

## Chapter 2

### PHYSICAL-CHEMICAL PROPERTIES OF MERCURY AND SELECTED POPs

This chapter is focused on physical-chemical properties used in the model calculations of mercury, PCB and  $\gamma$ -HCH long-range transport. The basic properties of the considered pollutants: partitioning between the gaseous, aqueous and particle phase, removal processes and chemical degradation reactions are discussed below. For all these compounds temperature dependences of some physical-chemical characteristics and degradation rate constants are given. Besides the description of Mercury Depletion Events (MDE) phenomenon is also presented.

The model parameterization for considered contaminants is based on literature data on physical-chemical properties. Some papers include the evaluation of the accuracy of physical-chemical constants. Scattering of literature values determined by experimental and computational methods can to some extent characterize uncertainty of these constants. In addition available information on standard deviations for a number of physical-chemical constants is presented in this chapter.

#### 2.1. Physical and chemical properties of mercury

Mercury undergoes numerous physical and chemical transformations in the atmosphere. Understanding and adequate reproduction of properties of mercury and its compounds is a very important condition of realistic simulation. Continuously growing knowledge of mercury behaviour in the atmosphere and modern investigations appearing in the scientific literature constrain us to revise or even substantially modify the model parameterization.

##### 2.1.1. Mercury forms in the atmosphere

Mercury appears in the atmosphere both in the elemental form and in the form of various chemical compounds. Since properties of the compounds significantly differ from each other and from elemental mercury, it is very important to define the variety of the most important mercury species transported in the atmosphere.

First and the prevailing mercury species is elemental mercury ( $Hg^0$ ). Due to its physical properties (temperature dependence of saturated vapour pressure) elemental mercury occurs in the atmosphere under the realistic conditions solely in the form of vapour. Even at the absolute temperature minimum over the Earth surface (the Antarctic, Siberia) partial pressure of mercury vapour is several times lower than the pressure of saturated vapour [Fursov, 1983; Lindqvist *et al.*, 1991].

Besides, atmospheric mercury occurs in the form of different compounds – inorganic and organic. Inorganic compounds include, first of all, mercury chloride ( $HgCl_2$ ) and mercury hydrate ( $Hg(OH)_2$ ). The composition of gaseous inorganic mercury compounds has not been adequately investigated yet [Ebinghaus *et al.*, 1999b].

Organic mercury is represented in the atmosphere mainly by compounds with one and two methyl groups. The first type of compounds include  $CH_3HgCl$ ,  $CH_3HgOH$ ,  $CH_3HgBr$  etc. and have a generalized name monomethyl mercury (MMM), the second one is  $Hg(CH_3)_2$  – dimethyl mercury (DMM).

At last, mercury in the solid phase is incorporated into the composition of aerosol particles. According to [Schroeder *et al.*, 1991], the solid phase mercury in the atmosphere can be presented by the following compounds:  $HgO$ ,  $HgS$ ,  $HgCl_2$ ,  $HgSO_4$ ,  $Hg(NO_3)_2$ .

Atmospheric transport of mercury compounds in the solid phase is mainly determined by properties of particles-carriers. One of the most important aerosol characteristics is the size distribution defining removal processes of mercury from the atmosphere. Under the conditions of continental atmosphere size distribution of particles was studied in [Milford and Davidson, 1985]. Mean aerodynamic diameter of aerosols containing mercury was found to be 0.61  $\mu m$ . G. Keeler and co-workers [Keeler *et al.*, 1995] investigated the composition and size distribution of particulate mercury in various regions of the USA. It was obtained that maximum of the distribution spectrum is shifted toward larger sizes in contaminated industrial areas, whereas it amounts to 0.68  $\mu m$  in relatively clean regions.

Another important property of particulate mercury is solubility of its compounds in cloud and precipitation water. This property is essential for mercury chemical transformations in cloud water [Ryaboshapko *et al.*, 2001]. Besides, it defines mercury availability for biota and controls thereby negative impact on the environment.

R. Ebinghaus *et al.* [1999a] assume that the insoluble part of particulate mercury in precipitation varies from 90% in contaminated regions to 10% in relatively clean ones. Another study of particulate mercury [Sakata and Marumoto, 2002] has demonstrated that only 5–50% of aerosol mercury content was leached by dilute hydrochloric acid (0.33 mol/L  $HCl$ ) in a highly contaminated urban area. Presumably, solubility of particulate mercury is even lower in neutral or sub-acid water of the cloud environment. Among mercury compounds occurring in the atmosphere bromide ( $HgBr_2$ ), iodide ( $HgI_2$ ), sulphide ( $HgS$ ) and oxide ( $HgO$ ) have the lowest solubility. According to [Brosset and Lord, 1991] 50% of mercury in rainwater is represented by insoluble compounds. This agrees with conclusions of other researchers [Fitzgerald *et al.*, 1991; Lamborg *et al.*, 1995]. Besides, C. Lamborg and co-workers point out that the portion of particulate mercury in snow is greater than in rainwater.

### 2.1.2. Physical and chemical transformations

Mercury transformations in the atmosphere include transitions between the gaseous, aqueous and solid phase, chemical reactions in the gaseous and aqueous environment. Hereafter we shall use term the “aqueous phase” for all species dissolved in cloud water and those in composition of solid particles suspended in a droplet.

#### *Inter-phase equilibrium*

All gaseous mercury compounds to this or that extent are soluble in cloud and rain droplets. Droplet sizes are small enough therefore the equilibrium between the solution and gas is established rather rapidly. As a rule, equilibrium states are described by Henry's law with allowance made for the temperature effect. The same approach can be used for the description of equilibrium between the atmospheric air and sea or lake water surface. In this section for the convenience of comparison the

water-air Henry's law constants<sup>1</sup> are given in the dimensionless form (i.e. as the ratio of concentration in the liquid to air concentration).

For the last five years no new publications have been found which could change to any extent the notion of conditions of elemental mercury equilibrium between air and water. Earlier the authors used the following temperature dependence of Henry's law constant obtained in multiple measurements of its value within the temperature range from 278K to 298K [Ryaboshapko and Korolev, 1997]:

$$H_{Hg} = 0.00984 \cdot T \exp \left[ 2800 \left( \frac{1}{T} - \frac{1}{298} \right) \right]. \quad (2.1)$$

This expression gives a value practically coinciding at 278K with that used by *W. Schroeder et al.* [1991] and by *G. Petersen et al.* [1998].

For seawater the following dependence suggested in [Wängberg et al., 1999] was used:

$$H_{Hg} = \exp(4633.3 / T_w - 14.52), \quad (2.2)$$

where  $T_w$  is the seawater temperature in K.

Both expressions provide the same result at 25°C but they differ almost 2 times at 0°C. It is difficult to say whether this difference is due to the influence of seawater chemical composition.

It is assumed that the main gaseous mercury compound in the atmosphere is chloride. The most often cited values of its Henry's law constant are  $3 \cdot 10^7$  (at 298 K) and  $8.3 \cdot 10^7$  (at 283 K) [Lidqvist et al., 1984]. *J. Sommar et al.* [1999] give higher values of the constant for  $HgCl_2$  –  $4.9 \cdot 10^7$  (at 298 K) and  $3.6 \cdot 10^7$  (at 323 K). *A. Ryaboshapko et al.* [2001] roughly approximated the temperature dependence of Henry's law constant for mercury chloride in the "air-water" system by the expression:

$$H_{HgCl_2} = 1.054 \cdot 10^5 T \exp \left[ 5590 \left( \frac{1}{T} - \frac{1}{298} \right) \right]. \quad (2.3)$$

Henry's law constants of other gaseous mercury compounds and individual reactants for different values of temperature are given in Table 2.1.

As it follows from the table the major part of DMM in the "air-water" system should be in the gaseous state. The reverse relationship should be for  $CH_3HgOH$ ,  $Hg(OH)_2$  and, particularly, for  $HgO$ .

Equilibrium conditions of ozone in the "air-water" system were studied in [Sander, 1997]. In this work *R. Sander* has suggested the following expression for temperature dependence of ozone Henry's law constant:

$$H_{O_3} = 9.51 \cdot 10^{-4} T \exp \left[ 2325 \left( \frac{1}{T} - \frac{1}{298} \right) \right]. \quad (2.4)$$

Although (as it was demonstrated above) metallic mercury cannot exist in the atmosphere in the liquid or solid state its sorption by aerosol particles is possible. Quantitative characteristics of the process depend first of all on the "gas – solid matter" interface area as well as on the composition of particles.

<sup>1</sup> It should be mentioned that there are two opposite determinations of dimensional Henry's law constant in the scientific literature devoted to physical-chemical properties of mercury and POPs. Henry's law constant is traditionally expressed either as the ratio of dissolved concentration in water to gas-phase partial pressure of a chemical in the case of mercury compounds or as inverse ratio in the case of POPs. Thus for mercury we identified this value in the chapter related to physical-chemical properties as water-air Henry's law constant ( $H$ ) and for POPs - as air-water Henry's law constant ( $K_H$ ).

**Table 2.1.** Henry's law constants for mercury compounds and different reactants

Compound	Henry's law constant	Temperature	Reference
$(CH_3)_2Hg$	6.7	273 K	Lindqvist and Rodhe, 1985
	3.2	298 K	
	3.2	298 K	Seigneur et al., 1994
$CH_3HgCl$	$6.25 \cdot 10^4$	288 K	Lindqvist and Rodhe, 1985
	$5.3 \cdot 10^4$	298 K	
	$5.39 \cdot 10^4$	298 K	Seigneur et al., 1994
$CH_3HgOH$	$5.9 \cdot 10^6$	288 K	Petersen, 1992
	$3.7 \cdot 10^6$	293 K	
$Hg(OH)_2$	$6.25 \cdot 10^5$	283 K	Lindqvist and Rodhe, 1985
	$3.1 \cdot 10^5$	298 K	
	$2.9 \cdot 10^5$	298 K	Seigneur et al., 1994
$HgO$	$3.2 \cdot 10^6$	?	Petersen et al., 1998
$Cl_2$	$2.7 \cdot 10^5$ *	?	Lin and Pehkonen, 1998
$\cdot OH$	600	298 K	In: [Lin and Pehkonen, 1998]
$HO_2\cdot$	$4.9 \cdot 10^4$	298 K	
$SO_2$	30	298 K	
$H_2O_2$	$1.8 \cdot 10^7$	298 K	

\* This constant was obtained on the following assumptions. Chlorine solubility in cloud drops strongly depends on pH and chloride concentration. C.-J. Lin and S. Pehkonen [1998] suggested the formula for calculations of effective Henry's law constant (mole/L/atm):

$$H_{eff} = 7.61 \cdot 10^{-2} \left( 1 + \frac{10^{-3.3}}{[Cl^-][H^+]} + \frac{10^{-10.8}}{[Cl^-][H^+]^2} \right).$$

According to data from [Baltensperger et al., 1998; Couture et al., 1998; Kimec et al., 1998; Vong et al., 1997]  $[H^+]$  and  $[Cl^-]$  concentrations in the marine atmosphere can be estimated by an order of magnitude as  $3.2 \cdot 10^{-5}$  and  $10^{-4}$  mole/L respectively. Hence it follows that effective Henry's law constant for chlorine will be equal to  $1.2 \cdot 10^4$  mole/L/atm or  $2.7 \cdot 10^5$  in the dimensionless representation.

