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**HEXACHLOROBENZENE:  
PROPERTIES, EMISSIONS AND CONTENT  
IN THE ENVIRONMENT**

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## ***Introduction***

Hexachlorobenzene (CAS: 118-74-1) belongs to hazardous persistent organic pollutants due to its carcinogenic effects. According to the classification of the International Agency on Cancer Research (IACR) it refers to carcinogen group 2B (2b).

The input of HCB to the environment takes place with the use of it as a pesticide, with emissions and wastes of industrial and municipal plants, exhaust gases of transport etc.

HCB is a chemical compound widely used as a semi-product (reagent) in organic synthesis. It is used in the production of aniline dyes, synthetic rubber (as a softener for polyvinylchloride and a peptizer for polyvinylstyrene rubber), pentachlorophenol and other pesticides, pyrotechnic mixtures and electrodes (as a regulator of porosity) and in other products and goods.

Industrial production of HCB is based on the reaction of benzene chlorination at the temperature of about 200°C at the atmospheric pressure and at the presence of ferrous oxide as a catalyst. Catalytic chlorination of intoxic isomers of hexachlorocyclohexane (HCH) is an alternative process. In this case HCB release is 80-95% of the theoretical one without additional application of chlorine [*Pesticide Manufacturing and Toxic Materials Control Encyclopedia*, 1980; *Melnikov*, 1974,1987].

In accordance with the Protocol on persistent organic pollutants signed under the Convention on Long-Range Transboundary Air Pollution HCB is included to the list of chemicals which emissions should be inventoried and controlled (Article 3 and Appendix III). HCB total emissions are to be reduced on the annual basis and its use as a pesticide should be prohibited.

HCB is very stable in all the environmental compartments. HCB interactions with gaseous components and different radicals in the air are very slow. There are no data on photodecomposition rates. HCB life-time in the atmosphere is defined by the rate of interaction with hydroxyl-radical and it is 2-3 years depending on the geographical latitude. Due to its weak solubility in water it is poorly washed out with precipitation and its

concentration in water bodies is very low. The main process defining HCB degradation in water is hydrolysis with the formation of pentachlorophenol [HSDB, 2000]. In water HCB is subjected to biodegradation. Under aerobic conditions it takes 2-3 years and under anaerobic conditions - 10 years. In bottom sediments and particulate matter its content is high enough. HCB half-life is maximum among other chlorinated benzenes and according to estimates of *D.Mackay et al.*, [1992] it is not less than 6 years in water.

After the input to soil HCB is kept there for a long period of time. The decrease of its content depends on climatic conditions, soil type as well as on temperature and water regime that explains a wide range of HCB half-life values in soil suggested by different authors. The estimates can differ as much as 10 times [*Pesticide profiles*, 1997; *Wania and Mackay*, 1995]. HCB degradation in soils can be due to chemical transformations, hydrolysis and living organisms impact (biodegradation) under aerobic and anaerobic conditions. It is difficult to predict beforehand what processes prevail. Being weakly soluble in water HCB can be run off by ground waters and HCB content in them cannot be always quantified even by modern analytical methods, though sometimes it reaches sufficiently high values (5 ng/l). HCB is well accumulated in food chains of aqueous and terrestrial ecosystems, for example, the bioaccumulation coefficient in algae is more than 500, in fish –  $10^3$ - $10^4$  [*Anliker et al.*, 1988; *Isnard and Lambert*, 1988], in terrestrial vegetation –  $10^5$ - $10^7$  [*Muir et al.*, 1993].

The study is aimed at substantiation of the selection of parameters for HCB transboundary transport modelling. The report contains the sections of HCB physical-chemical properties, peculiarities of distribution with different environmental compartments and emission data.

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# I. *Physical-chemical properties of hexachlorobenzene*

Formula - C<sub>6</sub>Cl<sub>6</sub>.

Molecular mass - 284.7840, IUPAC Table of International Atomic Weights, 1991.

Under normal conditions hexachlorobenzene is a crystal substance with density 2.044 g/cm<sup>3</sup> at 23°C.

## 1. Boiling and melting point

Temperatures of a substance transition from one aggregate state to another one are basic physical-chemical constants. Differences in boiling and melting temperature values published in the literature are due to differences in methods employed for the determinations of these characteristics and purity of a sample studied. At present there are a sufficient number of handbooks containing basic constants of organic substances and there are published experimental results of their determination and refinement, some of them are demonstrated in tables 1 and 2.

**Table 1:** Hexachlorobenzene melting point

Melting point, °C(Tm)	Reference	Note
228.7 (501,85 K)	<i>Howard P.H. and Meylan W., 1997, Kuehne R. et al., 1995</i>	
231	<i>Chemical Encyclopaedia, 1988</i>	
226	<i>Pesticide profiles, 1997</i>	
228	<i>Miller M. et al., 1984</i>	
229	<i>Banerjee S. et al., 1990</i>	
228.5	<i>Dannenfels R.M. et al., 1991</i>	Mean of 8 values of different authors
230	<i>Mackay D. et al., 1992</i>	Recommended values in most common use for modelling and calculations
	<i>Delle Site A., 1997</i>	
231.8	<i>HSDB, 2000</i>	( <a href="http://toxnet.nlm.nih.gov">http://toxnet.nlm.nih.gov</a> ) on February 10, 2000
229.4	<i>Paasivirta J. et al., 1999</i>	

**Table 2:** Hexachlorobenzene boiling point

Boiling point, °C	Reference	Note
319.3	<i>Howard P.H. and Meylan W., 1997</i>	
322	<i>Miller M. et al., 1984</i>	
309.4	<i>Chemical Encyclopaedia, 1988</i>	
332	<i>Banerjee S. et al., 1990</i>	
321	<i>Dannenfelser R.M. et al., 1991</i>	Mean of 4 values of different authors
322	<i>Mackay D. et al., 1992</i>	Recommended values
325	<i>HSDB , 2000</i>	( <a href="http://toxnet.nlm.nih.gov">http://toxnet.nlm.nih.gov</a> ) on February 10, 2000

## 2. HCB thermodynamic properties

### 2.1. Entropy

In thermodynamic calculations of HCB properties the entropy value of melting is often used. It characterizes the transition of a substance from the solid to liquid state. The entropy value of the process has been determined and averaged by many authors (see table 3).

**Table 3:** HCB melting entropy values determined by different authors

Phase transition	Entropy, $\Delta S$ , J/mol·K		
	Value	Reference	Note
Melting, $\Delta S_m$	50.20	<i>Domalski E.S. and Hearing E.D., 1996</i>	
	57.36	<i>Tsonopoulos C. and Prausnitz J.M., 1971</i>	Cited from <i>Mackay D. et al., 1992</i>
	44.80	<i>Miller M.M. et al., 1984, Dannenfelser R.M. et al., 1991</i>	Selected value for calculations of vapor sorption of non-polar organic compounds by snow and ice, <i>Hoff R.M. et al., 1995</i>
	46.10	<i>Hinckley D.A. et al., 1990</i>	Selected value from literature data
	46.10	<i>Paasivirta J. et al., 1999 with reference on Hinckley D.A. et al., 1990</i>	Value selected for calculations

## 2.2. Enthalpy

Another important thermodynamic constant characterizing phase transitions of a substance is enthalpy. For HCB data on the following processes are available, see table 4.

**Table 4:** Enthalpy of phase transitions

Phase transition	Enthalpy, $\Delta H$ , kJ/mol		
	Value	Reference	Note
Melting, $\Delta H_m$	20.55	<i>Dannenfelser R.M. et al.</i> , 1991	Mean of two values, recommended value – 20.6
	25.18	<i>Domalski E.S. and E.D.Hearing</i> , 1996	At temperature 502.02 K
	24.96	<i>Domalski E.S. and E.D.Hearing</i> , 1996	At temperature 501.87 K
	25.2	<i>Ruelle P. and Kesselring U.W.</i> , 1997	
Sublimation, $\Delta H_s$	79.3	<i>Chemical Encyclopaedia</i> , 1988	
	101.3	<i>Farmer W.J. et al.</i> , 1980	Cited from <i>Delle Site A.</i> , 1997
	$77.4 \pm 0.8$	<i>Wania F. et al.</i> , 1994	
	72.96	<i>Govers H.</i> , 1993	
Dissolution, $\Delta H_{sw}$	33.7	<i>Shiu W.Y. et al.</i> , 1997	
Substance transition from the aqueous phase to the atmosphere, $\Delta H_{wa}$	- 49	<i>ten Hulschen T.E.M. et al.</i> , 1992	Cited from <i>Wania F. et al.</i> , 1998b
Substance transition from the aqueous phase to octanol, $\Delta H_{wo}$	-24.4	<i>Bahadur N.P., et al.</i> , 1997	
Substance transition from octanol to air, $\Delta H_{OA}$	-75.2	<i>Harner T. and Mackay D.</i> , 1995	

### 3. Saturated vapor pressure of a matter in the solid and subcooled liquid state

The transition of a substance from the solid state to the vaporous one is called sublimation and from the liquid state - evaporation. Vapor pressure in equilibrium with the liquid (or solid substance) is called saturated vapor pressure. Saturated vapor pressure at a constant temperature is one of the most important constants.

#### 3.1. HCB saturated vapor pressure in the solid state

Saturated vapor pressure over solid HCB obtained in different ways by experiments and calculations are given in the first two columns of table 5. There are also values from different handbooks alongside values used for modelling of HCB behavior in the environment.

**Table 5:** Hexachlorobenzene saturated vapor pressure (solid state)

Saturated vapor pressure values of solid matter, Pa			
Experimental results	Calculation results	Recommended values	Accepted for modelling
(1.092 ±0.123)E-03 20 °C, GS, <i>Wania F. et al.</i> , 1994	1.15E-03 20-30 °C, average from literary data, <i>Dannenfeiser R.-M. et al.</i> , 1991	2.3E-03 25 °C, <i>Mackay D. et al.</i> , 1992, vol.1	1.85E-03 25 °C, <i>Mackay D. and Wania F.</i> , 1995
1.14E-03 20 °C, GS, <i>Farmer W.J., et al.</i> , 1980, cited from <i>Delle Site A.</i> , 1997	5.4E-03, 25 °C, UNIFAC, <i>Banerjee S. et al.</i> , 1990	1.45E-03 25 °C, <i>Hornsby A.D. et al.</i> , 1996	1.74E-03 25 °C, <i>Wania F. and Mackay D.</i> , 1995
2.29E-03 25 °C, GS, OECD, Guidelines for testing of chemicals, cited from <i>Delle Site A.</i> , 1997	4.34E-03, 25 °C, modified Watson equation, <i>Paasivirta J. et al.</i> , 1999	2.39E-03, 25 °C, <i>Howard H.P. and Meylan W.</i> , 1997	1.5E-03 25 °C <i>Mackay D. and Paterson S.</i> , 1991
1.5E-03 20 °C, GS, <i>Rordorf B.F. et al.</i> , 1986, cited from <i>Delle Site A.</i> , 1997		1.45E-03, 20-30 °C, <i>Pesticide Profiles</i> , 1997	1.5 E-03 25 °C, <i>Paterson S. et al.</i> , 1991
2.87E-03 25 °C, M, <i>Rordorf B.F. et al.</i> , 1986, cited from <i>Delle Site A.</i> , 1997			1.03E-03 25 °C, <i>Nash R.G.</i> , 1989

continued

Saturated vapor pressure values of solid matter, Pa			
Experimental results	Calculation results	Recommended values	Accepted for modelling
1.48E-03 20 °C, M, <i>Sears G.W. and Hopke E.R.</i> , 1949, cited from <i>Delle Site A.</i> , 1997			1.0E-03 20 °C, <i>Riederer M.</i> , 1990
4.6E-04 20 °C, RV, <i>Dobbs A.J. and Cull M.R.</i> , 1982, cited from <i>Delle Site A.</i> , 1997			1.0E-03 20 °C, <i>Bacci E. et al.</i> , 1990a
7.39E-04 20 °C, RV, <i>Gueckel W. et al.</i> , 1982, cited from <i>Delle Site A.</i> , 1997			2.61E-04 7.5 °C, <i>Pacyna J.M. et al.</i> , 1994
1.49E -03 GC, <i>Bidleman T.F.</i> , 1984			2.5E-03 ~17°C, <i>Scheringer M.</i> , 1997
1.14E-03 GC, <i>Bidleman T.F.</i> , 1984			2.6E-04 10 °C, <i>McLachlan et al.</i> , 1990
6.49E-04 20 °C, GC, <i>Hinckley D.A. et al.</i> , 1990			
1.11E-03 25 °C, GC, <i>Hinckley D.A. et al.</i> , 1990			

Abbreviations in table 5 used for denoting experimental methods:

GS - method of gas saturation;

M - manometric method;

GC – method of gas chromatography;

RVR - method of relative evaporation rate.

Reviewing abundant material on the determination of saturated vapor pressure of poorly volatile substances *A.Delle Site* [1997] came to a conclusion that most reliable are the results of three experimental methods: method of gas saturation (GS), gas chromatography method (GC) and the method of relative evaporation rate (RVR). GS is the method of direct measurement of the saturated vapor pressure of a substance over the solid state. The manometric method (in the table it is denoted by the letter M) and the effusive method can be also referred to direct measurements. The disadvantage of the two methods is their sensitivity to the measured substance purity. RVR is an indirect method for saturated vapor pressure determination. The method is based on the determination of relative evaporation

rate of the substance and more often water plays the role of a comparable substance since for insoluble (or poorly soluble) in water substances solid matter vapor pressure does not depend upon presence of water. The established dependencies between molecular masses and saturated vapor pressure of two substances (see eq.1) allow us to calculate saturated vapor pressure values of a studied substance from the results of distillation of its suspension in water:

$$W_A/W_B = (M_A P_A) / (M_B P_B), \quad (1)$$

where  $W_A$  and  $W_B$  - evaporation rates of *A* and *B* substances;

$M_A$  and  $M_B$  - molecular masses of *A* and *B*;

$P_A$  and  $P_B$  - saturated vapor pressure of *A* and *B*.

GC is an indirect method of saturated vapor pressure determination which makes a direct measurement of retention times (volumes) of substances for which correlation dependencies with certain values are determined.

The key equation connecting the retention time and saturated vapor pressure of two substances, one of which is a reference substance, can be written as:

$$\log (t_{S2}/ t_{S1}) = \log (P_1/P_2) + \log (\gamma_{1 SP}/ \gamma_{2 SP}) \quad (2)$$

where  $t_S$  - retention time;

$P$  - saturated vapor pressure;

$\gamma_{SP}$  - stationary phase activity coefficient;

log – here and hereinafter means decimal logarithm.

While measuring two conditions should be met - constant temperature and polarity of the stationary phase.

For a great number of substances only GC method made it possible to determine saturated vapor pressure values in the solid and subcooled liquid state, since for various reasons it is impossible to do it by direct methods.

The third group of methods is conventionally called “calculated” ones. It combines both sufficiently simple calculations by Clapeyron-Clausius equation as modified by Antoine and Watson-Grain and rather sophisticated calculation methods, for example, QSAR model based on correlation dependencies between saturated vapor pressure and some topological indices derived from a substance chemical structure - the method of quantitative structure - activity relationships (QSAR).

Basic Clapeyron-Clausius equation is:

$$d \ln P/dT = \frac{\Delta H_{vap}}{\Delta Z \cdot RT^2} \quad (3)$$

where  $P$  - vapor pressure;

$T$  - absolute temperature;

$\Delta H_{vap}$  – enthalpy of vaporization;

$R$  - universal gas constant;

$\Delta Z$ - compressibility factor determined as  $\Delta Z = P\Delta V/RT$ , where  $\Delta V$  – volume increment in the vaporization of 1 mol of substance. The simplest equation, obtained by integration of (3) is:

$$\ln P = A_1 - B_1/T, \quad (4)$$

in this form it can be employed as an equation for saturated vapor pressure dependence on temperature.

Basic equation UNIFAC connects saturated vapor pressure with solvate-chromic parameters:

$$\log P = 6.94 - (2.25V_u + 4.23 \log \gamma_C) - 0.577 \log \gamma_R - 0.01 (T_m - 25) \quad (5)$$

where  $V_u$  - molecular volume;

$\gamma_C$  and  $\gamma_R$  - activity coefficients,  $C$  - combinatorial and  $R$  - residual;

$T_m$  - melting point, °C.

*J.Paasivirta et al.* [1999] calculated  $P_S$  using the relationship between  $P_S$  and  $P_L$  - vapor pressure of a substance in the solid state and subcooled liquid state:

$$\Delta S_m = \ln (P_S/P_L) R / (1 - T_m / T) \quad (6)$$

where  $\Delta S_m = 46.1$  J/mol·K - melting entropy;

$T_m = 229.4$ °C - melting point.

$P_L$  value is determined from equation:

$$\log P_L = A_{RT} - B_{RT} \cdot RRT \quad (7)$$

where  $A_{RT}$  and  $B_{RT}$  - coefficients in temperature dependence equation, determined by calculations using measurements by gas chromatography [*Hickley et al.*, 1990];

RRT - relative retention time. It is determined by gas chromatography method. RRT is a constant for a given stationary phase and temperature. RRT values are of a reference character.

### **3.2. Saturated vapor pressure of HCB in the subcooled liquid state**

Vapor pressure of the subcooled liquid are presented like saturated vapor pressure of HCB in the solid state.

