

Estimation of vapour pressure, solubility in water, Henry's law function, and Log Kow as a function of temperature for prediction of the environmental fate of chemicals

J. Paasivirta

Department of Chemistry, University of Jyväskylä, Finland

Abstract

Environmental risk R estimation of a chemical is based on predicting exposure of biota (PEC) in media and harmful effect potency as PNEC from (eco) toxicology. For default emission E_0 , numerical relative risk is expressed as $R_0 = PEC/PNEC$. Using the risk limit $R_0 \geq 1$, the risk emission is $RE = E_0/R_0$. PEC can be estimated by the fate modeling. Our FATEMOD model computes the fate of chemicals in an environment defined as a catchment area. In this model, the substance properties (liquid state) of vapour pressure P_l , water solubility S , Henry's law coefficient H (P_l/S), lipophilicity K_{ow} , and the reaction half-life times are automatically computed as a function of temperature. This feature is unique, thus far, in fate models. The physical properties in the environmental temperature range are obtained from the equation: $\text{Log Prop}(i) = A_i - B_i/T$ (T in degrees Kelvin). We have learnt to determine the coefficients A_{pl}, B_{pl} (for P_l), A_s, B_s (for S), A_h, B_h (for H) and A_{ow}, B_{ow} (for K_{ow}) from thermodynamic equations of these properties as functions of molecular parameters and temperature T by dividing the equation into two parts: 1) T absent and 2) T present. The results compare well with expensive direct measurement results and also with results from retention time comparisons by temperature-controlled GC (for P_l) and HPLC (for S). In reasonable risk predictions for variable climates such as in Nordic countries, the ambient temperature cannot be ignored. Examples of temperature-adjusting FATEMOD runs in chemical risk estimations are given.

Keywords: degradation rates, physical properties, regional model, relative risk, temperature corrections, thermodynamics.



1 Introduction

Environmental fate estimation of anthropogenic chemicals is increasingly important for management of their risk of causing harmful effects to man and ecosystems. The risk can be presented as a product of exposure and the effect of potency of the chemical on the target species. Harmful effects of potency are evaluated by methods of (eco)toxicology e.g. as numerical value PNEC (predicted no-effect concentration, inverse to the potency). Exposure, as value PEC (predicted environmental concentration) for the chemical in each media (air, water, soil /plants, sediment, suspended solids, aerosols, depositions, food). Recently, mathematical modelling to predict environmental fate of chemical has been developed as an effective tool to assess exposure of biota in media. Modelling is a low-cost method to expand and complete the information from expensive analyses to make practical environmental risk management for large number of possibly hazardous substances feasible. The risk management scheme for an anthropogenic chemical emitted to environment is illustrated in Figure 1.

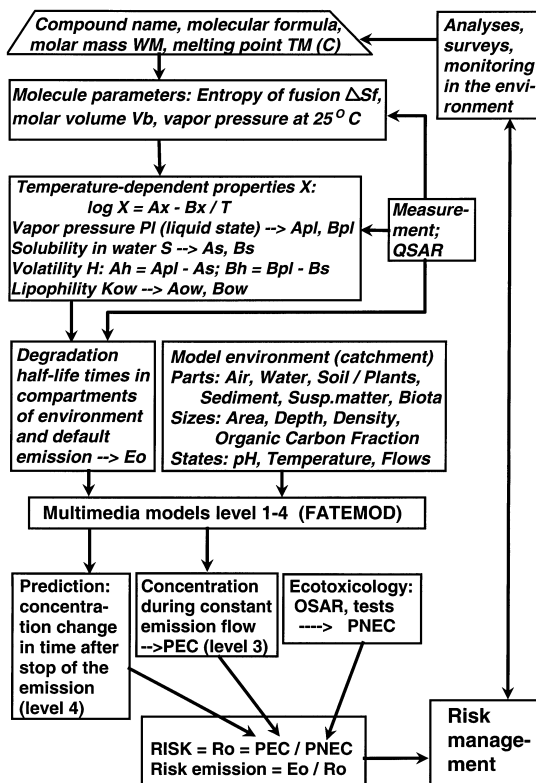


Figure 1: Scheme of the use of modelling in the environmental risk estimation and management of chemicals