B. Lyon et al. [1999] considered two types of particles – small (diameter 0.3  $\mu m$ ) and coarse (5.7  $\mu m$ ) and accepted that the distribution in the system is proportional to the contact surface area. The relationship of areas appeared to be equal to 93:7 respectively.

Most likely soot particles possess the highest sorption capability. C. Seigneur et al. [1998] analysed literature data published in [Krishnan et al., 1994; Livengood et al., 1995; Accurex Environmental, 1995] (cited from [Seigneur et al., 1998]) on  $Hg^0$  and  $Hg(II)$  absorption from the gaseous phase by activated charcoal and estimated redistribution coefficients  $K_{a/s}$  in the dimension "liter of air per gram of soot". The coefficient  $K_{a/s}$  was estimated to be equal to 10 L/g for  $Hg^0$  and  $3 \cdot 10^5$  L/g for  $Hg(II)$ . C. Seigneur et al. [1998] indicate that it is not clear so far whether activated charcoal and atmospheric particles have the same chemical properties. Besides the redistribution value should depend on the temperature but nothing is known about it as yet.

In the comparison of various mercury liquid-phase chemistry schemes [Ryaboshapko et al., 2001] it was demonstrated that mercury partition in the "liquid – solid matter" system considerably affects mercury accumulation in cloud and rain droplets. Above all it is defined by mercury accessibility to chemical transformations in the liquid phase and non-accessibility in the sorbed state. Soot particles contained in drops may serve as the most probable sorbent.

C. Seigneur and co-workers [Seigneur et al., 1998] also analysed data of [Thiem et al., 1976; Ma et al., 1996] (cited from [Seigneur et al., 1998]) on the absorption of  $Hg(II)$  from water by activated charcoal and estimated the redistribution coefficient  $K_{w/s}$  in the dimension "liter of water per gram of soot". For atmospheric conditions in the first approximation the coefficient is equal to 3700 L/g of  $Hg(II)$ .

Special experiments with rain water for the determination of partitioning coefficient  $K_p$  with shaking of aerosol matter in pure water and for the determination of desorption coefficient  $K_d$  showed that these coefficients are of the same order of magnitude [Seigneur *et al.*, 1998]. However,  $K_p$  varies from 100 to 600 L/g and  $K_d$  – from 200 to 1400 L/g. The experiment with adsorption of dissolved forms on sampled aerosol matter made for the determination of the adsorption coefficient  $K_a$  evidenced that  $K_a$  is lower by an order of magnitude than  $K_d$ . Most likely it is connected with the occurrence of insoluble mercury forms (oxide and sulphide) in aerosol matter. The nature of aerosol matter can drastically affect the coefficient values. Values of  $pH$  actually did not influence the investigated coefficients.

### Gas-phase reactions

In the atmosphere there is a number of chemical substances capable of oxidizing elemental mercury and its organic compounds in the gaseous phase. Photochemical processes leading to decay of molecules are also possible. The integral indicator of the significance of this or that reaction for mercury atmospheric cycle is mercury lifetime in the atmosphere relative to a given reaction. Based on this indicator it is reasonable to consider only those reactions, which make a tangible contribution to mercury atmospheric cycle. It is also important to know reaction products since their rate of scavenging from the atmosphere essentially depends on their phase state.

It is recognized that ozone is the most important oxidant in the gas phase. In the majority of modern models describing mercury behaviour in the atmosphere the reaction rate of oxidation by ozone suggested by *B. Hall* [1995] and equal to  $(3 \pm 2) \cdot 10^{-20}$  cm<sup>3</sup>/molec/s at 20°C is used. First of all it should be mentioned that this estimate has an essential uncertainty. *B. Hall* [1995] also investigated the temperature effect of this reaction at 22°C, 55°C and 75°C. With temperature decrease the reaction rate should decline (activation energy about 10 kJ/mole, pre-exponential multiplier  $2.1 \cdot 10^{-18}$  cm<sup>3</sup>/molec/s). With the use of these data we obtained the following temperature dependence of this reaction rate (cm<sup>3</sup>/molec/s):

$$k = 2.1 \cdot 10^{-18} \exp(-1246/T). \quad (2.5)$$

In a rough assessment mean temperature of the troposphere is 0°C, it gives the oxidation reaction rate equal to  $2.2 \cdot 10^{-20}$  cm<sup>3</sup>/molec/s. At the average concentration of ozone in the troposphere  $7.5 \cdot 10^{11}$  molec/cm<sup>3</sup> mean lifetime of elemental mercury in the troposphere relative to this reaction is about 2 years. Therefore this reaction is one of most important in the atmospheric mercury chemistry.

It is difficult to say what compound may be a product of  $Hg^0$  oxidation by ozone. Most probably the oxide is formed. *G. Petersen* and co-workers [Petersen *et al.*, 1998] consider the reaction product to be gaseous. On the contrary experts from *US EPA* [1997] suppose that actually the reaction product is immediately adsorbed by aerosol particles and then behaves itself in the atmosphere in accordance with properties of particles-carriers. We believe if mercury oxide is the product of oxidation by ozone, it cannot exist in the atmosphere as a gas due to its poor volatility [Sommar *et al.*, 2001; Schroeder and Munthe, 1998]. It should be immediately and irreversibly trapped either by particles or cloud drops.

*J. Sommar et al.* [1999; 2001] studied the reaction of elemental mercury oxidation by hydroxyl radical. The reaction can go on in two stages:



Thus, the resulting reaction can be written as follows:



with the reaction rate  $k = (8.7 \pm 2.8) \cdot 10^{-14} \text{ cm}^3/\text{molec/s}$ .

At the mean concentration of atmospheric hydroxyl  $10^6 \text{ molec/cm}^3$  the  $\text{Hg}^0$  lifetime relative to this reaction will be less than a year. Thus this reaction may be even more important than the reaction of oxidation by ozone. The high value of the  $\cdot\text{OH}$  radical oxidation rate has not been confirmed by any independent laboratory yet. Hence one should be careful operating with this high value. The temperature dependence of the reaction rate is also unknown.

The reaction of  $\text{Hg}^0$  oxidation by chlorine [Seigneur *et al.*, 1994; Tokos *et al.*, 1998] may be important for the atmosphere over the ocean:



where reaction rate  $k \leq 4 \cdot 10^{-16} \text{ cm}^3/\text{molec/s}$  at  $25^\circ\text{C}$ . B. Hall (cited from [Tokos *et al.*, 1998]) showed that the reaction rate does not depend on temperature. In the atmosphere near the oceanic water surface chlorine concentration is about  $3 \cdot 10^9 \text{ molec/cm}^3$ . Under these conditions mean lifetime of  $\text{Hg}^0$  relative to this reaction will be estimated by days. However, it should be mentioned that in the atmosphere chlorine could exist only at night, only over the ocean and only in the lowest atmospheric layer.

Gaseous hydrogen peroxide may be another oxidant of elemental mercury:



Available in the literature information about this reaction rate is contradictory. For instance, E.Constanttinou *et al.* [1995] use the rate constant up to  $4.1 \cdot 10^{-16} \text{ cm}^3/\text{molec/s}$  at  $25^\circ\text{C}$ . J.J.S.Tokos *et al.* [1998] give a considerably lower value –  $6 \cdot 10^{-19} \text{ cm}^3/\text{molec/s}$ . It is essential to note the reaction rate should strongly depend on temperature. On the base of data on activation energy (75 kJ/mole) we can suggest the following temperature dependence of the reaction rate constant ( $\text{cm}^3/\text{molec/s}$ ):

$$k = 8.4 \cdot 10^{-6} \exp(-9021/T) \quad (2.10)$$

If, as before, we take that mean temperature of the troposphere is  $0^\circ\text{C}$ , then the oxidation rate will be  $3.7 \cdot 10^{-20} \text{ cm}^3/\text{molec/s}$ . At the mean atmospheric concentration of gaseous  $\text{H}_2\text{O}_2$  equal to  $2.5 \cdot 10^{10} \text{ molec/cm}^3$  elemental mercury lifetime in the atmosphere will be about 30 years. Most likely it is the minimum value since hydrogen peroxide is a daytime oxidant [Lin and Pehkonen, 1999]. For this reason gas phase oxidation reaction of  $\text{Hg}^0$  by hydrogen peroxide can be neglected.

Mercury organic compounds, for example, DMM are sufficiently rapidly destructed in the atmosphere at the reaction with OH radical [Niki *et al.*, 1983]. The reaction product is either elemental mercury [Niki *et al.*, 1983] or MMM [Schroeder and Munthe, 1998]. The reaction rate constant is  $2 \cdot 10^{-11} \text{ cm}^3/\text{molec/s}$ . At mean radical concentration  $10^6 \text{ molec/cm}^3$  atmospheric lifetime of DMM should not exceed several hours [Lin and Pehkonen, 1999]. Besides, M. Horvat [1996] points to a possibility of photochemical destruction of DMM leading to even shorter lifetime.

Theoretically mercury reduction in the gas phase to the elemental state is not excluded. For example, photochemical destruction of molecules containing mercury can lead to the formation of  $\text{Hg}^0$  but quantitative information on such reactions is not available yet [Seigneur *et al.*, 1994].

### Aqueous-phase reactions

Schemes of aqueous-phase transformations used in modern models of mercury transport assume a simultaneous action of two mechanisms – oxidation and reduction of elemental mercury. These schemes are described in detail in the work [Ryaboshapko *et al.*, 2001]. The main oxidants may be dissolved ozone and chlorine as well as hydroxyl radical formed directly in a droplet. Sulphite complexes and hydroperoxide radical may be reducing agents. Photoreduction of some compounds is also possible. Modern ideas about aqueous-phase mercury chemistry are described in detail in the work [Lin and Pehkonen, 1999].

Many investigators studied the reaction of  $Hg^0$  oxidation by ozone in the water environment. C.-J. Lin and S. Pehkonen [1999] take the reaction rate constant equal to  $(4.7 \pm 2.2) \cdot 10^7$  (mole/L) $^{-1}$ s $^{-1}$ . In order to estimate the uncertainty of this value, Table 2.2 summarizes the rate constants used by different modellers in the chronological order. As it follows from the table the reaction rate published by J. Munthe in 1992 is used in models. The dependence of the rate on solution temperature and pH may be neglected. It may be supposed that the reaction with ozone is the basic one for elemental mercury oxidation.

