

## Temperature dependences of vapor pressures and solubilities of PCBs, PCDDs and PCDFs for modeling their environmental fate

Jaakko Paasivirta and Seija Sinkkonen

Department of Chemistry, University of Jyväskylä, P. O. Box 35,  
FIN-40351, Jyväskylä, Finland.

### Introduction

To predict fate of a chemical substance in environment by modeling a limited number of substance properties (parameters) must be known. Temperature-dependent vapor pressure (P) of solid substance (Ps) and of liquid or subcooled liquid (Pl) and water solubility (S) are the most important physical-chemical parameters that determine the partition of chemicals between different compartments. Most measurements of these properties have been made for single temperature, 25 or 20°C, thus far. However, for regions having large seasonal temperature variations, data in a range of temperatures must be known in reasonable accuracy. Measurements of Ps, Pl and S of persistent organic pollutants (POPs) in several temperatures over such ranges occur in literature only in few cases, thus far. Therefore, we have been working to obtain useful estimates of them as function of environmental temperature to be used as input values to environmental fate models for seasonally highly variable climates, such as Baltic Sea Region. Detailed report on methods and results of estimations for 54 different POPs will be published in near future /1/. Aim of the present report is to give estimations for eight common PCBs and for seventeen 2,3,7,8-substituted PCDDs and PCDFs compared to independent literature data.

### Temperature dependences

Vapor pressures and solubilities are connected with each other by Henry law constant:

$$H [\text{Pa m}^3 \text{ mol}^{-1}] = P_s / S_s = P_l / S_l \quad (1)$$

where Ps is the vapor pressure of solid and Pl that of (subcooled) liquid [Pa]. Ss is the solubility of solid substance and Sl that of liquid [mol m<sup>-3</sup>]. The vapor pressures, solubilities and Henry law constant have analogous log-linear dependences on the inverse values of temperature (T in Kelvins) /1/:

$$\log P_s = A_{ps} - B_{ps}/T ; \log P_l = A_{pl} - B_{pl}/T \quad (2)$$

$$\log S_s = A_{ss} - B_{ss}/T ; \log S_l = A_{sl} - B_{sl}/T \quad (3)$$

$$\log H = A_h - B_h/T \quad (4)$$

One intercept (A..) and slope (B..) factor can be calculated from two known factors:

$$A_{ss} = A_{ps} - A_h ; B_{ss} = B_{ps} - B_h ; A_{sl} = A_{pl} - A_h ; B_{sl} = B_{pl} - B_h \quad (5)$$

### Conversions and estimations

Temperature dependence for limited number of POPs have been measured for  $P_s$ ,  $P_l$ ,  $S_s$  and  $H/1$ . If only one pair of factors in equations (2-4) is known e.g. from regression of the measurements results at several temperatures, the other factors needed for modeling must be calculated using some estimations. Conversion between  $P_s$  and  $P_l$  is obtained from the following equation:

$$\log P_s = \log P_l + (\Delta S_f / R) \times (1 - T_m/T) / 2.3026 \quad (6)$$

where  $\Delta S_f$  is the entropy of fusion [ $J K^{-1} mol^{-1}$ ],  $R = 8.3143 [J K^{-1} mol^{-1}]$  and  $T_m =$  melting point [K]. Because melting is a reversible isothermic process,  $\Delta S_f$  can be calculated from the enthalpy of fusion by  $\Delta H_f = T_m \times \Delta S_f$ . If not available as measured value from literature  $\Delta S_f$  can be estimated (calculated) from pair of known values  $P_s$  and  $P_l$  at the same temperature as follows /1,2/:

$$\Delta S_f = \ln(P_s/P_l) \times R / (1 - T_m/T) \quad (7)$$

If factors for the temperature dependence of either  $P_s$  or  $P_l$  (equations (2)) are known, the other pair of vapor pressure factors is obtained by the following conversion formula:

$$A_{ps} = A_{pl} + \Delta S_f / (2.3026 R) \quad (8)$$

$$B_{ps} = B_{pl} + \Delta S_f \times T_m / (2.3026 R) \quad (9)$$

If only one  $P_s$  value in some temperature is known,  $A_{ps}$  and  $B_{ps}$  can be estimated by a modified Watson method from MW (molecular mass g/mol), structure type parameters and  $T_m$  /3/. A GWBASIC program VPES3 (J.Paasivirta 1996) estimates  $P_s$  values at a selected temperature range in one degree intervals and derives  $A_{ps}$  and  $B_{ps}$  by linear regression of estimated  $P_s$  values according to equation (2).