For preliminary estimation of environmental risk, the exposure assessment part (Figure 1) produces PEC in air, water, soil/vegetation and sediment. While obtained by multimedia modelling on the environmental fate of the chemical [1,2], PEC is practical for evaluating instant (acute harmful effect) risk to biota. Risk estimation of long-term (chronic) effects needs additional analyses, modelling and QSAR estimations of bioaccumulation processes [3-5]. The risk assessment result can be computed by fate model using default emission as input parameter E_o . Then risk ratio is $R_o = PEC/PNEC$ and defined risk emission $RE = E_o/R_o$. The lowest value for significant risk could be $RE = 1$, although a guideline for tolerable emission can be some lower RE value - for safety.

The modelling of PEC requires input data of the certain properties of the model environment and chemical. They can be written as a database to the model program for their fluent use. Such predictive models for chemical exposure prediction were evaluated and completed in a series of international European projects, our research team as partners, during 1989-2002 [6-8]. We learnt that ambient temperature was an essential factor in all model predictions of the fate of chemicals in the environment, but automatic temperature corrections of physical and chemical properties of the target substances were absent in their program codes. These procedures were, first time, taken in to our FATEMOD where all temperature dependent physical (Pl, S, H and Log Kow) and chemical (degradation life-times) properties of chemical (Figure 1) were instantly corrected to the ambient temperature [9-11]. Development of these temperature adjustments and their applications in PEC modelling is reviewed in this paper.

2 Temperature coefficients of the compound properties

2.1 Development

Our first paper on necessary temperature correction coefficients in fate model, paper on vapour pressures, solubilities and Henry's law coefficients as function of temperature for 72 POPs was published in 1999 [8]. Secondly, we published assessment rules for degradation rates of very persistent POPs [9]. Thirdly, our research group contributed in the evaluation and chromatographic validation of the temperature-dependent properties, including also LogKow, of twelve environmentally important synthetic musks. There, also an example of automatic use of temperature correction coefficients in risk estimation by modelling was presented [10].

2.2 Vapour pressure: VPLEST

Temperature dependence of vapour pressure has been known over 150 years. It is applied in PEC modelling by simple integrals of Clausius-Clapeyron equation (1) and (2), where T is the ambient temperature in degrees Kelvin. In case that A_{ps} and B_{ps} only are known, FATEMOD converts them to A_{pl} and B_{pl} by eqn. (3) and eqn. (4). ΔS_f = entropy of fusion ($J K^{-1} mol^{-1}$), TMK = melting point (K), and $19.1444 = \ln 10 * R$ (gas constant in $J K^{-1} mol^{-1}$).



$$\text{Solid state vapour pressure: } \log P_s = A_{ps} - B_{ps} / T. \quad (1)$$

$$\text{(Subcooled) liquid state vapour pressure: } \log P_l = A_{pl} - B_{pl} / T. \quad (2)$$

$$\text{Conversion of intercept: } A_{pl} = A_{ps} - \Delta S_f / 19.1444 \quad (3)$$

$$\text{Conversion of slope: } B_{pl} = B_{ps} - \Delta S_f * TMK / 19.1444. \quad (4)$$

For organic molecular substances, only P_l (liquid state vapour pressure) is needed for modelling of PEC. Determination of coefficients A_{pl} and B_{pl} can be performed by gas chromatography [11]. However, good results can be obtained also by QSAR methods, as well. Method of Crain [12] is capable to produce eqn. (2) for liquid state vapour pressure P_l from one known value (P_{l1} at T_1) with no other approximations needed than structure parameter K_F . It was adopted in our program VPLEST to derive A_{pl} and B_{pl} coefficients [10] by regression at given temperature (from 0 to +30 °C as the usual environmental range). Comparison of P_l assessments by VPLEST and gas chromatography [13] are shown in Figure 2.