**Table 6:** HCB saturated vapor pressure (in the subcooled liquid state)

Vapor pressure of the subcooled liquid, Pa			
Experimental results	Calculation results	Recommended values	Accepted for modelling
0.0778 20 °C, GC, <i>Hinckley D.A. et al.</i> , 1990	0.24 25 °C, <i>Govers H.</i> , 1993	0.251 25 °C, <i>Mackay D. et al.</i> , 1992, vol.1	0.251 25 °C, <i>Wania F. and Mackay D.</i> , 1995
0.119 25 °C, GC, <i>Hinckley D.A. et al.</i> , 1990	0.186 20 °C, <i>Bidleman T.F. et al.</i> , 1986, calculations by eq.4, values of A and B see in table 7		0.0584 7.5 °C, <i>Pacyna J.M.</i> , 1994
0.122 25 °C, GC, <i>Bidleman T.F.</i> , 1984	0.0821 25 °C, <i>Paasivirta J. et al.</i> , 1999, calculations by eq.4, values of A and B see in table 7		0.13 20 °C, <i>Bacci E. et al.</i> , 1990 b
0.159 25 °C, GC, <i>Bidleman T.F.</i> , 1984	0.271 25 °C, <i>Paasivirta J. et al.</i> , 1999, by eq. 6 and 7		0.01 0 °C, <i>Cotham W.E. and Bidleman T.F.</i> , 1991
	0.1041 25°C, calculations by eq.6 for this review*		0.25 <i>Wania F. and Mackay D.</i> , 1996
	0.1478 25 °C, by eq.6 for this review**		
	0.1823 25 °C, by eq.6 for this review***		

If equation (6) and different values of  $\Delta S_F$  and  $T_m$  are used the discrepancy of calculated values can be as much as 1.5 time, see table 6, column 2:

\*  $\Delta S_F = 46.1 \text{ J/mol}\cdot\text{K}$  - *Hinckley D.A. et al.*, 1990;

$T_m = 230 \text{ °C}$  и  $P_S = 2.3\text{E-}03 \text{ Pa}$  - *Mackay D. et al.*, 1992, vol.1;

\*\*  $\Delta S_F = 50.2 \text{ J/mol}\cdot\text{K}$  – *Domalski E.S. and Hearing E.D.*, 1996;

$T_m = 228.7 \text{ °C}$  и  $P_S = 2.39\text{E-}03 \text{ Pa}$  - *Howard H.P. and Meylan W.*, 1997;

\*\*\*  $\Delta S_F = 50.2 \text{ J/mol}\cdot\text{K}$  - *Domalski E.S. and Hearing E.D.*, 1996;

$T_m = 230 \text{ °C}$  - *Mackay D. et al.*, 1992, vol.1;

$P_S = 2.87\text{E-}03 \text{ Pa}$  - *Delle Site A.*, 1997.

The question of its importance for the long-range transport modelling needs a special investigation. The values obtained by us are sufficiently close to measured ones but somewhat lower than those presented in papers by *H.Govers* [1993] *J.Paasivirta et al.* [1997] and recommended by *D.Mackay et al.* [1992].

### 3.3. *Temperature dependence of saturated vapor pressure*

The dependence of saturated vapor pressure on temperature (T) can be calculated by Antoine equation:

$$\log P = A - \frac{B}{C + T} \quad (8)$$

For HCB in the subcooled liquid state *R.M.Stephenson and S.Malanowski* [1987] give the following coefficient values for equation (8).

$$A = 7.35248; \quad B = 2786.78; \quad C = -61.33$$

Temperature dependence of saturated vapor pressure can be described by equation (4). Values of A and B in (4) determined for HCB by different authors are summarized in table 7.

**Table 7:** Coefficients in the equation of temperature dependence of saturated vapor pressure

Coefficient values		Reference
<b>A</b>	<b>B</b>	
11.11	3582	<i>Hinckley D. A. et al., 1990</i>
11.04	3561	<i>Bidleman T.F. 1984 cited from Hinckley D.A. et al., 1990</i>
8.5	2873	<i>Hoff R.M. et al., 1995</i>
8.42	2834	<i>Paasivirta J. et al., 1999</i>

For the comparison of saturated vapor pressure variations with temperature growth we have made calculations using coefficients of temperature dependence from table 7. The results are demonstrated in table 8.

**Table 8:** HCB saturated vapor pressure as a function of temperature

Temperature, °C	Vapor pressure of the subcooled liquid, Pa			
	<i>Hinckley D.A. et al., 1990</i>	<i>Bidleman T.F. 1984, cited from Hinckley D.A. et al., 1990</i>	<i>Hoff R.M. et al., 1995</i>	<i>Paasivirta J. et al., 1999</i>
- 10	3.162E-03	3.236E-03	3.8019E-03	4.4668E-03
- 5	5.623E-03	5.97E-03	6.166E-03	7.943E-03
0	9.772E-03	1.0E-02	9.55E-03	1.096E-02
5	1.698E-02	1.905E-02	1.479E-02	1.698E-02
10	2.884E-02	2.884E-02	2.239E-02	2.570E-02
15	4.786E-02	4.786E-02	3.338E-02	3.80E-02
20	7.762E-02	7.762E-02	5.012E-02	5.623E-02
25	12.589E-02	12.589E-02	7.244E-02	8.128E-02
30	19.498E-02	19.498E-02	10.471E-02	11.749E-02

The coefficients calculated by *D.A.Hinckley et al.* [1990] and *T.F.Bidleman* [1984], are rather close, therefore HCB saturated vapor pressure calculated by them coincide in many points. The parameter variation obtained with the coefficients suggested by *R.M.Hoff et al.* [1995] is in the intermediate position and in a good agreement but in the pair with *J.Paasivirta et al.* [1999]. The last variant results in less abrupt pressure increase with temperature.

## 4. Solubility

Solubility is another important property of a substance, which along the saturation vapor pressure defines the character of its behavior in the environment. The rates of conversion between different phases directly or indirectly depend on solubility in water. Solubility defines vertical motions in the soil, the distribution in the water depth and the availability of a substance in the dissolved form or sorbed on particles. Solubility plays a crucial role in the input of a substance from the soil to a plant and in scavenging from the lower troposphere.

From the viewpoint of thermodynamics solubility defines substance concentration in the solution being in equilibrium with its own solid phase.

HCB is weakly soluble in water and well soluble in acetone, benzene and other organic liquids. This property can be determined experimentally (by direct or indirect methods) as well as it can be calculated by models based on a substance structure and its behavior at dissolving. HCB solubility has been measured and calculated by many authors, see table 9.

**Table 9:** HCB solubility in water (in the solid state)

Hexachlorobenzene solubility in water, $S_w$ , g/m <sup>3</sup>			
Experimental results	Calculation results	Recommended values	Accepted for modelling
0.005 SF, 25 °C, <i>Yalkowsky S.H. et al.</i> , 1979	0.0086, 20-30 °C, average from literary data, <i>Dannenfelser R.-M. et al.</i> , 1991	0.005, 25 °C, IUPAC, 1985	0.005, 25 °C, <i>Mackay D. and Paterson S.</i> , 1991.
0.00544 ± 0.00018 GC, 25 °C, <i>Shiu W.Y. et al.</i> , 1997	0.006, 25 °C, <i>Isnard P. and Lambert S.</i> , 1988,	0.005, 25 °C, <i>Mackay D. et al.</i> , 1992, vol. 1	0.005, 25 °C, <i>Paterson S. et al.</i> , 1991.
0.035, 25 °C, <i>Isnard P. and Lambert S.</i> , 1988	0.00518, 25 °C, <i>Kuehne R. et al.</i> , 1995	0.005, 25 °C, <i>Hornsby A. et al.</i> , 1996	0.0063, ~17 °C, <i>Scheringer M.</i> , 1997
0.047, GC, 25 °C, <i>Miller M.M. et al.</i> , 1984	0.00588, 25 °C, <i>Pinsuwan S. et al.</i> , 1995	0.0062, 25 °C, <i>Howard H.P and Meylan W.</i> , 1997	0.002, 10 °C, <i>McLachlan M. et al.</i> , 1990
0.00595, 25 °C, <i>Kuehne R. et al.</i> , 1995	0.0506, 25 °C, <i>Ruelle P. and Kesselring U.W.</i> , 1997		0.03987, * 20 °C, <i>Riederer M.</i> , 1990
			0.020, * 25 °C, <i>Mackay D. and Wania F.</i> , 1995
			0.020, * 25 °C, <i>Wania F. and Mackay D.</i> , 1995

\*- calculated from the relationship of saturated vapor and Henry's law constant.

Conventional symbols used in the table and their concise description:

SF - shake flask - a routine method for the determination of substance solubility by shaking or stirring by magnetic agitator and thermostating for not less than 48 hours. Then the substance content in the liquid state is determined by gas chromatography or by high performance liquid chromatography.

GC - generator column is a method for the determination of a hydrophobic compound solubility using a special so-called "generator column". At first the substance is dissolved in an organic solvent which is put on a sorbent with which the generator column is filled. Then water is passed through the sorbent with substance and the saturated solution is led to extracting column where the compound studied is sorbed at a specially selected phase. The compound extraction is made by a solvent mixture which at the same time is the mobile phase at subsequent determination by high performance liquid chromatography (HPLC). Both methods are employed for the determination of HCB solubility. SF method sometimes gives overestimated results due to the formation of fine crystal particulate in the water phase. This issue is discussed in detail by *W.Y. Shiu et al.* [1997].

The works of *P. Isnard and S. Lambert* [1988, 1989] are dedicated to studies and refinement of dependencies between hydrophobic substance solubility, "octanol-water" partition coefficients ( $K_{OW}$ ) and bioaccumulation factor (BCF). Solubility and  $K_{OW}$  are well correlated and nowadays there are more than ten various regression equations the coefficients for which can be calculated or obtained experimentally. HCB solubility values are demonstrated in table 9. The second column contains calculated values obtained by introduction to the regression equation of the third term connecting solubility  $K_{OW}$  and melting point. The authors consider that the inclusion of this parameter raises the result quality. A profound analysis of many calculation methods for the solubility determination of 694 organic species is made in the paper by *R. Kuehne et al.* [1995]. The main criterion for the estimation of the obtained value was the discrepancy between calculated and measured values not exceeding 0.38 log. For liquids the calculation results were better than for a solid matter. To obtain better results the authors suggest to pay more attention to variability of melting entropy and use the melting temperature as a parameter.

*P.Ruelle and U.W.Kesselring* [1997] take a general thermodynamic equation and transformed it to a rather simple form for hydrophobic substances. The following physical-chemical properties are used as parameters: melting enthalpy and temperature, molar aqueous volume and molar volume of the substance investigated. 531 species have been studied by this method and a relative error does not exceed 0.37 log.

Solubility of any substance is a function of temperature. This dependence for HCB was studied by *W.Y.Shui et al.* [1997]. The data presented in table 10 clearly demonstrate HCB content increase in solution with temperature increase.

**Table 10:** HCB solubility growth with temperature increase

Solubility, g/m <sup>3</sup>	Temperature, °C				
	5	15	25	35	45
	0.0022 ± 0.00011	0.0035 ± 0.0001	0.00544 ± 0.00018	0.00853 ± 0.0002	0.014 ± 0.00025

The equation coefficients of the form  $\log S_w = A - B/T$  determined by different authors are shown in table 11.

**Table 11:** Coefficients in the equation of temperature dependence for solid HCB solubility

Coefficient values		Reference
A	B	
0.254	1314	<i>Mackay D. and Wania F.</i> , 1995; <i>Wania F. and Mackay D.</i> , 1995
- 1.55	380	<i>Hoff R.M. et al.</i> , 1995

In a subcooled liquid state HCB solubility  $S_L$  is not so widely employed in calculations including model calculations unlike the vapor pressure. Only *E.Bacci et al.* [1990b], while investigating organic substance vapor bioconcentrations, used  $S_L$  in their calculations. They chose the results of *L.R.Suntio et al.* [1988], ( $S_L=0.2848$  g/m<sup>3</sup>) but not those of *D.W.Hawker and D.W.Conell* [1989] ( $S_L=0.86$  g/m<sup>3</sup>) or the  $S_L$  value recommended by *D.Mackay et al.* [1992] ( $S_L=0.5325$  g/m<sup>3</sup>).

Temperature dependence  $S_L$  with coefficients calculated by *J.Paasivirta et al.* [1999] are given below:

$$\log S_L = 0.45 - 1212/T \quad (9)$$

## 5. Henry's law constant ( $H$ )

The equilibrium at the interface of the water surface and the atmosphere is described by Henry's law which states that at constant temperatures and moderate pressures gas solubility in the liquid is directly proportional to the pressure of this gas over the liquid. The behavior of moderately volatile organic substances is characterized by "air-water" partition coefficient  $K_{AW}$  or by Henry's law constant connected by the equation:

$$K_{AW} = H/RT \quad (10)$$

where  $R$  - universal gas constant equal to 8.314 J/mol·K;

$T$  - absolute temperature, K.

A direct determination of Henry's law constant can be made by the measurement of equilibrium concentration of a substance in solution and its concentration in the vapor phase over the liquid. At the same time it is sufficient to determine the variation of substance concentration in the saturated solution when a gas flux is passing through it. A specific decrease of a substance in the aqueous solution of a limited volume can be described by the kinetic equation of the first order:

$$\ln (C_W/C_{W0}) = - \frac{GK_{AW} t}{V_W} \quad (11)$$

where  $C_W$  and  $C_{W0}$  - substance concentration in the solution at  $t$  time and at the beginning of the experiment:

$G$  - gas flow rate;

$V_W$  - water volume.

Substance concentration measurements form the basis of the well-known gas stripping method. For calculations of Henry's law constant value relationships (12) and (13) can be used:

$$\log H = \log P_S - \log S_m \quad (12)$$

where  $H$  – Henry's law constant, Pa m<sup>3</sup>/mol;

$P_S$  - vapor pressure of the solid matter, Pa;

$S_m$  - melting entropy, J/mol·K.

and

$$\log H = \log P_S - \log S_W - 6 \quad (13)$$

where  $H$  – Henry's law constant, Pa m<sup>3</sup>/mol;

$S_W$  - substance solubility in water, mol/l.

The application of different values of saturated vapor pressure and solubility values leads to an appreciable scattering of estimates (Table 12). The table also provides reference Henry's law constant values and the value employed in modelling HCB behavior in the environment.

**Table 12:** Henry's law constants for HCB

Henry's law constants, Pa m <sup>3</sup> /mol			
Experimental results	Calculation results	Recommended values	Accepted for modelling
132.9, 23 °C, gas stripping, distilled water, <i>Atlas E. et al.</i> , 1982	2.9 – 148, 25 °C, <i>Suntio R.L. et al.</i> , 1988, cited from <i>Cotham W. and Bidleman T.</i> , 1991	131 25 °C, <i>Mackay D. et al.</i> , vol.1, 1992	24.76 25 °C, <i>Mackay D. and F.Wania</i> , 1995
172.3, 23 °C, gas stripping, sea water, <i>Atlas E. et al.</i> , 1982	7.12, 25 °C, <i>Suntio R.L. et al.</i> , 1988 cited from <i>Finizio A. et al.</i> , 1997	172, 25 °C, <i>Howard H.P. and Meylan W.M.</i> , 1997	24.76, 25 °C, <i>Wania F. and D.Mackay</i> , 1995
71.4, 23 °C, gas stripping, distilled water, <i>Atlas E. et al.</i> , 1983	58.3 20 °C, <i>Dannenfelser R.-M. et al.</i> , 1991	58.8 25 °C, <i>HSDB</i> , 2000	49.6, 25 C, <i>Wania F. et al.</i> , 1998b
73.8, 23 °C, gas stripping, lake water, <i>Atlas E. et al.</i> , 1983	69 25 °C, <i>Govers H.</i> , 1993		11, 25 °C, <i>Nash R.G.</i> , 1989
100.9, 23 °C, gas stripping, sea water, <i>Atlas E. et al.</i> , 1983	139, 25 °C, <i>Mueller et al.</i> , 1994		132, ~ 25 °C, <i>Scheringer M.</i> , 1997
170, 25 °C, <i>Murphy T.J. et al.</i> , 1987, cited from <i>McConnell L.L. et al.</i> , 1996	131, 25 °C, <i>Shiu W.Y. and Mackay D.</i> , 1997		15 – fresh water; 18 – sea water, 0 °C, <i>Cotham W. and Bidleman T.</i> , 1991
30, 25 °C, <i>ten Hulschen T.E.M. et al.</i> , 1992, cited from <i>Iwata H. et al.</i> , 1995.	10.1 – 11.8 – winter; 18.8 – 40.7 – summer, <i>Hoff R.M. et al.</i> , 1996		131.5, 20 °C, <i>Bacci E. et al.</i> , 1990, a
	140 25 °C, <i>Ballschmiter K. and Wittlinger R.</i> , 1991		131, 25 °C, <i>McLachlan M. et al.</i> , 1995
			37.7, 10 °C, <i>McLachlan M. et al.</i> , 1990
			7.14, 20 °C, <i>Riederer M.</i> , 1990

As seen from table 12 Henry's law constant values for HCB, a well studied compound, vary within a wide range. Besides experimental data demonstrate different behavior of the compound at the "air-water" interface at different salinity of the solution. For example, according to *E.Atlas et al.* [1983] data, salinity increases Henry's law constant for distilled and sea water. The difference reaches 1.4 time.

