelements etc.), aeration and hydrothermal conditions. There are several integral methods for the evaluation of microbial process intensities. For instance, it is possible to use such an indicator as **soil humus type**. It is determined by the relationship of humic and fulvic-acids ($C_{\text{ha}}:C_{\text{fa}}$) and indicates the extent of soil organic matter transformation (Table 1).

Table 2 presents other characteristics, which may be integral indicators of soil biological activity. It is soil respiration or calculated from this value the **half-life (T_{50}) of active protected soil humus**. These half-lives vary

substantially depending on growing vegetation, climate, and the cultivation extent. At the same time the half-life of very condensed old humus accounting for more than a half of SOM amount is about 2500 years [Paul and Clark, 1996]. The table shows that the T_{50} for soils of temperate climate is within the range from 10 to 40 years. Probably for model calculations it is possible to use T_{50} equal to 25 years.

The **indicator of phytomass decomposition intensity** (PDI), which defines the relationship of litter mass to yearly litterfall mass is suggested to use for indication of biological process intensities (Table 3).

2. Pathways of POP input to soil and levels of contamination

This review mainly considers the following classes of pollutants (some of them are presented in Fig. 1):

- Polychlorinated biphenyls (PCBs), tri- and more chlorinated isomers are mostly toxic and persistent among them.
- Polycyclic aromatic hydrocarbons (PAHs), with benzo[a]pyrene (B[a]P) as a characteristic compound of these chemicals.
- Dioxins/furans (PCDD/Fs) combining polychlorinated-p-dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). The most toxic congeners contain four atoms of chlorine in positions 2,3,7,8 (TCDD or TCDF) or in addition to them chlorine atoms in other positions.
- Chlorinated organic pesticides, among which most important are bis-(4-chlorophenyl)-2,2,2-trichloroethane (DDT), hexachlorobenzene (HCB) and α,β,γ -isomers of hexachlorocyclohexane (HCH).

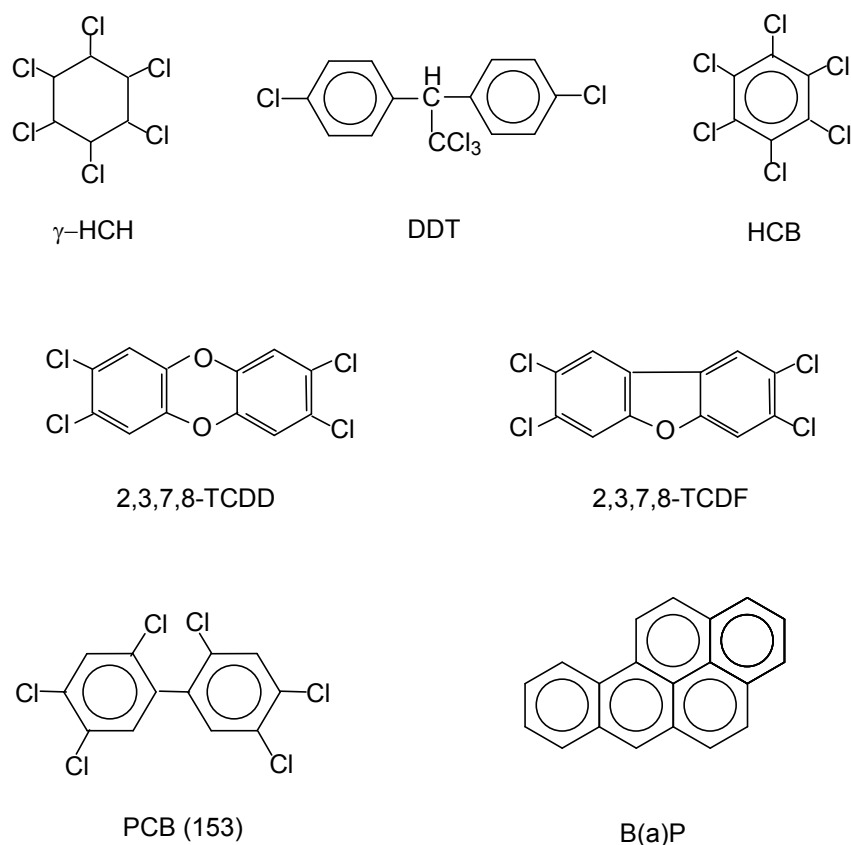


Figure 1. Some representatives of persistent organic pollutants

Airborne contaminants enter soil as a result of direct gas exchange between soil and air and as wet and dry depositions. Recently more attention is paid to the role of vegetation in POP accumulation in soil. Vegetation, in particular forests, intensively catch POPs from the atmosphere due to the developed surface and high content of lipids in tree bark and leaves as well as to the contact with huge volumes of air. Then chemicals enter the soil with washout from plant surfaces and with eroded cuticular waxes or leaf and tree litterfall. Therefore concentrations of some POPs (PCDD/Fs, PCBs, PAHs) in the forest soil can exceed substantially their concentrations in agricultural and meadow soil.

Current characteristic of POP levels in soil are presented in Table 4. It is evident from the table that the background concentrations of some classes of POPs are considerably

different. These values vary in the following limits (mg/kg): total PAHs – 0.002-186 (including B[a]P 0.001-0.13); total PCBs – 0.0001-1; total DDT – not detected–70 mg/kg; HCH - not detected–1; HCB - 0.00001-0.01; and total PCDD/Fs – 0.0000001-0.006.

Table 4. Current measured concentrations of some POPs in non-industrial soils

| POPs | Concentrations, $\mu\text{g}/\text{kg}$ | References |
|-----------------|---|--------------------------------|
| PAHs: Total* | 9 – 75 | <i>Milukaite, 1998</i> |
| | 260 | <i>Cousins and Jones, 1998</i> |
| | 60-300 | <i>Шпырбор, 2000</i> |
| | 60 – 320 | <i>Wilke and Amelung, 2000</i> |
| | 100 – 12,000 | <i>Trapido, 1999</i> |
| | 2 - 18.000 | <i>Kohl and Rice, 1998</i> |
| | 200-186,000 | <i>Krauss et al., 2000</i> |
| B[a]P | 0.1 – 3 | <i>Kohl and Rice, 1998</i> |
| | < 5 | <i>Шпырбор, 2000</i> |
| | 30 – 60 | <i>Milukaite, 1998</i> |
| | 1 - 130 | <i>Barkan et al., 2000</i> |

Table 4. continued

| POPs | Concentrations $\mu\text{g}/\text{kg}$ | References |
|--------------------------------------|--|--------------------------------|
| PCBs: Total* | < 0.1 | <i>Meijer et al., 2001</i> |
| | 20 – 30 | <i>Alcock et al., 1993</i> |
| | 0.3 – 30 | <i>Lead et al., 1997</i> |
| | 1 – 160 | <i>Krauss et al., 2000</i> |
| | 100 – 900 | <i>Бобовникова и др., 2000</i> |
| | 8 – 3100 | <i>Wilke and Amelung, 2000</i> |
| HCB | 0.008 | <i>Kohl and Rice, 1998</i> |
| | 0.1 – 0.2 | <i>Meijer et al., 2001</i> |
| Total HCH** | 0.3 – 0.5 | <i>Kim and Smith, 2001</i> |
| | 2.5 | <i>Meijer et al., 2001</i> |
| | nd-3 | <i>Bidleman, 1999</i> |
| | 0.08 – 3 | <i>Harner et al., 1999</i> |
| | 0.1 – 10 | <i>Kohl and Rice, 1998</i> |
| | 150 | <i>Finizio et al., 1998</i> |
| | 190 – 1100 | <i>Willett et al., 1998</i> |
| Total DDT*** | 0.5 | <i>Kohl and Rice, 1998</i> |
| | 1.4 – 2 | <i>Meijer et al., 2001</i> |
| | 1 – 4 | <i>Kim and Smith, 2001</i> |
| | 0.2 – 500 | <i>Harner et al., 1999</i> |
| | nd-2000 | <i>Bidleman, 1999</i> |
| PCDD/Fs, sum of toxic congener | 0.001 | <i>Cosins and Jones, 1998</i> |
| | 0.0005 – 0.2 | <i>Revich et al., 2001</i> |
| | 0.0003 - 2 | <i>Brzuzy and Hites, 1996</i> |

* - 20 - 32 main representatives,

** - all isomers;

*** - o,p'- and p,p'-isomers and their metabolites, mostly DDD and DDE.

3. POP distribution between soil components

The most important process affecting the rate of all other processes in soil (degradation, migration along the soil profile, volatilization etc.) is partitioning between soil components: air, soil solution and solid matrix. As usual POPs enter the soil solution and then they partitioning among the soil components. When initially POPs enter as a nonaqueous phase (oil and oil products, condenser oil, soot particles etc.) the process of a chemical solution and/or its distribution from the nonaqueous phase to the three soil components take place in parallel.

