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Physical-Chemical Properties of Chlorinated Dibenzo-*p*-dioxins

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■ Reported and newly determined experimental data for aqueous solubility, octanol-water partition coefficient, vapor pressure, and Henry's law constants of the polychlorinated dibenzo-*p*-dioxins are presented and reviewed. Correlation equations are derived for these properties as a function of chlorine number and molar volume, which enable the solubility and octanol-water partition coefficients of most congeners to be estimated with an accuracy within a factor of 2 and vapor pressure and Henry's law constant within a factor of 5. It is suggested that properties of homologous series are best correlated by a two-stage process. In the first stage, treated here, simple correlations are developed to establish approximate values as a function of molar volume and chlorine number. This should be followed by a more rigorous second stage treating isomer differences and using more refined molecular descriptors. The data presented here should be sufficiently accurate for many environmental assessment purposes.

Introduction

The polychlorinated dibenzo-*p*-dioxins (PCDDs) are a group of 75 chemicals, which are primarily discharged to the environment in gaseous emissions from incinerators, in water leachates from dump sites, in accidents, and as contaminants in other products (1, 2). To assess the potential harmful effects of this group of chemicals on humans and other organisms, knowledge about PCDD toxicity and exposure are required. Several dioxin congeners have been shown to be extremely toxic to some organisms (3). Although the precise mechanism of dioxin toxicity has not been fully elucidated, increasingly reliable structure-activity relationships for dioxin toxicity in mammals are being developed (4-6).

To estimate exposure it is necessary to determine the environmental pathways between sources and target organisms and to determine rates and extents of uptake. These tasks require accurate physical-chemical property data, since these data control partitioning between air, water, soils, sediments, and biota and thus dictate the primary media of accumulation and the rates of transfer. The key properties include water solubility C^S , octanol-water partition coefficient K_{OW} , vapor pressure P^S , and Henry's law constant H .

It is believed that the data reviewed and presented here provide a sufficiently reliable data base for environmental modeling and exposure assessment. At present few data exist, and there is considerable variation between reported values, in some cases by a factor of 1000. This work is thus viewed as one step closer to the ultimate goal of establishing a reliable, critically reviewed data base of experimentally determined values.

Specifically, we present a systematic procedure for correlating these physical-chemical properties, review the existing data, report new data, and develop and discuss approximate predictive correlations for the entire set of congeners in terms of the fundamental and easily deter-

mined molecular descriptors of chlorine number and molar volume.

Experimental Section

Solubility Determinations at University of Toronto.

All the PCDD chemicals were obtained from Foxboro/Analabs except for 2,8-dichlorodibenzo-*p*-dioxin, which was kindly supplied by the University of Amsterdam. The dioxins were of the highest available commercial quality and were used without further purification. Methanol [high-performance liquid chromatography (HPLC) grade] was obtained from Caledon Laboratory, Ontario. Milli-Q ultrapure deionized water was used for all experiments.

The dynamic-coupled-column liquid chromatography (or generator column) method previously described by May et al. (7, 8) was used. Saturated aqueous solutions were prepared by pumping water through a 0.64 cm o.d. by 30 cm long stainless steel generator column packed with prewashed (acetone, hexane, and toluene) Chromosorb W, 30/60 mesh, and coated with 0.1-0.5% by weight of the chemical. The generator column was thermostated with an Alltech water jacket, and the temperature was controlled to ± 0.02 °C. The saturated solution then flowed through an extractor column (0.64 cm \times 6 cm long stainless steel tubing) packed with 37-50 μ Bondapak/Corasil (Waters Associates). By switching an eight-port Valco valve the absorbed chemical was extracted by the mobile phase (methanol-water, 85:15 by volume, in isocratic mode) and directly injected onto the analytical column. The instrument was a Waters' HPLC system consisting of a Model 6000 solvent delivery system, a Model M45 solvent delivery system, a Model 720 system flow controller, and a Model 440 UV absorbance detector with 254- and 280-nm kits. The analytical column was a Waters' 3.9 mm o.d. \times 300 mm long μ Bondapak C₁₈ column. Integration of the peak area was recorded by a Waters Model 730 data module.

Solubility and Octanol-Water Partition Coefficient Determinations at University of Wisconsin. Reagents.

All polychlorinated dibenzo-*p*-dioxin and dibenzofuran congeners were obtained from Ultra Scientific Inc. (Hope, RI; 99.9% purity) and were used without further purification. The octanol was purchased from Fisher Chemical (certified grade). Pesticide-grade isooctane was used for gas chromatography. Milli-Q water (Millipore Corp., Milford, MA), irradiated with UV light to destroy any residual trace organics, was used for all solubility determinations.