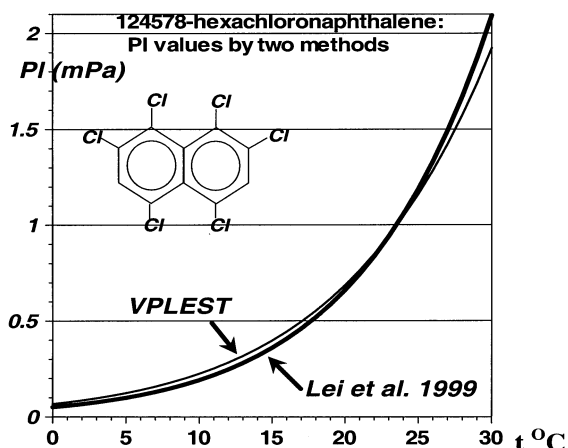


Figure 2: Comparison of P_l values determined by QSAR program VPLEST by author and gas chromatography by Lei et al. [13].

2.3 Solubility in water: WATSOLU

For organic molecules, there exists only one kind of solubility S which is relevant in environment [6,8,14,15]. Experimental determination of S for hydrophobic compounds are very inaccurate – in these cases water solubility estimated by mobile order thermodynamics presented by Ruelle and his coworkers [15-17] are more reliable. Unfortunately, all their results are only for one temperature (25°C). WATSOLU program is our modification of Ruelle's equations [16,17] to consist of separate temperature non-dependent and dependent parts for calculation of A_s and B_s coefficients to use in eqn (5) and first applied to the A_s and B_s evaluation for selected POPs [8] and synthetic musks [10].

WATSOLU calculations:



$$\text{Solubility in water (mol m}^{-3}\text{): } \quad \text{Log } S = A_s - B_s / T. \quad (5)$$

$$A_s = \Delta S_f / (R * \text{Ln}10) - 0.036 * V_b - 0.217 * \text{Ln} V_b + \sum N_{OH} * (2 + boh) / \text{Ln}10 + a_{Acc} + a_{Don} + 5.154. \quad (6)$$

$$B_s = \Delta S_f * TMK / (R * \text{Ln}10) + (DB - 20.5)^2 * V_b / (19.1444 * (1 + MAXW / 18.1)). \quad (7)$$

$$\text{Association terms: } \quad a_{Acc} = \sum v_{Acc}(i) * \text{Log}(1 + K_{Acc}W(i) / 18.1). \quad (8)$$

$$a_{Don} = \sum v_{Don}(i) * \text{Log}(1 + K_{Don}W(i) / 18.1). \quad (9)$$

Terms $v_{Acc}(i)$ and $v_{Don}(i)$ are numbers of active sites, and $K_{Acc}W(i)$ and $K_{Don}W(i)$ are stability constants for proton acceptor and donor groups in water. R (gas constant) = 8.3143. $R * \text{Ln}10 = 19.1444$. V_b = liquid state molar volume $\text{cm}^3 \text{mol}^{-1}$ = sum of increments [17]. N_{OH} = sum of the hydroxyl groups. Term $boh = 1, 2$ or 2.9 or prim., sec. or tert. OH, respectively. 18.1 is molar volume of pure water. TMK = melting point (K). DB = solubility parameter of Ruelle [16]. $MAXW$ = the greatest value of $K_{Acc}W(i)$ or $K_{Don}W(i)$ in water.

Together with melting point (TKM in Kelvins), thermodynamic parameter ΔS_f is most important for evaluation temperature coefficients A_s and B_s . It is ratio of the heat of fusion ΔH_f (J mol^{-1}) and TKM (K). An accurate method to determine ΔH_f is thermoanalysis of the pure crystals by differential scanning calorimetry (DSC) [18]. By measuring some members of a congener group by DSC to obtain accurate heats of fusion values, the results can be expanded using multiple regression with molecular descriptors to other compounds in the congener group [19]. A QSAR method to estimate ΔS_f is to calculate it as sum of molecular increments [20]. The results are often equal between isomers, and therefore less accurate than from method above.

HPLC at different temperatures can be used for validation the completely theoretical results from WATSOLU. This has been successfully done by us in the musk study [10]. Another example of comparison of WATSOLU and HPLC-derived values of S for 4,5,6-trichloroguaiacol (Figure 3).