The content of contaminants in soil solution plays the key role in their fate in soil. Although a small part of a chemical remains in the liquid phase (for POPs less than a fraction of percent) just a dissolved chemical claimed to be degraded and dispersed in the environment. The dissolved POPs are consumed by plants and living macro- and microorganisms, volatilizes, and leache down to soil profile up to entering ground waters. In the absence of nonaqueous phase, the dissolved POP fraction is the main source of their input to the soil air whence it can volatilize to the atmosphere. A minor part of POPs migrates as a result of weathering. POPs are partly transported from soil to surface waters by runoff process as dissolved molecules and being adsorbed by soil particles in course of soil erosion.

3.1. Concept of equilibrium POP distribution between soil components

At present the concept of equilibrium distribution of organic chemicals between medium components is widely used for the mathematical description of their degradation and migration processes in soil and other environmental compartments. The equilibrium distribution means the reversible partitioning of the chemicals at equilibrium conditions between the components. Distribution of a chemical in soil is described with the help of partition coefficients, i.e. the ratios of equilibrium concentrations in soil air, soil solution and solid matrix. It is also assumed that the equilibrium is set up immediately. Figure 2 represents a diagram of the relationship of partition coefficients of an organic pollutant between three soil phases: gaseous, liquid and soil organic matter (the principal indicator of the chemical distribution in the soil matrix) and associated physicalchemical properties of the pollutant [Andren et al., 2000].

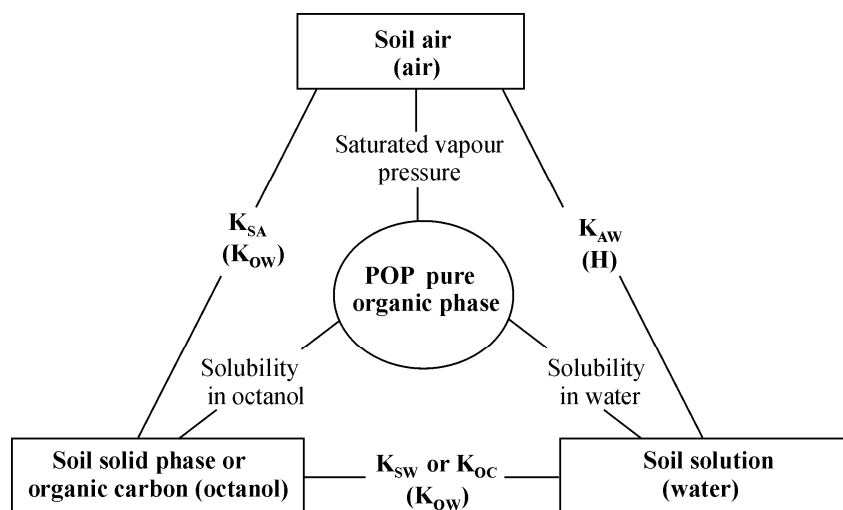


Figure 2. The diagram represents relation of partition coefficients describing POP partitioning between main soil components and respective physical-chemical properties of the chemicals given in brackets.

The following physical-chemical properties and related partition coefficients affect the distribution of a persistent organic chemical in soil:

- Saturated vapor pressure of a pure solid substance (P_s) or of its subcooled liquid (P_L) is an indicator of the substance volatility. For the main POPs P_s varies within $10^{-0.6}$ (monochlorobiphenyl) to 10^{-10} (OCDD) Pa. The majority of POPs belongs to semi-volatile compounds except for highly condensed PAHs (B[a]P etc.) and highly chlorinated (hepta- and octa-) congeners of PCDD/Fs. The chemical vapor pressure increases about 2 times with temperature increase by each 10°C .
- The indicator of volatility from the water surface is Henry's law constant (H) or the coefficient of air/water distribution K_{AW} determined as a relationship of concentrations in air and water ($K_{AW}=C_A/C_W$). This coefficient is connected with H by the equation: $K_{AW} = H/RT$, where R is the gaseous constant ($R=8.314 \text{ Pa}\cdot\text{m}^3/\text{mol}\cdot^{\circ}\text{K}$) and T is the temperature ($^{\circ}\text{K}$). Henry's law constant can be obtained experimentally but it is often calculated by the relationship $H=P_L/S_L$ where S_L is water

solubility of the chemical. For the main POPs, Henry's law constant varies from 1.86×10^{-5} (B[a]P) to 0.67 (HCH) $\text{Pa}\cdot\text{m}^3/\text{mol}$ [Cousins *et al.*, 1999; Andren *et al.*, 2000]. Thus, for many POPs the possibility to volatile from the water surface is rather high. Note that Henry's law constant strongly depends upon temperature, it should be taken into account in the simulation [Cousins *et al.*, 1999; Shatalov *et al.*, 2000].

- Partition coefficient between n-octanol and water (K_{OW}) is an indicator of a compound hydrophobicity and its capability to be accumulated in natural organic phases (soil organic matter, microorganisms, algae, plants and higher organisms). It is shown that living and nonliving organic matter has similar sorption properties relative to non-polar organic pollutants and very similar absorption capability with octanol. In spite of low content of the specific organic matter in the majority of soils, the soil organic phase exhibits high specific storage capacity for hydrophobic organic contaminants. Therefore K_{OW} is most important in the description of POP behaviour in soil. K_{OW} values for many

POPs can be found in [Mackay *et al.*, 1992 a,b,c]. They vary from $10^{3.7}$ (γ -HCH) to $10^{10} - 10^{13}$ (OCDD). According to UNEP standards, POP criterion in the environment is the $\log K_{OW} > 5$, however HCH isomers with $\log K_{OW}$ within the range of 3.7-3.8 are also of interest due to their wide spread in the environment. K_{OW} dependence on temperature is not strong [Andren *et al.*, 2000].

- Partition coefficient between octanol and air (K_{OA}) is determined by the relationship of chemical concentrations in octanol and air ($K_{OA} = C_O/C_A$) and it is used as an indicator of partitioning between air and condensed organic phase and consequently it determines a substance capability to volatile from soil. Its use is also based on the assumption that sorption properties of soil organic matter are similar to those of octanol. This coefficient is used for the description of partitioning between solid and gas phase of soil as well as between soil and the atmosphere. K_{OA} value for the majority of POPs is very high and it varies from 10^8 to 10^{10} at 25°C. These coefficients can be measured or estimated from the ratio K_{OW}/K_{AW} providing that these two coefficients were determined at the same temperature.
- The K_{OA} is directly connected with the soil - air partition coefficient of pollutant K_{SA} which is determined as the ratio of solid phase to air concentrations ($K_{SA} = C_S/C_A$). It is more convenient to determine this value through the relationship $K_{SA} = K_{SW}/K_{AW}$. Recently direct measurements of K_{SA} have been made for a range of POPs, and excellent agreement was found between the measured and calculated values, suggesting that this approach is valued [Hippelein and McLachlan, 1998]. K_{SA} values vary from

10^4 (HCB) to 10^{10} (OCDF). The coefficients K_{OA} and K_{SA} also strongly depend on temperature. Both coefficients K_{SA} and K_{OA} drastically decrease with temperature increase and correspondingly POP volatilization from the soil surface increases. The connection between K_{SA} and soil moisture is established as well: $\log K_{SA}$ linearly increases with decrease of relative soil moisture from saturation to 25%. Beyond this point, the rate of this increase in K_{SA} accelerates sharply [Hippelein and McLachlan, 2000].

