

PREDICTED AND OBSERVED FATE OF SELECTED
PERSISTENT CHEMICALS IN THE ENVIRONMENT

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ABSTRACT

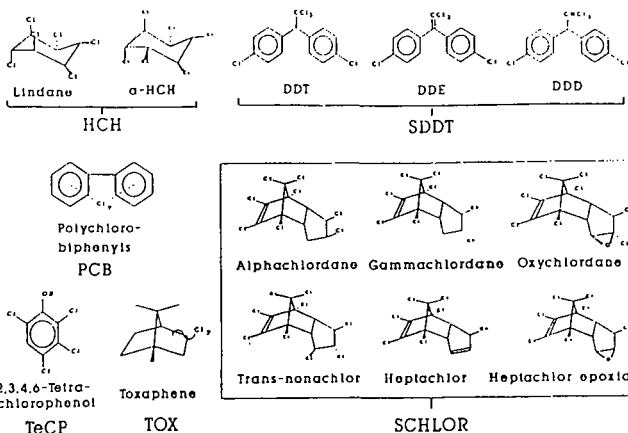
The observed environmental fate of the persistent organochlorine compounds HCH, DDT, PCB, 2,3,4,6-tetrachlorophenol, chlordanes and toxaphene is compared with results from unit world fugacity level I and II modeling. The results indicate that prediction of the environmental fate of a new chemical is possible by modeling from a limited set of property data. However, prediction of the food chain enrichment is more complex due to metabolic differences of various species.

INTRODUCTION

For prevention of future damages of chemicals released into the environment, methods to predict their fate have been developed. Fastest and most economical are procedures based on modelings involving some physical, chemical and biological properties which are readily obtainable for the compound of interest.^{1,2} To test the reliability and predictive power of modeling it is useful to compare fate values obtained by some models to the observations on some widely released and persistent anthropogenic compounds in the environment. A trial comparison is done in this paper.

CHEMICALS SELECTED

Persistent environmental traces of pesticides, industrial chemicals and wastes have been studied intensively especially within the group of organochlorines. Therefore, the following compounds are investigated in the present study:



Technical lindane (γ -HCH) which contains other isomers of hexachlorocyclohexane (HCH) is a widely used insecticide. Total cumulative production of HCH is about ten million tons. Lindane and its persistent transformation product α -HCH (alpha-HCH) are the major HCH:s in the environment.³ DDT is an insecticide produced in about million tons, thus far. Its two metabolites DDE and DDD are very persistent and therefore found in comparable levels in environmental samples. DDE is responsible of the extinction of some bird populations due to its eggshell thinning effect.⁴ Chlordanes and toxaphene are polycyclic polychloroinsecticide residues which appear also in regions where they never have been used.⁵ PCB, mixture of polychlorobiphenyls, has been produced in about million tons during 1929-1973 for technical uses.³ It was found as persistent, food-chain enriched biocide in 1966 and then its high levels were found to cause reproductive damages in seals.⁵⁻⁷ TeCP, 2,3,4,6-tetrachlorophenol, is a major wood preservative, chlorination and combustion product and, consequently, found as a very common contaminant everywhere.³⁻⁶

MODELING

The environment taken to the trial modeling is one square kilometer unit world column from an industrialized region with agriculture. An example of such region is Seto Inland Sea in Japan which has a total area of 17 107 km², a human population of 34 million and organochlorines intensively studied.⁸ This area gives an opportunity to use data for HCH, DDT and PCB from the period of their high releases in 1970ties and information on these and chlordanes in later times.

Another area for comparisons is Finland which is studied by laboratory of the author. Information on the fate of all selected chemicals there, also Baltic Sea and Arctic coast included in some extent, has been obtained since 1970. Fate of the chemical in the unit world can be estimated using the fugacity model of Mackay and his coworkers.^{1,2} Level I calculation procedure of this method gives the equilibrium distribution of compound between the compartments of environment when the compound is assumed to be persistent. Then, level II calculation which considers the removal processes gives the residence time for the compound in the unit world of the model. If a constant input of compound to the unit world is given, the model, named here as CHEMFATE, calculates also concentrations of the compounds in each compartment at steady state. Results are shown in Table 1.