**Table 2.2.** Rate constants of  $Hg^0$  oxidation by ozone in the aqueous phase

Rate constant, (mole/L) $^{-1}$ s $^{-1}$	Dependencies		Reference
	on temperature	on pH	
$(4.7 \pm 2.2) \cdot 10^7$	Independent	Independent	Munthe, 1992
$4.7 \cdot 10^7$	at 25°C	–	Seigneur <i>et al.</i> , 1994
$4.5 \cdot 10^7$	–	–	Pleijel and Munte, 1995
$4.7 \cdot 10^7$	at 25°C	–	Constantinou <i>et al.</i> , 1995
$4.5 \cdot 10^7$	–	–	Lin and Pehkonen, 1997
$4.7 \cdot 10^7$	at 5°C	–	Petersen <i>et al.</i> , 1998
$4.7 \cdot 10^7$	–	Dependent	Lin and Pehkonen, 1998
$(4.7 \pm 2.2) \cdot 10^7$	Independent * (5 - 35°C)	Independent * (5.2 - 6.2)	Lin and Pehkonen, 1999

\* Independent within the interval

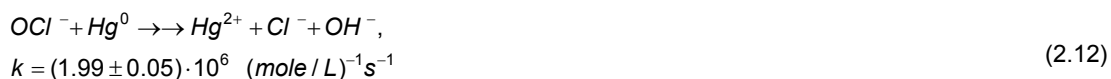
$Hg^0$  oxidation by hydroxyl radical takes place only in the daytime since the radical itself is a product of photochemical reactions. C.-J. Lin and S. Pehkonen [1997] estimated that the reaction rate is equal to  $2 \cdot 10^9$  (mole/L) $^{-1}$ s $^{-1}$ . K. Gårdfeldt *et al.* [2001] suggest a very close value –  $(2.4 \pm 0.3) \cdot 10^9$  (mole/L) $^{-1}$ s $^{-1}$ .

H. Herrmann and co-workers [Herrmann *et al.*, 2000] investigated variations of hydroxyl radical concentrations in cloud water. First of all, the concentration depends on the atmosphere pollution by substances capable either to generate radicals or react with them. Besides, there is a strong dependence on a droplet size. In the daytime OH concentration variation may be roughly described by the function of square of sine.

The calculated OH concentration in water at noon is  $3.7 \cdot 10^{-15}$  mole/L. In this case the constant of pseudo-first order reaction will be  $7.4 \cdot 10^{-6}$  s $^{-1}$  [Lin and Pehkonen, 1997]. Aqueous-phase reactions of oxidation by ozone and OH radical compete: at the ozone air concentration below 4 ppb radical oxidation prevails. At concentrations more than 10 ppb the contribution of radical reaction is about 20%, and at 20 ppb – only 10%.

Under certain conditions the reaction of  $Hg^0$  oxidation by dissolved chlorine may be important. In solution chlorine may occurs in two forms – hypochlorine acid (HOCl) and hypochlorite ion (OCl $^-$ ),

which relationship depends on solution  $pH$ . Oxidation by chlorine can take place mainly in the ocean atmosphere and only at night since  $Cl_2$  and  $HOCl$  are decomposed at light. Both hypochlorine acid and pyrochlorite ion can oxidize mercury [Lin and Pehkonen, 1999]:



It was considered earlier that the main agent responsible for the mercury reduction to the elemental state was sulphite ion ( $SO_3^{2-}$ ) forming unstable complexes with mercury ion [Munthe *et al.*, 1991]. As a result of the complex decays an atom of elemental mercury comes to the aqueous phase. Photoreduction of  $Hg(OH)_2$  was indicated also as a possible reduction mechanism [Pleijel and Munthe, 1995]. During recent years radical mechanism of reduction at the reaction of mercury ion or dissolved compounds with  $HO_2$  radical was investigated [Lin and Pehkonen, 1997; 1998].

Chemistry of mercury sulphite complexes is not sufficiently studied up till now. In a general form the scheme of the sulphite mechanism at present is represented in the following way.

At the first step sulfur dioxide is dissolved in a water drop with the formation of three forms of 4-valent sulfur: non-dissociated  $H_2SO_3$ , bisulphite-ion ( $HSO_3^-$ ), and sulphite-ion ( $SO_3^{2-}$ ). At real  $pH$  values of cloud water within the range of 3 - 5 the bulk of  $S^{IV}$  is represented by the first two forms, although in any case concentrations of sulphite-ion trace quantities will be higher than concentrations of dissolved mercury.

Sulphite-ion can react with divalent mercury ion forming mercury sulphite. Further it combines with another sulphite-ion producing sulphite-mercury complex [Constantinou *et al.*, 1995]:

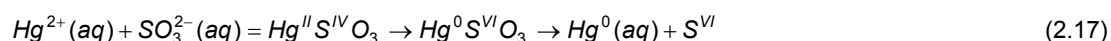


Note that G. Petersen *et al.* [1998] considers this pathway to be impossible on the assumption that primary the complex is formed. Then it dissociates with the formation of mercury sulphite. In any case mercury sulphite complex dominates among all other mercury compounds with four-valence sulphur [Lin and Pehkonen, 1997].

Mercury sulphite and probably sulphite-mercury complex decay and mercury is reduced to the elemental state [Constantinou *et al.*, 1995]:



In a general form the intramolecular redox process may be represented by the following reaction chain [van Loon *et al.*, 2000]:



Thus the availability of  $S^{IV}$  in a drop provides the action of negative feedback increasing elemental mercury concentration in a drop and preventing its additional solution from the ambient air.



G.Petersen and co-workers [Petersen et al., 1998] believe that mercury reduction process is limited by reaction of  $Hg(SO_3)_2^{2-}$  dissociation. Data on the rate of the indicated reactions are very contradictory. It is demonstrated in Table 2.3.

**Table 2.3.** Reaction rates of sulphite reduction of mercury in the aqueous phase

Reaction	Equilibrium or rate parameter	Temperature	Reference
$Hg^{2+} + SO_3^{2-} \rightarrow HgSO_3$	$5 \cdot 10^{12} M^{-1}$	25°C	Constantinou et al., 1995
$HgSO_3 + SO_3^{2-} \leftrightarrow Hg(SO_3)_2^{2-}$	$2.5 \cdot 10^{11} M^{-1}$	25°C	
$Hg(SO_3)_2^{2-} \rightarrow Hg^0$	$1 \cdot 10^{-4} s^{-1}$	25°C	
$HgSO_3 \rightarrow Hg^0 + SO_3^{2-}$	$0.6 s^{-1}$	25°C	
$Hg^{2+} + 2SO_3^{2-} \rightarrow Hg(SO_3)_2^{2-}$	$1.1 \cdot 10^{-21} ([SO_2(g)]/10^{-2pH})^2 s^{-1} *$	5°C	Petersen et al., 1998
$Hg(SO_3)_2^{2-} \rightarrow HgSO_3 + SO_3^{2-}$	$4.4 \cdot 10^{-4} s^{-1}$	5°C	
$HgSO_3 \rightarrow Hg^0$	$0.6 s^{-1}$		Munthe et al., 1991
$HgSO_3 \rightarrow Hg^0 + products$	$0.6 s^{-1}$		Lin and Pehkonen, 1999
$Hg(SO_3)_2^{2-} \rightarrow Hg^0$	0		Munthe, 1994
$Hg(HSO_3)^- \rightarrow Hg^0 + S^{VI}$	$4 \cdot 10^{-6} s^{-1}$		Munthe et al., 1991

\* Concentration of  $SO_2$  is in ppb.

While considering the importance of sulphite reduction mechanism one should take into account several things. First, if water solution has chloride, mercury ions mainly form mercury chloride [Prokofiev, 1981; Lindqvist et al., 1984; Lin and Pehkonen, 1998]. At the same time the probability of sulphite compounds formation drastically decreases. Under real atmospheric conditions the content of chloride in cloud water varies from  $2 \cdot 10^{-5}$  to  $4 \cdot 10^{-4}$  mole/L [Baltensperger et al., 1998; Couture et al., 1998; Kimec et al., 1998]. The content of chloride is particularly high in the atmosphere over the ocean – up to  $4 \cdot 10^{-4}$  mole/L [Vong et al., 1997]. Observations in Europe under EMEP [Ilyin et al., 2001] show that chloride content in precipitation is always higher than  $2 \cdot 10^{-6}$  mole/L used in the work [Petersen et al., 1998]. The model analysis of the chemical scheme sensitivity to chloride content demonstrated that actually sulphite mechanism of reduction starts acting only when chloride concentration is lower than  $5 \cdot 10^{-6}$  mole/L [Ryaboshapko et al., 2001].

Second, sulphite in cloud water are rapidly oxidized to sulfate. According to data from [Lin and Pehkonen, 1998] in 5 hours sulphite-ion content becomes negligible and the sulphite reduction mechanism ceases to act (it is assumed that at cloud formation the bulk of sulphur dioxide is dissolved in cloud water). It is also important that at high concentrations of sulphite-ion the sufficiently stable complex  $Hg(SO_3)_2^{2-}$  (see Table 2.3) is mainly formed [Lin and Pehkonen, 1998].

Third, as it was mentioned above the probability of sulphite-ion formation is strongly dependent on solution *pH*. According to [Petersen et al., 1998] the rate of mercury-sulphite complex formation is defined by the solution acidity (see Table 2.3). Model assessments showed [Ryaboshapko et al., 2001] that sulphite reduction mechanism begins to act at *pH* more than 5.

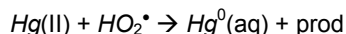
Finally, sulphite reduction rate drastically decreases with temperature decrease. According to [van Loon et al., 2000] at temperature decrease from 25°C to 0°C the rate declines more than 20 times.

C.-J. Lin and S. Pehkonen [1999] consider that in general  $SO_2$  is not important in mercury reduction since sulfur oxidation to 6-valence state goes on quickly. Ozone is the principal oxidant in the continental atmosphere both in the daytime and at night, and in the marine atmosphere – in the daytime. At night chlorine is the main oxidant in the oceanic atmosphere.

A part of oxidized mercury can be represented by hydrate. Under real conditions it can take place only at high *pH* and when chlorides are practically absent. Under the impact of solar light hydrate can

decay forming elemental mercury. Z. Xiao and co-workers [Xiao *et al.*, 1994] estimated that even at summer noon in the latitude of Stockholm this reaction is very slow ( $k = 3 \cdot 10^{-7} \text{ s}^{-1}$ ).