- The linear relationship between the K_{OW} and partition coefficients of a great range of organic contaminants between particulate and liquid phases of soil (K_{SW}) is established. It is determined as the relationship of POP concentration in the solid liquid phase and soil solution ($K_{SW} = C_S/C_W$). In addition a linear correlation between K_{SW} and organic matter content in soil or bottom sediments is also quantified. For this reason the organic carbon partition coefficients (K_{OC}) are often used to characterize adsorptive properties of POPs in respect of soil organic matter carbon and soil solution. K_{OC} is K_{SW} normalized to the unit of soil humus and determined by the next equation:

$$K_{OC} = K_{SW}/f_{OC},$$

where f_{OC} is the humus fraction in weighted fraction of organic carbon relative to the mass of the soil solid phase. K_{OC} is often used for modelling the POP migration and transformation rate in the environmental compartments. The K_{OC} can be determined experimentally or estimated from K_{OW} by regression equation:

$$K_{OC} = a \cdot K_{OW}.$$

According to *S.W.Karikhoff et al.* [1979] and *R.Seth et al.* [1999] the regression coefficient a equal 0.4 and scattering of K_{OC} is within 2.5 orders of magnitude. These values were obtained for a set of chemicals including the majority of POPs. It was also indicated that for PCBs and PAHs the relation between K_{OC} and K_{OW} is not quite linear in particular for the most hydrophobic substances of these groups. It is explained by slow establishment of thermodynamic equilibrium between dissolved and adsorbed fractions. Therefore real K_{OC} values estimated for highly hydrophobic POPs in field soils can differ from the calculated ones by several orders of magnitude [*Krauss and Wike, 2001*].

An important property of soil solution influencing POP partitioning between soil phases is the presence of dissolved organic carbon (DOC). The relation of concentrations of POPs sorbed by DOC and dissolved as actual molecules is characterized by the partition coefficient K_{DOC} . A close 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:

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

$$\log K_{DOC} = 0.93 \log K_{OW} - 0.54$$

Since the regression dependence between K_{DOC} and K_{OW} for PCBs is in a wide range of $\log K_{OW}$ (from 3 to 8), the last equation obviously can be used for the assessment of K_{DOC} for other POPs. In particular $\log K_{DOC}$ measured value for DDT - 5.15 [*Schulten, 1999*] is consistent with this equation.

POP sorption by DOC appreciably changes the relationship between the mobile and

sorbed fraction of a pollutant in soil. It results in a significant increase of a pollutant concentration in soil solution and, as a consequence, in deeper penetration of the pollutants into soil and in the increase of accumulated pollutant amount. Below (Section 4) we demonstrate the results of numerical calculations performed for the assessment of the effect of dissolved organic carbon on POP accumulation in soil and their revolatilization.

Knowing partition coefficients K_{SA} it is easy to assess POP concentrations in the soil solution at any level of contamination and SOM content. Since the pollutant concentration in the soil solution is the most important characteristic defining its behaviour in soil, characteristic POP concentrations in soil solution were calculated at three contamination levels in mineral soils (Table 5). Further (Part 2) this database will be used for analyzing processes of POP microbial degradation in terms of the excess of the threshold level about 1 $\mu\text{g/l}$.

Thus, in according to concept of equilibrium distribution, the relation of an organic pollutant concentration in the soil solid and liquid phase is constant at any moment. This statement is a special case of Freundlich's equation describing the sorption of a substance by a sorbent (in this case by soil organic matter). It is valid only for low concentrations of pollutants when the sorbent is far from being saturated and the concentration of a pollutant in the solid phase is directly related to its concentration in the solution.

Table 5. POP concentrations in soil solution (C_p) at their three concentrations in soil (C_s) calculated from K_{OC}

| POPs | C_p ($\mu\text{g/l}$) at different levels of C_s | | |
|----------------------------------|--|-----------------|------------------|
| | 10 mg/kg | 1 mg/kg | 0.1 mg/kg |
| <u>COP</u> | | | |
| γ -HCH | 100 – 1000 | 10 – 100 | 0.1 – 1 |
| α -HCH | 77 – 770 | 8 – 77 | 0.8 – 8 |
| HCB | 2 – 5 | 0.2 – 2 | 0.02 – 0.2 |
| DDT | 0.5 – 5 | 0.05 – 0.5 | 0.005 – 0.05 |
| <u>PAH</u> | | | |
| B[a]P | 0.0006 – 1 | 0.05 – 0.5 | 0.005 – 0.05 |
| <u>Homologous group of PCBs</u> | | | |
| Mono-chlorine | 13 – 350 | 1 – 25 | 0.1 – 3 |
| Di-chlorine | 0.3 – 250 | 0.03 – 25 | 0.003 – 2.5 |
| Tri-chlorine | 0.001 – 400 | 0.06 – 63 | 0.006 – 6.3 |
| Tetra-chlorine | 4 – 10 | 0.5 – 8 | 0.005 – 0.8 |
| Penta-chlorine | 0.04 – 20 | 0.004 – 5 | 0.0004 – 0.5 |
| Hexa-chlorine | 0.005 – 7 | 0.0005 – 0.7 | 0.00005 – 0.1 |
| Hepta-chlorine | 0.003 – 0.2 | 0.0003 – 0.2 | 0.00003 – 0.03 |
| Octa-chlorine | 0.02 – 0.3 | 0.002 – 0.04 | 0.0002 – 0.002 |
| Nona-chlorine | 0.003 – 0.03 | 0.0003 – 0.003 | <0.0001 – 0.0003 |
| Deca-chlorine | 0.003 – 0.03 | 0.0003 – 0.003 | <0.0001 – 0.0003 |
| <u>Homologous group of PCDDs</u> | | | |
| Mono-chlorine | 2 – 63 | 0.2 – 6 | 0.02 – 0.6 |
| Di-chlorine | 0.01 | 0.01 | 0.002 – 0.01 |
| Tri-chlorine | 0.2 – 0.4 | 0.02 – 0.2 | 0.002 – 0.02 |
| Tetra-chlorine | 0.02 – 4 | 0.002 – 0.4 | 0.0002 – 0.04 |
| Penta-chlorine | 0.03 – 0.2 | 0.002 – 0.2 | 0.0002 – 0.03 |
| Hexa-chlorine | 0.008 – 0.02 | 0.0008 – 0.008 | <0.0001 – 0.0008 |
| Hepta-chlorine | 0.001 | 0.0003 – 0.001 | <0.0001 – 0.0005 |
| Octa-chlorine | 0.001 | 0.0001 – 0.001 | 0.00001 – 0.0003 |
| <u>Homologous group of PCDFs</u> | | | |
| Mono-chlorine | 0.5 – 5 | 0.05 – 0.5 | 0.005 – 0.05 |
| Di-chlorine | 0.2 – 4 | 0.02 – 0.4 | 0.002 – 0.04 |
| Tri-chlorine | 0.2 – 3 | 0.02 – 0.3 | 0.002 – 0.03 |
| Tetra-chlorine | 0.02 – 0.5 | 0.006 – 0.3 | 0.006 – 0.03 |
| Penta-chlorine | 0.05 – 0.1 | 0.005 – 0.05 | 0.0005 – 0.005 |
| Hexa-chlorine | 0.004 | 0.002 – 0.004 | <0.0001 – 0.0001 |
| Hepta-chlorine | <0.0001 – 0.002 | <0.0001 – 0.001 | <0.0001 – 0.0001 |
| Octa-chlorine | 0.0007 | 0.0007 | 0.0007 |

Notes: The concentrations are calculated for soil containing organic carbon from 0.5% to 5% at 22-25°C

3.2. POP sorption by dissolved organic matter and its role in the pollutant migration down to soil profile

As indicated above, POP sorption by dissolved organic matter is of a particular interest. DOC consists of specific polymeric humic compounds as well as non-specific compounds formed in the course of vegetable and living litterfall decay or exudates of microorganisms, animal or plants (sugar, amino acids, lipids etc.) [Zsolnay, 1996]. By the size particles the specific DOC approach to colloids (0.001 - 0.1 μm) and their mean molecular weight is 6364 [Schulten, 1999]. Due to the developed specific surface (on the average 3853 m^2/g) and high hydrophobicity, DOC possesses high absorbing capacity relative to different cations and organic compounds.