Table 1. Environmental fate relevant data and results of CHEMFATE modeling. Assumed temperature 20°C and fraction of organic carbon in soil 0.04. Compartments: a = air, s = soils, w = water and f = fish (biota).

Compound		HCH	DDT	PCB	TeCP	SCHLOR	TOX
References		3,9,10	2,9	3,9,11,12	8,13-15	16,17	16
Molecular mass		290.8	354.5	326.4	231.9	409.8	413.8
Water solubility ppm		10.00	.0017	.0430	100.0	0.357	1.500
log Kow		3.3	5.98	6.1	4.25	5.1	3.3
Bcf		96	45840	60428	854	6043	96
Vapour pressure mmHg		4.65E-5	1E-7	2.5E-5	4.5E-3	5.9E-5	1.4E-5
Henry constant		7.4E-5	1.14E-3	1.04E-2	5.7E-4	3.7E-3	2.1E-4
Level I distribution in ppm	Na	304051	4476	30194	88770	97245	112696
	Ns	216410	990728	966209	729677	871950	275913
	Nw	479493	4586	3393	181399	30619	611332
	Nf	45.92	210.23	205.03	154.84	185.03	58.55
Half-life times in days:							
Hydrolysis		191	8021	-1	-1	-1	-1
Photolysis		22	54480	8000	1.0	-1	-1
Biodegradation (soil)		365	5327	-1	280	240	1000
Residence time in days		37	7233	273886	5	395	4198
Assumed daily input kg		0.868	0.042	0.010	2.000	0.050	0.200
Steady-state conc. mg/l							
In air	Ca	1.6E-6	2E-7	1.2E-5	2E-7	2E-7	5.3E-6
In soil	Cs	0.101	3.04	35.3	0.116	0.171	1.169
In water	Cw	2.1E-3	1.3E-4	1.2E-3	2.7E-4	5.7E-5	2.4E-2
In fish (biota)	Cf	0.203	6.08	70.6	0.232	0.341	2.339

Bcf = bioconcentration factor, here calculated from log Kow

HCH is sum of the hexachlorocyclohexanes, mainly α -HCH and γ -HCH (lindane).

PCB is mixture of P=5-10 polychlorobiphenyls; chromatographic pattern of the PCB in fish resembles that of Clophen A-60 or Arochlor 1260. However, pentachlorobiphenyl is here taken to be the model PCB molecule. It corresponds an average PCB mixture released, e.g. Arochlor 1254 (54 % Cl).

-1 = Not known. Half-life time infinite ($k_1=0$) is assumed.

Properties needed for modeling were taken from the literature.^{2,10-11} The daily inputs of HCH, DDT and PCB were estimated from the amounts used until 1976 in the Seto Inland Sea area.⁹ HCH and DDT input was taken as 10^{-11} times and PCB inflow as $0.5 \cdot 10^{-11}$ times the total load there. TeCP, SHCLOR and TOX inputs were approximated from production and releases related to those of HCH and DDT.^{3,5,6} The assumed environmental conditions were: temperature 20°C and fraction of organic carbon in soil/sediments 0.04. Bioconcentration factor (Bcf) varied very much depending on test species and conditions for each compound. Therefore, logarithm of the octanol-water partition coefficient (log Kow) was used as basis in calculations. Kow gives $Bcf = 0.048 \cdot Kow$.

Level I distribution (assuming full persistence and equilibration) was obtained as parts per millions normalizing $N_a + N_s + N_w = 10^6$ and calculating then $N_f = Bcf \cdot N_w / 10^6$. For level II calculation, hydrolysis, photolysis and biodegradation were considered as half-life times $t_{1/2}$. The corresponding rate constants are $k_i = 0.693 / t_{1/2}$. Biodegradation in water was approximated as 1/10 of the rate in soil and the hydrolysis in soil as 1/10 of hydrolysis in water. The diffusion to stratosphere and the sediment burial were also used as degradation processes as suggested by Mackay et al.². Their influence to the result, however, was negligible.