Solubility. The aqueous solubilities were measured by the generator column technique in a Pyrex tube 40 cm long with a 2-mm i.d. The packing was Chromosorb W, 60/80 mesh (Johns-Manville, Denver, CO), which was held in place by two glass wool plugs. The column temperature was controlled to within ± 0.1 °C with a water jacket connected to a constant-temperature circulator. Water was pumped through the generator column and a C₁₈ Sep-Pak (Waters Associates, Milford, MA) from a thermostated glass reservoir by either a HPLC pump (Model M-45, Waters Associates, Milford, MA) or a metering pump (Model 312, ISCO, Lincoln, NE). The procedure used was

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a modification of the method of Stolzenberg and Andren (9) and is briefly described below.

The column packing was a 1% by weight coating of the compound on 5 g of Chromosorb W, held in place with glass wool plugs. Before a determination with a newly packed column, or if the temperature was changed, water was pumped through the system for several hours to allow the entire system to reach equilibrium.

For each determination, a sufficient volume of water was pumped from the reservoir through the column at 1–2 mL/min, through a Sep-Pak, and into a tared flask. The Sep-Pak was removed and a gentle stream of nitrogen used to remove water. The solute was eluted from the Sep-Pak with 10 mL of isooctane and the amount of solute quantitated by gas chromatography (GC). The aqueous solubility was calculated by dividing the amount of solute collected by the volume of water pumped through the column.

Octanol–Water Partition Coefficient. The generator column method used to determine K_{OW} has been described previously (10) and only a brief description is presented here. The 24-cm column segment was hand-packed with silanized Chromosorb W (3 g, 60/80 mesh) retained by a coarse, ground glass frit at the bottom and a plug of silanized glass wool at the top. The column was thermostated at 25 °C. A C₁₈ Sep-Pak (Waters Associates, Milford, MA) was used to extract the compound from the column effluent. A Hewlett-Packard gas chromatograph (5840A), equipped with an electron capture detector (Ni63), was used for quantitation.

Approximately 10 mg of the solute was dissolved in 100 mL of octanol, and 15 mL of this solution was stirred with 120 mL of organic-free water for 14–18 h. An aliquot of the octanol phase was diluted with isooctane, and the concentration of the compound was determined by GC. The remaining octanol phase was coated on the generator column.

The aqueous phase generated by pumping octanol-saturated water through the octanol-coated column was passed through a C₁₈ extraction column (Sep-Pak) and was collected in a tared weighing flask. When an amount of compound sufficient for analysis was collected on the Sep-Pak, it was removed from the generator column and eluted with 10 mL of hexane and the amount of compound determined by GC. K_{OW} was calculated by dividing the compound concentration in the octanol phase by that in the aqueous phase. The aqueous solute concentration exiting the generator column was found to be independent of flow rate in the range 0.05–2.0 mL/min and of the volume of water passed through the column. Extraction efficiency of the Sep-Pak exceeded 90%.

Thermodynamic Basis

The various physical–chemical equilibrium properties of dioxins can be described by a series of thermodynamic equations in terms of basic molecular properties. These relationships have been discussed previously (11, 12) and are only summarized here.

The vapor pressure $P^S(\text{Pa})$ (superscript S indicating saturation) of a liquid or subcooled liquid (subscript L) or solid (subscript S) solute can be equated to the fugacity f_L under most environmental conditions. The solubility (expressed as mole fraction x) of a pure, non-ionizing, sparingly soluble liquid solute can be expressed by the fugacity equation:

$$f_L = x\gamma_w P_L^S \quad (1)$$

where γ_w is the activity coefficient in water, and P_L^S is the

vapor pressure of the liquid solute. The solubility C_L^S , mol/m³, is then

$$C_L^S = x/v_w = 1/(\gamma_w v_w) \quad (2)$$

where v_w is the molar volume of water of approximately 18×10^{-6} m³/mol. For a solid solute the fugacity equation is (13)

$$f_S = x\gamma_w f_L \quad (3)$$

and the solubility becomes

$$C_S^S = (f_S/f_L)/\gamma_w v_w = F/\gamma_w v_w \quad (4)$$

where F is (f_S/f_L) the fugacity ratio, or the ratio of vapor pressure of the solid to that of the hypothetical subcooled liquid vapor pressure. It also equals the corresponding ratio of solubilities.