C.-J. Lin and S. Pehkonen [1997, 1998] found that hydroperoxide radical can be a very effective reducing agent:



According to their data the reaction rate is  $1.7 \cdot 10^4 (\text{mole/L})^{-1} \text{ s}^{-1}$  and typical level of  $\text{HO}_2^\bullet$  radical concentration in the liquid phase is  $1 \cdot 10^{-8} \text{ mole/L}$ . It is particularly important that this radical reacts both with free mercury ions and with molecular compounds of  $\text{HgCl}_2$  type. At the same time it is assumed that molecules of mercury compounds sorbed by particles are not accessible for this reduction mechanism. The reaction is dependent on  $\text{pH}$  but the quantitative description of this dependence is not available so far. The diurnal dynamics of the radical concentration was investigated in detail by H. Herrmann *et al.* [2000] under different external conditions. Like in the case with radical  $^\bullet\text{OH}$  in the daytime  $\text{HO}_2^\bullet$  concentration variations can be described by a function square sine. On the base of said above it seems important to include this reaction to the model calculation scheme.

It is known that the major part of cloud water does not fall out as precipitation but it is evaporated. For modeling of mercury behaviour in the atmosphere the interpretation of mercury fate after a droplet evaporation is important. The literature provides very contradictory information on this issue. Earlier it was supposed [Lindqvist *et al.*, 1991] that reactive oxidized mercury after water evaporation is reduced to the elemental form due to photo-dissociation. Only chemically persistent compounds (like  $\text{HgS}$ ) are remained in the solid state. G. Petersen *et al.* [1998] in their model assume that at drop evaporation all mercury compounds are transferred to the gaseous phase. Experts of US EPA [1997] consider that after drop evaporation an aerosol particle is formed containing in its composition all earlier dissolved and insoluble mercury compounds.

### 2.1.3. Arctic mercury depletion

Rising of mercury content in vulnerable Arctic ecosystems and increase of mercury input to human organism in the Arctic is of a particular concern [AMAP, 1998]. Only few years ago it was difficult to find any geophysical explanation of increased mercury content in the Arctic. Mercury behaviour in the atmosphere suggests that elevated  $\text{Hg}$  depositions in high latitudes are impossible. Indeed, it is commonly accepted that even if  $\text{Hg}^0$  is scavenged from the atmosphere due to dry deposition, the process can be realized only in low and middle latitudes through "soil-plant-atmosphere" interaction [US EPA, 1997].  $\text{Hg}^0$  uptake by snow cover is usually disclaimed. Oxidized gaseous and particulate  $\text{Hg}$  has restricted atmospheric lifetime, and their anthropogenic emissions in middle latitudes cannot account for noticeable contribution to total  $\text{Hg}$  deposition in the Arctic [Petersen *et al.*, 2001; Ilyin *et al.*, 2001].

However, recently discovered Mercury Depletion Events (MDE) phenomenon during springtime [Schroeder *et al.*, 1998] allows hypothesizing other ways of high  $\text{Hg}$  deposition in the Arctic (and Antarctic). The main point of the MDE consists in abrupt dropping of TGM concentration in high latitudes during springtime. The drop can be very quick (during few hours) and very deep – practically to total disappearance of elemental mercury. In a short time the TGM concentration can sharply rise to its usual values. Sometimes the period of super low  $\text{Hg}^0$  concentration can last several hours and even days [Lu *et al.*, 2001; Lindberg *et al.*, 2002; Berg *et al.*, 2001; Ebinghaus *et al.*, 2002]. Sharp droppings can repeat several times, and the total duration of the phenomenon is about 4-6 weeks.

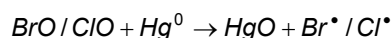
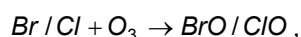
Both in the Northern and Southern Hemisphere the phenomenon can be observed only in springtime [Lu *et al.*, 2001; Ebinghaus *et al.*, 2002]. In the Northern Hemisphere it lasts from mid-March to mid-June.

Elemental mercury has relatively long atmospheric lifetime and theoretically cannot have such sharp variations [Junge, 1972]. Evidently, elemental mercury must be extremely quickly transformed into any other mercury-containing products during MDE. Most likely, they are oxidized mercury compounds presented by either gaseous oxidized forms or particulate oxidized forms. The products were experimentally determined both as reactive gaseous mercury (RGM) and  $Hg_{part}$  [Lu *et al.*, 2001; Lindberg *et al.*, 2002]. The concentration of oxidized mercury can be of the same level as usual TGM concentration (up to 1 ng/m<sup>3</sup>). Such concentrations are much higher than those ones, which are typically observed in the vicinity of strong anthropogenic sources.

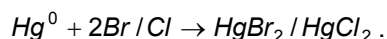
Very probably, the phenomenon embraces only the first kilometre height of the atmospheric layer [Ebinghaus *et al.*, 2002]. This is supported by aircraft measurements of oxidation products [Schroeder *et al.*, 2001; Lindberg *et al.*, 2002]. For example, at the surface level RGM concentration was 70 pg/m<sup>3</sup>, while at 1 km height – only 2 pg/m<sup>3</sup> [Lindberg *et al.*, 2002]. The total gaseous mercury (TGM) concentration rises with height and achieves its ordinary values at 1 km [Schroeder *et al.*, 2001]. This height is practically coincides with the top of the boundary layer. Hence, since the oxidation process is very fast the vertical profile of oxidation products is opposite to the TGM profile.

It is commonly believed that the sunrise in the Arctic provokes quick photochemical (catalytic) oxidation of elemental mercury in reactions with *Br*-related radicals [Ebinghaus *et al.*, 2002]. Recently S. Lindberg *et al.* [2002] presented a possible mechanism of the *Hg* depletion. The mechanism suggested can be described by several consecutive:

1. Occurrence in the atmosphere sea-salt aerosol particles in the frozen form (negative air temperature is an obligatory condition)
2. Influence of UV solar radiation on concentrated on the particle surface *Br/Cl* compounds. The compounds can be concentrated on the surface in the process of freezing
3. Formation of halogen radicals and halogen oxide radicals as a result of autocatalytical hetherogenic reactions
4. Destruction of ozone and oxidation of elemental mercury in the following reactions:



and/or



5. Abrupt stopping step 2 when air temperature is rising above zero. Formation of a water drop instead of the frozen particle and dissolution of the salts homogeneously within the drop.

The mechanism seems to be very reasonable. However, it cannot explain an “explosion” character of the process beginning. In our opinion such a “trigger” is formation of areas of open water near seashore (or polynyas) in ice cover. In springtime ice cover becomes movable due to ice drift provoked by sea currents or wind pressure. Such alternations can be very fast – in few hours a wide area of open water can appear even at low air temperature. In this case the formation of frozen sea-salt aerosol is quite natural. S. Lindberg *et al.* [2002] showed that elevated levels of RGM accompanied very often with periods of sea-surface roughness and formation of marine aerosol.

S. Lindberg *et al.* [2002] expect that primary product of elemental mercury oxidation is RGM. Then some RGM can be converted into  $Hg_{part}$ . On the contrary, Lu *et al.* [2001] believe that RGM and  $Hg_{part}$  are formed simultaneously, and the formation of  $Hg_{part}$  is preferable. T. Berg *et al.* [2002] also observed simultaneous formation both of  $Hg_{part}$  and RGM. Lifetime of  $Hg_{part}$  and RGM even in the stable polar atmosphere is much shorter than that of  $Hg^0$ , and their deposition should lead to additional Hg pollution of the Arctic environment. Measurements of mercury concentration in snow-pack conducted in series with atmospheric observation at Barrow station (Alaska, USA) showed clearly that the depletion phenomenon is accompanied by the rise of mercury content in snow [Lindberg *et al.*, 2002]. Canadian experts provided a broad survey of mercury content in northeastern Canada and Greenland. They found that the depletion phenomenon is widespread and lead to considerable rising of mercury content in snow-pack during springtime [Lu *et al.*, 2001]. However, S. Lindberg *et al.* [2002] noted that mercury concentration in snow-pack reaches its maximum leeward from polynyas and open water areas. Besides, the concentrations drop with distance from the seashore. These facts confirm that the MDE is closely connected with seashore line.

It was noted in recent works that the depletion is connected with elevated concentrations of BrO. Satellite observations showed that both in the Arctic and the Antarctic the zones of elevated BrO concentrations have ring shape – they connected with the seashores, and they appear in spring [Steffen *et al.*, 2001; Drummond, 2001; Lu *et al.*, 2001; Ebinghaus *et al.*, 2002]. If hypothesis of BrO involvement into Hg depletion is correct, it means that not the whole Arctic is influenced by the phenomenon but only seashore zones. Most likely, that the central parts of the Arctic and Antarctic are not affected by the MDE. Nowadays it is difficult to say how far southward the phenomenon can be extended. It observed at least within the Polar Circle in the Arctic.

## 2.2. Physical-chemical properties of selected POPs

Basic differences in POP environmental behaviour result from some peculiarities of their physical-chemical properties.

The key characteristics required for modeling POP behaviour in the environment are considered below.

Saturated vapour pressure ( $p^0$ , Pa) characterizes the capability of a pure substance to be transmuted to the gaseous state (for liquid this process is called vaporization, for solid substances - sublimation). The saturated vapor pressure for subcooled liquid -  $p_L^0$  is considered in this work. The value of  $p_L^0$  depends on the air temperature and increases with increasing temperature for all considered compounds. With the help of  $p_L^0$  one can characterize the partitioning of an organic compound between its particle and gaseous phase in the atmosphere.

Partitioning of a substance between the gaseous and particle phase in the atmosphere ( $\phi$ ) is determined in accordance with the Junge-Pankow model [Junge, 1977; Pankow, 1987]. POP fraction adsorbed on particle surfaces is:

$$\phi = c\theta / (p_L^0 + c\theta), \quad (2.18)$$

where

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

Thus POPs with lower vapour pressure are better sorbed on atmospheric aerosol particles thereby increasing the probability of their subsequent deposition and washout with precipitation.

Air-water Henry's law constant ( $K_H$ , Pa·m<sup>3</sup>/mol) is the ratio of equilibrium partial pressure  $P_A$  of a substance in the air to its concentration in water  $C_W$  which equals the ratio of its saturated vapour pressure  $p^0$  and its solubility  $S$ , i.e. the proportion:

$$\frac{P_A}{C_W} = \frac{p^0}{S} = K_H \quad (2.19)$$

is fulfilled. Here  $K_H$  is the Henry's law constant, in this case measured in [Pa·m<sup>3</sup>/mol] on the assumption that the species concentration in water is measured in mol/m<sup>3</sup>. Expressing the saturated vapour pressure of a substance in terms of its air molar concentration using the Mendeleev-Clapeyron equation, one can represent the Henry's law constant in the dimensionless form  $K'_H$ :

$$\frac{C_A}{C_W} = K_{AW} = K'_H = \frac{K_H}{RT} \quad (2.20)$$

here  $K_{AW}$  is the dimensionless air-water partition coefficient;  
 $C_A$  is the substance concentration in air;  
 $R$  is the universal gas constant;  
 $T$  is the absolute temperature, K.