The equilibrium in the "air-water" system and correspondingly equilibrium concentration values in these compartments depend on the temperature. Temperature dependence equation is similar to the equations for temperature dependence of saturated vapor pressure and substance solubility and it has the form like equation (4):

$$\log H = A - B/T$$

where  $H$  – Henry's law constant, Pa m<sup>3</sup>/mol;

$A$  and  $B$  - dimensionless coefficients.

Their values obtained by different authors are shown in table 13.

**Table 13:** Temperature dependence coefficients of Henry's law constant (Pa m<sup>3</sup>/mol)

Coefficient values		Reference
A	B	
9.98	2560	<i>ten Hulschen T.E. et al.</i> , 1992, cited from <i>Wania F. and Mackay D.</i> , 1995
9.88	2560	<i>ten Hulschen et al.</i> , 1992, sea water, cited from <i>Vozhennikov O.I. et al.</i> , 1997
10.05	2493	<i>ten Hulschen et al.</i> , 1992, fresh water, cited from <i>Hoff R. M. et al.</i> , 1995
7.97	1622	<i>Paasivirta J. et al.</i> , 1999

## 6. “Air-water” partition coefficient and wet deposition ratio

“Air-water” partition coefficient -  $K_{AW}$  is dimensionless Henry’s law constant. The value inverse to  $K_{AW}$  is called wet deposition ratio  $W_V$  of a substance occurring in the atmosphere as vapors. This value can be determined experimentally using the ratio of substance concentrations in wet depositions and in the air or it can be calculated by the equation:

$$W_V = C_{\text{rain}}/C_{\text{air}_g} = RT/H, \quad (13)$$

where  $C_{\text{rain}}$  - equilibrium concentration of a substance in wet depositions,  $\text{pg}/\text{m}^3$ ;

$C_{\text{air}_g}$  - equilibrium concentration of a substance in the air in the vapor-phase,  $\text{pg}/\text{m}^3$ ;

$R$  - universal gas constant equal to  $8.314 \text{ J}/\text{mol K}$ ;

$T$  - absolute temperature, K;

$H$  – Henry’s law constant,  $\text{Pa m}^3/\text{mol}$ .

Experimental values  $W_V$  obtained by different authors and estimates obtained with different Henry’s law constant values made for this review are presented in table 14.

**Table 14:** HCB washout ratio

HCB wet deposition ratio, $W_V$	Method of determination	Reference	Note
$1.02 \times 10^3$	Calculations using ratios of concentrations in air and precipitation (experimental data)	<i>Hoff R.M. et al.</i> , 1996	Mean annual concentrations in the region of Eagle Harbor, MI, (Superior)
$5 \times 10^4$	-«-	-«-	Sleeping Bear Dunes, (Michigan)
$5 \times 10^4$	-«-	-«-	Sturgeon Point, NY, (Erie)
$2.3 \times 10^3$	-«-	-«-	Point Petre, ON, (Ontario)
$1.5 \times 10^3$	-«-	<i>Eisenreich S. et al.</i> , 1981	The Great Lakes, Canada
348.15	Calculations by formula (13) using different values of Henry’s law constant, $T=25 \text{ }^\circ\text{C}$	<i>Finizio A. et al.</i> , 1997	$H = 7.12$
18.92	-«-	<i>Mackay D. et al.</i> , 1992, vol.1	$H = 131$
14.41	-«-	<i>Howard H. P. and Meylan W.M.</i> , 1997	$H = 172$
42.16	-«-	<i>HSBD</i> , 2000	$H = 58.8$
50.00	Calculations using ratio to $K_{aw}$	<i>Wanya F. et al.</i> , 1998b	$K_{aw} = 2.0 \times 10^{-2}$

34.72	-«-	<i>Atlas E. et al., 1983</i>	$K_{aw} = 5.4 \times 10^{-2}$
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The analysis of Table 14 data reveals that calculated values  $W_V$  differ from measurements by one or two orders of magnitude. Using the minimum value of Henry's law constants selected we obtain the best agreement with observations. Thus in calculations of HCB scavenging from the atmosphere using  $H$  values from column "Note" of the table it can be expected that we obtain underestimated substance fluxes onto the water surface.

## 7. Partition coefficients

### 7.1. “Octanol-water” partition coefficient ( $K_{OW}$ )

( $K_{OW}$ ) is a value determined as the ratio between substance concentration in the water phase and its concentration in octanol. This coefficient is a measure of substance hydrophobic property and reflects its capability to be accumulated in soil and bottom sediments and the hazard to be accumulated in fat tissues of biological organisms (bioaccumulation). Value  $K_{OW}$  can be determined experimentally or it can be calculated on the basis of correlation dependencies between substance hydrophobic property and its solubility, retention time determined by method in reversed-phase high pressure liquid chromatography (HPLC) and other characteristics. Usually  $K_{OW}$  is expressed as a decimal logarithm ( $\log K_{OW}$ ). Table 15 presents  $K_{OW}$  calculated and measured HCB values and values used in further calculations.

**Table 15:** Partition coefficient  $K_{OW}$

log $K_{OW}$ (25 °C)			
Experimental results	Calculation results	Recommended values	Accepted for modelling
5.47, GC, <i>Doucette W.J. and Andren A.</i> , 1988	5.41, <i>Dannenfelser R.-M. et al.</i> , 1991	5.5, <i>Mackay D. et al.</i> , 1992, vol.1	5.5, <i>Mackay D. and F.Wania</i> , 1995, <i>Wania F. and D.Mackay</i> , 1995, <i>McLachlan M. et al.</i> , 1990
5.46 ±0.02, SF, <i>Bahadur N.P. et al.</i> , 1997	5.665, <i>Pinsuwan S. et al.</i> , 1995	5.73, HSDB, 2000	5.47, <i>Paterson S. et al.</i> , 1991, <i>Mackay D. and Paterson S.</i> , 1991, <i>Riederer M.</i> , 1990
5.73, SF, <i>De Bruijn et al.</i> , 1989	5.49, <i>Govers H.</i> , 1993	5.31, Medchem Database, cited from <i>Mueller J.F. et al.</i> , 1994	5.31, <i>Schering M.</i> 1997
5.731±0.009, SF, <i>Sabljić A. et al.</i> , 1993	5.14, <i>Paasivirta J.</i> , 1999		6.0 <i>Bacci E. et al.</i> , 1990 b
5.22 cited from <i>Isnard P. and S.Lambert</i> , 1988	5.66, <i>Isnard P. and S.Lambert</i> , 1988		

continued

log $K_{OW}$ (25 °C)			
Experimental results	Calculation results	Recommended values	Accepted for modelling
6.00, <i>Suntio L.R. et al.</i> , 1988 – cited from <i>Finizio et al.</i> , 1997	6.42, method A, <i>Doucette W.J. and Andren A.</i> , 1988		
5.47, GC, <i>Miller M. et al</i> , 1984	6.53, method B, <i>Doucette W.J. and Andren A.</i> , 1988		
	6.22, method C, <i>Doucette W.J. and Andren A.</i> , 1988		
	5.80, method D, <i>Doucette W.J. and Andren A.</i> , 1988		
	5.22, method E, <i>Doucette W.J. and Andren A.</i> , 1988		
	4.75, method F, <i>Doucette W.J. and Andren A.</i> , 1988		

For the experimental determination of  $K_{OW}$  the same methods as for the determination of solubility are employed. It is the simplest and cheapest method based on the extraction after intensive mixing (shake-flask). Its essential disadvantage is the formation of abundant and true emulsion. *J.Sangster* [1989] considers that this method is not applicable to a substance with  $\log K_{OW}$  exceeding 4.5. *N.P.Bahadur et al.* 1997 have made good use of this method for the evaluation of  $K_{OW}$  temperature dependence. The experimental results are demonstrated in table 15. Another widely used method is the method of “generator column” (GC). In this case the column for liquid chromatography is adapted for  $K_{OW}$  measurements. The column is filled with silanized silica gel as a sorbent. The substance is put into the column in the form of a solution in octanol saturated with water. Then the substance is eluted by water saturated octanol and analysed either by HPLC method or by gas chromatography (GC).

The calculation methods presented in Table 15 include first of all a simple compilation as have been done by *R.-M.Dannenfelsler et al.* [1997], and by *H.Govers* [1993]. Many authors use correlation dependencies. The comparison of different correlation dependencies for the determination of  $K_{OW}$  value was made by *W.J.Doucette and A.Andren* [1988]. The least discrepancy between calculated and measured values was obtained when molecular connectivity indices were used, see table 16.

**Table 16:** Mean errors in calculations of  $K_{OW}$ , %

Method	Mean error	Regression equation
A (Hansch and Leo)	10.34	-
B (Nys and Rekker)	10.03	-
C (HPLC – RT)	7.01	$\log K_{OW} = -1.87 (RT)^2 + 7.04 (RT) + 1.29$
D (MW)	6.17	$\log K_{OW} = -1.35 \cdot 10^{-5} (MW)^2 + 0.021 (MW) + 1.03$
E (MCI)	4.19	$\log K_{OW} = -0.05 (MCI)^2 + 1.27 (MCI) - 0.085$
F (TSA)	6.11	$\log K_{OW} = 0.024 (TSA) - 0.099$

Conventional designations used in the table:

Method A - is suggested by *Hansch and Leo* [1978]. It is based on fragment constants obtained empirically and structural factors for direct calculations of  $\log K_{OW}$  using only substance structural formula;

Method B – is a direct method of calculations using only the structural formula and relevant constants of hydrophobic fragments, [*Nys and Rekker*] 1973;

Method C – is a method of  $K_{OW}$  correlation with retention time (RT) in reverse-phase HPLC;

Method D - is based on  $\log K_{OW}$  correlation with molecular mass (MW) of a substance;

Method E - is based on  $\log K_{OW}$  correlation with molecular connectivity indices (MCI);

Method F – is based on correlation with total surface area (TSA) of the molecule.

*L.Paasivirta et al.* [1999] used the following equation for  $K_{OW}$  calculation:

$$\log K_{OW} = A_Z - B_Z \log S_L \quad (14)$$

where  $A_Z$  and  $B_Z$  are the coefficients determined by  $S_L$  measurement data of a great number of organic species at 25°C carried out by HPLC;

$S_L$  - substance solubility in the subcooled liquid state.

## Log $K_{OW}$ temperature dependence

Log  $K_{OW}$  value decreases with temperature increase.  $K_{OW}$  numerical values in the temperature range of 5-45°C were measured and presented in the paper by *N.P.Bahadur et al.* [1997], see table 17.

**Table 17:** Log  $K_{OW}$  temperature dependence

Temperature, °C	log $K_{OW}$
5	5.74 ± 0.04
15	5.60 ± 0.07
25	5.46 ± 0.02
35	5.30 ± 0.01
45	5.17 ± 0.05

Log  $K_{OW}$  dependence on temperature is described by equation:

$$\log K_{OW} = A - \Delta H / 2.303 RT \quad (15)$$

where  $A$  - dimensionless constant equal to 1.806 for HCB;

$\Delta H_{WO}$  - enthalpy of substance transfer from the water phase to octanol one.

$\Delta H_{WO}$  for HCB is -24.4 kJ/mol.

## 7.2. “Organic carbon-water” partition coefficient ( $K_{OC}$ )

Coefficient  $K_{OC}$  characterizes the process of substance adsorption on soil particles, bottom sediments and particulate matter in the air and water.  $K_{OC}$  determination in experiment is made by equation:

$$K_{OC} = C_{OC} / C_W \quad (16)$$

where  $C_{OC}$  - equilibrium concentration of a substance associated with particulate organic carbon of the test medium;

$C_W$  - equilibrium concentration of a substance in the water phase (true solution);

$K_{OC}$  is the dimensional value usually expressed in m<sup>3</sup>/kg, ml/g and the like.

The coefficient of partitioning between particulate organic carbon of soil, bottom sediments or particulate matter is directly connected with another coefficient characterizing sorption on particles -  $K_d$  by the following relationship:

$$K_d = K_{OC} f_{OC} \quad (17)$$

where  $f_{OC}$  - mass fraction of organic particulate carbon on particles which amounts to 0.1-0.2 [Bidleman, 1999] for aerosol particles; for soil - 0.02, bottom sediments - 0.004; for particulate in the depth of fresh waters and seas - 0.2 [Mackay and Wania, 1995].

Measurements of  $K_{OC}$  is rather a complicated problem since many factors such as, pH, size of particles and their mineral composition etc. influence its value. At present calculation methods based on correlation dependencies between  $K_{OC}$  and other physical-chemical constants and properties of organic compounds are being developed and widely used.

$K_{OC}$  values obtained by different methods are shown in table 18.

**Table 18:**  $K_{OC}$  partition coefficient values

log $K_{OC}$ (25 °C)			
Experimental results	Calculation results	Recommended values	Accepted for modelling
4.77, HPLC, bottom sediments, <i>Hodson J. and Williams N.A.</i> , 1988	3.92, soils, <i>Dannenfesler R.-M. et al.</i> , 1991	4.9 ; 5.5 – bottom sediments of fresh waters, HSDB, 2000	3.915, soils, <i>Nash R.G.</i> , 1989
4.54,* soils, <i>Sacan M.T. and Balcioglu I.A.</i> , 1996	4.67, soils, <i>Sacan M.T. and Balcioglu I.A.</i> , 1996	3.6; 4.0 – soils, HSDB, 2000	5.25, soils, <i>Beck A.J. et al.</i> , 1996
3.53,* particulate matter in water, <i>Luehrs D.C. et al.</i> , 1996	3.28, particulate matter in water, <i>Luehrs D.C. et al.</i> , 1996		
	3.99, soils, <i>Sabljić A. et al.</i> , 1995		

\* - the method of determination is not indicated.

We have not made the comparison of measured data from table 18 since  $K_{OC}$  were determined for particles of different origin. However, *J.Hodson and N.A.Williams* [1988] analysed  $K_{OC}$  values by HPLC method and published their results. The authors had to recognize that the method used gives overestimated values. Calculation methods are more widely presented in table 18. *R.-M.Dannenfesler et al.* [1991] used simple averaging of literature data, i.e.  $K_{OC}$  values for soil. *M.T.Sacan and I.A.Balcioglu* [1996] used the model based on quantitative structure property relationship (QSPR) and the basic regression equation of the form:

$$\log K_{OC} = (\pm 0.034) 1.034 \text{ CRI} + (\pm 0.113) 0.441, \quad (18)$$

where CRI - characteristic root index.

While studying adsorption of many organic substances by activated carbon a limitation factor of the process has been established – energy of linear solvation. For this reason for  $K_{OC}$  calculations *D.C.Luehrs et al.* [1996] used the regression equation connecting a great number of parameters characterizing a molecule - polarity/polarizability, molar volume, bond indices etc. *A.Sabljić et al.* [1995] used a set of OSAR models and systematized by classes and chemical domains of organic compounds all correlation dependencies between  $K_{OC}$  and  $K_{OW}$  developed by that time. This work allows us to calculate an unknown coefficient for one substance by the known coefficient of another substance included to the same chemical domain.

### 7.3. “Octanol-air” partition coefficient ( $K_{OA}$ )

This coefficient represents the ratio between equilibrium substance concentrations in octanol and air and it is denoted as  $K_{OA}$ . It characterizes quantitatively a capability of different surfaces (soil, vegetation) to absorb pollutants.  $K_{OA}$  values are measured for a small number of persistent organic pollutants (POPs). The coefficient, however, was included by *F.Wania and D.Mackay* [1996] to the parameters which are the criteria of POP behavior in the terrestrial environment.

**Table 19:** Octanol-air partition coefficient  $K_{OA}$

log $K_{OA}$ (25 °C)			
Experimental results	Calculation results	Recommended values	Accepted for modelling
6.90, <i>Harner T. and Mackay D., 1995</i>	6.78, <i>McLachlan M. S. et al., 1995</i>		6.80, <i>Wania F. and Mackay D., 1996</i>
	8.54, <i>Finizio A. et al., 1997</i>		6.74, <i>Paterson S. et al., 1991,</i> cited from <i>Tolls J. and McLachlan M.S., 1994</i>
	7.07, <i>Beck A.J. et al., 1996</i>		6.90, <i>Horstmann M. and McLachlan M.S., 1998</i>

In the experimental determination of  $K_{OA}$  the calculation is made by the relationship:

$$K_{OA} = C_O / C_A \quad (19)$$

where  $C_O$  - equilibrium substance concentration in octanol;

$C_A$  - equilibrium concentration in air.

The method suggested by *T.Harner and D.Mackay*, [1995] made it possible to determine experimentally  $K_{OA}$  values of six chlorinated benzenes, five polychlorinated biphenyls and p,p'-DDT. Based on the definition and some trivial transformations the relation of  $K_{OA}$  with other partition coefficients is apparent.

$$K_{OA} = C_O/C_A = (C_O/C_W) / (C_A/C_W) = K_{OW} / K_{AW} \quad (20)$$

For example,  $K_{OA}$  value is obtained by *M.S.McLachlan et al.* [1995] and by *A.J.Beck et al.* [1996] (see table 19) from the relationship:

$$K_{OA} = K_{OW} RT/H \quad (21)$$

where  $K_{OW}$  is the "octanol-water" partition coefficient;

$R$  is the universal gas constant equal to 8.314 Pa m<sup>3</sup>/mol K;

$T$  is the temperature, K;

$H$  is Henry's law constant, Pa m<sup>3</sup>/mol.