Temperature dependence of solubility  $S_i$  can be calculated from known  $A_{pi}$ ,  $B_{pi}$ ,  $A_h$  and  $B_h$  using a simple conversion by eq. (5). In case that part of these factors are unknown, a recent application of mobile order thermodynamics /4/ offers a simple nearly predictive solubility equation which can be modified to give the temperature dependence parameters. Our modification resulted to the calculation procedure for factors  $A_{ss}$  and  $B_{ss}$ :

$$A_{ss} = \Delta H_f / (2.3 \times R \times T_m) + 5.154 - 0.036 \times V_b - 0.217 \times \ln V_b + C \quad (10)$$

$$B_{ss} = \Delta H_f / (2.3 \times R) \quad (11)$$

where  $V_b$  is molar volume of the solute B (in "hypothetical subcooled liquid state"/4/) and  $C$  is a solute-water interaction correction term /4/. Values of  $C$  are zero for planar aromatics (e.g. for PAHs, PCDDs and PCDFs), 0.4249 for PCBs, 1.4584 for polychlorinated cyclic insecticides, and 3.2105 for oxy-polychloro-insecticides.

For calculation of Ass and Bss, a GWBASIC program TDSOLU was constructed (J.Paasivirta 1998). The calculation can also be done following equations (10,11) by a scientific hand calculator.

### Results and discussion

The factors Ass and Bss actually correspond to solid substance solubility Ss, not to that of subcooled liquid, as was clear from the results. In contrary, SOFA method for estimation of the solubilities of PCDDs and PCDFs produced SI values /5/. These 25 °C values could be converted by multiplying with fugacity ratio (Ps/Pl) to Ss values which were in close agreement with the present TDSOLU estimation results. Names, molecular masses (MW g/mol), melting points (Mp °C) and estimated, converted or measured values of  $\Delta S_f$ , Aps, Bps, Apl, Bpl, Ass and Bss of the selected PCBs, PCDDs and PCDFs are collected in Table 1.

TABLE 1. Known, estimated (# VPES3, \*TDSOLU), converted (αequations 7,8 or 3), or measured (Ref. in slashes /) property values for eight PCBs, seven OCDDs and ten PCDFs. £ Default value (assumed the same as for other similar isomer).