The value of the Henry's law constant is used in the description of the gaseous exchange between the atmosphere and soil, between the atmosphere and seawater, and for the determination of wet scavenging of the POP gaseous phase.

The washout ratio for the particle phase ( $W_p$ ) can be calculated by the following relationship:

$$W_p = C_p / C_{A,a} \quad (2.21)$$

where  $C_p$  is the substance concentration in precipitation in the particle phase, ng/m<sup>3</sup>;  
 $C_{A,a}$  is the substance concentration in air in the particle phase, ng/m<sup>3</sup>.

Coefficients of partitioning between different media ( $K_{OW}$ ,  $K_{OA}$  – dimensionless;  $K_{OC}$ , dm<sup>3</sup>/kg):

The octanol-water partition coefficient ( $K_{OW}$ ) is a measure of substance hydrophoby and characterizes its partitioning between water and lipid media substituted for octanol. It is determined as the ratio of equilibrium concentrations in octanol  $C_O$  (mol/l) and in water  $C_W$  (mol/l):

$$K_{OW} = C_O / C_W \quad (2.22)$$

$K_{OW}$  is used for the estimation of the partition coefficient in the organic carbon-water system ( $K_{OC}$ ), the partition coefficient in the octanol-air system ( $K_{OA}$ ), and the bioconcentration factor (BCF).

The octanol-air partition coefficient ( $K_{OA}$ ) is used for the description of a substance partitioning between air and the cuticle of plants, between the gaseous phase and the organic film of atmospheric aerosol particles, etc. In experiments this coefficient is determined by the ratio of equilibrium concentrations of a substance in octanol and air.

$$K_{OA} = C_O / C_A = K_{OW} / K_{AW} = K_{OW} \cdot RT / K_H \quad (2.23)$$

where  $C_O$  is the equilibrium concentration of a substance in octanol;  
 $C_A$  is the equilibrium concentration of a substance in air.

Additionally, this coefficient can be defined with the use of coefficients “octanol-water” and “air-water”.

The organic carbon-water partition coefficient ( $K_{OC}$ , dm<sup>3</sup>/kg) is used for the description of POP sorption by soil and bottom sediments. It is determined as:

$$K_{OC} = K_P / f_{OC}, \quad (2.24)$$

where  $K_P$  is the partition coefficient equal to the ratio of POP concentration in the solid state of soil (bottom sediments) to that in the water phase;

$f_{OC}$  is the mass fraction of organic carbon in soil and bottom sediments.

Molecular diffusion coefficients ( $D_A$ ,  $D_W$ , cm<sup>2</sup>/s) are used in the description of the POP air-soil exchange process. The molecular diffusion coefficient of an organic compound in air ( $D_A$ , cm<sup>2</sup>/s) can be estimated by the formula [Schwarzenbach *et al.*, 1993]:

$$D_A = 10^{-3} \cdot \frac{T^{1.75} [(1/M_{air}) + (1/M)]^{1/2}}{p [\bar{V}_{air}^{1/3} + \bar{V}_m^{1/3}]^2} \quad (2.25)$$

where  $T$  is the absolute temperature, 298 K;

$M_{air}$  is the mean molecular air weight, ~29 g/mol;

$M$  is the molecular weight of an organic substance, g/mol;

$p$  is the pressure, 1 atm;

$\bar{V}_{air}$  is the mean molar gas volume in the air, ~20.1 cm<sup>3</sup>/mol;

$\bar{V}_m$  is the molar volume of an organic substance, cm<sup>3</sup>/mol.

For the determination of molecular diffusion coefficients for organic substances in water ( $D_W$ , cm<sup>2</sup>/s), the following ratio [Schwarzenbach *et al.*, 1993] can be used:

$$D_W = \frac{13.26 \times 10^{-5}}{\mu^{1.14} \cdot (\bar{V}_m)^{0.589}} \quad (2.26)$$

where  $\mu$  is the solution viscosity in centipoise at a certain temperature, taken to be equal to water viscosity, 0.894 cps at 298K;

$\bar{V}_m$  is the mean molar volume of a substance, cm<sup>3</sup>/mol.

For POP modeling it is necessary to know:

- temperature dependencies of physical-chemical characteristics (subcooled liquid-vapour pressure, Henry's law constant, octanol-air partition coefficient);
- data on the distribution of low volatile POPs with particle sizes in the atmosphere;
- degradation constants in environmental compartments.

The above-mentioned characteristics used for modeling PCB congeners and  $\gamma$ -HCH are described below in relevant subsections. Physical-chemical properties and the parameterizations of PCB individual congeners and  $\gamma$ -HCH used in the multi-compartment model are presented in several MSC-E reports [Pekar *et al.*, 1999, Shatalov and Malanichev, 2000, Erdman *et al.*, 2001, Shatalov *et al.*, 2001]. The analysis of physical-chemical properties of the considered POPs available in the literature as well as parameters employed by other modellers for the long-range transport evaluation allowed us to improve the model parameterization.

### 2.2.1. Polychlorinated biphenyls (PCBs)

Polychlorinated biphenyls (PCBs) belong to a class of organochlorine aromatic compounds long used for industrial purposes in many countries. There are 209 PCB congeners with different physical-chemical properties and toxicity depending on the number and position of the chlorine atoms in the biphenyl molecule. According to the classification of the International Agency for Research on Cancer (IARC), PCBs belong to group 2A of probable carcinogens for man [IARC, 1987 cited from *HSDB*, 2002]. In addition, PCBs can affect the human reproductive system and impose toxic impacts on an embryo [Avkhimenko, 2000]. PCBs without substituents in ortho-position relative to the internuclear bond C<sub>1</sub>-C<sub>1</sub> (coplanar), as well as some PCB mono-ortho-substituted congeners, exhibit toxicity similar to that of polychlorinated dibenzo-*p*-dioxins/furans. Eleven congeners of PCBs beginning with tetra- to heptachlorinated isomers possess toxicological properties with international toxic equivalency factors from 0.00001 to 0.1 I-TEF relative to 2,3,7,8-tetrachlorodibenzo-*p*-dioxin isomer [Klyuev and Brodsky, 2000].

PCBs are typical POPs because they are persistent to external impacts. They have high thermal and photo stability and small reactive capability. Due to high lipophily, PCBs may be accumulated in adipose tissues of man, animals, birds and aqueous organisms. In addition, these compounds are readily sorbed on particle and soil surface. Numerous measurements demonstrate that they are omnipresent in environmental objects even in such remote regions as the Arctic [Breivik *et al.*, 2002].

The following individual PCB congeners were selected for the evaluation of the long-range transport to the Arctic: PCB-28, 118, 153 and 180. They represent light, medium and heavy homologues of PCBs. It should be mentioned that PCB-118 possesses toxicological properties (0.0001 I-TEF). This selection was also conditioned by the fact that physical-chemical properties of these congeners are well studied and the availability of measurement data on concentrations in different natural objects allow us to verify model results.

General information on four PCB congeners is demonstrated in Table 2.4.

**Table 2.4.** Structural formulas, composition and some properties of the PCB studied

Compound	Chemical names (IUPAC)	CAS RN	Molecular formula	Molecular weight, g/mol	Structural formula
PCB-28	2,4,4'-Trichlorobiphenyl	7012-37-5	C <sub>12</sub> H <sub>7</sub> Cl <sub>3</sub>	257.5	
PCB-118	2,3',4,4',5-Pentachlorobiphenyl	31508-00-6	C <sub>12</sub> H <sub>5</sub> Cl <sub>5</sub>	326.4	
PCB-153	2,2',4,4',5,5'-Hexachlorobiphenyl	35065-27-1	C <sub>12</sub> H <sub>4</sub> Cl <sub>6</sub>	360.9	
PCB-180	2,2',3,4,4',5,5'-Heptachlorobiphenyl	035065-29-3	C <sub>12</sub> H <sub>3</sub> Cl <sub>7</sub>	395.3	

Below, physical-chemical properties of PCB congeners modeled in the AMAP project are described.

### Temperature dependence of PCB subcooled liquid-vapour pressure

The coefficients for the dependence of the subcooled liquid-vapour pressure  $p_L^0$  on the temperature in the form (2.27) for 180 PCB congeners were determined by *R.L.Falconer and T.F.Bidleman* [1994].

$$\log p_L^0 (\text{Pa}) = -A/T(K) + B. \quad (2.27)$$

These coefficients for four PCB congeners are listed in Table 2.5.

**Table 2.5.** Coefficients of the dependence of subcooled liquid-vapour pressure (Pa) on temperature for four PCB congeners [Falconer and Bidleman, 1994]

Compound	A	B
PCB-28	4075	12.20
PCB-118	4664	12.72
PCB-153	4775	12.85
PCB-180	5042	13.03

Parameters for calculating the temperature dependence of  $p_L^0$  for 32 PCB congeners were derived [Falconer and Bidleman, 1994] from previously obtained gas chromatographic data (GC). From this information the coefficients were estimated for another 148 PCBs for which vapour pressure had been reported only at a fixed temperature. According to [Falconer and Bidleman, 1994], these A values should have a similar degree of reliability as the GC results, which ranged from –16 to +18%, with a mean of +3% (percentage of literature values). The values of  $p_L^0$  (Pa) calculated by these dependences for different ambient temperatures are given in Table 2.6.

**Table 2.6.** Values of subcooled liquid-vapour pressure (Pa) at different temperatures for three PCB congeners

Compound	$P_L^0$ , Pa			
	-10°C	0°C	+10°C	+25°C
PCB-28	$5.1 \cdot 10^{-4}$	$1.9 \cdot 10^{-3}$	$6.3 \cdot 10^{-3}$	$3.4 \cdot 10^{-2}$
PCB-118	$9.7 \cdot 10^{-6}$	$4.3 \cdot 10^{-5}$	$1.7 \cdot 10^{-4}$	$1.2 \cdot 10^{-3}$
PCB-153	$4.9 \cdot 10^{-6}$	$2.3 \cdot 10^{-5}$	$9.5 \cdot 10^{-5}$	$6.7 \cdot 10^{-4}$
PCB-180	$7.2 \cdot 10^{-7}$	$3.6 \cdot 10^{-6}$	$1.6 \cdot 10^{-5}$	$1.3 \cdot 10^{-4}$

As evident from Table 2.6, for all the congeners  $p_L^0$  values increase with temperature rise, resulting in a reduction of their adsorption on particles (see Eq. (2.18)).

### Henry's law constant dependence on temperature for PCBs

The Henry's law constant is a key parameter in model calculations of the long-range transport. The temperature dependence of Henry's law constant can be expressed by Eq. (2.28):

$$\log K_H = \log K_{H298} + \frac{\Delta H_{AW}}{2.303R} \left( \frac{1}{T_0} - \frac{1}{T} \right), \quad (2.28)$$

where  $K_{H298}$  is the Henry's law constant (Pa·m<sup>3</sup>/mol) at 25°C (298K);  
 $\Delta H_{AW}$  is the enthalpy of volatilization from water, kJ/mol;  
 $R$  is the universal gas constant, 8.314·10<sup>-3</sup> kJ/(mol·K);  
 $T$  is the absolute temperature, K.