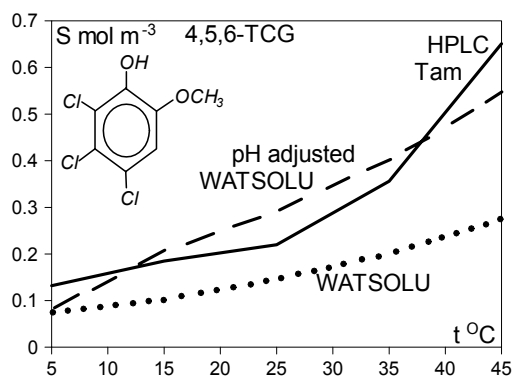


Figure 3: Solubility of 4,5,6-trichloroguaiacol in water at different temperatures [21] with HPLC compared to WATSOLU results: lower curve without and upper curve with correction to pH of the solvent in HPLC.

Temperature-controlled HPLC study of chloroguaiacols had been done in the University of Toronto by Tam et al. [21]. The HPLC and WATSOLU values without considering pKa of the substrate and pH of the elution solvent were not in agreement. But after making correction the WATSOLU values of the substrate (phenol) to pH of the HPLC solvent, the values coincide.

2.4 Octanol-water partition coefficient: TDKLOW program

Ruelle applied the mobile order thermodynamics for Log Kow at 25 °C [16]. The procedure was to subtract solubility equations for Log S in water-saturated n-octanol and in pure water from each other, which resulted to equation of Log Kow. We isolated temperature independent and dependent parts from these equations to produce coefficients Aow and Bow in eqn (10). Most temperature dependence was eliminated by subtraction, but some remained by polyfunctional molecules. The first application was presented in paper from our musk study [10].

TDLKOW calculations:

$$\text{Octanol water partition: Log Kow} = Aow - Bow / T. \quad (10)$$

$$Aow = \Delta B + \Delta F + \Delta Acc + \Delta Don. \quad (11)$$

$$\Delta B = (0.5 * Vb * (1/124.2 - 1/18.1) + 0.5 * Ln * (18.1/124.2)) / Ln 10. \quad (12)$$

$$\Delta F = (Vb * (rw/18.1 - ro/124.2) - \sum N_{OH}(j) * (boh + rw - ro)) / Ln 10. \quad (13)$$

$$\Delta Acc = \sum vAcc(i) * (\log((1 + KaccO(i)/124.2) / (1 + KaccW(i)/18.1))). \quad (14)$$

$$\Delta Don = \sum vDon(i) * (\log((1 + KdonO(i)/124.2) / (1 + KdonW(i)/18.1))). \quad (15)$$

$$Bow = (Vb/19.1444) * ((db - 20.5)^2 / (MAXW/18.1) - (db - 16.38)^2 / (1 + MAXO/124.2)). \quad (16)$$

Most molecular descriptors are defined in previous chapter (2.3). Here 124.2 is the reduced molar volume of water-saturated n-octanol, rw is structuration factor of water = 2.0, ro is structuration factor for water-saturated n-octanol (= 1.275). KaccO(i) and KdonO(i) are stability constants of proton acceptor and donor groups in octanol, and MAXO the greatest value of KoO(i) and KohO(i) for solute in n-octanol [16].

2.5 Volatility: Henry's law function

Henry's function is used for volatilisation the estimate in FATEMOD. Its value is temperature-dependent, expressed by eqn (17). At environmental temperature range the values can be approximated as $H = P_l / S$ for cases of low solubility compounds which are not miscible in water [22]. Then, Ah and Bh are obtained by simple subtractions (eqns (18) and (19)). For more hydrophilic compounds other methods to calculate H in the fate modelling are needed [22].