For  $K_{OA}$  calculations *A.Finizio et al.* [1977] used its relation with the vapor and aerosol phase partition coefficient  $K_p$ :

$$\log K_p = a + b \log K_{OA} \quad (22)$$

for HCB ratio  $K_p/K_{OA}$  is equal to  $5 \times 10^{-12} \mu\text{g}/\text{m}^3$ .

The temperature dependence of  $K_{OA}$  is obtained by *T.Harner and D.Mackay* [1995] in the experiment and it is described by equation:

$$\log K_{OA} = A + B/T = A + \Delta H_{OA} / RT \quad (23)$$

where  $A = - 6.3$ ;

$B = 3928$ ;

$\Delta H_{OA} = 75.2 \text{ kJ/mol}$ .

In the next section we consider the dependence of  $K_p$  on saturated vapor pressure of the subcooled liquid ( $P_L$ ) testifying to the relation between  $K_{OA}$  and  $P_L$ .

#### **7.4. Vapor/aerosol partition coefficient ( $K_p$ )**

Partitioning of persistent organic compounds in the air between particles and vapors depends on a number of factors:

- physical-chemical properties of a substance and first of all on the saturated vapor pressure;
- ambient temperature;
- aerosol content in air;
- air aerosol composition in particular the content of organic matter etc.

At present for the description of possible mechanisms of the connection between organic matter vapors and atmospheric aerosol two models based on different processes (adsorption and absorption) are suggested. The adsorption model of Junge-Pankow predicts the substance fraction associated with aerosol by the equation:

$$\varphi = c\theta / (P_L^0 + c\theta) \quad (24)$$

where  $c$  is the constant depending on the difference between the heat of desorption from the particle surface and the heat of substance evaporation and on aerosol surface properties. The “ $c$ ” value is equal to 17.2 Pa/cm;

$\theta$  - specific surface of aerosol particles expressed in  $\text{cm}^2$  of aerosol/ $\text{cm}^3$  of air.

For the urban regions  $\theta=1.1 \times 10^{-5}$ , for clean area -  $3.5 \times 10^{-6}$ , for the continental background -  $4.2 \times 10^{-7}$  (*Whitby's data* [1971] cited from *T.F.Bidleman* [1999]);

$P_L^0$  - subcooled liquid-vapor pressure, Pa.

For HCB under conditions of high concentration of aerosols in urban air:

$$\varphi_u = 17.2 (1.1 \times 10^{-5}) / (0.25 + 17.2 (1.1 \times 10^{-5})) = 0.07 \% \quad \text{or } < 0.1\%$$

in the background regions:

$$\varphi_b = 17.2 (4.2 \times 10^{-7}) / (0.25 + 17.2 (4.2 \times 10^{-7})) = 0.003\%$$

In calculations  $P_L^0$  value recommended by *D.Mackay et al.* [1992] is used. If  $P_L^0$  value obtained experimentally by *D.A.Hinckley et al.* [1990] and *T.F.Bidleman* [1984] (table 6 in column 1) is used then the aerosol phase fraction would be even less.

The fraction of a substance associated with aerosol can be calculated from equation:

$$\varphi = K_p [\text{TSP}] / (1 + K_p [\text{TSP}]) \quad (25)$$

where  $K_p$  - coefficient quantifying the partitioning of a substance between vapors and particles,  $\text{m}^3/\mu\text{g}$ ;

TSP – total suspended particulate matter concentration,  $\mu\text{g}/\text{m}^3$ .

The connection of  $K_p$  with the saturated vapor pressure demonstrates the following equation:

$$\log K_p = \log (c\theta / \text{TSP}) - \log P_L^0 \quad (26)$$

*J.Pankow et al.* [1984] suggested also an absorption model which was later modified by other investigators such as *T.Harner and T.F.Bidleman* [1998], *A.Finizio et al.* [1997] etc. It is based on the assumption that the substance is partitioned between the vapor phase and a thin film of the organic matter covering the aerosol surface. In this case the partition coefficient can be described as:

$$K_p = 10^{-6} RT f_{\text{om}} / M_{\text{om}} \gamma_{\text{om}} P_L \quad (27)$$

where  $R = 8.314$  - universal gas constant,  $\text{Pa m}^3/\text{mol K}$ ;

$T$  – temperature of the process,  $\text{K}$ ;

$f_{\text{om}}$  – mass fraction of organic matter in the particle that can absorb gaseous POPs;

$M_{\text{om}}$  - mean molecular mass of the organic matter phase aerosols,  $\text{g}/\text{mol}$ ;

$\gamma_{\text{om}}$  - activity coefficient of a compound in the organic matter phase;

$P_L$  - subcooled liquid-vapor pressure,  $\text{Pa}$ .

*A.Finizio et al.* [1997] introduced “octanol-air” partition coefficient to the previous equation and obtained the following equation:

$$K_p = 1.22 \times 10^{-12} K_{\text{OA}} f_{\text{om}} (M_o \gamma_o / M_{\text{om}} \gamma_{\text{om}}) \quad (28)$$

where  $K_{\text{OA}}$  - “octanol-air” partition coefficient;

$M_o$  and  $M_{\text{om}}$  - molecular mass of octanol and aerosol organic matter,  $\text{g}/\text{mol}$ ;

$\gamma_o$  and  $\gamma_{\text{om}}$  - activity coefficients of the substance in the octanol and organic matter phase;

or in a simplified form:

$$K_p = B K_{\text{OA}} \quad (29)$$

where  $B = 1.22 \times 10^{-12} f_{\text{om}} (M_o / M_{\text{om}} (\gamma_o / \gamma_{\text{om}}))$

Independent of the model used the association of organic matter with atmospheric aerosol the  $K_p$  value can be calculated as the ratio of equilibrium concentrations of a substance in

the vapor phase ( $C_g$ ) to its content on particles ( $C_p$ ) with allowance made for the content of particulate:

$$K_p = C_p / C_g \text{ (TSP), m}^3/\mu\text{g} \quad (30)$$

where  $C_p$  - concentration of a substance on aerosol particles,  $\text{pg/m}^3$ ;

$C_g$  - concentration of a substance in the vapor-phase,  $\text{pg/m}^3$ ;

TSP – total suspended particulate matter concentration,  $\mu\text{g/m}^3$ .

The  $K_p$  values presented in table 20 we calculated on the basis of HCB concentrations measured in the air of Canada and Germany at different time.

**Table 20:** HCB partitioning between air and aerosol particles

Air concentration			$K_p$	Log $K_p$	Site location	Reference
HCB, $\text{pg/m}^3$		TSP, $\mu\text{g/m}^3$				
$C_g$	$C_p$					
156	0.46	50*	5.9E-05	- 4.229	Central Europe, Germany, warm season	<i>Horstmann M. and McLachlan M.S., 1998</i>
210	0.43	50*	4.1E-05	- 4.387	Central Europe, Germany	-»-
110	4	50*	7.3E-04	- 4.137	Central Europe, Germany	<i>Ballschmiter K. and Wittlinger R., 1991</i>
98	0.2	10	2.0E-04	- 3.699	The Great Lakes, L.Superior, r.Eagle Harbor, mean annual, 1994	<i>Hoff R.M. et al., 1996</i>
80	0.2	30	8.3E-05	- 4.08	The Great Lakes, L.Erie, Sturgeon Point, mean annual, 1994	-»-
70.3	2.7	9	4.3E-03	- 2.37	The Great Lakes, Turkey Lake, May, July, October, 1987	<i>Lane D.A. et al., 1992</i>
68.9	2.1	12	2.6E-03	-2.589	The Great Lakes, L.Ontario, Point Petre, November, Mart, 1988/1989	-»-

\* - TSP selected value for urban areas

As evident from table 20 values of  $K_p$  observed in Germany and at the Great Lakes are rather close and agree well with the calculated value [*Finizio et al., 1997*] -4.43. It follows from calculations that at such HCB concentrations on aerosol particles their input to HCB air concentrations does not exceed 1%. *T.F.Bidleman et al. [1986]* estimated the contribution of the aerosol phase in Columbia, SC, at 0°C and at 20°C and it was 0.7% and 0.1% respectively. Hence one is inclined to think that at positive temperatures the bulk of HCB is

in the vapor phase and its content on aerosol is negligible. The results of the air monitoring program in southern Germany (near Augsburg) do not contain measurements of HCB on particles [Kaupp et al., 1996].

Consequently measurement data on HCB air content testify that this chemical fits into the group occurring only in the vapor phase. At very low temperatures characteristic of the polar regions HCB condenses from the atmosphere. According to calculations of *F.Wania and D.Mackay* [1996] HCB condensation temperature is  $-36^{\circ}\text{C}$ .

In order to describe the dependence of substance partitioning in the atmosphere on temperature *T.F.Bidleman et al.* [1986] used the following equation:

$$\log [C_p (\text{TSP})/ C_g] = m/T + b \quad (31)$$

where  $C_p$  - concentration of a substance on aerosol particles,  $\text{pg}/\text{m}^3$ ;  
 $C_g$  - concentration of a substance in the vapor phase,  $\text{pg}/\text{m}^3$ ;  
TSP - total suspended particulate matter concentration,  $\mu\text{g}/\text{m}^3$ ;  
 $T$  - ambient temperature, K.

By their determination the coefficients “ $m$  and  $b$ ” for HCB are:  $m=-3328$  and  $b=16.117$ . The correlation coefficient is sufficiently high - 0.687.

*H.Kaupp et al.* [1996] suggested another equation for the description of temperature dependence of HCB concentration in the vapor phase:

$$C_G = A e^{-k/T} \quad (32)$$

where  $C_G$  - air concentration,  $\text{pg}/\text{m}^3$ ;  
 $A$  - “air-sorbent” partition coefficient for HCB equal to  $21.0 \text{ pg}/\text{m}^3$ ;  
 $K = Qm/R = -4404$ ;  
 $Qm$  - enthalpy of the phase transition of compound from air to sorbent,  $\text{kJ}/\text{mol}$ ;  
 $R$  – universal gas constant equal to  $8.314 \text{ Pa}/\text{mol}\cdot\text{J}$ .

Using HCB concentrations [Lane et al., 1992] observed in Ontario Province we obtained  $K_p$  values which differ by up to two orders of magnitude from those of other authors. The authors also could not reveal the dependence of HCB air concentrations on the ambient temperature that contradicts other authors’ results.

## 7.5. Molecular diffusion coefficient

The molecular diffusion coefficient can be calculated from the semi-empirical equation (R.P.Schwarzenbach et al. [1993]):

For air ( $D_A$ , cm<sup>2</sup>/s)

$$D_A = 10^{-3} \frac{T^{1.75} [(1/M_{\text{air}}) + (1/M)]^{1/2}}{P [\bar{V}_{\text{air}}^{1/3} + \bar{V}^{1/3}]^2} \quad (33)$$

where  $T$  - absolute temperature, K, normal conditions ( $T=298.15$  K);

$M_{\text{air}}$  - air mean molecular mass equal to about 29 g/mol;

$M$  - substance molecular mass for HCB equal to 284,78 g/mol;

$P$  - pressure (1 atm);

$\bar{V}_{\text{air}}$  - mean molar gas volume in the air equal to approximately 20.1 cm<sup>3</sup>/mol;

$\bar{V}$  - molar volume of an organic substance (cm<sup>3</sup>/mol).

For water ( $D_W$ , cm<sup>2</sup>/s)

$$D_W = \frac{13.26 \times 10^{-5}}{\mu^{1.14} \cdot (\bar{V})^{0.589}} \quad (34)$$

where  $\mu$  - solution viscosity (centipoise) is accepted to be equal to aqueous viscosity, at 298.15K it is 0.894 centipoise;

$\bar{V}$  - molar volume of an organic substance (cm<sup>3</sup>/mol).

To calculate the molecular diffusion coefficient it is necessary to determine the molar volume using the density of a substance and its molecular mass. Substance density is dependent on temperature. Reference data (table 21) on HCB, however, give one and the same value at different temperatures. Therefore to calculate the molecular diffusion coefficient under normal conditions we used data on molar volumes calculated by different authors (table 22).

**Table 21:** HCB density

Substance density, g/cm <sup>3</sup>	Temperature, C	Note	Reference
1.5691	23.6		<i>Mackay D. et al.</i> , 1992, vol.1
2.044	20		<i>Mackay D. et al.</i> , 1992, vol.1
2.044	25		<i>Chemical Encyclopaedia</i> , 1988
2.044	23	Cited from CRC Handbook of Chemistry and Physics, 76 th, Ed by Lide D.R., Boca Raton, FL: CRC Press Inc., 1995-1996	HSDB, 2000

**Table 22:** HCB molar volume at 25°C

Molar volume, cm <sup>3</sup> /mol	Reference	Note
181.5	<i>Dannenfelser R. M. et al.</i> , 1991	
154.31	<i>Govers H.</i> , 1993	
166.8	<i>Ruelle P. and Kesselring U.W.</i> , 1997	
186	<i>Mackay D. et al.</i> , 1992, vol.1	
221.4	<i>Mackay D. et al.</i> , 1992, vol.1	Method Le Bas
221	<i>Riederer M.</i> , 1990	The value used for calculation of substance input from the air to vegetation
222	<i>Kerler F. and J.Schoenherr</i> , 1988	-«-
195.8	<i>McLachlan M.S. et al.</i> , 1995	-«-

For calculations of molecular diffusion coefficients we have chosen four values (table 23) out of eight ones. Table 23 contains also the obtained  $D_A$  and  $D_W$  values and the coefficients used in modelling the transport and in exchange processes between environmental compartments (“air-water”, “air-soil” and “air-vegetation”).

**Table 23:** Molecular diffusion coefficients

Diffusion coefficient, m <sup>2</sup> /s		Reference	Note
$D_A$	$D_W$		
5.87E-06	6.94E-10	<i>Mackay D. et al.</i> , 1992, vol.1	$\bar{V} = 186$ cm <sup>3</sup> /mol used in calculation
6.38E-06	7.75E-10	<i>Govers H.</i> , 1993	$\bar{V} = 154.31$ cm <sup>3</sup> /mol used in calculation
6.17E-06	7.4E-10	<i>Ruelle P. and Kesselring U.W.</i> , 1997	$\bar{V} = 166.8$ cm <sup>3</sup> /mol used in calculation
5.42E-06	6.25E-10	<i>Kerler F. and Schoenherr J.</i> , 1988	$\bar{V} = 222$ cm <sup>3</sup> /mol used in calculation
4.97E-06	4.97E-10	<i>Mackay D. and Wania F.</i> , 1995; <i>Wania F. and Mackay D.</i> , 1995	
11.1E-06	11.1E-10	<i>Mackay D. and Paterson S.</i> , 1991	

Calculated values of  $D_A$  and  $D_W$  agree well enough with literature data.

## 8. HCB degradation in the environment

HCB in the atmosphere is involved in different processes controlling its behaviour. HCB can undergo chemical reactions and in this case most important are the interaction with hydroxyl-radical. It can be destructed by UV radiation. Measured and calculated values of HCB reaction rates with hydroxyl-radical are illustrated in table 24.

**Table 24:** Constants of rate HCB reaction with hydroxyl-radical

Reaction rate constants with OH <sup>*</sup> , $k_{OH^*} \times 10^{-14}$ cm <sup>3</sup> /molecule·s	Reference	Note
2.7 (2.0 - 3.8)	<i>Brubaker W.W. and Hites R.A., 1998</i>	Calculations were based on experimental data using the equation: $k = A e^{-E_a/RT}$ at $T = 298$ K
1.3 (0.9 – 1.9)	-«-	at $T = 277$ K
1.71	<i>Howard P. and Meylan W.M., 1997</i>	The calculated value was introduced by the authors to Reference data

Rate constants of gaseous HCB decomposition in the atmosphere can be calculated from the equation:

$$K_{OH^*} = k_{OH^*} [OH] \quad (35)$$

where  $K_{OH^*}$  the pseudo first-order rate constants, s<sup>-1</sup>,

$k_{OH^*}$  is the rate constant for hydroxyl-radical reaction, cm<sup>3</sup>/molecule s;

[OH] is the hydroxyl-radical concentration in air, molecule/cm<sup>3</sup>.

Hydroxyl-radical air concentration depends on the latitude and season. For example, at the location in 45°N [OH] value is:

for summer -  $2 \times 10^6$  molecule/cm<sup>3</sup>;

for spring and fall -  $0.8 \times 10^6$  molecule/cm<sup>3</sup>;

for winter -  $0.09 \times 10^6$  molecule/cm<sup>3</sup>;

mean annual decomposition rate constant is  $0.8 \times 10^6$  molecule/cm<sup>3</sup> [Yu Lu and Khall, 1991]. The calculated HCB rate constants in the reaction with hydroxyl-radical are presented in table 25.

**Table 25:** Reaction rate of gaseous HCB with atmospheric hydroxyl-radical

Compound	$k_{OH^\bullet}$ , $\text{cm}^3/\text{molecule}\cdot\text{s}$	$K_{OH^\bullet}^*$ , $\text{s}^{-1}$			
		Summer	Fall/Spring	Winter	Mean annual
HCB	$1.71 \times 10^{-14}$ <i>Howard P. and Meylan W.M., 1997</i>	$3.42 \times 10^{-8}$	$1.37 \times 10^{-8}$	$0.15 \times 10^{-8}$	$1.37 \times 10^{-8}$
	$1.3 \times 10^{-14}$ <i>Brubaker W.W. and Hites R.A., 1998</i>	$2.6 \times 10^{-8}$	$1.04 \times 10^{-8}$	$0.12 \times 10^{-8}$	$1.04 \times 10^{-8}$

The calculation results of HCB half-life made for this review and their comparisons with estimates of other authors are demonstrated in table 26.