OBSERVATIONS OF THE LEVELS

After comprehensive studies in 1973-77, environmental distribution of HCH, DDT (as DDT+DDE+DDD) and PCB at the Seto Inland Sea area could be presented. The order of concentrations in sediments, fish and birds were $PCB > DDT > HCH$ quite opposite to the amounts released, and to the concentrations in rainwater.⁹ CHEMFATE could have predicted this result, as seen in the comparison of the levels in fish (mullet):

	HCH	DDT	PCB
Observed level ng/g	3.16	158	1000
Observed relative level	1	50	316
Predicted relative level (Table 1)	1	30	348

Later, the usages of HCH, DDT and PCB were restricted in Japan. Chlordanes, however, were continuously used as antitermite agents mainly in the western part of the country. The present levels in Japanese biota are typically such as measured in *Lateolabrax japonicus* in Osaka Bay in 1986:⁹

	HCH	DDT	PCB	SCHLOR
Observed level ng/g	4	21	150	74
Observed relative level	1	5.25	37.5	18.5
Table 1 prediction	1	30	348	1.7

Obviously, the continuous input model does not work between these residues in the present Japanese conditions, where e.g. HCH is mainly transported atmospherically from other countries, leakages of DDT and PCB are decreasing and chlordane is a new contaminant.⁹

In the present Finnish and Baltic conditions, input of the selected organochlorines is small except that of TeCP which has been leaked from wood preservative uses, and emits continuously from chlorinations such as pulp chloro-bleaching and combustion processes. Atmospheric transport distance before deposition, however is much shorter for chlorophenols than for chlorohydrocarbons, as seen e.g. in snow studies.¹⁰

Average levels in muscles of Baltic salmon from the Kemi River (central northern Finland) were in 1982-85:^{10,11}

	HCH	DDT	PCB	TeCP	SCHLOR	TOX
Observed levels ng/g lb	4.7	436	553	5.0	27.4	109
Observed relative levels	1	93	118	1.1	5.8	23
Table 1 relative levels	1	30	348	1.1	1.7	11.5

Considering the uncertainty in setting the relative inflow amounts, CHEMFATE predicted this past result remarkably well.

LOCAL EFFECTS TO FATE

Local leakages cannot be completely modeled by such general calculations as CHEMFATE. For example, PCB and chlorophenols have some point sources to water courses in Finland where their concentrations in fish and incubated mussels rise to significantly higher values than those in the above salmons or in fish of other areas where PCB and chlorophenol pollution is mainly airborne.^{5,8,19-23} However, modeling from properties could predict the local/global nature of persistent chemicals. In that way such globally hazardous pollutants as, at present, HCH, SCHLOR and TOX could be restricted in advance. Concentration ratios of certain organochlorines in Baltic and Arctic (northern Norway and Finland) fish and predatory bird species B/A can be taken as measures of the local/global nature of the pollutant:^{19,24,25}

MOST	HexaCN	SDDT		γ-HCH	α-HCH	TOX	MOST
!-----!-----!-----!-----!-----!-----!-----!-----!							
LOCAL	PCB	2378TeCDF		SCHLOR	HCbz	GLOBAL	
B/A	18	7	6	5	4	3	2 2 1

Then, hexachloronaphtalene is the most locally, toxaphene the most globally distributed organochlorine. But, exceptionally, chlordanes and toxaphene levels in fish of the lakes of East Finland are significantly higher than elsewhere in Finland.^{19, 24, 26}

FOOD CHAIN ENRICHMENT IN THE FATE

High bioaccumulation rate and persistency in CHEMFATE predict the possible food chain enrichment which is one of the most serious effects to cause hazardous exposure of wildlife and humans. Comparison of levels in species on different trophic levels gives an estimate of enrichment (Fig. 1).