$$\text{Temperature dependence of Henry's law function: } \log H = Ah - Bh / T. \quad (17)$$

$$\text{Approximation of coefficients: } Ah = Apl - As. \quad (18)$$

$$Bh = Bpl - Bs. \quad (19)$$



2.6 Estimation of the degradation lifetimes

Degradation rates $R(i) \text{ h}^{-1}$ and half-life times $HL(i)$ (hours) of the compound in each of the four major compartments ($i = 1-4$) are necessary factors for fate prediction [9]. The values of $R(i)$ and $HL(i)$ depend with different weight of significance in different compartments on rate constants of the photodegradation ($k(p)$), hydrolysis $k(h)$ and biodegradation $k(b)$:

$$\text{In Air: } R(1) = k(p) \quad HL(1) = \ln 2 / R(1). \quad (20)$$

$$\text{In Water: } R(2) = k(p)/12 + k(h) + k(b)/12. \quad HL(2) = \ln 2 / R(2). \quad (21)$$

$$\text{In Soil/Plants: } R(3) = k(h)/12 + k(b). \quad HL(3) = \ln 2 / R(3). \quad (22)$$

$$\text{In Sediment: } R(4) = k(h)/12 + k(b)/12. \quad HL(4) = \ln 2 / R(4) \quad (23)$$

There are “thumb rules” for temperature correction of the $HL(i)$ values: 10°C decrease of temperature (T) from reference value HLT increases degradation lifetime in air by a factor of 1.2, and in other major compartments by a factor of 2 [9]. The corresponding correction equations are:

$$HL(1)_{corr} = HL(1)_{ref} * 1.2^{((HLT-T)/10)}. \quad (24)$$

$$HL(2)_{corr} = HL(2)_{ref} * 2^{((HLT-T)/10)}. \quad (25)$$

$$HL(3)_{corr} = HL(3)_{ref} * 2^{((HLT-T)/10)}. \quad (26)$$

$$HL(4)_{corr} = HL(4)_{ref} * 2^{((HLT-T)/10)}. \quad (27)$$

3 FATEMOD applications: role of temperature

3.1 Model program

FATEMOD is a practical tool for PEC predictions for relatively persistent chemicals or their more persistent metabolites in environment. The results, together with effect potency (PNEC) data could give a reasonably realistic risk estimate (Figure 1) for management of pollution (e.g. source detection and discharge guidelines), need of restrictions or remediation, groundwater quality control, obstacles for use of the chemical in agriculture, and assessment of potential ecosystem damages. In addition, it is a realistic tool for fast prediction of environmental risks of chemicals for the planned EU-wide management.

The model environment in FATEMOD consist of single box (catchment) of six compartments (parts in Figure 1). Air, Water, Soil/plants and Sediments contribute in the mass balance calculation. For exposing concentrations, also compartments Suspended solids and Fish are included. Examples of environments are: SWF = catchment areas of rivers flowing to the Bothnian Sea (South-West Finland) and KemR = Kemijoki River catchment area (North Finland).

Database of compounds in FATEMOD lists following property parameters: CAS Nr, molecular mass WM, melting point TM (in Celsius), entropy of fusion ΔS_f (in $\text{J K}^{-1} \text{ mol}^{-1}$), pKa value, temperature coefficients (see above) for vapour pressure (Apl, Bpl or Aps, Bps), water solubility (As, Bs), LogKow (Aow, Bow),



and degradation half-life times HL at reference temperature HLT in parts Air, Water, Soil/plants and Sediment.

3.2 Risk estimation of dimethoate application in Finland

Dimethoate is the most used insecticide in Finland while it possesses low toxicity to man and mammals. However, its estimated PNEC value to fish is about 0.3 mg L^{-1} . By FATEMOD model run with $E_o = 500 \text{ mg/ha h}^{-1}$ to soil/plants, PNEC to fish was exceeded, but recovered in five months in South-West Finland but in North Finland not before winter (Figure 4).

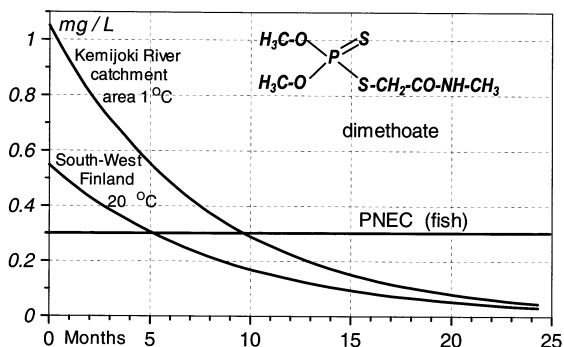


Figure 4: FATEMOD concentrations (PEC) of the insecticide dimethoate in the water at mean spring-summer temperature after stop of emission of 500 mg/ha h^{-1} to soil/plants.

