Estimation of degradation half-life times of PCDDs, PCDFs and PCBs for environmental fate modeling

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Introduction
POPCYCLING-BALTIC is one of the 15 projects under EU program ELOISE (European Land-Ocean Interaction StudiEs). The project aims to develop a multicompartmental model to study the fate and behaviour of persistent organic pollutants (POPs) in the Baltic Sea environment including the surrounding catchment areas. Our task since start of the project (1.6.96) has been to develop estimates of substance parameters for modeling. First results were presented in the first ELOISE conference /1,2/.

Many physical-chemical substance parameters needed in environmental fate modeling of POPs are temperature dependent. Vapour pressure (P), water solubility (S) and Henry's law constant (H) are the most important physical-chemical parameters that determine the partition of chemicals between different compartments. Our contribution to the estimation of these parameters is presented in other reports. This report handles another essential input parameter: degradation half-life time ($t_{1/2}$) of the substance.

Degradation processes
The degradation reactions are collected in model as a half-life time in each compartment. The overall half-life time ($t_{1/2}$) of a substance is:

$$t_{1/2} = 0.693 / (k_H + k_B + k_P) \quad (5)$$

where k_H, k_B and k_P are (pseudo) first-order rate constants of hydrolysis (H), biodegradation/metabolism (B) and photolysis (P), respectively.

Hydrolysis
The hydrolysis of POPs in environmental conditions is extremely slow and can be neglected.

Biodegradation

The rate of biodegradation depends greatly on composition of the microbial community in each compartment, on the compartment characteristics and also on the local/regional history of pollution. Still, biodegradation rate in soil depends on soil temperature and soil moisture content. The EC FOCUS Group has suggested that increasing temperature by 10 degrees is characterized by a concomitant increase in the degradation rate by a factor of 2.2, and vice-versa for decrease in temperature /3/. This has later been confirmed to apply to the great majority of biodegradable chemicals by Walker /4/. Arnold and Briggs have presented a factor of 2.5-3 for each 10 $^{\circ}$C rise in temperature. Rates increase also with increased availability of moisture /5/. Numerous correlations have been developed to relate chemical structure and/or physical-chemical properties and biodegradability /6,7,8/. In addition, laboratory measurements e.g. with standard soils are used. However, best estimates of biodegradation half-life times are preferably obtained from field monitoring results. As a rule, the biodegradation half-life times of POPs in environment are very long; from years to tens of years.

Photochemical degradation

Photodegradation in air and water includes direct photolysis and reactions with OH radicals, ozone, nitrogen oxides and other photochemically generated radicals. Usually the reaction with OH reaction is the most important pathway of photochemical degradation of POPs /9,10/. Generally, it is assumed that the photodegradation rate in water is about the tenth part of the photodegradation rate in the atmosphere. In soil photochemical degradation is possible only near the air-soil interface.

Direct photolysis. For the estimation of the rate of direct photolysis data on intensity of solar radiation, absorption characteristics of chlorinated aromatic compounds, quantum yield information and ambient concentrations are needed /11,12/. Measurements of spectral solar irradiation at the earth's surface are scarce. Some tables of the spectral photon irradiance are available /13/. Usually the rates of direct photolysis are slow because of the poor spectral overlap between the absorption spectra of chlorinated compounds and the tropospheric solar spectrum /14/. In aquatic environment most UV light is absorbed in the top 2 m of natural fresh and coastal marine waters /11/. The photolysis rates fall off directly with the depth of the water column. Photochemical reactions of organic chemicals in solution show a weak temperature dependence. A 10^{0}C increase (decrease) in temperature accelerates (slows down) the reaction only by a factor between 1.15 and 1.5 /15,16/. Photolysis in soil is restricted to less than the top 1 mm of soil /17/.

Reactions with OH radical. For more than 90 % of the organic compounds in the vapour phase of the troposphere the transformation by reactions with OH radical is the most rapid mechanism. The reaction with ozone is generally of secondary importance. For the calculation of the half-life time of photodegradation by reactions with OH radical, the OH radical concentration and the OH reaction rate constant have to be known. The OH concentration in atmosphere is dependent on latitude, height, season etc. A scientific assessment (1989) by United Nations suggest a relatively constant average tropospheric OH radical concentration of 6.5 ($\pm$2) x 10^{5} molecules cm^{-3} /18/. Prinn et al. have recently (1995) calculated a temperature and atmospheric density-

weighed average OH concentration of $(9.7 \pm 0.6) \times 10^5$ molecules cm^{-3} /19/. No measured or modelled OH concentrations at the higher northern latitudes (>60 ^{0}N) could be obtained. The rate constants of organic compounds with OH radicals in the atmosphere are dependent on temperature and pressure (20). The reaction rate constant has been found to be 1.5 to 2.0 fold when the temperature was increased from 265 K to 298 K. At lower temperatures the effect of the decrease in temperature on the OH reaction rate constant are larger /20/. In natural aquatic environment the separation between photo- and biodegradation is difficult. In natural waters the OH radical concentrations are so low that photooxidation by OH radicals probably is not important.

Degradation half-life times

In view of the existing knowledge, any accurate estimations of degradation half-life times for PCBs, PCDDs and PCDFs cannot be done. The present suggestions for imput parameters are very arbitrary. Our interim evaluation is presented in Table 1.

TABLE 1. Degradation lifetimes ($t_{1/2}$ d) of selected PCBs, PCDDs and PCDFs in average weather conditions of Bay of Bothnia (5°C)

Compound		4 x 25°C value in Ref. 21			New literature based value*		
		Air	Water	Sedim.	Air	Water	Sedim.
PCB28	244'-trichloro-	83	283	283	5.3	900	900
PCB52	22'55'-tetra-	133	500	500	70	3600	3600
PCB101	22'455'-penta-	167	833	833	70	3600	3600
PCB105	233'44'-penta-	1667	12000	12000	70	2600	2600
PCB118	23'44'5-penta-	1667	12000	12000	70	2500	2500
PCB138	22'344'5-hexa-	2833	9167	9167	200	6800	6800
PCB153	22'44'55'-hexa-	2833	9167	9167	200	6800	6800
PCB180	22'344'55'-hepta-	2833	9167	9167			
Tetra-CDDs		2833	9167	9167	48	35000	35000
Penta-CDDs		2833	9167	9167	86	40000	40000
Hexa-CDDs		2833	9167	9167	180	60000	60000
Hepta-CDDs		2833	9167	9167		35000	35000
Octa-CDD		2833	9167	9167		52000	52000
Tetra-CDFs		2833	9167	9167	84	22000	22000
Penta-CDFs		2833	9167	9167	123	19000	19000
Hexa-CDFs		2833	9167	9167	360	24000	24000
Hepta-CDFs		2833	9167	9167		13000	13000
Octa-CDF		2833	9167	9167		10000	10000

*Air values /22/, water and sediment values /23/

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