Measured values of  $\Delta H_{AW}$  for relevant PCB homologous groups with from three to seven chlorine atoms are summarized in the paper [Wania, 1997] and presented in Table 2.7.



**Table 2.7.** Measured values of  $\Delta H_{AW}$  for four PCB homologous groups

Homologue groups	$\Delta H_{AW}$ , kJ/mol	Reference cited from [Wania, 1997]
Trichlorobiphenyls	61.8	<i>Burkhard et al.</i> , 1985
Pentachlorobiphenyls	67.2	
Hexachlorobiphenyls	69.4	
Heptachlorobiphenyls	71.3	

From Eq. (2.28) the temperature dependence of the Henry's law constant can be expressed in the form:

$$\log K_H = -A/T(K) + B, \quad (2.29)$$

where  $A = \Delta H_{AW}/2.303R$ ;

$$B = \log K_{H298} + \Delta H_{AW}/2.303R(298).$$

Values of Henry's law constant at 25°C for four PCB congeners published in [Dunnivant et al., 1992] are given in Table 2.8. Calculation of  $K_H$  (25°C) for PCBs was performed on the basis of the Quantitative Structure-Property Relationship (QSPR) model. This model agrees well with other model predictions and is capable of accurately calculating  $K_H$  for structurally similar PCB congeners. The statistical analysis of the calculated and experimental  $\log K_H$  data showed a high regression coefficient ( $r = 0.9476$ ) and a low standard error ( $s = 0.662$  or 1.9% of the mean value), which are indicative of reasonable model predictions [Dunnivant et al., 1992].

**Table 2.8.** Values of Henry's law constant at 25°C for four PCB congeners,  $\text{Pa} \cdot \text{m}^3/\text{mol}$ 

Compound	$K_{H298}$ , calculated value	Reference
PCB-28	28.58	<i>Dunnivant et al.</i> , 1992
PCB-118	12.56	
PCB-153	16.48	
PCB-180	10.74	

Using  $\Delta H_{AW}$  values from Table 2.7 and Henry's law constants at 25°C from Table 2.8, the coefficients of temperature dependences of Henry's law constants (2.29) were estimated and used for modeling in this work. Table 2.9 gives selected  $A$  and  $B$  values (they are given in bold) in comparison with the temperature dependence coefficients available in the literature.

**Table 2.9.** Coefficients of the temperature dependences of Henry's law constants for four PCB congeners

Compound	A					B				
	1*	2	3	4	5	1	2	3	4	5
PCB-28	2611	<b>3227</b>	3100	1821	3418	10.22	<b>12.28</b>	11.97	7.69	12.92
PCB-118		<b>3510</b>	3535	2727	3416		<b>12.88</b>	13.44	10.71	12.70
PCB-153		<b>3625</b>	3662	3577	3413		<b>13.38</b>	14.05	13.72	12.68
PCB-180		<b>3724</b>	3910	7628	3414		<b>13.53</b>	14.71	27.16	12.49

1 – *ten Hulscher et al.*, 1992 cited from [Pekar et al., 1999]; 2 - estimated (see text) on the basis of data from [Wania, 1997 and Dunnivant et al., 1992]; 3 – [Paasivirta et al., 1999]; 4 – [Bamford et al., 2000]; 5 – estimated on the basis of data from [Iwata et al., 1995].

### Temperature dependence of the octanol-air partition coefficient for PCBs

Parameters of temperature dependences of octanol-air partition coefficients for 15 PCBs were determined by *T. Harner and T.F. Bidleman* [1996] for the temperature range from -10°C to + 30°C in the form:

$$\log K_{OA} = A/T(K) - B. \quad (2.30)$$

It should be mentioned that for trichlorobiphenyls the experimental dependence was estimated for PCB-29 only [Harner and Bidleman, 1996]. For this reason, coefficient  $A$  of this dependence (2.30) for PCB-28 was taken to be equal to the corresponding coefficient for PCB-29 (3792). Further, using data from Table 2.5, the subcooled liquid-vapour pressure at 20°C (293 K) was calculated. Then using the regression Eq. (2.31) derived by T. Harner and T.F. Bidleman [1996], the octanol-air partition coefficient at 20°C was estimated.

$$\log K_{OA} = (-1.268) \log p_L^0 + 6.135, \quad r^2 = 0.995 \quad (2.31)$$

Coefficient  $B$  was calculated by the formula:

$$B = A/293 - \log K_{OA}^{293}, \quad (2.32)$$

where  $K_{OA}^{293}$  is the octanol-air partition coefficient at 20°C (293K).

The dependences determined experimentally and estimated are presented in Table 2.10.

The octanol-air partition coefficients at 20°C determined on the basis of these dependences are given in Table 2.11.

**Table 2.10.** Octanol-air partition coefficient dependence on temperature for three PCB congeners

Compound	A	B	Reference
PCB-28	3792	4.63	Estimate (see text)
PCB-118	4693	5.92	Harner and Bidleman, 1996
PCB-153	4695	6.02	
PCB-180	4535	4.70	

**Table 2.11.** Octanol-air partition coefficients at 20°C for four PCBs

Compound	Chlorine atom positions	$K_{OA}$
PCB-28	2,4,4'	$2.04 \times 10^8$
PCB-118	2,3',4,4',5	$(1.21 \pm 0.10) \times 10^{10}$
PCB-153	2,2',4,4',5,5'	$(1.11 \pm 0.08) \times 10^{10}$
PCB-180	2,2',3,4,4',5,5'	$(5.64 \pm 0.71) \times 10^{10}$

### PCB molecular diffusion coefficients

The molecular diffusion coefficients of PCB-153 in air and in water were estimated by Eq. (2.25) and (2.26). Diffusion coefficients of the rest of the congeners were estimated by the following formulas:

$$\frac{D_A}{D_A^{153}} \cong \left[ \frac{M^{153}}{M} \right]^{1/2} \quad (2.33)$$

$$\frac{D_W}{D_W^{153}} \cong \left[ \frac{M^{153}}{M} \right]^{1/2}, \quad (2.34)$$

where  $D_A^{153}$  and  $D_W^{153}$  are the molecular diffusion coefficients of PCB-153 in air and in water, respectively;

$D_A$  and  $D_W$  are the molecular diffusion coefficients of a given PCB congener in air and in water, respectively;

$M^{153}$  is the molecular weight of PCB-153, g/mol (see Table 2.4);

$M$  is the molecular weight of a given PCB congener (see Table 2.4).

Table 2.12 demonstrates values of molar volumes for four PCB congeners taken from [Mackay *et al.*, 1992; Ruelle and Kesselring, 1997] and molecular diffusion coefficients for air and water calculated with the use of these values. Molecular diffusion coefficients of PCBs selected for modeling in this work were estimated on the basis of molar volume presented in [Mackay *et al.*, 1992].

**Table 2.12.** Molar volumes ( $\bar{V}$ ,  $\text{cm}^3/\text{mol}$ ) and obtained values of molecular diffusion coefficients in air and water at  $25^\circ\text{C}$  of four PCB congeners ( $D_A$ ,  $D_W$ ,  $\text{m}^2/\text{s}$ )

Compound	$\bar{V}$ , $\text{cm}^3/\text{mol}$		$D_A$ , $\text{m}^2/\text{s}$	$D_W$ , $\text{m}^2/\text{s}$
	Values	References		
PCB-28	<b>247.3</b>	Mackay <i>et al.</i> , 1992	<b><math>5.42 \cdot 10^{-6}</math></b>	<b><math>6.09 \cdot 10^{-10}</math></b>
	198.7	Ruelle and Kesselring, 1997	$5.18 \cdot 10^{-6}$	$5.87 \cdot 10^{-10}$
PCB-118	<b>289.1</b>	Mackay <i>et al.</i> , 1992	<b><math>4.82 \cdot 10^{-6}</math></b>	<b><math>5.40 \cdot 10^{-10}</math></b>
	224.5	Ruelle and Kesselring, 1997	$4.81 \cdot 10^{-6}$	$5.35 \cdot 10^{-10}$
PCB-153	<b>310</b>	Mackay <i>et al.</i> , 1992	<b><math>4.58 \cdot 10^{-6}</math></b>	<b><math>5.14 \cdot 10^{-10}</math></b>
	237.4	Ruelle and Kesselring, 1997	$4.66 \cdot 10^{-6}$	$5.14 \cdot 10^{-10}$
PCB-180	<b>330.9</b>	Mackay <i>et al.</i> , 1992	<b><math>4.38 \cdot 10^{-6}</math></b>	<b><math>4.91 \cdot 10^{-10}</math></b>
	-	Ruelle and Kesselring, 1997	-	-

Values used for modeling are given in bold.

Data of Table 2.12 show that the molecular diffusion coefficients both in air and water decrease with the increase in the degree of chlorination.

### Partitioning of PCBs between the gaseous and particle phase in the atmosphere

Fractions of PCB adsorbed on particles were calculated from Eq. (2.18) [Junge, 1977; Pankow, 1987] for the background aerosol ( $\theta = 1.5 \cdot 10^{-4} \text{ m}^2/\text{m}^3$ ) and the data of Table 2.6. Obtained values  $\phi$  for different temperatures are given in Table 2.13.

**Table 2.13.** PCB fractions adsorbed on atmospheric aerosol particles at different temperatures, %

Compound	$\phi \times 100$ , %			
	$-10^\circ\text{C}$	$0^\circ\text{C}$	$10^\circ\text{C}$	$25^\circ\text{C}$
PCB-28	5	1	0.4	0.1
PCB-118	72	37	13	2
PCB-153	84	53	21	4
PCB-180	97	88	61	16

As evident from Table 2.13, fractions of PCBs bound with particles increase with the increase of the degree of chlorination. Moreover, for all congeners the extent of adsorption increases with temperature decrease.

### PCB sorption by soil and bottom sediments

PCB sorption by soils and bottom sediments is characterized quantitatively by the organic carbon-water partition coefficient ( $K_{OC}$ ,  $\text{m}^3/\text{kg}$ ).  $K_{OC}$  for PCBs were calculated with the use of the following relation:

$$K_{OC} = 0.41 K_{OW} \quad [\text{Karickhoff, 1981}] \quad (2.35)$$

Table 2.14 gives partition coefficients in the “octanol-water” system selected for modeling and

partition coefficients for the “organic carbon-water” system estimated with the use of these coefficients for four PCB congeners. Besides ranges of  $\log K_{OW}$  values determined by experimental and computational methods and available in literature are presented in this table.