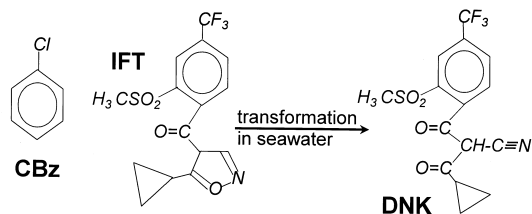


Figure 5: Waste chemicals discharged to purification ponds (waste stream WS) and further to the recipient sea area (RSA).

3.3 Determination of guidelines for discharge

The risk based guidelines were needed for the waste chemicals of a factory led through a purification plant (WS) to a coastal recipient sea area (RSA). The wastes were solvent/reagent chlorobenzene (CBz) and herbicide isoxaflutole (IFT). The latter is melabolized in water to a more persistent diketonitrile (DNK; Figure 5). PECs of these compounds were estimated by FATEMOD modelling with default emission to WS $E_o = 1 \text{ Kg h}^{-1}$. Output from WS was used as emission to RSA (two successive modellings). PNEC values were taken from the

acute ecotoxicity test results with *Daphnia*, Fish and Algae. Results as Ro and RE values and discharge guidelines led from them are shown in Table 1.

Observe that the mean water temperatures in winter and summer in these water flows were 5 and 20 °C, respectively. However, the risk emission values did not differ very much. This is due the dominance of water the compartment in the model systems.

Table 1: Risk levels of the chemical discharges at RSA sea area.

Values of ecotoxicity			<i>Daphnia</i>		Fish		Algae	
Code	Toxic level --> Compound		LC50 mg L ⁻¹	PNEC µg L ⁻¹	LC50 mg L ⁻¹	PNEC µg L ⁻¹	LC50 mg L ⁻¹	PNEC µg L ⁻¹
CBz	Chlorobenzene		5.8	580	22.0	2200	12.5	1250
IFT	Isoxaflutole				1.7	170	0.33	33
DKN	Diketonitrile				1.7*	170	0.33*	33
RE determination			<i>Daphnia</i>		Fish		Algae	
Code	t °C	PEC µg L ⁻¹	Ro	RE Kg h ⁻¹	Ro	RE Kg h ⁻¹	Ro	RE Kg h ⁻¹
CBz	5	2.319	0.004	250	0.0011	949	0.0019	539
CBz	20	2.229	0.0038	260	0.0010	987	0.0018	561
IFT	5	2.529			0.0149	67	0.0766	13
IFT	20	1.566			0.0092	109	0.0475	21
DKN	5	3.458			0.0203	49	0.1048	10
DKN	20	3.386			0.0199	50	0.1026	10

* Assumed toxicity for DKN was the same as for its precursor IFT

Risk ratio Ro = PEC / PNEC (for discharge from factory Eo = 1 Kg h⁻¹)

Risk emission RE = 1 / R (Kg h⁻¹ to the first waste basin)

Guidelines: RE / 10 (safety factor) for CBz = 25 and for IFT 1 Kg h⁻¹

References

- [1] Mackay, D., Multimedia Environmental Models. The Fugacity Approach. Lewis, Chelsea, MI, USA, **L-242**, 1991.
- [2] Paasivirta, J., *Chemical Ecotoxicology*. Lewis, Chelsea, MI, USA, **L366**, 1991.
- [3] Gobas, F.A.P.C., & J.A. McCorquodale (eds.), *Chemical Dynamics in Fresh Water Ecosystems*. Lewis, Chelsea, MI, USA, **L-511**, 1992.
- [4] Paasivirta, J., Long-term effects of bioaccumulation in ecosystems, Chapter 3. In: *The Handbook of Environmental Chemistry, Vol. 2 Part J. bioaccumulation*, ed. B. Beek, Springer, Berlin, pp. 201-233, 2000.
- [5] Calamari, D., (ed.) *Chemical Exposure Predictions*. Lewis, **L-852**, 1993.
- [6] Trapp, S. & Matthies, M. *Chemodynamics and Environmental Modeling, An Introduction*. Annex: Baumgarten, G., Reiter, R., Scheil, S., Schwartz, S. & Wagner, J.O., *CemoS User's Manual and included program diskette*. Springer, Berlin, 1998.
- [7] Pacyna, J.M., Brorström-Lunden, E., Runge, E., Paasivirta, J., Münch, J., Fudala, J. Calamari, D. & Broman, DS., *Environmental Cycling of Selected Persistent Organic Pollutants (POPs) in the Baltic Region*. ENV4-CT96-0214 / EU. Executive Final Summary Report, NILU, Kjeller, Norway, 1999.