**Table 26:** HCB half-life in the atmosphere

Season	Half-life in the atmosphere, days				
	Calculations are made for this Technical note using data of:		<i>Kwok and Atkinson, 1995, cited from Bidleman T.F., 1999</i>	<i>Scheringer M., 1997</i>	<i>Mackay D. et al., 1992, vol.1</i>
	<i>Howard P. and Meylan W.M., 1997</i>	<i>Brubaker W.W. and Hites R.A., 1998</i>			
Summer	233	308			
Fall/Spring	586	770			
Winter	5370	6667			
Mean annual	586	770 429*	579	1240	708

\* - the calculations are performed for the temperature interval 290-298 K and  $[\text{OH}^\bullet] = (0.8-1.0) \times 10^6 \text{ molecule}/\text{cm}^3$ .

HCB half-life in the atmosphere of the Great Lakes calculated on the basis of multi-annual monitoring of air pollution by pesticides at the monitoring stations [*Cortes et al., 1998*] are:

- Eagle Harbor - 4526 days;
- Sleeping Bear Dunes - 1200 days;
- Sturgeon Point - 2482 days.

Presented half-life values were calculated on the assumption that no further emission of HCB occurs.

The authors assessed virtual date of HCB full decomposition as 2060 year. It is much more than for all other known pesticides.

The observed values substantially exceed the calculated data given in table 26. HCB half-lives determined by *M.Scheringer*, fit best the observations.

The decrease of HCB concentration in natural water is defined by the following processes: evaporation, sorption and transformation reactions. The evaporation of a substance from the water surface depends on Henry's law constant, but theoretical calculations of a substance flux from the water actually provide essentially lower values due to sorption processes. Since HCB is hydrophobic to a large extent it is sorbed by particulate matter and with time it is sedimenting onto the bottom. In bottom sediments intensive processes of biodegradation take place and half-life periods differ in 4 times for aerobic and anaerobic conditions. The hydrolytic decomposition of HCB in the water depth goes on very slowly and as a rule it is not considered [*Capel and Larson*, 1995]. Photolytic degradation of HCB in the water occurs as the first-order reaction with reaction rate constant  $k=1.3 \times 10^{-6} \text{ s}^{-1}$ . The availability of various organic species as in the case of natural surface waters makes a sensitizing effect and accelerates HCB photodecomposition. *M.Hirsch and O.Hutzinger* [1989] found experimentally that aromatic amines and proteins contained in water increase the reaction rate constant by one-two orders of magnitude. The values as high as  $k = 1.7 \times 10^{-4} \text{ s}^{-1}$  and  $k = 7.2 \times 10^{-4} \text{ s}^{-1}$  were observed at the presence of triptophane and diphenylamine respectively.

Nowadays HCB half-life in water, bottom sediments and soils is estimated by equal values which as *D.Mackay et al.* [vol.1 1992] believe is on the average 55000 hours or approximately 6 years. Similar estimates are obtained by *M.Scheringer* [1997] and *D.H.Bennet et al.* [1999] according to their opinion HCB half-life in the soil and other compartments except the air is 53000 hours (6 years).

While modelling HCB global airborne transport *F.Wania and D.Mackay* [1995] used different half-life periods depending on climatic conditions. Half-life for different climatic zones and natural environmental compartments are presented in table 27.

**Table 27:** Half-life for different climatic zones [*Wania and Mackay*, 1995]

Half-life, days	Climatic zone
<b>Air</b>	
230	Tropical and subtropical
708	Temperate and boreal
2292	Polar
<b>Other compartments</b>	
708	Tropical
2292	Subtropical and temperate

7081	Boreal
22922	Polar

## 9. Biological accumulation factors

Bioaccumulation of different chlororganic compounds in water ecosystems has been a subject of investigations of many scientists for last 20 years. Terrestrial ecosystems have attracted general attention relatively recently. The motion and concentration of species in food chains of any ecosystem is difficult to be studied and requires long time for obtaining plausible results. *M.S.McLachlan* [1996] made a suggestion that estimates of bioaccumulation in food chains based on different assumptions (theoretical calculations) unsatisfactory agree with the experiment due to lack non-attainment of equilibrium of processes taking place in the system.

In a general form the bioaccumulation factor is a ratio of the concentration in a biological object to the concentration in habitat as well as to concentration in the food staff used by a living organism.

The most trivial case is the accumulation of pollutants from the air by vegetation and bioaccumulation factor (BCF) is calculated from the relationship:

$$\text{BCF} = \frac{m_l}{m_a} \quad (36)$$

where  $m_l$  - pollutant mass in foliage mass,  $m_a$  - pollutant mass in the air volume.

A pollutant being in the vapor or gas phase can enter directly leaf stomata or it can be dissolved in the cuticle layer. Exactly cuticle plays the role of accumulator of lipophilic compounds. The input of non-electrolytes inside a cuticle is defined by pollutant solubility and mobility in it. Quantitatively this exchange is characterized by the "plant cuticle-water" ( $K_{CW}$ ) partition coefficient. Different plants with different cuticle layers have different capability to accumulate pollutants. For HCB  $K_{CW}$  values have been found experimentally and calculated by the correlation dependence between  $K_{CW}$  and  $K_{OW}$ . Table 28 illustrated  $K_{CW}$  obtained by *F.Kerler and J.Schoenherr* [1988].

**Table 28:**  $K_{CW}$  experimental and calculated values

Plant	$\log K_{CW}, 25\text{ }^{\circ}\text{C}$	
	Experiment	Calculation
<i>Citrus</i>	5.70	$\log K_{CW} = 0.975 \log K_{OW} - 0.021 = 5.81$
<i>Ficus</i>	5.74	$\log K_{CW} = 0.962 \log K_{OW} + 0.034 = 5.3$
<i>Lycopersicon</i>	5.83	$\log K_{CW} = 0.977 \log K_{OW} + 0.061 = 5.41$
<i>Capsicum</i>	5.80	$\log K_{CW} = 0.979 \log K_{OW} + 0.123 = 5.48$
Mean	5.771	5.367

\* -calculated for  $K_{OW} = 5.47$

A. Sabljic *et al.* [1990] established the correlation dependence between  $K_{CW}$  and molecular connectivity indices which were earlier used for setting up the connections between different parameters - POP sorption by the soil, association with dissolved humic substances, bioconcentration, biodegradation and toxicity for water ecosystems.  $K_{CW}$  is calculated from the equation:

$$\log K_{CW} = 0.37 (\pm 0.16) + 1.31 (\pm 0.05) (^3\chi^4) - 1.49 (\pm 0.19) (\text{no. OH}_{\text{aliph}}) \quad (37)$$

where  $^3\chi^4$  - valence third-order molecular connectivity index which is 3.996 for HCB.

(no.  $\text{OH}_{\text{aliph}}$ ) - number presence of aliphatic hydroxy groups. They are absent in HCB therefore the last term of equation (37) is equal to zero.

In this case  $K_{CW}$  value is 5.60. It is in a good agreement with the values of table 28. The authors also suggest the equation of correlation dependence of  $K_{CW}$  upon  $K_{OW}$ :

$$\log K_{CW} = 0.057 + 0.970 \log K_{OW} \quad (38)$$

and upon solubility in water ( $S_w$ )

$$\log K_{CW} = 1.118 - 0.569 \log S_w \quad (39)$$

The partition coefficient of a stable hydrophobic organic substance in the "air-vegetation" system (BCF) or bioconcentration factor was calculated by [Mueller *et al.*, 1994] with the help of regression relation including  $K_{OW}$ ,  $H$  and volume fractions of different leaf components. The main contribution to BCF for hydrophobic substances is made by lipid fractions.

To calculate BCF the authors used a number of dependencies between coefficients in this system. Value obtained in this way is close to experimental data are presented in table 29.

**Table 29:** BCF values obtained in different ways

Plants	log BCF	
	calculaiton, <i>Mueller J. et al.</i> , 1994	experiment, <i>Bacci E. et al.</i> , 1990a and <i>Reischl A. et al.</i> , 1987
Azalea	5.00	5.62
Spruce	5.32	5.97

*M.Riederer* [1990] using Fugacity-Based Model calculated log BCF for HCB which is 4.39.

*E.Bacci et al.* [1990b] have determined log BCF by extrapolation. It also may be calculated from the equation:

$$\text{BCF} = 0.022 K_{\text{OW}}/ K_{\text{AW}} \quad (40)$$

or

$$\text{BCF} = L K_{\text{OA}} \quad (41)$$

where  $L$  - volumetric percentage of the lipid fraction in a plant.

“Plant lipids-air” partition coefficient was introduced by *J.Tolls and S.McLachlan* [1994] in studies of POP partitioning between the air and *Lolium multiflorum* (Welsh Ray Grass) using for calculations the ratio of fugacity capacity -  $Z_L/Z_A$ . They found the correlation of this partition coefficient with “octanol-air” partition coefficient with high correlation coefficient:

$$\log Z_L/Z_A = 0.91 \log K_{\text{OA}} + 0.68 \quad r^2 = 0.90 \quad (42)$$

$$\log Z_L/Z_A = \log K_{\text{OA}} \quad r^2 = 0.89 \quad (43)$$

Log  $Z_L/Z_A$  value for HCB determined in the experiment is 6.83 and  $\log K_{\text{OA}}=6.74$ .

The distribution of a substance in different parts of plants was studied by *S.Paterson et al.* [1991] on the example of soya bean. Based on principles:

- 1 - that substance concentration is determined by two values -  $f$  - its fugacity (Pa) and  $Z$  - fugacity capacity ( $\text{mol}/\text{m}^3\text{Pa}$ ) from equation:  $C = f Z$ ;
- 2 - at the superposition of two adjacent phases their fugacity is equal to:

$$C_1/C_2 = f Z_1/ f Z_2 = Z_1/ Z_2 \quad (44)$$

While considering HCB partition in the “soil-plant-air” system *S.Paterson et al.* [1991] determined correlation dependencies for each particular part of the system including separately for roots, stem and leaves. Table 30 gives the budget of HCB content in different parts of soya bean.

**Table 30:** The balance of HCB content in different parts of soya bean

System	Z, mol/m <sup>3</sup> Pa	Concentration, g/m <sup>3</sup>	%
Roots	40.3	1.74	17.4
Stem	18.6	0.80	7.85
Leaves	69.1	2.99	74.74
Intercellular air	4.04 10 <sup>-4</sup>	1.75 10 <sup>-5</sup>	< 0.001
Intercellular water	1.17 10 <sup>-2</sup>	5.06 10 <sup>-4</sup>	0.01

The time of equilibrium setting up in different parts of the plant does not coincide as well as half-life of HCB in them (table 31) [*Paterson et al.*, 1991; *Skurlatov et al.*, 1994].

**Table 31:** Indices characterizing residence time of HCB in a plant

System	Fugacity, μ Pa			Time of equilibrium setting up, h	Half-life, h
	General	Soil	Air		
Roots	1570	1570	-	3280	2420
Stem	1498	1497	1.0	1480	4020
Leaves	39.7	12.7	27	125	170
Intercellular air					5.7 x 10 <sup>5</sup> 3 x 10 <sup>5</sup>

How we can see from table 31, the equilibrium with the air in soya bean leaves is set faster and faster degradation of substances takes place there. HCB enter roots most slowly and is held in stem for the longest time.

## II *HCB properties selected for modelling. Parametrization*

### 1. Temperature dependence of Henry constant (H)

$$H(T) = H(Tr) \exp[m (1/Tr - 1/T)],$$

where  $m = -5800$

$$H(Tr) = 7.12 \text{ (Pa m}^3\text{/mol) at 25 }^\circ\text{C} \quad [\textit{Finizio et al., 1997}]$$

### 2. Temperature dependence of saturated vapor

$$\log P_L \text{ (Pa)} = 11 - 3582 / T \quad [\textit{Hinckley et al., 1990}]$$

$$\log P_L = -0.90$$

$$P_L = 12.589\text{E-}02 \text{ Pa at 25 }^\circ\text{C}$$

### 3. Temperature dependence of the “octanol-water” partition coefficient

$$\log K_{ow} \text{ (dm/kg)} = 1.1806 - 1274/T \quad [\textit{Bahadur et al., 1997}]$$

$$\log K_{ow} \text{ (dm/kg)} = 5.46$$

$$K_{ow} = 2.884\text{E+}05 \quad \text{at 25 }^\circ\text{C}$$

### 4. “Organic carbon – water” partition coefficient:

$$\log K_{oc} = 4.54 \quad [\textit{Sacan and Balcioğlu, 1996}]$$

$$K_{oc} = 3.46737\text{E+}04$$

### 5. Temperature dependence of «octanol-air» coefficient

$$\log K_{oa} = -6.3 + 3928/T \quad [\textit{Harner and Mackay, 1995}]$$

$$\log K_{oa} = 6.90 \text{ at 25 }^\circ\text{C}$$

## 6. Washout ratio of HCB

$$W_v = 3.5 \times 10^2 \quad \text{at } 25 \text{ }^\circ\text{C}$$

## 7. Molar volume

$$\bar{V} = 186 \text{ cm}^3/\text{mol} \quad \text{at } 25 \text{ }^\circ\text{C} \quad [\text{Mackay et al., 1992, vol.1}]$$

## 8. Molecular diffusion coefficients:

$$\text{air: } D_A, \text{ m}^2/\text{s} = 4.97\text{E-}06 \quad [\text{Mackay et al., 1992, vol.1}]$$

$$\text{water: } D_W, \text{ m}^2/\text{s} = 4.97\text{E-}10$$

## 9. Degradation time (half-life):

*air:*

$$\text{Winter} - 1.2 \text{ E-}09 \text{ s}^{-1}$$

calculation from [Yu Lu and Khalil, 1991] and [Brubaker and Hites, 1998]

$$\text{Spring/Fall} - 1.04\text{E-}08 \text{ s}^{-1}$$

$$\text{Summer} - 2.6\text{E-}08 \text{ s}^{-1}$$

*water:*

$$5.24\text{E-}09 \text{ s}^{-1}$$

[Scheringer, 1997]

*soil:*

$$5.24\text{E-}09 \text{ s}^{-1}$$

## 10. «Plant cuticle–water» distribution coefficient

$$\log K_{CW} = 5.77$$

[Kerler and Schoenherr, 1988]

$$K_{CW} = 5.8884\text{E+}05$$

### ***III. Sources of hexachlorobenzene emission to the atmosphere***

Small amounts of HCB are formed in the production of any chlorine-organic compound and in the combustion of any kind of organic fuel and wastes under the conditions of free burning and in pyrolysis. There are few works dedicated to the study of HCB formation in different industrial processes as well as to emissions from stationary sources. This effect is due to the fact that HCB was for many years considered only as vegetation protection agent (pesticide).

Pesticide properties of halogen derivatives of benzene were widely studied and used in practice but HCB does not belong to chemicals with strong insecticide and herbicide properties. On the other hand, it has maximum fungicide activity among all chlorobenzenes. Its use as a disinfectant to control cereal fungus disease most frequently in combination with fungicide - ethyl mercuric chloride allowed to reduce the total toxicity of the used agent due to the decrease of mercuric fungicide amount.

By the early 80-s the information on HCB use in agriculture was submitted to FAO by 14 countries. In 1988 HCB was used in three countries - India, Pakistan and Oman. The total consumption amounted to more than 36 thous. tonnes. The main consumer was India. Its fraction in the total consumption volume is accounted for 90% to actually 100% in different years [*Food and Agriculture Production Yearbook*, 1989]. The information on HCB use in agriculture in European countries in *Yearbook of Food and Agriculture Organization of the United Nations* [1989] is not available.

The methodology of estimates of emissions from HCB application to agriculture is a multiplication of HCB use by emission factor. According to different authors the emission factor is from 20% to 50% of the total amount used [*Pacyna et al.*, 1999; *Yearbook. Pesticide Monitoring in natural objects of the Russian Federation*, book 1, 1993; *Atmospheric Emission Inventory Guidebook, Joint EMEP/CORINAIR, vol.3*, 1999]. Global HCB emission estimated by us on the basis of FAO data could reach in 1988 7.2 to 18 thous. tonnes.

According to the expert estimates of *Pacyna J.M. et al.*, [1999] in 1970 HCB emissions in Europe reached 192 tonnes and by 1995 they has reduced to 23 tonnes. A great fraction (80%) resulted from its use in agriculture. According to these estimates the emission reduction went on by different rates. For example, in France and Spain emissions to the air decreased in almost 20 times, in Germany - in 13.5 times and in countries of Eastern Europe - in 3-4 times. Our review of data on the use of chemicals containing HCB in agriculture the Russian Federation and some other eastern European countries demonstrated that by the early 90-s it has been completely excluded from the list of applied means for vegetation protection.

Apart from agriculture among HCB emission sources there are many sectors of industry - non-ferrous metallurgy, pulp and paper and chemical industries and other fields of economic activity, for example, wood treatment for conservation as well as heat generation and municipal economy and first of all waste incineration. Transport is another source of HCB emission to the atmosphere since in the combustion process of gasoline and diesel fuel there are conditions for HCB formation. Emission factors for all kinds of activity are demonstrated in table 1.