DOC exists in soil in three fractions. About 30% as highly resistant DOCI is inside micropores of size $< 0.2 \mu\text{m}$. 50% as average resistant DOCII is present in mezopores (0.2-6 μm) and 20% - as the most labile fraction DOCIII being in the soil solution. The last fraction and probably partly DOCII usually account for the major share of mobile organic matter migrating along the soil profile. DOCIII represents soil organic matter most accessible for microorganisms. It is separated by the method of soft extraction by light shaking of soil with 4mM CaSO_4 during a minute with a subsequent filtration through a filter with pores of 0.5-0.6 μm or by centrifugation [Zsolnay, 1996]. DOC content in soil varies widely depending on soil texture and hydrothermic conditions. DOC content reaches its maximum in summer and autumn and tens times decreases in winter. Table 6 presents data on water extractable DOC content in different soil profiles estimated in some investigations. They indicate that the content of water-extractable

DOC can vary within a wide range and it does not change substantially with depth, in particular within two upper horizons.

Table 6. The content of water extractable dissolved organic matter in different horizons of cultivated soils

| Investigation | Depth of sampling (cm) or horizon | Water extractable organic matter, mg/kg |
|---------------|-----------------------------------|---|
| 1 | A | 296 (134)* |
| | B | 50 (22) |
| | C | 37 (20) |
| 2 | 2.5 – 10 | 162 – 781 |
| | 10 – 17.5 | 178 – 659 |
| | 17.5 - 25 | 149 – 587 |
| 3 | 0 – 10 | 30 – 410 |
| | 10 – 30 | 30 – 460 |
| | 30 – 60 | 40 – 460 |
| 4 | 0 – 7.5 | 104 – 253 |
| | 7.5 – 15 | 93 – 240 |
| | 0 – 7.5 | 76 – 154 |
| | 7.5 – 15 | 113 – 213 |
| 5 | A | 9 (2) |
| | B | 10 (2) |
| | C | 7 (2) |
| 6 | 0 – 30 | 11 (3) |
| | 30 – 60 | 9 (2) |
| | 60 – 90 | 8 (3) |
| 7 | 5 – 10 | 26 (11) |
| | 20 – 55 | 17 (6) |
| | 110 – 115 | 23 (5) |
| 7** | 5 – 10 | 31 (5) |
| | 20 – 55 | 25 (5) |
| | 110 - 115 | 14 (2) |

* in brackets standard deviations are given;

**meadow soil.

Mobile organic matter is determined in water collected in different depths of a soil. The quantity of a mobile organic matter is the most stable value. In forest soils, for which the majority of measurements were made, its value in the horizon B is 5 times lower than in the horizon A, and in the horizon C it further declines about 2 times. The content of mobile

organic substances in forest soils varies in the horizon A within the limits of 5-70 (in some case to 440), in the horizon B 2-24 and in the horizon C 1-2 mg/l [Zsolnay, 1996].

Non-specific dissolved organic compounds (primarily decomposition products of natural organic compounds – sugar, amino acids and fatty acids) are very labile. Rate constants of their decomposition reach $0.006-0.12\text{ d}^{-1}$, that approaches the rate constant of glucose decomposition. The rest of DOC (polymeric humic compounds) is decomposed slower ($k=0.0005\text{ d}^{-1}$) [Zsolnay, 1996]. Thus the bulk of DOC is sufficiently resistant to microbial transformations and its half-life is about 3.8 years.

The importance of DOC for POP removal increases for highly lipophilic compounds. It is explained by the elevated strength of interactions between substances and polymeric molecules. It is calculated that presence of 10 mg DOC per liter of soil solution positively affects on profile migration of chemicals with solubility less than 0.02 mg/l [Hutchins *et al.*, 1985]. It is demonstrated by gel filtration that DOC accelerates migration of many highly hydrophobic chemicals [Madhum *et al.*, 1986]. It is proved that leaching of phenanthrene and DDT in soil is accelerated at DOC concentration of 80 mg/kg [Magee *et al.*, 1991; Ballard, 1971].

K.Kalbitz and P.Popp [1999] found out that β -HCH content in water extracts from contaminated soil in the basin of the Mulde River closely correlated with DOC content and both values varied with seasons reaching maximum in summer and autumn. β -HCH content in the soil solution deviated from 0.01 to 2.2 $\mu\text{g/l}$ and in some cases exceeded its solubility in water as much as 10-20 times [Kalbitz and Popp, 1999].

Obviously just sorption by dissolved organic matter can explain the noticeable migration of

highly hydrophobic and poorly dissolved POPs over soil profiles, while the bulk of POPs is usually localized in the soil top layer (0-5 cm). For instance, in some forest soils far from pollution sources, dioxins were found at the depth up to 1 m [Brzuzy and Hites, 1995]. In different background soils of Lithuania, B[a]P was detected till the depth of 20 cm and deeper [Milukaite *et al.*, 1998]. In laboratory experiments with 10 cm soil columns continuously washing with water the content of 2,3,7,8-TCDD and DDT in the eluate was about 0.7 mg/l, and concentrations of both chemicals at the soil depth of 2.5 cm was appreciably higher than it can be expected on the base of their equilibrium partitioning between the solid and liquid phase without regard for POP migration with DOC.

Thus, it is necessary to make allowance for POP sorption by DOC for the correct consideration of their profile migration in soil. For approximate estimates it may be considered that DOC accounts for 1% of total soil organic matter [Zsolnay, 1996].

3.3. Sorption-desorption interactions between POPs and soil solid phase

In the context of high storage capacity of the soil solid phase for POPs, the processes of their sorption and desorption to soil solution are of a particular importance. POP sorption is realized primarily due to low energetic bonds (Van der Waals, hydrogen) as well as due to hydrophobic interactions of POPs with the non-polar parts of SOM through partitioning mechanism. In view of lack of chemically active or ionized groups in POP molecule the role of ionic or highly energetic (covalent) bonds is not essential for their sorption. These bonds can make a noticeable contribution to the pollutant binding only after

their microbial or chemical degradation (for instance, hydroxylation of molecules).

Recently more and more evidences appear that real sorption-desorption interactions between POPs and soil differ drastically from equilibrium ones. It is connected with SOM 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 SOM micropores, the establishment of thermodynamic equilibrium between the dissolved and adsorbed phase requires considerable time (usually from one to six months). POP desorption in the inverse direction is also non-uniform and delayed.

There are several investigations illustrating these processes. Sorption of the major part of pyrene and phenanthrene in soil suspension performed for the first 4 days, however full equilibrium distribution in the system was established only after 2 or 6 months [Braidà *et al.*, 2001]. Studying of sorption of HCB and three PCB congeners (mono-, di- and hexachlorinated) by sediments revealed a biphasic configuration of this process [Lick *et al.*, 1997]. After the relatively rapid (hours) step of these compound partitions between water and suspended sediment particles, a slow process of increasing sorption with almost equal rates for all the compounds started. In a month the partition coefficients increased approximately by 0.4-0.5 units, and finally these values were an order of magnitude higher than initial ones. Desorption kinetic of the chemicals was similar: a rapid process followed by slow desorption. Hereby full desorption of HCB from sediments with water required 1 month and HxPCB – 1 year [Lick *et al.*, 1997].

Desorption rate constants of some main POPs (PCBs and PAHs) from contaminated field soils and sediments were determined in

various investigations. For this purpose, the contaminants were extracted by water with some additions of solvents or floating resins Tenax and XAD for the imitation of biological object impacts. Desorption of the majority of POPs proceeded primarily in two steps and it was described by the introduction of readily and slowly desorbing fractions of the solute. Desorption rate constant of the readily desorbed fraction was 10^{-2} - 10^{-1} and the slowly desorbed one – 10^{-3} d⁻¹. For modelling purposes the first (ready) fraction can be considered as equilibrium adsorbed POPs while the characteristic exchange time (T_{50}) for the second (slow) fraction may probably be taken equal to 1 year. The quantity of the first fraction depended on pollutant hydrophobicity and residence time in soil. For example, in sediments of New York harbor (total content of PCB – 0.5 and PAH - 5 mg/kg), the readily extracted fraction for PCB-18, 49, 52, 101, 138 and 180 reached 60, 50, 10, 5, 1 and less than 1% respectively [Lamoureaux and Brownawell, 1999]. Meantime, in the subsurface layer of long aged sediments, the content of the readily desorbed fraction was considerably lower: 10-20% for PCB and 2-3% for PAH [Ten Hulsher *et al.*, 1999]. M.Krauss with coauthors [2000, 2001] studied 25 samples of urban and rural soils in Germany contaminated with POPs at the background levels (total content of PCBs – 0.001-0.16 and PAHs – 400-186 mg/kg). They indicated that the readily extracted fraction of PCB containing 2, 3, 4, 5, 6, 7 and 8 chlorine atoms was respectively 80±20, 62±20, 55±15, 35±10, 30±15, 25±10 and 10±5%. Meanwhile, the same value for naphthalene, phenanthrene, anthracene, pyrene, and benzo[a]pyrene was 55±10, 53±7, 51±5, 40±10, and 10±5% respectively. It was also demonstrated for PCB-153 and B[a]P that at the background pollution the relative content of readily desorbed fraction was little dependent on pollutant concentrations. Contrary to PAHs,