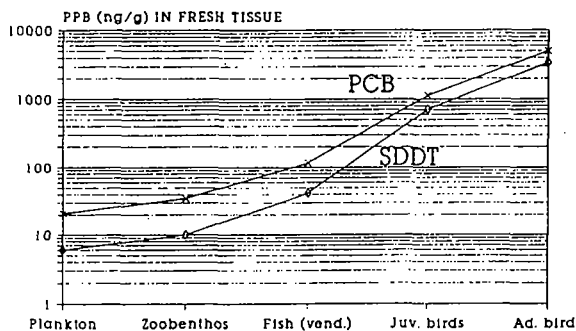


Fig. 1. Average concentrations of PCB and SDDT in five different trophic levels in the Lake Päijänne ecosystem.²⁷

Comparisons are, however, obscured by significant metabolic differences between species which are also specific to each type of compound. For example, levels of HCH, DDT and PCB in Japanese humans were all about 1 ppm but very different in fish (see above).⁹ Levels in Baltic salmon and white-tailed eagles measured in 1986 showed also specific differences:²⁸

	HCH	SDDT	PCB	SCHLOR	TOX
Conc. ng/g in salmon	13.3	176	332	63	76
Conc. ng/g in eagles	ND	34000	245000	3110	ND

where ND is concentration less than 3 ng/g. Accordingly, the eagle seems to collect very much DDT, PCB and chlordanes residues from its food but metabolize effectively HCH and toxaphene components. Also the chlorophenol levels are low in eagles, except in one case of rotten old eagle body which contained high amounts of pentachlorophenol.

In food chain enrichment studies it is useful to compare total amounts of the residue in individuals at their different life stages. In case of aquatic (fish-eating) birds, enrichment was studied by comparison of biocides in eggs, juveniles and adults.²⁹ Comparison of the contents gave no direct measure for enrichment in local food chain where the juveniles were eating fish (vendace) from the lake. Eggs contained biocides laid by the mothers and juveniles had even lower contents than eggs. However, while the total biomass of the individuals were known, one could calculate average total amount of each biocide in individual specimens. Then, in most cases, amount in juveniles [A(juv)] was higher than amount in egg [A(egg)]. This was a firm proof that the pollutant did bioaccumulate to the juvenile from its food. Comparison of the enrichment power between SDDT, PCB and MetHg (methyl mercury) cannot be done correctly by calculating A(juv)/A(egg), because their contents in vendace were very different. In contrary, the relative enrichment factors (Erf) based on increase of the amount in juvenile compared to the concentration in food could be used:

$$\text{Erf} = \frac{\text{A(juv)} - \text{A(egg)}}{\text{C(ven)}}$$

Results of Erf calculation are collected in Table 2.

Table 2. Amounts µg/specimen, concentration in fresh fish (vendace) µg/kg and relative enrichment factors of three biocides in Lake Päijänne birds 1972-75.²⁹

Species	Biocide	A(juv)	A(egg)	C(ven)	Erf
Great crested grebe	SDDT	138	234	42	*
	PCB	466	204	117	2.24
	MetHg	266	30	415	0.57
Common tern	SDDT	42	11	42	0.74
	PCB	103	64	117	0.33
	MetHg	73	33	415	0.10
Black-headed gull	SDDT	33	53	42	*
	PCB	110	109	117	0.01
	MetHg	103	16	415	0.21
Common gull	SDDT	85	176	42	*
	PCB	144	218	117	*
	MetHg	350	20	415	0.80
Herring gull	SDDT	712	668	42	1.05
	PCB	1525	930	117	5.09
	MetHg	523	51	415	1.14
Black-backed gull	SDDT	863	672	42	4.55
	PCB	1203	453	117	6.41
	MetHg	496	56	415	1.06

* No enrichment: juveniles excrete more than collect.

The Erf values indicate that PCB has the highest enrichment power in three, SDDT in one and methyl mercury in two of the six species studied. In case of the large predatory birds like osprey and white-tailed eagle, and marine mammals, PCB, however, appears to be the organochlorine of highest known toxic exposure through enrichment. Some congeners of PCB are similarly toxic as dioxins and enriched in food chain to significantly higher levels than the latter (toxic PCDDs and PCDFs).^{20, 20, 21}

CONCLUSIONS

Prediction by a general unit world method using some property data and degradation rates gives exposure-related fate of a persistent organochlorine compound in environment up to first bioaccumulation stage with a reasonable accuracy in cases when the compound is at least regionally distributed. Very locally behaving chemicals released from point sources need more local models for exposure estimation. To predict hazardous exposure of targets at higher trophic levels simple models work only occasionally. Other methods than modeling, for example structure-activity relationship evaluations and model ecosystem tests are needed to cover this area of environmental risk assessment.

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