Chlorine chemistry (chlororganic synthesis) is considered to be the major source of HCB emission to the atmosphere. The assortment of commodity products and semiproducts of chlororganic synthesis is extremely wide. Among these are light chlorinated hydrocarbons with short saturated chain (methyl chloride, chloroform, tetrachloromethane, 1,2-dichloroethane and other chlorinated paraffins), unsaturated chain (chlorinated methylene, vinyl chloride, trichloroethylene, epichlorohydrin etc), chlorinated aromatic compounds (different chlorobenzenes, chlorinated toluenes and anilines), and chlorinated polynuclear aromatic compounds (polychlorinated biphenyls and terphenyls). The production of chlorinated hydrocarbons has the highest emission factors and the output volumes can reach hundreds of thousands and millions of tonnes [*Fedorov*, 1993].

**Table 1.** HCB emission factors for different source categories

HCB sources of emission to the atmosphere	Emission factor, $\mu\text{g/t}$	Reference
<b>Combustion of organic fuel</b>		
Coal	16	<i>Pacyna J. et al., [1999]</i>
Wood	60	--
<b>Industrial processes</b>		
Production of chlorinated hydrocarbons:		
Tetrachloromethane	$(1-20) \times 10^6$	<i>Pacyna J. et al., [1999]</i>
Trichloroethylene	$(1-6) \times 10^6$	--
Tetrachloroethylene	$(3-10) \times 10^6$	--
Copper smelting	$3.9 \times 10^4$	--
Secondary production of aluminium	$5 \times 10^6$	<i>Atmospheric Emission Inventory Guidebook, Joint EMEP/CORINAIR, vol. 1, [1999].</i>
<b>Waste incineration</b>		
Solid municipal	$10 \times 10^3$	<i>Pacyna J. et al., [1999]</i>
Medical	$19 \times 10^3$	--
Waste water sediment	$5 \times 10^6$	--
<b>Industrial waste</b>		
Tetrachloromethane	$8 \times 10^3$	<i>Holoubek I. et al., [1993]</i>
Trichloroethylene	$3 \times 10^3$	--
Tetrachloroethylene	$6 \times 10^6$	--
Polyvinylchloride	$5 \times 10^6$	--
<b>Motor transport*</b>		
Leaded gasoline	0.87	<i>Pacyna J. et al., [1999]</i>
Unleaded gasoline	0.024	--
Diesel fuel	21	--
<b>Agriculture</b>		
Used as fungicide	$5 \times 10^{11**}$	<i>Atmospheric Emission Inventory Guidebook, vol.3, [1999].</i>

\* - emission factors for motor transport is given in ng/km.

\*\* - emission factor is 0.5 of use

On the basis of expert estimates of tetrachloromethane and trichloroethylene volumes produced in the USSR in 1988 [Fedorov, 1993] we calculated HCB emissions from this kind of sources. The results and initial data are shown in table 2.

**Table 2.** HCB emissions from the production of light chlorinated hydrocarbons

Chlorine chemistry product	Production output in 1988, thous.t <i>Fedorov L.A., 1993</i>	Emission factor*, g/t, <i>Pacyna J.M. et al., 1999</i>	Emission, t
Tetrachloromethane	100	10	1
Trichloroethylene	105	4	0.4
Total	205		1.4

\* - in calculations mean emission factor values were used.

As follows from table 2 HCB emission from the production of only two commodity products of chlorine chemistry exceeds a tonne per year. On the basis of very incomplete data in the USSR by the end of the 80-s 2 mill. tonnes of chlorinated hydrocarbons have been produced and the emission from this reduction could amount to 10 tonnes.

Among stationary sources incineration plants can pose a severe hazard for the environment. Their emissions contain chlorinated aromatic hydrocarbons including HCB.

In waste incineration processes in burning and cooling zones of flue gases different reactions take place. At present mechanisms of heterogeneous reactions forming HCB molecules from ethane, ethylene and acetylene at the presence of chlorine containing compounds, metal oxides and silica are described in the literature [Froese and Hutzinger, 1996a,b]. Chemistry of incomplete waste incineration ( $t \cong 400^{\circ}\text{C}$ ) is defined by gas-phase reactions of organic compounds based of radical processes. In this case reactive compounds are radicals  $\cdot\text{H}$ ,  $\cdot\text{OH}$ ,  $\cdot\text{O}$ ,  $\cdot\text{O}_2\text{H}$ , etc. which in the process of chain reactions form hydrogen chloride (HCl). Maximum amount of chlorinated benzene is formed on fly ash particles acting as catalysts in chlorination of benzene structures. The extent of benzene chlorination and concentrations in the output depends on many factors. They are availability of chlorine-donor compounds, temperature regime, availability of heterogeneous surfaces and their chemical nature. HCB concentrations measured by *K.L.Froese and O.Hutzinger*, 1996b in the outlet of incinerator reach  $400 \text{ ng/m}^3$  with the total content of chlorinated benzene more than  $1500 \text{ ng/m}^3$ . Similar values of chlorinated benzene in flue gases of incinerators were determined by *K.Ballschmitter et al.* [1988]. HCB concentration range in

incinerator flue gases is several orders of magnitudes: 9.5-1100 ng/m<sup>3</sup> [HSDB, 2000]. HCB emission factors for incineration of different kinds of wastes are illustrated in table 1.

Waste incineration can contribute essentially to the total emissions of a country. For example, *I.Holoubek et al.* [1993] estimated HCB emissions in the Czech Republic and Slovakia for 1992 to be 3-6 tonnes and 80% was accounted for HCB emission from incineration of tetrachloroethylene (perchloroethylene), trichloroethylene and polyvinylchloride (PVC).

Since HCB is included to the Protocol of 1998 on persistent organic pollutants countries submit emission data to the ECE Secretariat. Official data on PCB emissions at least for one year from 1985 to 1998 was submitted by 13 countries. These data are given in table 3 (the data are received from MSC-W database as of the beginning of April, 2000).

**Table 3.** Official data of HCB emissions in European countries (kg/yr)

Country	1985	1990	1991	1992	1993	1994	1995	1996	1997	1998
Belgium		488				30 <sup>1</sup>	238	21.3 <sup>1</sup>		
Bulgaria		544					79	87	47	75.6
Croatia		300						0	0	
Germany		86								
Hungary	0.486	0.304	0.506	0.678	0.632	0.476	0.660	0.660	0.678	0.712
Iceland	0	0	0	0	0	0	0	0	0	
Netherlands	0					0	0	0	2.1	2.1
Norway							172	200	200	
Poland		0					0	0		
Spain		9227	8641	14703	7065	7733	6088	6065		
Switzerland		0	0	0	0	0	0	0	0	
Russian Federation		1.637	1.637	1.637	1.7	1.6	1.3	1.1	0.979	0.95
United Kingdom		1267	1259	1280	1255	1240	1248	1241	893	893

<sup>1</sup> – only Wallonia

Expert estimates of HCB emission during 1970-95 were made within the framework of POPCYLCING-Baltic project [*Pacyna et al.*, 1999]. For basic years these data are presented in table 4.

**Table 4.** Expert estimates of HCB emissions in European countries (kg/yr)

Country	1970	1975	1980	1985	1990	1995
Albania	249	249	165	170	88	55
Armenia*	163	164	111	110	55	50
Austria	2097	2018	1959	240	81	81
Azerbaijan*	615	620	417	415	206	187
Belarus	1762	1752	1161	1155	573	471
Belgium	1500	1593	1226	418	73	75
Bosnia and Herzegovina*	447	447	299	300	150	50
Bulgaria	1156	1176	795	789	398	300
Croatia*	704	703	471	473	236	78
Czech Republic*	1049	1049	696	695	317	216
Denmark	3181	3166	3024	319	131	115
Estonia	289	281	181	177	87	71
Finland	3160	3132	2915	290	127	126
France	25662	25621	23197	3776	1276	1285
Georgia*	519	523	353	351	175	158
Germany	20486	20969	17857	5259	1654	1555
Greece	4672	4628	4510	493	195	175
Hungary	1341	1336	877	863	427	305
Iceland	85	96	151	16	7	7
Ireland	1646	1485	1289	139	47	46
Italy	20123	17274	15767	2792	839	795
Kazakhstan* **	2431	2449	1649	1641	817	740
Latvia	501	483	309	310	155	128
Lithuania	631	644	437	431	213	176
Luxembourg	83	77	72	10	3	3
Netherlands	1423	1470	1370	389	93	92
Norway	1014	991	995	129	45	45
Poland	3907	3901	2612	2634	1321	930
Portugal	4740	4645	3651	416	159	145
Republic of Moldova	383	390	269	278	144	100
Romania	2847	2887	1940	1955	970	740
Russian Federation*	32365	32613	21971	21860	10868	9846
Slovakia*	445	445	295	295	174	118
Slovenia*	139	139	93	93	47	15
Spain	25384	25848	23899	3084	1175	1172
Sweden	3800	3720	3493	413	161	161
Switzerland	633	648	727	185	59	56
The FYR of Macedonia*	275	275	184	185	92	30
Ukraine	7759	7840	5292	5263	2619	2095
United Kingdom	11071	10926	9707	2175	548	511
Yugoslavia*	1239	1237	828	831	416	137
Total, t/yr	192	190	157	62	27	23

\* - estimated on the basis of spatial emission distribution [*Pacyna et al.*, 1999] over Czechoslovakia, USSR and Socialist Federal Republic of Yugoslavia.

\*\* - part of Kazakhstan, Uzbekistan and Turkmenia within the EMEP grid

The comparison of the expert estimates [*Pacyna et al.*, 1999] with the available official data pointed out that the expert estimates differ from the official data both to higher and lower sides. Probably it is connected with the fact that in many countries HCB was not used as a pesticide beginning with the 90-s whereas in the expert estimates [*Pacyna et al.*, 1999] it is the main emission constituent. Beside not all official data include all kinds of activity.

The aforesaid characterizes HCB as a pollutant which has a wide range of emission sources. Contrary to PAH and PCDD/F HCB is a pollutant which is specially synthesized for industrial purposes and unlike lindane and DDT it is used not only in agriculture but also in industry. Besides HCB is a by-product of many kinds of activity.

It is important to include an estimate of emissions from chemical industry and different kinds of waste incineration in HCB source inventory otherwise HCB emission will be underestimated.



## IV. Levels of hexachlorobenzene content in the environment

### 1. HCB content in the air

HCB is studied well enough. Many authors investigated its behavior and distribution with environmental objects and a great number of measurements have been carried out in different regions of the globe. Table 1 demonstrates observed HCB content in the air.

**Table 1.** HCB air content

Region of observations	Observation period	HCB concentration, pg/m <sup>3</sup>	Reference
1	2	3	4
<b>Clean areas</b>			
<b>Pacific ocean</b>			
Enewetak Atoll, Marshall Islands, (12 °N, 162 °E)	April-August 1979	<u>100</u> 95–130	<i>Atlas E. and Giam C.S., 1981</i>
Chuckchee and Bering Seas	July-August 1988	<u>210</u> 144-324	<i>Hinckley D.A., et al., 1991</i>
<b>Indian ocean</b>			
Reunion Island (21 °S, 56 °E)	March 1986	<u>7</u> 4–12	<i>Wittlinger R. and Ballschmiter K., 1990</i>
<b>Atlantic ocean</b>			
Sargasso Sea, North Atlantic	End of the 70-s	150	<i>Atlas E. and Giam C.S., 1981</i>
Bermuda Islands, north-west of Atlantic	April 1985	<u>101±66</u>	<i>Knap A.H and Binkley K.S., 1991</i>
	June 1986	28-205	
		<u>108±44</u> 47-173	
<b>Seas</b>			
Baltic Sea	1986	150-400	<i>Wodarg D. and K.H.Reinhardt, 1992</i>
	1987-1989	<u>264</u>	
North Sea	1986	<u>125</u>	

continued

1	2	3	4
<b>Canadian Arctic</b>			
Axel Heiberg Island (80 °57' N, 97 °35.5' W)  (81 °4.6' N, 96 °48.6' W)	May-June	<u>73±18</u>	<i>Hargrave B. et al., 1988</i>
	and August-September 1986	<u>63±16</u>	
Ellesmere Island (81 °N, 100° W)	August-September 1986	<u>189</u> 131-233	<i>Patton G.W. et al., 1989</i>
	June 1987	<u>147</u> >44-155	
Alert, Meteorological station (82.5°N, 62.3° W)	January-June and October-December 1993	<u>57</u> 27-75	<i>Hargrave B.T. et al., 1997</i>
<b>European Arctic</b>			
Norway			
Lillestroem	May 1981	<u>162</u> 55-234	<i>Oehme M. and Manoe S. 1984</i>
Bear Island	September 1980	<u>40</u> 29-45	
	February 1981	<u>111</u> 59-188	
Hopen Island	1982/1983	100-250	<i>Oehme M. and Ottar B., 1984</i>
Jan Mayen Island	1982/1983	50-200	
Bjørnøja	1982	<u>120</u> 78.4-200	<i>Pacyna J.M. and Oehme M., 1988</i>
	1983	<u>134</u> 88-180	
	Winter-spring 1983	<u>124</u> 87-201	
	Summer 1984	<u>57</u> 42-149	
Jergul	Summer 1984	<u>71±25</u> 36-114	<i>Oehme M., 1991</i>
	Winter 1984	<u>126±22</u> 93-172	

continued

1	2	3	4
Ny-Ålesund Spitzbergen (Svalbard), (79°N, 12° E)	September 1980	<u>71</u> 50-85	<i>Oehme M. and Manoe S. 1984</i>
	February 1981	<u>86</u> 71-95	
	1982	<u>123</u> 75-169	<i>Pacyna J.M. and Oehme M., 1988</i>
	1983	<u>186</u> 158-227	
	Winter-spring 1983	<u>144</u> 112-187	
	Summer 1984	<u>154</u> 20-200	
	Winter-spring 1984	<u>151</u> 29-389	
	1992	<u>205.2±59.9</u> 121.1-372.5	<i>Oehme M. et al., 1995</i>
	April–December 1993	63-164	<i>Oehme M. et al., 1996</i>
	1997	<u>106.5</u> 45.8-244.7	<i>Berg T. and Hjell- brekke A.-G., 1999</i>
Kårvath	Summer 1984	<u>102±86</u> 62-153	<i>Oehme M., 1991</i>
	Winter 1984	<u>131±43</u> 55-177	
	1992	<u>103.2±28.9</u> 56.3-149.3	<i>Oehme M. et al., 1995</i>
Birkenes (58°N, 8° E)	Summer 1984	<u>65±24</u> 30-103	<i>Oehme M., 1991</i>
	Winter 1984	<u>95±45</u> 52-211	
Svanvik	1992	<u>107.9±30.3</u> 55.1-188.4	<i>Oehme M. et al., 1995</i>
Lista	1992	<u>182.6±53.1</u> 102.0-280.6	
		1997	<u>92.9</u> 1.2-125.5
Storhofdi, Iceland	1997	<u>10.25</u> 1.18-23.64	

continued

1	2	3	4
<b>North America, Great Lakes</b>			
Canada, Great Lakes	Up to 1980	<u>200</u> 100-300	<i>Eisenreich S.J., et al.</i> 1980
Province Ontario, Egbert (44°14' N, 79° 47' W) 100 km to the north of Toronto city	1988-1989	<u>&gt;54</u> 0.04 – 640	<i>Hoff R.M. et al.,</i> 1992
Turkey Lake, 40 km away from Sault Ste Marie, central Ontario Province	May and October 1987	<u>74</u> 26-97	<i>Lane D.A. et al.,</i> 1992
Eagle Harbour (47°28' N, 88° 09' W) Superior Lake	1992-1994 Programme IADN	<u>98.2</u>	<i>Hoff R.M. et al.,</i> 1996
Sleeping Bear Dunes (44 °46' N, 86 °04' W) Michigan Lake	-"	<u>120.1</u>	
Sturgeon Point (42 °42' N, 79 °04' W) Erie Lake	-"	<u>80.2</u>	
Pt.Petre (49 °51' N, 77 °09' W) Ontario Lake	November 1988 and March 1989	<u>71</u> 39-87	<i>Lane D.A. et al.,</i> 1992
	1992-1994	<u>130</u>	<i>Hoff R.M. et al.,</i> 1996
<b>Asia</b>			
Baikal Lake	June-July 1991	<u>194±47</u> 180-251	<i>McConnell L.L. et al.,</i> 1996
	May – June 1992	70-170	<i>Iwata H. et al.,</i> 1995
Listvyanka, (Bank of Angara river at inflowing to Baikal Lake)	June-July 1991	144-250	<i>McConnell L.L. et al.,</i> 1996
<b>Urban regions</b>			
<b>Europe</b>			
Germany			
Ulm	Winter 1987	<u>250</u> 70-520	<i>Wittlinger R. and Ballschmitter K.,</i> 1987
	Winter 1987	114	<i>Ballschmitter K. and Wittlinger R.,</i> 1991
Hamburg	1986-1987 April to April	<u>600</u> 300-2500	<i>Bruckmann P. and W.Kersten,</i> 1988
Augsburg	March – November 1992	180-470	<i>Kaup H. et al.,</i> 1996
	January-February 1993	160	

continued

1	2	3	4
Sweden			
Aspvreten (58°43' N, 17°23' W)	1983-1985	54- >165	<i>Bidleman T.F. et al., 1987</i>
Stockholm	1983-1985	>47-130	
Netherlands, Deft	1979-1981	100	<i>Guicherit R. and Schulting F.L., 1983, cited from Bruckmann P. and W.Kersten, 1988</i>
France			
La Ferté sous Jouarre	March-Sept. 1992	9.0–2400	<i>Chevreuil M. et al., 1996</i>
	April – July 1993	50–140	
Strasbourg	April - May 1993	<u>483</u>	<i>Sanusi A. et al., 1999</i>
	June - July 1994	130-688	
Meteostation 5 km to the south from Colmar	April - May 1993 June - July 1994	<u>317</u> 145-968	
Czech Republic Southern Bohemia, Košetice	July - December 1994	<u>207.6</u> 100–340	<i>Holoubek I. et al., 1995</i>
	November 1996 – December 1998	<u>181</u> 45–835	<i>Holoubek I. et al., 1999</i>
<b>Northern America</b>			
USA			
Columbia, SC	1977-1982	290	<i>Bidleman T.F., et al., 1986</i>
Denver, CO	1980	240	
College Station, Texas	End of the 70-s	200	<i>Atlas E. and Giam C.S., 1981</i>
Pigeon Key, Florida	End of the 70-s	120	
Portland, Oregon	February - April 1984	50-110	<i>Ligocki M.P. et al., 1985</i>
Adirondack Mountains, NY	July 1985	<u>198</u> 25-282	<i>Knap A.H and Binkley K.S., 1991</i>
Chicago, IL	June - August 1991, Programme (LMUATS)	<u>68±40</u>	<i>Pirrone N. et al., 1995</i>
South Haven, MI		<u>55±23</u>	
Green Bay, WI		<u>160±87</u>	<i>McConell L.L. et al., 1996</i>
Georgetown, SC		<u>120±40</u>	