for which did not exhibit any significant relation between the readily extractable fraction and SOM content, the weak inverse correlation between these values for PCBs was established. It was also demonstrated that the readily available fractions of all the studied POP representatives corresponded to their availability to earthworms [Krass *et al.*, 2000]. Close correlation between their bioaccumulation factors BCF obtained for PCBs and PAHs and the content of the chemicals extracted by methanol-water (1:1) mixture was established [Kraus *et al.*, 2000; Kraus and Wilke, 2001; Lamourex and Brownawell, 1999]. Close correlation has been demonstrated between readily extractable (with Tenax) fraction of DDT and its accumulation in earthworms [Morrison *et al.*, 2000]. The amount of readily extractable DDT reached 35+/-10% in old contaminated agricultural soils (49 year after application, total DDT 19 mg/kg) [Morrison *et al.*, 2000].

Strong connection between the amount of readily extractable POP fraction and their bioavailability was proven in a number of publications. However, the amount of the fraction available to various biological objects differed substantially. Contrary to plants, which consume POPs only from the soil solution, soil invertebrates, for example, absorb slightly greater quantity of the chemicals due to a closer contact with soil organic matter when soil moves along the gut [Kraus *et al.*, 2000; Kraus and Wlicke, 2001; Lamourex and Brownawell, 1999]. The most complete deliverance of the adsorbed chemicals takes place under the impact of microorganisms. The relationship of fractions available to plants, earth invertebrates and microorganisms can be roughly represented as 1:10:100 [Chiou *et al.*, 2001]. Some microorganisms possess an elevated capability to decompose adsorbed POPs due to the secretion of extracellular exudates with

surfactant properties. Biomass of microorganisms and experimental conditions are also important. For example, microorganisms decomposed by 10-15% more POPs in the soil suspension than when incubated in soil, what can be explained by breaking soil aggregates. An addition, large biomass of some specific microorganisms introduced directly into soil can increase POP bioavailability by 25-40 % and more [Schwartz and Scow, 1999]. Obviously the pollutant concentration also can be of a significant importance since soil adsorptive capacity is limited.

As it was indicated for a number of POPs, the pollutant fraction available to microbial degradation is actually close to the readily extractable one and equally reduced with time after the chemical introduction. For instance, after the input of phenanthrene (2 mg/kg) to sterile samples of mineral and peat soils, the quantity of the water-extractable chemical virtually coincided with its availability to degrading microorganisms. In 2 months, the readily extractable fraction of phenanthrene in the mineral soil reduced from 85 to 60% and in the peat soil – from 70 to 35% [White *et al.*, 1999]. Equal reduction of the chemical bioavailability and its readily available fraction were obtained in native soil after introduction of phenanthrene at a very low concentration (0.07 mg/kg). However, in this case the readily extractable fraction of phenanthrene reduced up to 10% after a month [Schwartz and Scow, 1999].

Some microorganisms are capable to extract greater quantities of a chemical than it could be expected on the basis of equilibrium partitioning between liquid and solid phases. However it is more characteristic of the least hydrophobic POPs, e.g. biphenyl [Freg *et al.*, 2000]. Meantime there are many evidences that a certain part of slowly disappearing (or potentially available) POPs remains in soil

even in the presence of inoculated degrading microorganisms.

In addition to potentially available extractable POPs, unextractable (bound) POP residues are usually accumulated in soil. It has been demonstrated in laboratory experiments with different ^{14}C -labeled POPs. While the bound ^{14}C -residues were accumulated as in sterile and native soil samples, their content in the later variant (at presence of soil microorganisms) was significantly higher. For instance, in 17 months after the input of ^{14}C -phenanthrene, pyrene or B[a]P to sterile soil (initial organic pollutant concentrations – 10 mg/kg) it was possible to extract by water with floating Tenax of 80, 70 and 23% of the introduced respective substances. Up to 15, 21 and 54% of the POPs respectively was extracted only by organic solvents and besides 5, 9 and 23% was not extracted at all [Northcott and Jones, 2001, 2001a]. As it is indicated in a number of works, the unextractable fraction of POPs formed in the absence of microorganisms (sterile conditions) consists primarily of their unchanged parent molecules [Johnson *et al.*, 2001; Johnson and Weber, 2001]. When POPs are introduced to

native soil the accumulation of bound ^{14}C -residues was much higher due to the formation of chemically bound transformations products. In this case only some amount of bound POPs is present as parent molecules [Guthrie and Pfaender, 1998].

Similar results were obtained with pyrene (100 mg/kg) introduced to soil with 3.5% of organic carbon (Fig. 3) [Guthrie and Pfaender, 1998]. The formation of bound pyrene in the native soil (variant B) almost twice exceeded its accumulation in sterile soil (variant A). It proves that microorganisms participate in the binding process obviously through the formation of hydroxylated metabolites. In the variant B the rapid processes of pyrene degradation and binding completed mainly over a month. In 9 months in the soil with indigenous microorganisms only 2.4% of the chemical was mineralized, about 40% still present as original solvent extractable pyrene, and 20% transferred to a low available fraction (extractable only by a solvent). In variant C inoculated by degrading microorganisms, up to 30% of pyrene was mineralized and no solvent extractable pyrene left.

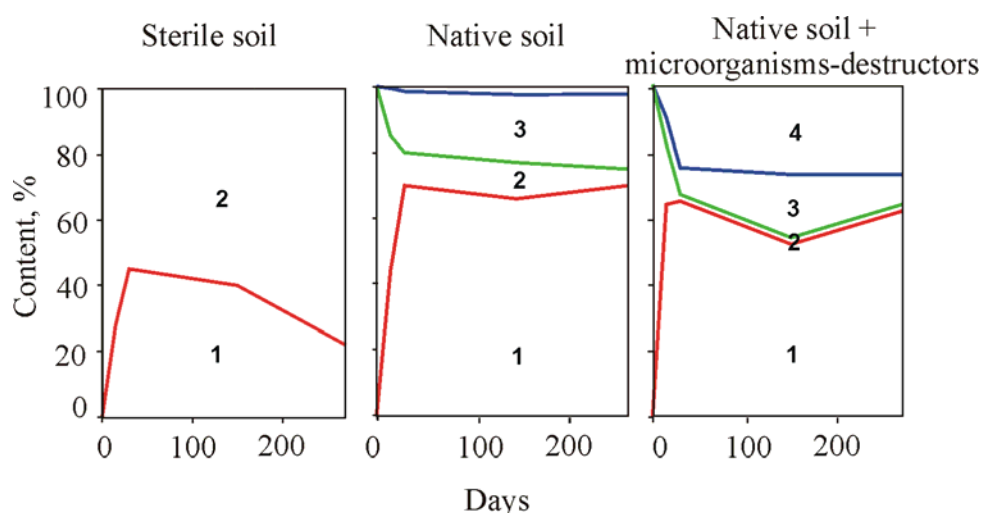


Figure 3. The content of ^{14}C -pyrene different fractions in soil [Guthrie and Pfaender, 1998]: 1 - bound ^{14}C ; 2 - extractable ^{14}C -pyrene; 3 - ^{14}C products of pyrene; 4- mineralized pyrene

Similar picture of inhomogeneity of POP sorbed by soil was found also in the analysis of their behaviour in the air/soil system. The laboratory experiments by *J.H. Duyzer and R.F. van Oss* [1997] carried out under conditions close to field ones taking place at the background air contamination of soils are of particular interest. In these experiments the concentration of the compound in 10 cm soil layer was about 2 – 3 $\mu\text{g}/\text{kg}$, which corresponds to about 10 $\mu\text{g}/\text{kg}$ after recalculation to the upper 3 cm layer where the bulk of the compound is accumulated. The obtained sorption of lindane by clear garden soil during 5 days occurred to be much larger than calculated on the basis of instantaneous equilibrium hypothesis [*Jury et al.*, 1983]. Good correspondence was got only for clear sand. During the subsequent re-emission period (5 days) 29% of totally sorbed chemical was volatilized from sand, 2.8% - from soil surface, 3.8 - from soil/sand mixture (1:1 or 4:1), and 3.9% - from grass. In the end of experiment 36% of lindane were extracted by solvents from sand and 28% - from soil.