- [8] Paasivirta, J., Sinkkonen, S., Mikkelsen, P., Rantio, T. & Wania, F., Estimation of vapour pressures, solubilities and Henry's law constants of selected persistent organic pollutants as functions of temperature, *Chemosphere* **39**, pp.811-832, 1999.
- [9] Sinkkonen, S. & Paasivirta, J., Degradation half-life times of PCDDs, PCDFs and PCBs for environmental fate modelling. *Chemosphere* **40**, pp.943-949, 2000.
- [10] Paasivirta, J., Sinkkonen, S., Rantalainen, A-L., Broman, D. & Zebühr, Y., Temperature Dependent Properties of Environmentally Important Synthetic Musks. *Environ. Sci. & Pollut. Res.* **9(5)**, pp. 345-355, 2002.
- [11] Hinckley, D.A., Bidleman, T.F. & Foreman, W.T., Determination of vapour pressures for nonpolar and semipolar organic compounds from gas chromatographic retention data, *J. Chem. Eng. Data* **35**, pp. 232-237, 1990.
- [12] Crain, C.F., Tables 14-4 and 14-5, Eqn 14-25 (Chapter 14): Vapor Pressure In: W. J. Lyman, W. F. Reehl and D. H. Rosenblatt, ed. *Handbook of Chemical Property Estimation Methods*, ACS, Washington, DC, 1990.
- [13] Lei, Y.D., Wania, F. & Shiu, W.Y., Vapour pressures of polychlorinated naphthalenes, *J. Chem. Eng. Data* **44**, pp. 577-582, 1999.
- [14] Schwarzenbach, R.P., Cschwend, P.M. & Imboden, D.M., *Environmental Organic Chemistry*, Wiley, New York, pp. 80-81, 1993.
- [15] Ruelle, P & Kesselring, U.W. Aqueous solubility prediction of environmentally important chemicals from the mobile order thermodynamics, *Chemosphere* **34**, pp.275-298, 1997.
- [16] Ruelle, P., The n-octanol and n-hexane/water partition coefficient of environmentally relevant chemicals predicted from the mobile order and disorder (MOD) thermodynamics, *Chemosphere* **40**, pp.457-512, 2000.
- [17] Ruelle, P., Farina-Cuendet, A. & Kesselring, U.W., The mobile order solubility equation applied to polyfunctional molecules: The non-hydroxy steroids in aqueous and non aqueous solvents, *Int. J. Pharm.* **157**, pp. 219-232 1997.
- [18] Plato, C., Differential scanning calorimetry as a general method for determining purity and heat of fusion of high-purity organic chemicals. Application to 64 compounds. *Anal Chem.* **44**, pp1531-1534, 1972.
- [19] Lahtinen, M., Paasivirta, J. & Nikiforov, V.A., Evaluation of entropies of fusion of polychlorinated naphthalenes by model congeners: a DSC study, *Thermochim. Acta*, in print, 2006.
- [20] Chickos, J.S., Braton, C.M. & Hesse, D.G., Estimating entropies and enthalpies of fusion of organic compounds *J.Org.Chem.* **56**, pp. 927-938,1991.
- [21] Tam, D.,Varhanickova, D., W-Yu. Shiu, W. Yu. & Mackay, D., Aqueous solubility of chloroguaiacols. *J. Chem. Eng. Data* **39**, pp. 83-86 1994.
- [22] Boethling, R.S., Howard, P.H. & Meylan W.M., Finding and estimating chemical property data for environmental assessment. *Environ. Toxicol. Chem.* **23**, pp. 2290-2308, 2004.