**Table 2.14.** Partition coefficients in the “octanol-water” and “organic carbon-water” system for four PCB congeners

Compound	Range of $\log K_{OW}^*$	Selected $\log K_{OW}$	Estimated $\log K_{OC}$ , $\text{dm}^3/\text{kg}$	$K_{OC}$ , $\text{m}^3/\text{kg}$
PCB-28	5.61-5.8	5.8 [Mackay et al., 1992]	5.41	259
PCB-118	6.39-7.12	6.74 [Hawker and Connell, 1988]	6.35	2253
PCB-153	6.72-7.75	6.9 [Mackay et al., 1992]	6.51	3257
PCB-180	6.7 - 8.27	7.36 [Hawker and Connell, 1988]	6.97	9393

\* Literature data include information from the following references: [Hawker and Connell, 1988; Mackay et al., 1992; McLachlan, 1996; Hovard and Meylan, 1997; Paasivirta et al., 1999; Sahsuvar, 1999; NIST, 2002].

As seen from Table 2.14, PCBs sorption by soils and bottom sediments increases with the number of chlorine atoms in the molecule.

### PCB wet deposition

Wet deposition is an important mechanism of PCB scavenging from the atmosphere. Total dimensionless ratio  $W_T$  for a substance washout with precipitation is determined by the Eq. (2.36):

$$W_T = W_G (1 - \phi) + W_P \phi, \quad (2.36)$$

where  $W_G$  is the washout ratio of the gas phase;  
 $W_P$  is the washout ratio of a substance associated with aerosol particles;  
 $\phi$  is the substance fraction associated with aerosol particles.

Due to sufficiently high values of Henry's law constants, the efficiency of gaseous PCB washout with precipitation is relatively low. Washout ratios  $W_G$  determined as inverse values to dimensionless Henry's law constant ( $RT/K_H$ ) at 25°C are of the order of  $10^1 - 10^2$ . Washout ratios of PCB scavenging with rain ( $W_P$ ) for particle-bound PCBs are substantially higher. [Franz and Eisenreich, 1998] summarized various published data indicating that  $W_P$  for scavenging with rain is  $10^2 - 10^6$ . For model calculations of PCB-118, PCB-153 and PCB-180, a  $W_P$  mean value equal to  $1.5 \cdot 10^5$  [Sweetman and Jones, 2000] was chosen. It should be mentioned that for gaseous and particle-bound PCB-28, the empirical washout ratio is equal to  $2.1 \cdot 10^4$  [Granier and Chevreuil, 1997]. Because the usage of theoretical ratios in preliminary calculations of this PCB leads to underestimation of scavenging with rain (this can be explained, for instance, by the occurrence of organic matter in raindrops), the above experimentally determined value of the washout ratio was used.

### PCB degradation in the environment

**The atmosphere.** Data of E.S.C.Kwok et al. [1995] show that the basic mechanism of PCB degradation in the atmosphere is reaction with hydroxyl radicals and that all other mechanisms can be neglected. The degradation process in the atmosphere is described by the following reaction:

$$\frac{dC}{dt} = -k_{air} \cdot C \cdot [OH], \quad (2.37)$$

where  $C$  is the pollutant concentration in air,  $\text{ng}/\text{m}^3$ ;  
 $[OH]$  is the air concentration of hydroxyl radical,  $\text{molec}/\text{cm}^3$ ;  
 $k_{air}$  is the degradation rate constant for air,  $\text{cm}^3/(\text{molec} \cdot \text{s})$ .

The atmospheric concentration of OH-radical shows wide seasonal and diurnal variations, as its major tropospheric source is the photochemical cleavage of ozone by sunlight [Sinkkonen and Paasivirta, 2000]. In the MSCE-POP model the variability of this factor is taken into account by the assumption that the value of the mean diurnal concentration of hydroxyl radicals depends only on the season. At a latitude of 45°N, the mean diurnal OH-radical concentration at the surface layer at a depth of 2 km is  $2 \cdot 10^6$  molec/cm<sup>3</sup> in summer,  $0.8 \cdot 10^6$  molec/cm<sup>3</sup> in spring and autumn and  $0.09 \cdot 10^6$  molec/cm<sup>3</sup> in winter at mean annual concentration  $0.8 \cdot 10^6$  molec/cm<sup>3</sup> [Yu Lu and Khall, 1991].

In modeling PCB long-range transport to the Arctic, it was reasonable to introduce the temperature dependence of rate constant of the gas-phase reaction with OH-radicals. In the work [Beyer and Matthies, 2001] this dependence is described by the Arrhenius equation:

$$k_{air} = A \cdot \exp(-E_a / RT) \quad (2.38)$$

where  $A$  is the pre-exponential multiplier value, cm<sup>3</sup>/(molec·s);

$E_a$  is the activation energy of interaction with an OH-radical in air, J/mol;

$R$  is the universal gas constant, J/(mol · K);

$T$  is the ambient temperature, K.

The same approach was applied to PCB atmospheric transport evaluation in [Sahsuvar, 1999]. Values of the pre-exponential multiplier and the activation energy for individual PCB congeners taken from [Beyer and Matthies, 2001] are displayed in Table 2.15.

**Table 2.15.** Coefficients in the equation of temperature dependence of rate constant in the reaction with OH-radical (2.38) according to [Beyer and Matthies, 2001]

Compound	$A$ , cm <sup>3</sup> /(molec·s)	$E_a$ , J/mol	Reference
PCB-28	$2.70 \cdot 10^{-10}$	13720	Anderson and Hites, 1996
PCB-118	$6.15 \cdot 10^{-11}$	12920	Degradation rate constant at 25 °C estimated with AOPWIN, version 1.90 and calculated reaction energy
PCB-153	$8.12 \cdot 10^{-11}$	15380	
PCB-180	$1.40 \cdot 10^{-10}$	17840	

The activation energy value for PCB-28 was experimentally determined and presented in [Anderson and Hites, 1996] with form  $-E_a/R$  (K) =  $1650 \pm 220$ . Uncertainty in this value is based on one standard error of the slope of the temperature dependence regression. The estimated rate constant of PCB-28 in the gas-phase reaction with OH-radical at 298 K amounts to  $1.1(0.8-1.4) \times 10^{-12}$  cm<sup>3</sup> s<sup>-1</sup> (95% confidence limits) [Anderson and Hites, 1996]. For the remaining PCBs, degradation rate constants in air at 298 K were determined using the computer program AOPWIN from molecular structure information [Beyer and Matthies, 2001]. The activation energy  $E_a$  (i.e. temperature dependence of reaction rate) of these PCBs was correlated with the degree of chlorination. Although the coefficient of determination is small ( $r^2 = 0.67$ ), the slope is significantly distinct from zero [Beyer and Matthies, 2001].

**Natural waters and soils.** PCB degradation in the aqueous and soil environment has not been thoroughly investigated. No data on temperature dependence of degradation constants in these environmental compartments have been found among relevant literature. Table 2.16 demonstrates estimates of half-lives for four PCB congeners in surface water and soils presented in [Mackay et al., 1992; Wania, 1999].

**Table 2.16.** PCB half-lives in surface water and soil according to literature data

Substance	Half-life*, h (surface water)	Half-life (soils), h	
	<i>Mackay et al.</i> , 1992; <i>Wania</i> , 1999	<i>Wania</i> , 1999	<i>Mackay et al.</i> , 1992
PCB-28	17000	10 000	55 000
PCB-118	55 000	100 000	55 000
PCB-153	55 000	550 000	55 000
PCB-180	55 000	1000 000	55 000

In recent investigations of *S.Sinkkonen and J.Paasivirta* [2000] carried out for the Baltic region, there are different estimates of four PCB half-lives, taking into account the temperature factor of surface water and soils. Table 2.17 exhibits half-lives for surface waters and soils taken from [*Sinkkonen and Paasivirta*, 2000] and the corresponding degradation constant values of the considered PCB congeners in these environmental compartments. Specifically these values were used for modeling in this work.

*Thus for modeling the hemispheric transport of the selected PCB in the Arctic region, we have used the above-discussed physical-chemical properties. The parameterization is described in section 3.3 below.*

**Table 2.17.** Degradation constants for water and soil [*Sinkkonen and Paasivirta*, 2000]

Substance	$k_d^{sea}$ , s <sup>-1</sup>	Half-life*, h. Surface water	$k_d^{soil}$ , s <sup>-1</sup>	Half-life*, h. soils
PCB-28	$1.33 \cdot 10^{-7}$	1450	$7.4 \cdot 10^{-9}$	26 000
PCB-118	$3.21 \cdot 10^{-9}$	60000	$3.21 \cdot 10^{-9}$	60000
PCB-153	$1.6 \cdot 10^{-9}$	120000	$1.17 \cdot 10^{-9}$	165 000
PCB-180	$8.02 \cdot 10^{-10}$	240000	$5.83 \cdot 10^{-10}$	330 000

\* - on the average for +7 °C

### 2.2.2. $\gamma$ -Hexachlorocyclohexane ( $\gamma$ -HCH)

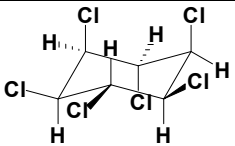
$\gamma$ -HCH is one of stereo isomers of 1,2,3,4,5,6 of hexachlorocyclohexane (HCH) referring to a group of organochlorine compounds. HCH occurs as eight stereo isomers among which  $\gamma$ -HCH possesses the highest insecticide activity.  $\gamma$ -HCH (as technical HCH or lindane) was intensively used all over the world for various purposes – for the treatment of people and animals (against ectoparasites), constructions, clothes, water (against mosquitoes), plants, forests, orchards, seeds, soil etc. [*Filov ed.*, 1990].  $\gamma$ -HCH exhibits mutagenic activity, embriotropic action and affects reproduction processes [*Izmerov ed.*, 1990]. Additionally people who have had occupational contact with this substance can develop allergies or experience other irritating effects.

$\gamma$ -HCH is one of the most volatile chemicals among organochlorine insecticides. It is poorly soluble in water but easily soluble in the majority of organic solvents. This chemical is extremely stable to temperatures up to 180°C and with acids, but in alkalis it undergoes dehydrochlorination [*HSDB*, 2002]. Once HCH isomers enter the environment, they are distributed globally and can be found in air, surface water, soil, and living organisms [*Walker et al.*, 1999]. But HCHs are much less bioaccumulative than other organochlorines because of their relatively low lipophily and short half-life in biota [*AMAP Assessment Report*, 1998]. HCHs are the most abundant pesticides in the Arctic

atmosphere and waters [Macdonald *et al.*, 2000]. The detectable presence of these substances in such remote regions, where lindane and technical HCH have not been used, is evidence of the long-range transport [Walker *et al.*, 1999].

Table 2.18 demonstrates general characteristics of  $\gamma$ -HCH.