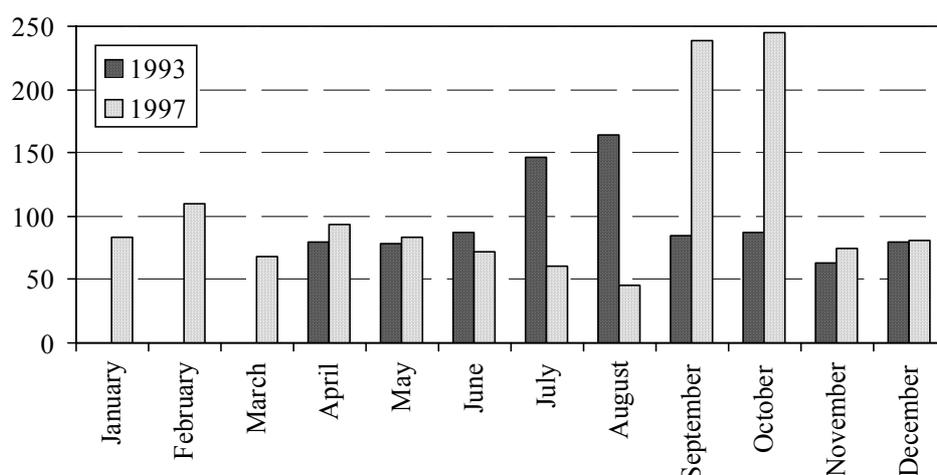
120±40 – mean value and confidential range of the value determined;

70-520 – concentration range;

250 – mean value.

The data presented in table 1 fairly well illustrate air pollution in the Arctic region (European and Canadian) and slightly worse in western Europe and the United States of America. No data on air pollution by HCB are available on Asian countries, Latin America and Africa, where HCB was used in agriculture for many years in volumes incomparable with those used in Europe and Canada for the same purposes. In Russia individual measurements were carried out in the region of Baikal Lake. Data on other regions are not available in the literature. On the basis of table 1 data the evaluated HCB air concentration field is rather uniform (100-200 pg/m<sup>3</sup>) practically invariable with time.

The monitoring programmes on air pollution by persistent organic pollutants (HCB included) implemented by Canada and EMEP are aimed at revealing of interannual and seasonal air concentration variations and they provide a possibility to compare observations with estimates obtained by transboundary transport modelling on the regional and global scale. Figure 1 shows HCB air concentration variations at the EMEP station in Ny-Ålesund, Svalbard, Norway in 1993 and 1997 [Oehme et al., 1996; Berg and Hjellbrekke, 1999].



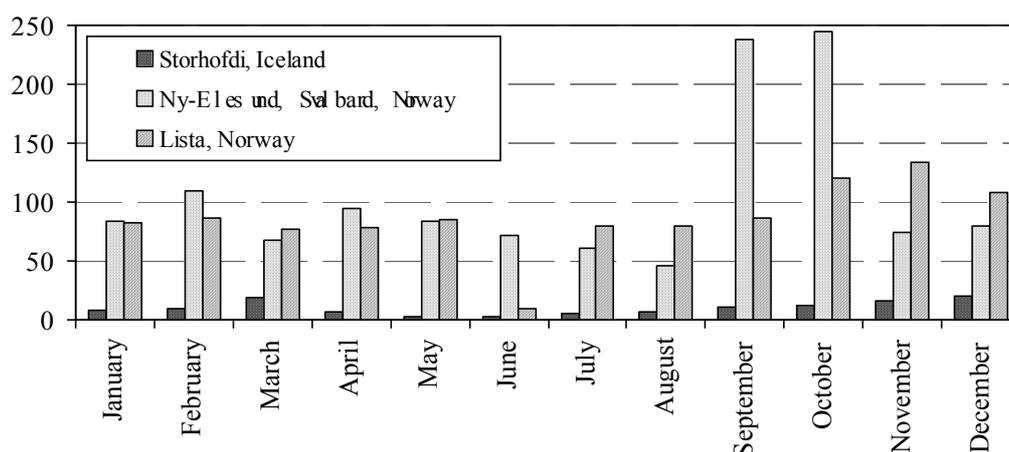
**Figure 1.** HCB air concentration (pg/m<sup>3</sup>) dynamics during an year at station Ny-Ålesund, Svalbard, Norway

As follows from figure 1 HCB concentration has a distinctive maximum. In 1993 the concentration growth was in July-August, in 1997 - in September-October. In spring and early in summer the concentrations were noticeably lower. In 1992-93 *M.Chevreuil et al.* [1996] observed an opposite picture in France where maximum concentrations were observed in May. Observations carried out in Canadian Arctic in 1993 [*Hargrave et al.*, 1997] demonstrated a pattern similar to Norwegian one - the concentration decrease coincides with a warm season beginning with May. For lack of data and complete observation series it is difficult to speak about a stable seasonal variation of HCB air concentrations so far.

The comparison of HCB air concentration levels at Norwegian stations in 1984 and 1992 indicates an inessential decrease of HCB mean annual concentrations (table 1). Judging by the data of Ny-Ålesund, Svalbard, Norway, for 1984, 1992 and 1997 the conclusion on the absence of trends may be suggested since mean annual concentrations were kept at the level of 100 pg/m<sup>3</sup>.

Thus during recent period of time covering more than a decade in spite of the prohibition and restriction of HCB use in agriculture, at EMEP stations air pollution concentrations are kept practically invariable.

The comparison of HCB air concentration variation during a year at EMEP stations is illustrated in figure 2.



**Figure 2.** HCB mean monthly concentration (pg/m<sup>3</sup>) variations at EMEP stations in 1997  
T.Berg and A.-G.Hjellbrekke, [1999]

The comparison of HCB air content at three EMEP stations during 1997 indicates no general regularities of HCB behaviour in northern Europe. The concentration levels recorded at Norwegian stations are similar but at Lista station they are somewhat lower than Ny-Ålesund, Svalbard, Norway, mean annual concentration is lower. At Lista the highest HCB concentrations are observed during autumn-winter period and November concentrations exceed those of June more than in 10 times (max/min ratio is 13.9). At station Ny-Ålesund, Svalbard, maximum concentrations are observed in September-October with absolute maximum for 1997 equal to 244.7 pg/m<sup>3</sup>. During summer months the concentrations decrease is about 3 times. In 1997 the lowest concentrations were observed

at station Storhofdi, Iceland. Here HCB mean annual concentration was almost 10 times lower than at Norwegian stations. In May and June HCB content was about 3 pg/m<sup>3</sup>, it is comparable with the air pollution level over the southern part of the Indian Ocean [Wittlinger and Ballschmiter, 1990].

During recent years there appeared works substantiating theoretically peculiarities of persistent organic pollutant (POP) distribution in the environment. *F.Wania and D.Mackay* [1993,1995,1996] suggested a model describing POP migration from regions with positive temperatures to polar regions which was called “global distillation or grass-hopper effect”. HCB being one of the most volatile compounds among POPs well suits to illustrate the model.

HCB calculated concentrations are shown in table 2.

**Table 2.** Calculated HCB air concentrations

Region	Period	Concentration, pg/m <sup>3</sup>	Note	Reference
Arctic regions	The 80-s	130	Averaged over measurements in Arctic regions	<i>Cotham W. and Bidleman T.F., 1991</i>
Ontario Lake		200	Regional model	<i>Mackay D. and Paterson S., 1991</i>
Geographical belts of Northern Hemisphere			Model of global distribution	<i>Wania F. and Mackay D., 1995</i>
Polar		54		
Boreal		53		
Temperate		50		
Subtropical		48		
Tropical		42		
Geographical belts of Southern Hemisphere				
Tropical		32		
Subtropical		33		
Temperate		35		
Polar		37		

While comparing HCB calculated concentrations obtained by the global distribution model with observations as usual we lack experimental data.

## 2. HCB content in precipitation

Data on HCB concentration levels in rain are represented by a variety of values which can differ by several orders of magnitude. For example, HCB content in wet precipitation in the region of the Great Lakes is within 0.04-0.3 pg/m<sup>3</sup>, in Europe - from 0.02 to 6.5 pg/m<sup>3</sup>. The analysis of measured values (table 3) does not allow us to identify characteristic HCB concentration levels in different regions of the world for insufficient number of experimental data. At present we can only state that HCB concentration in all the considered regions does not exceed 10 pg/m<sup>3</sup>.

**Table 3.** HCB content in wet depositions

Region of observations	Observation period	HCB concentration, pg/m <sup>3</sup>	Reference
1	2	3	4
<b>Clean areas</b>			
<b><i>Pacific ocean</i></b>			
Enewetak Atoll, Marshall Islands, (12 °N, 162 °E)	April-August 1979	<0.03	<i>Atlas E. and Giam C.S., 1981</i>
<b><i>Great Lakes</i></b>			
Eagle Harbour (47°28' N, 88° 09' W) Superior Lake	1992-1994 Programme IADN	0.1	<i>Hoff R.M. et al., 1996</i>
Sleeping Bear Dunes (44°46' N, 86° 04' W) Michigan Lake	--	0.06	
Sturgeon Point (42°42' N, 79° 04' W) Erie Lake	--	0.04	
Pt. Petre (49°51' N, 77° 09' W) Ontario Lake	--	0.3	
<b><i>European Arctic</i></b>			
Storhofdi, Iceland	January-December 1997	0.021	<i>Berg T. and Hjellbrekke A.-G., 1999</i>
Lista, Norway	January-December 1997	0.903	

continued

1	2	3	4
<b>Urban and semi-rural regions</b>			
<b>Europe</b>			
Germany, Zingst	January-December 1997	0.162	<i>Berg T. and Hjellbrekke A.-G., 1999</i>
France			<i>Chevreuil M. et al., 1996</i>
Paris	February–July 1992	1.8–17	
	January–September 1993	0.3–5.6	
La Ferté sous Jouarre	February–July 1992	2.5–4.5	
	January-September 1993	0.3–6.5	
<b>Northern America</b>			
Oregon Graduate Center, 12 km to the south-east from Portland, Oregon	March-April, October-December, 1982	<0.05-0.10	<i>Pankow J.F. et al., 1984</i>

Regular sampling of atmospheric precipitation and their monthly analysis of atmospheric are carried out only at EMEP stations. Data for 1997 [*Berg and Hjellbrekke, 1999*] are given in table 4.

**Table 4.** Comparison of HCB concentrations in wet depositions at EMEP stations

Month	HCB concentration, pg/m <sup>3</sup>		
	IS 0091R	NO 0099 R	DE 0009 R
	Storhofdi, Iceland	Lista, Norway	Zingst, Germany
January	0.03	1.00	---
February	0.03	1.20	0.01
March	0.02	0.90	0.11
April	0.03	0.80	0.01
May	0.05	0.70	0.11
June	0.01	1.10	0.01
July	0.01	0.30	0.01
August	0.01	1.30	0.01
September	0.02	0.80	0.32
October	0.01	0.90	0.85
November	0.01	0.60	0.01
December	0.02	0.70	0.01
Mean	0.02	0.86	0.12

At station Storhofdi, Iceland (IS 0091 R) the samples had the lowest HCB concentrations among all the EMEP stations. The highest concentration here was in May and it amounted to 0.05 pg/m<sup>3</sup>. On the contrary in Norway at Lista station (NO 0099 R) HCB concentrations were 0.30-1.30 pg/m<sup>3</sup> round the year. Two maximum values 1.10 pg/m<sup>3</sup> and 1.3 pg/m<sup>3</sup> were observed in June and August respectively. The minimum was determined in July but it was rather high - 0.30 pg/m<sup>3</sup>. At EMEP station Zingst (DE 0009 R), Germany, HCB content in precipitation was appreciably lower than at Norwegian station but higher compared to Iceland station. The concentration increase is observed in September-October, in October the concentration is maximum at this station and concentrations are very close to the data for this period recorded at station Lista. Concentration variations during a year do not coincide at EMEP stations.

### 3. HCB content in snow cover and ice

The snow cover in the Arctic region is characterized by essentially higher HCB concentrations [Cotham and Bidleman, 1991] than in central Europe [Ballschmiter and Wittlinger, 1991] (see table 5). HCB content in the sea ice can amount to tens of pg/l and as to the order of magnitude are similar to snow concentrations. Investigations of PCB content in ice samples taken in the glacier of Rocky Mountains (52 ° 11' N, 117 °19' W), located at 3506 m height were carried out by *D.Donald et al.*, [1999]. During the period from 1959 to 1994 the concentrations increased. In the early 60s they did not exceed 1 pg/l and in 1994 they reached their maximum - 50 pg/l. Later on the concentrations cut down and in 1997 amounted to 30 pg/l. In Canadian Arctic (Canadian Ice Island) the pollution of the sea ice by HCB does not exceed 6 pg/l [*Wania et al.*, 1998a].

**Table 5.** HCB content in snow and ice

Region	Period	Concentration, pg/l	Note	Reference
<b>Canadian Arctic</b>				
Axel Heiberg Island (80 °57' N, 97 °35.5' W) (81 °4.6' N, 96 °48.6' W)	May-June, August– September 1986	33±10 <2	Mean concentration in snow, HCB content in ice samples was less than 2 pg/l	<i>Hargrave B. et al.</i> , 1988
Arctic regions	Up to 1989	22		<i>Cotham W. and Bidleman T.F.</i> , 1991
Canadian Ice Islands	June 1987	<6	Sea ice	<i>Wania F. et al.</i> , 1998a
	June 1987	21	Sea ice including fractions of plants in particles	
Norwegian Sea	August 1979	80	Sea ice	<i>Wania F. et al.</i> , 1998a
	August 1985	40–50		
Rocky Mountains (52 ° 11' N, 117 °19' W)	1959	<1	Glacier	<i>Donald D. et al.</i> , 1999
	1962	1		
	1970	3.3		
	1980	6.0		
	1990	11		
	1994	50		
1995	34			
Germany, Ulm	1987	1.5		<i>Ballschmiter K. and Wittlinger R.</i> , 1991

## 4. HCB content in surface waters

Hexachlorobenzene is weakly dissolved in water and belongs to hydrophobic compounds therefore its concentrations in natural water bodies and water courses are not high and amount to several units - several hundreds of pg/l/. Measurement data on the surface water pollution are demonstrated in table 6.