Balance calculations show that the amount of the pollutant non-reversibly sorbed or degraded is 35% for sand and 68% for soil. In the course of similar experiment with phenantren, non-reversible sorption or degradation accounted for 35 and 70% for sand and soil, respectively [*Duyzer and van Oss*, 1997].

Modern ideas concerning different sorbed POP forms in soil and, their availability are schematically demonstrated in Figure 4. The forms of POPs in soil can be considered from different viewpoints: physical sense of sorption and its reversibility (C), availability to degradation and migration processes (B) and usual chemical analysis (CA) or fractionated analysis (FA) of the pollutants in soil.

First, after entering soil solution, POP is distributed between liquid phase (**dissolved** POPs) and solid matrix (primarily soil organic matter) through equilibrium partitioning mechanism and in accordance to partition coefficient $f_{OC} \cdot K_{OC}$. Hereby some amount of POP is **sorbed to DOC** in accordance to $f_{DOC} \cdot K_{DOC}$.

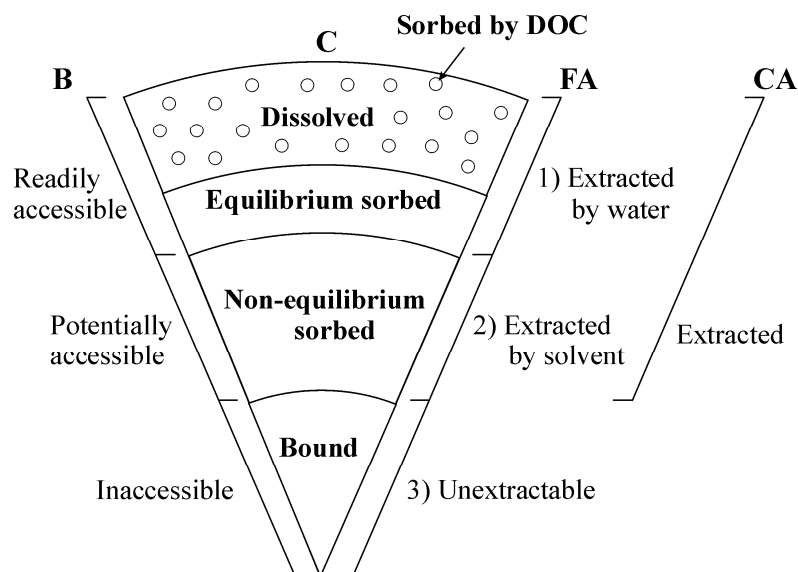


Figure 4. Schematic picture of a segment of soil particle surrounding by soil solution and of dissolved and sorbed POP forms (C) in accordance with the capability to be extracted in the course of regular chemical analysis (CA), fractionated analysis (FA) and POP availability to migration and to soil biota (B)

After that, pollutant molecules being adsorbed by particulate SOM gradually penetrate to deeper and more condensed structures (glassy kerogen type structures resembling micropores of activated charcoal). At the depletion of the dissolved phase by chemical molecules (due to degradation or migration) its desorption from the deeper layers proceeds slowly leading to non-equilibrium partitioning of the chemical between the solid and liquid phase. As a result two fractions of **reversibly sorbed** POPs are formed. While one fraction remains in the surface amorphous layer of SOM and considers to be **equilibrium sorbed** chemical, the other one penetrating to deeper layers regards as **non-equilibrium sorbed** chemical. The chemical transition from equilibrium to non-equilibrium sorption and vice versa proceeds during a long period of time (months or even years). This process is known as "aging" of pollutants in soil or sediments [Alexander, 1994]. In addition, the fraction of strongly or **irreversibly sorbed (bound)** POPs is formed, which is represented by molecules penetrating to highly condensed part of SOM and closed inside the pore space of humus molecules, which have a tendency to change their structure. In according to some investigations, the unextractable POP fraction can also be formed due to sorption by metal-organic parts of SOM protected from penetration of solvent molecules. After microbial or chemical degradation the transformed POP molecules (e.g. hydroxylated derivatives) can also be bound to SOM by covalent links.

The majority of official methods of chemical analysis are based on the determination of a chemical **extractable** by organic solvents. However, fractionated analysis provides more accurate insight into the extent of POP sorption. First fraction - **water extractable** (readily extractable) combines dissolved and equilibrium sorbed chemical. The second one -

slowly extractable by water can be defined as **solvent extractable**. It represents non-equilibrium adsorbed chemical. The remainder belongs to **unextractable** (or **bound**) POPs. At least partly they are present as unchangeable molecules. For their extraction humus dissolution by alkaline, super-critical extraction by water vapor under the pressure and other methods are used.

The content of a bound chemical usually is not regulated. Thus the capability to be extracted is taken as a criterion of risk for man and the environment. The fraction of unextractable chemical is considered actually **unavailable** to biota and nonparticipating in migration processes. From the viewpoint of biological availability the composition of extractable fraction is also non-uniform. It is divided into **readily available** and **low available** (or potentially available). At present there is insufficient experimental data in the literature to make an accurate description of low available POP fraction. For provisional calculations it may be assumed that the water extractable fraction is in equilibrium with dissolved fraction and therefore it is readily available to different processes of migration and degradation. The migration and transformation of the solvent extractable fraction is mainly limited by the rate of chemical release to the soil solution. At the same time the unextractable (bound) fraction can be referred to degradation processes of the chemical.

An accelerated reverse transition to the readily available form takes place, for example, when the arid period is changed for the rain period as well as in the course of freezing or melting when soil aggregates are partly destroyed. It was also demonstrated that PAHs, PCBs and HCB desorption rate increases as much as 7 times with temperature increase by each 10°C [Johnson and Weber, 2001].

Soot particles or coal particles originated by combustion and containing a lot of highly condensed PAHs and highly chlorinated PCDD/Fs and PCBs can play a particular role in long-term accumulation of chemicals in soil. Investigation of sediments in the Milwaukee harbor carried out by Ghosh with co-authors [2001] showed that about 63% of PAHs are contained in small in height light fraction (63 - 250 μm in diameter), consisting of thin coal and wooden particles and the rest of PAHs is found mainly in slimy or clay particles (<63 μm in diameter). By pyrene and fluoranthene it was exemplified that about 10% of PAHs in light coal fraction and up to 90% in heavy clay fraction are almost at equilibrium with the solute (T_{50} for the desorption is 0,4-0,9 days). The half-desorption times for the rest non-equilibrium sorbed part of these compounds from coal and clay fractions are 0.4 and 6 years, respectively. As a result half-desorption time from sediments themselves for non-equilibrium sorbed PAHs with molecular weight 178, 202, 228 и 252 increases up to 2.3, 6.1, 7.6 and 18.3 years, respectively.

It is found that the diffusion velocity for slowly desorbing POPs in coal particles is extremely small. For PAHs at standard temperature it is 10^{-17} - 10^{-19} cm^2/s . However at temperature increase from 10 to 37 $^{\circ}\text{C}$ diffusion velocity increases by two orders of magnitude. Nevertheless, calculations show that under standard conditions up to 40% of PAHs sorbed by coal particles will be retained up to 100 years.