Code	Structure	MW	Mp°C	$\Delta S_f$	Aps	Bps	Apl	Bpl	Ass	Bss
PCB28	244'-trichloro-	257.5	57	56.5£	15.15□	5049□	12.20 /2/	4075 /2/	0.232*	975.5*
PCB52	22'55'-tetra-	292	87	46.1 /4/	14.77□	5087□	12.36 /2/	4220 /2/	-0.790*	868.2*
PCB101	22'455'-penta-	326.4	77.4	56.9 /4/	15.64□	5556□	12.67 /2/	4514 /2/	-0.702*	1042*
PCB105	233'44'-penta-	326.4	105	56.5£	15.85□	5874□	12.90 /2/	4758 /2/	-0.723*	1117*
PCB118	23'44'5'-penta-	326.4	109	56.5£	15.67□	5792□	12.72 /2/	4664 /2/	-0.723*	1129*
PCB138	22'344'5'-hexa-	360.9	80	56.5£	15.76□	5842□	12.81 /2/	4800 /2/	-1.38*	1043*
PCB153	22'44'55'-hexa-	360.9	103.5	56.5£	15.80□	5800□	12.85 /2/	4688 /2/	-1.20*	1113*
PCB180	22'344'55'-hepta-	395.3	110	56.5£	15.98□	6173□	13.03 /2/	5042 /2/	-2.01*	1132*
DD1	2378-TeCDD	322.0	305	69.1 /4/	13.14#	6091#	9.53□	4004□	0.193*	2088*
DD2	12378-PeCDD	356.4	241	78.5£	13.26#	6298#	9.16□	4190□	0.209*	2111*
DD3	123478-HxCDD	391.0	273	88.1 /4/	13.60#	6848#	9.004	4335□	0.236*	2517*
DD4	123678-HxCDD	391.0	286	88.1£	13.63#	6885#	9.03□	4315□	0.235*	2576*
DD5	123789-HxCDD	391.0	244	88.1£	13.57#	6699#	8.97□	4411□	0.235*	2290*
DD6	1234678-HpCDD	425.2	265	100.2 /4/	13.83#	7225#	8.60□	4408□	0.393*	2821*
DD7	OCDD	460.0	332	101.5 /4/	14.16#	7846#	8.86□	4638□	-0.148*	3213*
DF8	2378-TeCDF	306.0	227	73.2 /4/	13.73#	5988#	9.91□	4076□	0.656*	1915*
DF9	12378-PeCDF	340.4		90.1£	12.99#	5848#	8.28□	3640□		
DF10	23478-PeCDF	340.4	196	90.4 /4/	13.17#	6129#	8.45□	3914□	1.08*	2219*
DF11	123478-HxCDF	374.9	225.5	96.4 /4/	13.45#	6576#	8.41□	4063□	0.914*	2517*
DF12	123678-HxCDF	374.9	232	96.4£	13.40#	6577#	8.43□	4063□	0.844*	2517*
DF13	123789-HxCDF	374.9		96.4£	13.54#	6749#	8.52□	4216□		
DF14	234678-HxCDF	374.9		96.4£	13.42#	6556#	8.41□	4023□		
DF15	1234678-HpCDF	409.3	236	105.9 /4/	13.67#	6977#	8.14□	4161□	0.934*	2820*
DF16	1234789-HpCDF	409.3	221	109.1 /4/	13.59#	7020#	8.06□	4287□	0.933*	2737*
DF17	OCDF	443.8	259	108.1 /4/	13.86#	7277#	8.21□	4272□	0.573*	3009*

The estimated  $P_s$  and  $S_s$  values were compared to independent (not used as basis of estimations) observed values in literature [1]. An overview of comparison is given in Figure 1.

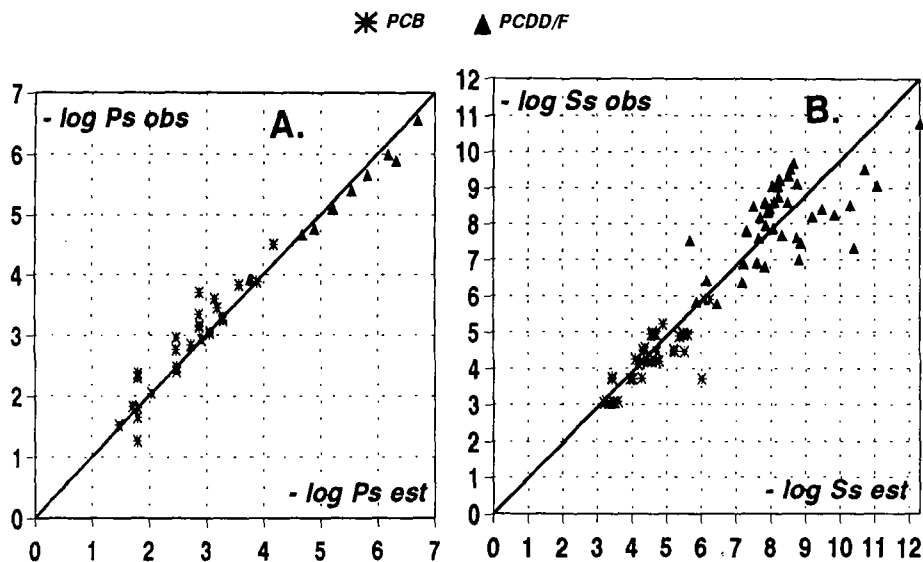


Fig. 1. Observed (independent) versus estimated vapor pressure (A) and solubility (B) values as negative logarithms.

All observed values of  $P_i$  and most of  $S_i$  are very near to the estimated ones (Fig.1). Consequently, the temperature dependence factors of vapor pressure and solubility, if not measured, estimated by aid of thermodynamic relations, like those presented here (Table 1) can be recommended as interim input values to environmental fate modeling.

#### Acknowledgements

Dr. Frank Wania is acknowledged for useful discussion and European Union for project (POPCYCLING-BALTIC) funding.

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