**Table 2.18.**  $\gamma$ -HCH general characteristics

Compound	Chemical names (IUPAC)	CAS RN	Molecular formula	Molecular weight, g/mol	Structural formula
$\gamma$ -HCH	(1,2,4,5/3,6)-gamma stereo isomer 1,2,3,4,5,6, – hexachlorocyclohexane	58-89-9	C <sub>6</sub> H <sub>6</sub> Cl <sub>6</sub>	290.8	

$\gamma$ -HCH physical-chemical properties required for model calculations are presented below. According to predictions based on the Junge-Pankow model,  $\gamma$ -HCH was assumed to be present in the atmosphere at moderate temperatures only in the gas phase.

### Temperature dependence of $\gamma$ -HCH subcooled liquid-vapour pressure

Coefficients for the temperature dependences of  $\gamma$ -HCH subcooled liquid-vapour pressure  $p_L^0$  (2.39) available in the literature are presented in the Table 2.19.

$$\log p_L^0(\text{Pa}) = A + B/T \text{ (K)} \quad (2.39)$$

**Table 2.19.** Coefficients of  $\gamma$ -HCH subcooled liquid-vapour pressure temperature dependences

Coefficients		Notes	References
A	B		
11.15	- 3680	calculated from experimental GC data	Hinckley <i>et al.</i> , 1990
13.63	- 4416	calculated from literature data	Hinckley <i>et al.</i> , 1990
13.80	- 4330	estimated	Paasivirta <i>et al.</i> , 1999

The first temperature dependence of  $\gamma$ -HCH subcooled liquid-vapour pressure was determined by D.A.Hinckley *et al.* [1990] from experimental data using capillary gas chromatography (GC). This method provides vapour pressures within a factor of two of average literature values for nonpolar compounds. Exactly this temperature dependence was used in the MSC-E model calculations of  $\gamma$ -HCH long-range airborne transport for 1999 - 2000. Additionally it was used in [Cotham and Bidleman, 1991] for the evaluation of  $\gamma$ -HCH fluxes in the Arctic regions.

### Henry's law constant dependence on temperature for $\gamma$ -HCH

Coefficients for Henry's law constant temperature dependence for  $\gamma$ -HCH in the form (2.40) have been determined by several authors.

$$\log K_H = A + B/T \quad (2.40)$$

These coefficients are presented in Table 2.20.

**Table 2.20.** Coefficients of Henry's constant temperature dependences, Pa·m<sup>3</sup>/mol

Coefficients		Notes	References
A	B		
7.54±0.54	-2382±160	experiment, distilled water	<i>Kucklick et al.</i> , 1991
8.68±0.96	-2703±276	experiment, sea water	
11.58	-3093	estimated	<i>Paasivirta et al.</i> , 1999
9.51	-3005	experiment	<i>Jantunen and Bidleman</i> , cited from <i>Paasivirta et al.</i> , 1999
10.10	-3183	Selected for previous MSC-E modeling [ <i>Pekar et al.</i> , 1999]	<i>Jacobs and van Pul.</i> , 1996

Temperature dependence of Henry's law constant for  $\gamma$ -HCH determined experimentally by *Kucklick et al.* [1991] for distilled water and seawater was used for modeling in this work. It is necessary to mention that this temperature dependence value was also used in [*Cotham and Bidleman*, 1991] for calculating pollutant fluxes in the Arctic regions.

### $\gamma$ -HCH molecular diffusion coefficients

Molecular diffusion coefficients of  $\gamma$ -HCH were estimated from dependences (2.25) and (2.26) suggested by [*Schwarzenbach et al.*, 1993], on the basis of molar volumes taken from [*Ruelle and Kesselring*, 1997; *Mackay et al.*, 1997].  $\gamma$ -HCH molar volumes and values of molecular diffusion coefficients in air and water are given in Table 2.21.

**Table 2.21.**  $\gamma$ -HCH molar volumes and calculated molar diffusion coefficients in air and water

$V_{mol}$ , cm <sup>3</sup> /mol	Molecular diffusion coefficients, m <sup>2</sup> /s	
	Air ( $D_a$ )	Water ( $D_w$ )
179.5 [ <i>Ruelle and Kesselring</i> , 1997]	$6 \cdot 10^{-6}$	$7 \cdot 10^{-10}$
243.6 [ <i>Mackay et al.</i> , v.5, 1997]	$5 \cdot 10^{-6}$	$5.9 \cdot 10^{-10}$

Molecular diffusion coefficients of  $\gamma$ -HCH selected for modeling were estimated on the basis of molar volume presented in the work [*Ruelle and Kesselring*, 1997].

### Coefficients of partitioning $K_{OW}$ and $K_{OC}$ for $\gamma$ -HCH

Among literature at present there is a large amount of data on measured and estimated values of  $\gamma$ -HCH partitioning in the "octanol-water" and "organic carbon-water" system. According to [*Mackay et al.*, 1997], experimentally determined values of log  $K_{OW}$  are within the range of 3.25 - 5.32 and values of log  $K_{OC}$  – within 2.38 - 3.40. The "octanol-water" and "organic carbon-water" partition coefficients selected for modeling  $\gamma$ -HCH under this project and recommended or used by other authors are given in Table 2.22.

**Table 2.22.** Partition coefficients  $K_{OW}$  and  $K_{OC}$  for  $\gamma$ -HCH

Partition coefficient	Units	Value	Reference
log $K_{OW}$	dimensionless	3.9	<i>Chu and Chan</i> , 2000
log $K_{OC}$	dm <sup>3</sup> /kg	3.0	<i>Mackay et al.</i> , 1997; <i>Chu and Chan</i> , 2000



### Temperature dependence of octanol-air partition coefficient for $\gamma$ -HCH

Reasoning from the requirement of consistency in parameters  $K_{OW}$  and  $K_{OA}$ , coefficients A and B of temperature dependence for  $\gamma$ -HCH partition coefficient in an "octanol-air" system in the form of Eq. (2.30) were calculated. For this purpose, we used coefficient A of temperature dependence (2.40) of Henry's law constant for fresh water (with a reverse sign) from [Kucklick *et al.*, 1991] and reference value  $K_{OA}$  at 25°C, calculated by the formula:

$$\log K_{OA} = \log K_{OW} - \log K_H/RT \quad (2.41)$$

where  $\log K_{OW} = 3.9$  (see Table 2.22);

$\log K_H/RT$  is estimated by Eq. (2.40) taken from [Kucklick *et al.*, 1991] for 25°C.

Thus the temperature dependence of partition coefficient in the "octanol-air" system for  $\gamma$ -HCH will be of the following form:

$$\log K_{OA} = 2382/T(K) - 0.25 \quad (2.42)$$

### $\gamma$ -HCH degradation in environment

**The atmosphere.** The main process in  $\gamma$ -HCH degradation is its interaction with OH-radical. Hence, as in the case of PCBs, the degradation of this species in air will be described by second order Eq. (2.37) taking into account seasonal values of OH-radical air content at the latitude 45° N taken from [Yu Lu and Khall, 1991]. The mean seasonal [OH] concentrations used are, for winter,  $9 \cdot 10^4$  molec/cm<sup>3</sup>, for autumn and spring,  $8 \cdot 10^5$  molec/cm<sup>3</sup>, and for summer,  $2 \cdot 10^6$  molec/cm<sup>3</sup>. According to [Brubaker and Hites, 1998], the temperature dependence of rate constants of the reaction with OH-radical in air for  $\gamma$ -HCH will be of the following form:

$$k_{OH} [\text{cm}^3/(\text{molec} \cdot \text{s})] = A \exp (-Ea/ (RT)) \quad (2.43)$$

where  $A = 6 \cdot 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ ;

$Ea = 14.2 \pm 1.7 \text{ kJ/mol}$ ;

$R$  is the universal gas constant, J/(mol, K);

$T$  is the ambient temperature, K;

Thus the rate constant ( $k_{Oh}$ ) estimated [Brubaker and Hites, 1998] for 298 K ranges within  $(1.4-2.5) \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$  with a mean value equal to  $1.9 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ .

**Natural waters.**  $\gamma$ -HCH degrades in aqueous environments through several processes: hydrolysis, photolysis and microbial degradation. The slowest degradation takes place in ground waters; the most rapid degradation processes are biodegradation under anaerobic conditions and hydrolysis in nearly alkaline medium (pH=9) at a temperature above 20°C. In the literature there are various estimates of  $\gamma$ -HCH degradation rate constants in water for the above-mentioned processes. According to these data, half-lives of  $\gamma$ -HCH degradation in waters due to different processes vary from 3 days [Mackay *et al.*, 1997] to 1720 days [Strand and Hov, 1996].

For calculations of  $\gamma$ -HCH degradation in the aqueous environment, we selected the temperature dependence of hydrolytic decomposition of HCH isomers at different pH determined in [Ngabe *et al.*, 1993]. The rate constant for alkaline (base) hydrolysis is related to the energy of activation and absolute temperature by the Arrhenius equation:

$$\log k_b = A - E_a/(2.303RT), \quad (2.44)$$

where  $k_b$  is the second-order rate constant for the base hydrolysis of a substance in water,  $M^{-1} \cdot \text{min}^{-1}$ ;  
 $A = 15.146$  is the pre-exponential factor;  
 $E_a = 84.6 \pm 7.8$  is the energy of hydrolysis process activation, kJ/mol;  
 $R = 8.314$  is the universal gas constant, J/(mol·K);  
 $T$  is the absolute temperature, K.

According to *B.Ngabe et al.* [1993], the pseudo first-order rate constant for the hydrolysis of a substance in water depends on the activity of hydroxide ions in the solution and is connected with the second-order rate constant by the following relationship:

$$k_{DW} \cong k_b \cdot a_{OH}/60, \quad (2.45)$$

where  $k_{DW}$  is the pseudo first-order rate constant for the hydrolysis of  $\gamma$ -HCH in water,  $s^{-1}$ ;  
 $a_{OH}$  is ion activity in the solution depending on pH value and temperature.

Under conditions close to natural ones (pH=7), the half-life of  $\gamma$ -HCH in an aqueous environment due to the hydrolysis on the base of  $k_{DW}$  calculated by formulas (2.44) and (2.45) for the temperature range from 0°C to 25°C will be from 1.5 to 34 years.

**Soils.** Obviously for  $\gamma$ -HCH, as for other POPs, important factors in the soil degradation process are soil type and humus content. The current version of the MSC-E model does not operate with such details of soil-top as of yet. Therefore in this project we have selected a mean value of degradation rate constant of this substance available in the literature and used by other modellers. It is equal to  $2 \cdot 10^{-8} s^{-1}$  [*Hornsby et al.*, 1996]. The half-life of  $\gamma$ -HCH degradation in soils calculated on the basis of this rate constant amounts to 400 days. Values of  $\gamma$ -HCH half-life in soil, according to data presented in [*Mackay et al.*, 1997], vary from 3 days to 3 years.

The model parameterization is described in Section 3.3.

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