Thus,

1. POP transport with the dissolved organic matter can appreciably affect their migration processes over the soil profile.
2. Partition coefficient that defines partitioning between molecular dissolved POP and that adsorbed by dissolved organic matter (K_{DOC}) can be parameterized by the regression dependence upon K_{OW} .
3. In the first approximation it may be taken that the quantity of mobile DOC is 1% of its total content in soil.
4. The sorption of highly hydrophobic POPs can be very essential. However, the establishment of thermodynamic equilibrium takes time. For this reason the relationship between the dissolved and adsorbed fraction can vary with time. Adsorbed POPs are distributed between three fractions: readily available, potentially available and unavailable to processes of transformation and migration. The third fraction actually does not participate in these processes and may be considered in the simulation of the POP degradation.
5. At the first stage of modelling, the readily available POP fraction can be taken equal to 30% on the base of results obtained by *M.Krauss et al.* [2000] for characteristic congener PCB-153 while investigating urban and rural soils in Germany. The characteristic time of exchange between readily- and potentially available fractions may be taken equal to 1 year and the half-life of potentially available POP fraction – 25 years. For more accurate modelling of the POP transitions from readily available to potentially available fractions it is necessary to define readily available fractions and the exchange rate parameters.
6. In further modelling of POP long-range transport it is necessary to make allowance for the effect of soil moisture on its sorption properties, in particular on K_{SA} .

4. Numerical experiments

In the previous sections on the review the significance of two new mechanisms of POP adsorption to soil organic matter has been revealed, which influence on migration and accumulation of these chemicals in soil. They are: 1 - POP adsorption to the dissolved organic matter and 2 - dividing of a POP adsorbed by particulate organic matter to equilibrium and non-equilibrium fractions or to readily and potentially available ones respectively. Some numerical experiments were carried out to demonstrate the importance of these processes in modelling the pollutants transport and accumulation in soil.

4.1. Model assumptions

Modelling was carried out with the use of the modified 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 adsorbed by solid phase ($f_{non-equil}$) or low available with individual degradation rate (Fig. 5).

The share of a substance adsorbed 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 $f_{DOC} = 0.01f_{SOM}$. K_{DOC} is assessed through the dependence given in Section 3.1. Note that the pollutant associated with DOC is transported with the soil solution.

According to model assumptions the solid non-equilibrium adsorbed fraction is adsorbed by 70% of soil organic matter. The rest organic chemical is equilibrium adsorbed 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 $T_{non-equil,50} = 1$ year. It is also assumed that the non-equilibrium adsorbed fraction degrades "slowly". Its degradation is practically coincides with the degradation rate of humus itself with half-life 25 years. A pollutant equilibrium adsorbed 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 5.

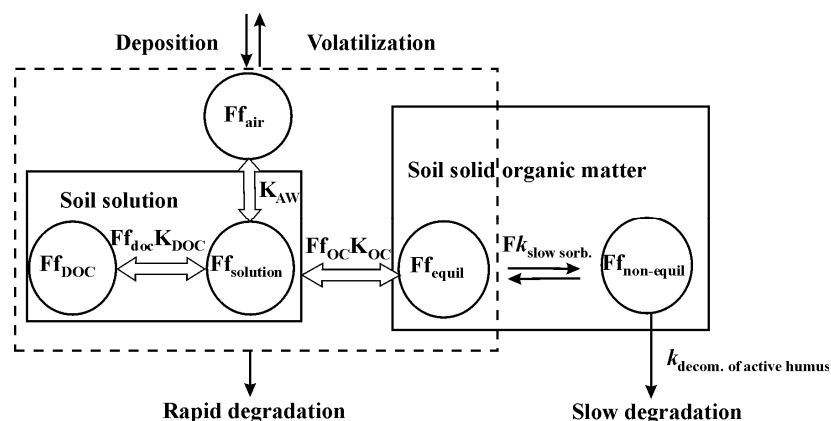


Figure 5. Model realization of POP partitioning between soil components and its degradation

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 adsorbed 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°C can be found in [Shatalov *et al.*, 2001]. Modelling 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.

4.2. Evaluation of the effect of POP fraction adsorbed by dissolved organic matter

To assess the DOC effect on POP transport, the calculation results with and without consideration of DOC adsorbed fraction are considered below (Fig. 6).

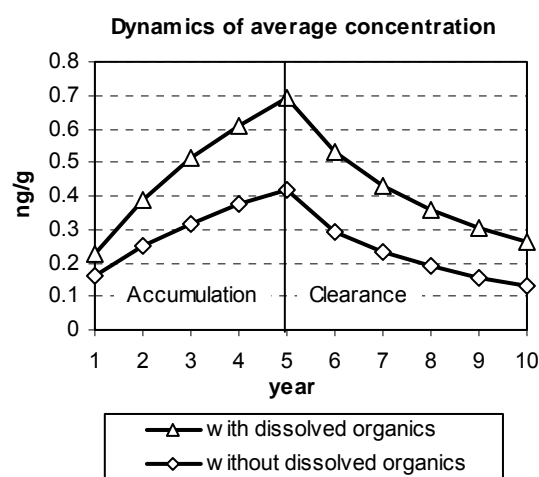


Figure 6. The comparison of calculation results of POP accumulation in soil and soil clearance with and without DOC consideration

The comparison of the curves depicted in figure 12 indicates that the consideration of DOC phase increases the pollutant concentration in soil as much as 1.75 times during 5 years. It is explained by more intensive transport of DOC dsorbed pollutant together with the water flow.

This process also significantly affects pollutant distribution down to soil profile. As evident from Figures 7.a and 7.b, the consideration of DOC phase slightly increases the depth of POP penetration. For example, by the 5th year the concentration in the third layer (Fig. 7.a) is 5 times higher than that obtained without DOC phase (Fig. 7.b).

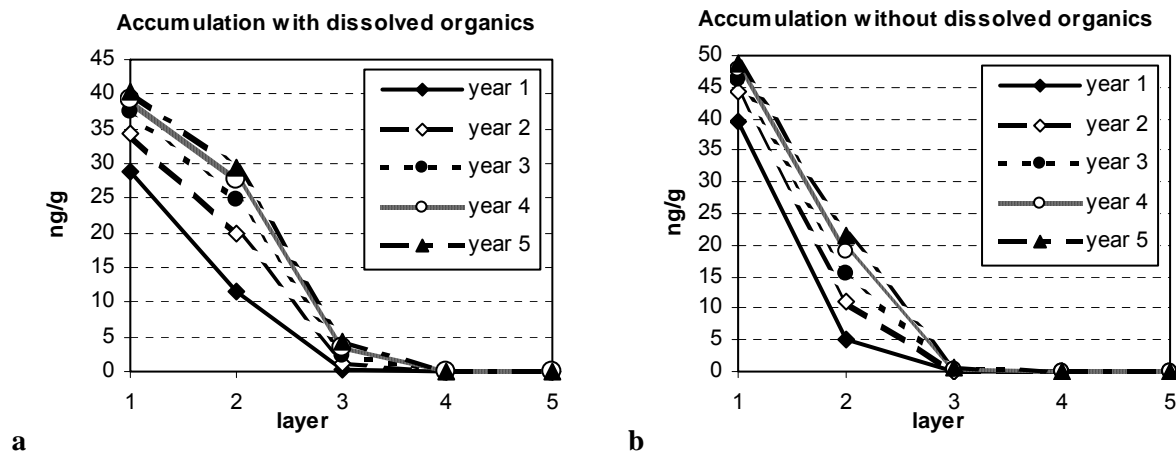


Figure 7. POP concentrations in the soil layers (1-5) during the accumulation period (5 years). Calculations with (a) and without (b) DOC consideration

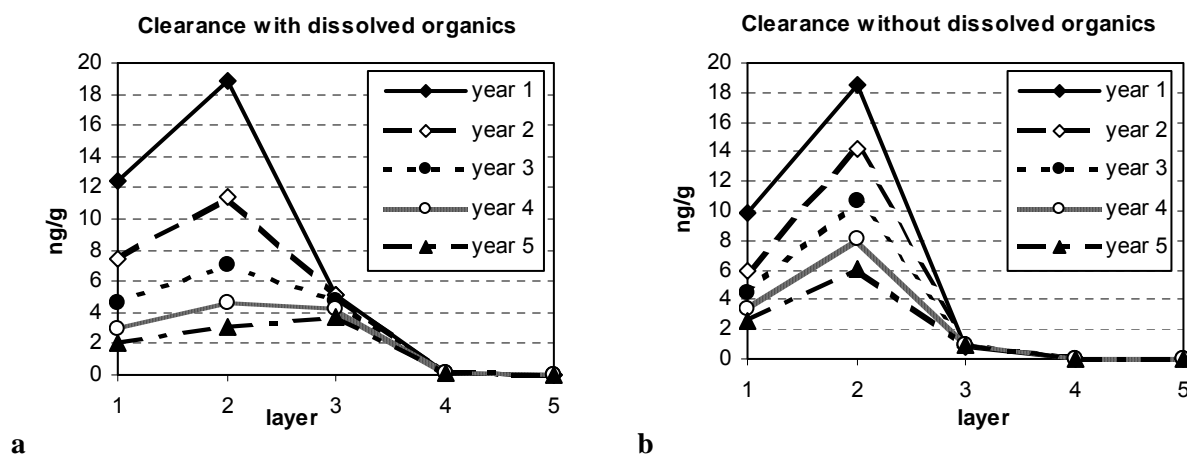


Figure 8. Pollutant concentrations in soil layers (1-5) during clearance period (5 years). Calculations performed with (a) and without (b) DOC consideration

As seen from Figures 8.a and 8.b at the stage of clearance the consideration of DOC phase considerably slows down soil clearance. With the consideration of DOC phase (Fig. 8.a) as before the concentration in the 3rd layer is 5 times higher than that obtained without DOC consideration (Fig. 8.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.