**Table 6.** HCB content in surface waters (sea and fresh water)

Region	Period	Concentration, pg/l	Note	Reference
1	2	3	4	5
<b>Clean areas</b>				
<b>Great Lakes</b>				
Superior Lake	1992-1994 programme IADN	10		<i>Hoff R.M. et al., 1996</i>
Michigan Lake	-"-	14		
Erie Lake	-"-	14		
Ontario Lake	-"-	45		
Huron Lake		7		
<b>Canadian Arctic</b>				
Axel Heiberg Island (80 °57' N, 97 °35.5' W) (81 °4.6' N, 96 °48.6' W)	May-June August-September 1986	$17 \pm 6$ $22 \pm 7$	Mean values of sea water content at the depth of 10-60 m	<i>Hargrave B. et al., 1988</i>
Oceanic station, cape Barrow (74 °42' N, 94 °50' W) Resolute Bay	1993	$15$ 14-18		<i>Hargrave B. et al., 1997</i>
<b>Seas</b>				
Chuckchee Sea, (57 °56' N, 175 °04' W)	July-September 1988	60	Surface water at the depth up to 2 m	<i>Hinckley D.A., et al., 1991</i>
		<5	Surface microfilm of 120 µm thickness	

continued

1	2	3	4	5
Mediterranean Sea				
Alfacs Bay	January 1985 – March 1986	<u>14.2</u>	Sea water	<i>Grimalt J.O. et al., 1988</i>
Fangar Bay		<u>21</u>		
Alfacs Bay		<u>32</u>	Brackish water, “river-sea” mixing zone	
Fangar Bay		<u>18.1</u>		
Barcelona harbour	1988	< 100	Surface water	<i>Bajona J. et al., 1991</i>
		$(1 \pm 0.5) \times 10^3$	Near bottom water at the depth of 5 m	
North Sea	1988–1989	30		<i>Wodarg D. and Reinhardt K.H., 1992</i>
Baltic Sea		30		
Skagerrak, Swedish west coast	April 1995	70		<i>Bergqvist P.-An. et al., 1998</i>
	May 1995	180		
<b>Fresh water courses and water bodies</b>				
Spain, Ebro, delta	January 1985 – March 1986	<u>655</u>		<i>Grimalt J.O. et al., 1988</i>
Russian Federation				
Dnieper*	1991	0–21		<i>Yearbook. Pesticide Monitoring in natural objects of the RF, 1992,1993</i>
Ob*	1991	0–368		
Volga in Bashkiria*	1991	<u>7</u> 0–167		
	1992	0–11		
Ural*	1991	0–2		
Baikal Lake	May-June 1992	7.0-28		<i>Iwata H. et al., 1995</i>

\* - measurement units: ng/l

In the water compartment HCB as a rule is sorbed on particulate matter and then settles onto the bottom as sediments and silt. As it is indicated [*Grimalt et al., 1988*] (table 7) in river systems subjected to the direct pollution HCB fraction associated with particles is 73.3-96.9%.

The concentrations in bottom sediments, soils and vegetation here and hereinafter are presented in ng/g of dry weight.

**Table 7.** HCB partitioning between dissolved and particulate phase in natural waters Ebro River delta

Sampling site location	HCB mean concentration, pg/l		HCB fraction associated with particles, %
	Dissolved phase	Particulate	
Site on the river	55	600	91.6
Site in Alfacs Bay, sea water	2.2	12	84.5
Site in Alfacs Bay, surface brackish water	1.0	31	96.9
Site in Fangar Bay, sea water	2.0	19	90.5
Site in Fangar Bay, surface brackish water	4.1	14	73.3
Site on irrigation channel	200	780	79.6

*J.Bajona et al.* [1991] indicates a considerable growth with depth as well. For example, in Barcelona harbour HCB content in the surface water is up to 100 pg/l and in the near bottom water – in 10 times more (table 6).

*B.Starndberg et al.* [1998] investigated HCB content on particulate matter in Bothnia Gulf and in the Baltic Sea. During the experiment (1991-93) they recorded an appreciable concentration of HCB (3.4 and 3.2 ng/g) on the stations far away from the offshore and at coastal stations - 0.49 and 0.69 ng/g.

Processes of HCB sorption on particulate matter surface in the water depth obviously define its concentration decrease in natural waters.

## 5. HCB content in bottom sediments

HCB content levels in bottom sediments of different water bodies are presented in table 8. The range of measured concentrations is very wide: from 0.005 ng/g in Baikal Lake to 440 ng/g in the Elbe River. Table 8 data characterize basically bottom sediment pollution of fresh water lakes. The concentration range for them is slightly narrower - from 0.09 ng/g in Sophia Lake (Canadian Arctic) to 38 ng/g in Ketelmeer Lake (the Netherlands).

**Table 8.** HCB content in bottom sediments

Region of observations	Observation period	HCB concentration, ng/g dry weight	Note	Reference
1	2	3	4	5
<b>Seas and see basins</b>				
Baltic Sea, northern part	1991-1992	0.79-0.94		<i>Strandberg B. et al., 1998</i>
Bothnia Gulf	1991-1992	0.84		
Mediterranean Sea, Barcelona Harbour	1988	10	Depth of sampling 0-2 cm	<i>Bajona J. et al., 1991</i>
<b>Fresh water and water courses</b>				
RF, Baikal Lake	1992	0.005 – 0.16		<i>Iwata H. et al., 1995</i>
Canada, Ontario Lake southern part		7		<i>Mackay D. and Paterson S., 1991</i>
Arctic lakes Canada				
L 375 (49 °45' N, 93 °47' W)	1988	0.43	Thin upper layer with depth up to 1.3 cm	<i>Muir D. et al., 1995</i>
L 382 (49 °42' N, 93 °41' W)	1987	0.36		
Hawk (63 °38' N, 90 °42' W)	1985	1.80		
Far (63 °42' N, 90 °40' W)	1986	0.29		
Sophia (75 °07' N, 93 °35' W)	1979	0.09		
Amituk (75 °03' N, 93 °48' W)	1980	1.14		
Buchaman (79 °30' N, 87 °30' W)	1985	1.03		
Hagen (81 °45' N, 71 °30' W)	1986	1.01		

continued

1	2	3	4	5
Ketelmeer Lake, Netherlands	1995	38	Upper layer	<i>ten Hulschen Th. et al., 1999</i>
	1995	37-39.1	Middle layers of sediment	
Czech Republic, river Labe (Elbe) and its confluents	1987-1990			<i>Nonderk L. and Frolikova N., 1991</i>
Jaromer		<1		
Pardubice		<1		
Preloc		7		
Kolin		<10		
Celakovice		1		
Melnik		7		
Litomerice		<1		
Lovosice		4		
Usti		440		
Decin		290		
Orlice		<1		
Jizera		<1		
Vltava		6		
Ohre		5		
Biline		10		

HCb content in the Labe (Elbe) river bottom sediments over the whole territory of the Czech Republic is uniform enough. The concentration range is one order of magnitude (from <1 to 10 ng/g). Only two sampling sites are exceptional: Usti and Decin located in an industrial region at the border with Germany. Here bottom sediments are appreciably polluted by HCB and the pollution level here exceeds the mean by two orders of magnitude. Mean concentration in the Labe River bottom sediments is about 7 ng/g the same as in the southern part of Ontario Lake, Canada. In bottom sediments of the background regions - Baikal and Arctic lakes of Canada HCB content is by one - two orders of magnitude lower than in other regions. Obviously the bottom sediment pollution is directly associated with the load inflicted on water bodies.

## 6. HCB content in soils

Wide use of HCB in agriculture seemingly could provide abundant data on its content in soils. However, in the literature data on soil pollution by HCB are scarce and often presented content levels are beyond the limits of sensitivity of analytical methods. Table 9 illustrates HCB concentrations in soils of different regions.

**Table 9.** HCB soil content

Region of observations	Observation period	HCB concentration, ng/g dry weight	Note	Reference
Germany, Bavaria	1989–1990	0.36	Unpolluted agricultural soils	<i>McLachlan M.S., 1996</i>
Czech Republic, Moravian Mountains, 6 sites sampling	1994	0.47–4.5	Soils from Moravian mountains, 1100 m above sea level	<i>Holoubek I. et al., 1999</i>
Praha		<u>3.9</u>	Capitol, large urban area, very high density of traffic and industry	<i>Podlešakova et al., 1998, cited from Holoubek I. et al., 1999</i>
Ostrava – Karvina		<u>2.8</u>	Urban area, very high density of industry and traffic (metallurgy and chemical industry)	
Sokolov		<u>3.5</u>	Industrial region, coal mining, coal conversion plant chemical industry	
Usti nad Labem		8.7-487	Urban area, chemical industry	
Teplice		6.4-10	Northern Bohemia, very high density industry	
Prachatice		6.9-10	Smaller industrial town, local heating system	
Košetice	1988-1998	<0.1-9	Regional background observatory	
	1996-1998	0.21-5.87		
RF, Baikal Lake region	1992	0.050 – 1.6	Agricultural fields surrounding Irkutsk city	<i>Iwata H. et al., 1995</i>

Investigations of POP content including HCB in soils in regions remote from potential sources were carried out and described by *W.A.Ockenden et al.* [1999]. Having investigated more than a hundred selected site the authors showed that in spite of a wide scattering of HCB concentrations in soils (from below the detection level to 5100 pg/g), high concentrations (more than 1000 pg/g) are rare. All HCB concentrations exceeding 200 pg/g were recorded at 30-60° N. Most measurement results are below the detection limit and in the first orders of magnitude.

As it was indicated by the authors HCB concentration distribution in soil is of a latitudinal character. It was not found at the latitudes from 60-90<sup>0</sup>S and it is very seldom determined at the latitude of 30-60<sup>0</sup>S and extremely rare at the latitudes but it was frequently recorded in soils of the Northern Hemisphere up to 90<sup>0</sup>N. Forest soils appeared to be more polluted by HCB than soils covered by herbaceous vegetation and the difference was about an order of magnitude (8 times).

## 7. HCB content in vegetation

The input of pollutants to vegetation can occur by different ways. First, they come from the atmosphere due to aerosol particles settling and then absorption of HCB gaseous compounds by vegetation respiration. Second, while absorbing nutrients by roots from the polluted soil. Nowadays it is widely believed that some plants in particular moss and lichen can be passive samplers for the air pollution control. Table 10 presents HCB concentrations in different vegetation species measured in different regions of the world.

**Table 10.** HCB content in vegetation

Region of observations	Observation period	Vegetation type	HCB concentration, ng/g dry weight	Reference
1	2	3	4	5
<b>Antarctic</b>				
	1985	<i>Usnea sulphurea</i> Lichen	0.72	<i>Villeneuve J.P. et al., 1988</i>
	1985 – 1987	Moss and lichen	0.5	<i>Bacci E. et al., 1988</i>
<b>Africa</b>				
Mali-Guinea	1985-1987	<i>Mangifera indica</i> Mango leaves	<0.1	<i>Bacci E. et al., 1988</i>
Ghana	--	--	<0.1	
Benin-Burkina Faso	--	--	<0.1	

continued

1	2	3	4	5
<b>Europe</b>				
<b>Moss and lichen</b>				
Monaco, mountains facing the Mediterranean Sea	May 1986	<i>Usnea barbata</i> Lichen	5.5	<i>Villeneuve J.P.</i> <i>et al.</i> , 1988
Southern France, Peira–Cava (h=1200 m) and Turini (h=1800 m)	May 1986	<i>Usnea barbata</i>	3.9 – 7.1	<i>Villeneuve J.P.</i> <i>et al.</i> , 1988
Italy	1984	<i>Lobaria pulmonaria</i> <i>Xanthoria parietina</i> Lichen	1.5	<i>Villeneuve J.P.</i> <i>et al.</i> , 1988
Sweden	1975	<i>Cladonia alpestris</i>	0.26	
Southern part	1982		0.8	<i>Thomas W. et al.</i> , 1984, cited from <i>Muir D. et al.</i> , 1993
Norway	1979	<i>Hypogymnia physodes</i>	<u>5.8</u> 1-11	<i>Carlberg G.E.</i> <i>et al.</i> , 1983, cited from <i>Muir D. et al.</i> , 1993
	1994	–“–	1.6–4.8	<i>Ockenden W.A.</i> <i>et al.</i> , 1998
Czech Republic, Košetice	1988-1998	Lichen	<0.1–18	<i>Holoubek I., et al.</i> , 2000
	1996–1998		0.67–1.1	
	1988–1998	Moss	<0.1–6.0	
	1996–1998		0.97-6.0	
<b>Needle</b>				
Austria				
Villach-Gratz	1991-1992	Pine needles	<u>7.7</u> 4.0-17	<i>Calamari D. et al.</i> , 1994
25 sites all over the country	October 1993	Fir-tree needles	<u>0.61</u> 0.34-1.06	<i>Weiss P.</i> , 1998
Netherlands, Island of Texel	1991-1992	Pine needles	<u>3.8</u> 3.2-4.3	<i>Calamari D. et al.</i> , 1994
Finland, Lapperanta–Imatra	–“–	–“–	<u>2.2</u> 2.0-2.8	
Northern Italy				
Lake Garda	–“–	–“–	<u>2.7</u> 1.8–3.4	
Val Grande	–“–	–“–	1.4	
Po Valley	–“–	–“–	4.4–5.0	

continued

1	2	3	4	5
Milan	--	--	<u>7.1</u> 5.5-9.8	<i>Calamari D. et al., 1994</i>
Southern Italy, Napoli	--	--	2.2	
Greece, Ithaca-Gerolimena	--	--	<u>5.9</u> 5.0-7.2	
Norway, 6 sites sampling	1994	<i>Pinus sylvestris</i>	<u>1.15</u> 0.68-2.1	<i>Ockenden W. et al., 1998</i>
Germany, Bavaria	1991	Grass <i>Lolium multiflorum</i>	26*	<i>Welsch-Pausch K. et al., 1995</i>
<b>North America, The Great Lakes</b>				
Region of Ontario Lake, 35 sites	1986	Moss, lichen	0.52-2.4	<i>Bacci E. et al., 1988</i>
	1987	--	0.4-1.5	
Bear Lake	1985-1987	--	<u>0.99±0.44</u> 0.46-1.75	<i>Muir D. et al., 1993</i>
Dunn's Valley	--	--	<u>0.62±0.36</u> 0.45-1.1	
Kakebeka Falls	--	--	<u>1.1±0.48</u> 0.24-0.96	
East Canada	1985	--	0.65 - 1.6	<i>Muir D. et al., 1993</i>

\* - of wet weight

HCB concentrations in vegetation samples (moss, lichen and mango) vary in the range <0.1 - 18 ng/g of dry weight. HCB content in herbaceous vegetation sampled in the vicinity of the University of Bavaria is 26 ng/g of wet weight [*Welsch-Pausch et al., 1995*]. The higher value in this case obviously was obtained because of the analysis of a fresh (not dried) sample.

The capability of plants to accumulate pollutants is quantified by a bioconcentration factor (BCF). To assess the accumulation of air pollutants we use a factor of bioconcentration for the atmosphere. It is the ratio of the pollutant mass present in a plant to the pollutant mass present in the air (see Chapter I, section 8). HCB bioconcentration factors for different vegetation species are demonstrated in table 11.

**Table 11.** Factors of HCB bioconcentration by different vegetation species

Region of observation	Vegetation type	Bioconcentration factor, BCF	Reference
Canada, Great Lakes	Lichen	$3.9 \times 10^6 - 1.7 \times 10^7$	<i>Muir D.C.G. et al., 1993</i>
European Arctic, Spitzbergen, Norway	Moss	$3.1 \times 10^7$	<i>Muir D.C.G. et al., 1993</i>
Southern Norway	Lichen ( <i>Hypogymnia physodes</i> )	$1.7 \times 10^7$	Calculation on the basis of data <i>Ockenden W. et al., 1998</i> и <i>Berg T. and Hjellbrekke A.-G., 1999</i>
Laboratory experiment	Azalea	$4.18 \times 10^5$	<i>Paterson S. et al., 1991</i> cited from <i>Muir D.C.G. et al., 1993</i>

according to measurements of *Muir D.C.G. et al.* [1993] lichen density is  $0.9 \text{ g/cm}^3$ .

Investigations of *Ockenden W. et al.*, [1998] indicated that lichen accumulate organic substances better than needles. In Norway HCB concentrations in needles (*Pinus sylvestris*) were lower than in lichen in 1.5-5 times.

The present review of literature data on HCB content levels in different environmental compartments proves the global character of HCB distribution. HCB is present in the atmosphere as vapors, therefore a sufficiently uniform concentration field in space and time is observed. However, at temperatures lower than  $-36 \text{ }^\circ\text{C}$  vapors condensation takes place. This phenomenon can explain the observed constant growth of HCB concentrations in polar ice. The environmental pollution by HCB does not manifest stable trends in HCB content in natural compartments in the regional and global scale.

## *Conclusions*

This report presents results of investigations which precede model calculations of HCB long-range transport.

The most part of our study was concentrated on HCB physical-chemical properties. Main properties of HCB affecting its behaviour in the environment are:

- high saturated vapour pressure and the presence of HCB gas-phase affect the distance of airborne transport;
- weak solubility in water and good solubility in organic liquids including lipids result in its insignificant washout from the atmosphere by precipitation and low content in natural waters and accumulation in biological objects;
- high partition coefficient values in "octanol-water", "octanol-air", "organic carbon-water" systems characterize its accumulation in soils, bottom sediments and food chains;
- chemical sluggishness ensures the stability in natural objects.

As a result of literature data review we have selected specific values of constants and HCB properties which are planned to be used as input parameters for the long-range transport modelling.

The range of HCB sources includes a wide number of industrial sources and agriculture. On the global scale agriculture was and remains the main source of HCB pollution. In European countries the contribution of agriculture constantly diminishes but the role of industrial and other sources is still significant.

Studies of emission sources and evaluation of HCB input to the atmosphere should be continued.

For the comparison of model results we have reviewed literature data on HCB content levels and on peculiarities of its distribution inside environmental compartments. Observations

show that HCB is revealed in all the environmental compartments. In the atmosphere and surface waters concentration fields are rather uniform and HCB distribution over soil is of a latitudinal character. The Northern Hemisphere seems to be well studied and the Southern Hemisphere has no sufficient measurement data. In all the environmental compartments minimum concentrations are observed in tropical and subtropical regions whereas in the Arctic area there is a danger of HCB accumulation.

In view of physical-chemical properties and the behaviour in the environment HCB corresponds to the notion of a global pollutant. It is confirmed by observations in different points of the globe it is reasonable to evaluate the long-range transport of HCB on hemispherical or global level.

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