4.3. Evaluation of the effect of non-equilibrium adsorbed POP fraction

To estimate the influence of non equilibrium adsorbed POP fraction, the calculation results with and without consideration of this fraction (Fig. 9). The figure shows that during 5-year accumulation period of a chemical 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.

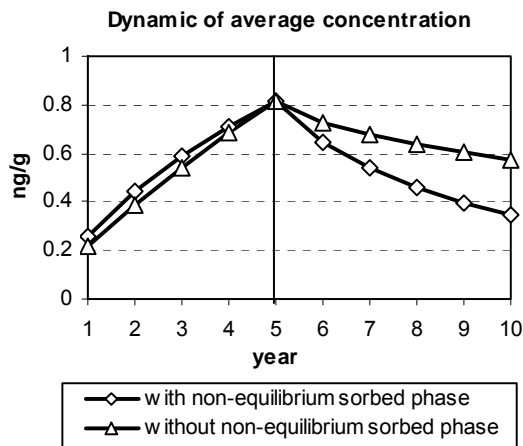


Figure 9. The comparison of calculation results with and without consideration of non-equilibrium adsorbed POP fraction

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 influences the pollutant vertical distribution in soil (Fig. 10). As follows from Figures 10.a and 10.b the consideration of the low available fraction

slightly increases the penetration depth of the pollutant. For instance, by the 5th year, the POP concentration in the 3rd layer with the consideration of the non-equilibrium adsorbed fraction (Fig. 10.a) is somewhat higher than those obtained without its consideration (Fig. 10.b). As to the 1st layer the pattern is reverse.

The comparison of Figures 11.a and 11.b 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 is 5 times higher than without the fraction consideration (Fig. 11.b).

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.

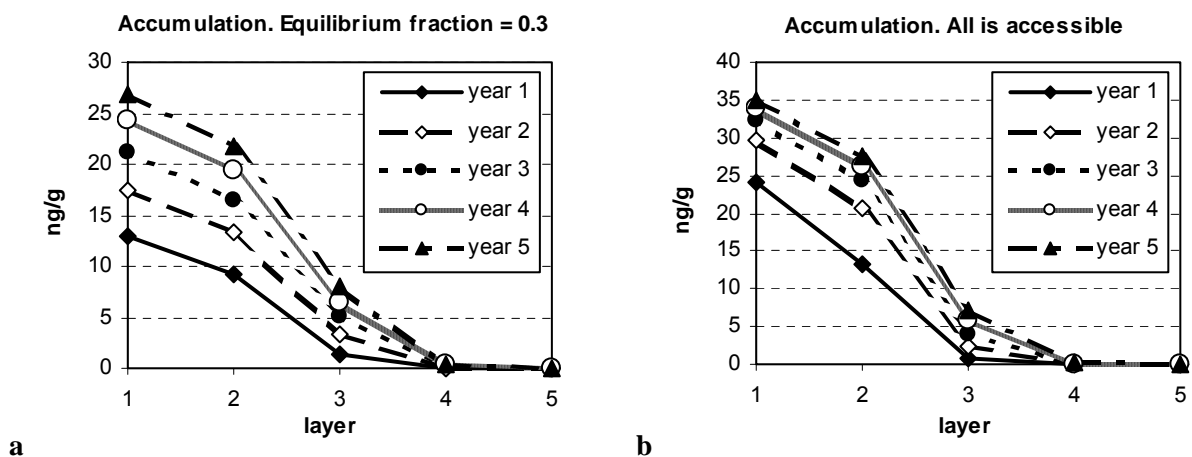


Figure 10. POP concentration in the soil layers (1-5) during the accumulation period (5 years). Calculations with (a) and without (b) consideration of the non-equilibrium adsorbed POP fraction

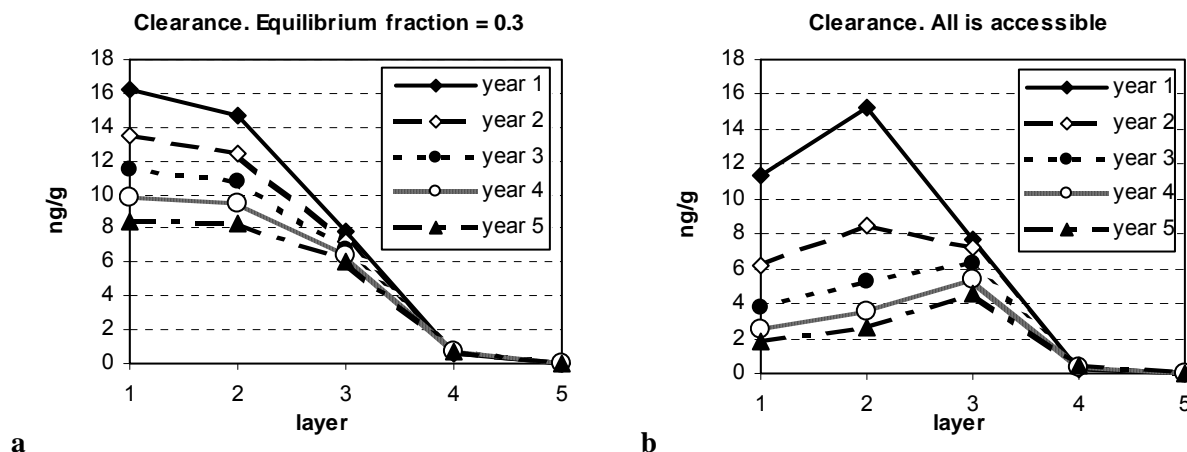


Figure 11. POP concentrations in the soil layers (1-5) at the stage of clearance (5 years). Calculations with (a) and without (b) consideration of the low available fraction

Conclusions

This technical note reviews the POP behaviour in soil from the viewpoint of their partitioning between different phases and the transport down to soil profile. On the base of the review, some recommendations for MSCE-POP model modification were suggested and numerical experiments were carried out.

1. According to literature data among the processes defining POP behaviour in soil an important role belongs to the transport down to soil profile with the dissolved organic matter (DOC) and partly non-equilibrium sorption by particulate soil organic matter. The consideration of these processes results in deeper penetration to and increased accumulation in soil.
2. In the model description of POP transport with the dissolved organics in the first approximation, its fraction can be taken equal to 1% of its total content in soil. Coefficients K_{DOC} of POP partitioning between real dissolved and DOC adsorbed fractions can be calculated through regression dependences on K_{OW} discussed in Section 3.1.
3. In the first approximation it may be assumed that the fraction of particulate soil organic matter, which sorbes POPs in equilibrium is 30% and the half-life of the other non-equilibrium adsorbed fraction is 25 years. The characteristic time of the non-equilibrium sorption is 1 year.
4. The model experiments with PCB-153 showed that the consideration of POP transport with the dissolved organics increases the total soil accumulation as much as 2 times and shifts POP distribution along the soil profile to deeper penetration of POPs. The consideration of non-equilibrium sorption decelerates essentially soil clearance due to emission and degradation reduction (1.7 times by the end of 5-year clearance period).
5. These investigations indicate the expedience and possibility of incorporation of these processes to the POP long-range transport model. Further refinement of parametrization of these processes is needed.

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