Prausnitz (13) has shown that the fugacity ratio F can be expressed approximately as

$$\ln F \approx -\Delta H_f(1/T - 1/T_M)/R = -\Delta S_f(T_M/T - 1)/R \quad (5)$$

or

$$F = f_S/f_L \approx \exp[-\Delta S_f(T_M/T - 1)]/R \quad (6)$$

where ΔH_f and ΔS_f are the enthalpy and entropy of fusion, respectively, of the solute at its melting point T_M , T is the system temperature, and R is the gas constant. The hypothetical subcooled liquid molar solubility and vapor pressure can thus be estimated as

$$C_L^S \approx C_S^S \exp[\Delta S_f(T_M/T - 1)/R] \quad (7)$$

$$P_L^S \approx P_S^S \exp[\Delta S_f(T_M/T - 1)/R] \quad (8)$$

The entropy of fusion ΔS_f can be calculated from the experimentally measured enthalpy of fusion as discussed by Miller et al. (14) or estimated from Walden's rule as reviewed by Yalkowsky (15) as 56 J/(mol·K), thus $\Delta S_f/R$ is approximately 6.79.

As discussed by Mackay and Shiu (16), partitioning of organic chemicals between air and water phases can be expressed by the Henry's law constant (H , Pa·m³/mol):

$$H = P_S^S/C_S^S = P_L^S/C_L^S = \gamma_w v_w f_L \quad (9)$$

The dimensionless air–water partition coefficient K_{AW} is given as

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

The octanol–water partition coefficient K_{OW} is defined as

$$K_{OW} = C_{ow}/C_{wo} = (\gamma_{wo} v_{wo})/(\gamma_{ow} v_{ow}) \quad (11)$$

where C is the concentration of the solute, γ is the activity coefficient, and v is the molar volume of the solvent, with subscript wo denoting water saturated with octanol and subscript ow denoting octanol saturated with water (17).

There have been many studies of relationships between aqueous solubility and octanol–water partition coefficient (17–21). Mackay et al. (21) and Banerjee et al. (18) have suggested that their product Q or $C_L^S K_{OW}$ is fairly constant. Recently as reliable experimental data on molecules of larger molar volume have become available, Miller et al. (17) have further observed that $\log Q$ varies as a function of molar volume V (cm³/mol) or chlorine number N as reported earlier (21, 22):

$$\log Q = A - BV = A' - B'N \quad (12)$$

where A , B , A' , and B' are constants.

The quantity Q can be regarded as an approximate or "pseudo" solubility of the chemical in octanol saturated

Table I. Properties of Chlorinated Dibenzo-*p*-dioxins

	chlorine no., <i>N</i>	<i>M_r</i>	mp, °C (25, 29, 45)	fugacity ratio, <i>F</i>	<i>V</i> , cm ³ /mol (Le Bas)
dibenzo- <i>p</i> -dioxin	0	184.0	123.0	0.107	192.0
1-chloro-	1	218.5	105.5	0.16	212.9
2-chloro-	1	218.5	89.0	0.233	212.9
2,3-dichloro-	2	253.0	164.0	0.0421	233.8
2,7-dichloro-	2	253.0	210.0	0.0148	233.8
2,8-dichloro-	2	253.0	151.0	0.0567	233.8
1,2,4-trichloro-	3	287.5	129.0	0.0936	254.7
1,2,3,4-tetrachloro-	4	322.0	190.0	0.0233	275.6
1,2,3,7-tetrachloro-	4	322.0	175.0	0.0328	275.6
1,3,6,8-tetrachloro-	4	322.0	219.0	0.0121	275.6
2,3,7,8-tetrachloro-	4	322.0	305.0	0.0017	275.6
1,2,3,4,7-pentachloro-	5	356.4	196.0	0.0204	296.5
1,2,3,4,7,8-hexachloro-	6	391.0	273.0	0.00352	317.4
1,2,3,4,6,7,8-heptachloro-	7	425.2	265.0	0.00423	338.3
octachloro-	8	460.0	332.0	0.00115	359.2

Table II. Aqueous Solubility of Some PCDDs at 25 °C

	solubility, µg/L	<i>C_S^S</i> , mmol/m ³	selected <i>C_S^S</i> , mmol/m ³	selected <i>C_L^S</i> , mmol/m ³	ref	method ^b
dibenzo- <i>p</i> -dioxin	842	4.58	4.7	43.93	<i>a</i>	gen col HPLC
	900	4.89			<i>a</i>	gen col GC
1-chloro-	417	1.91	1.91	11.94	<i>a</i>	gen col HPLC
2-chloro-	278	1.27	1.35	5.79	<i>a</i>	gen col HPLC
	318	1.46			<i>a</i>	gen col GC
2,3-dichloro-	14.9	0.059	0.059	1.4	<i>a</i>	gen col HPLC
2,7-dichloro-	3.75	0.0148	0.0148	1	<i>a</i>	gen col HPLC
2,8-dichloro-	16.7	0.066	0.066	1.16	<i>a</i>	gen col HPLC
1,2,4-trichloro-	8.41	0.0261	0.0261	0.279	<i>a</i>	gen col HPLC
1,2,3,4-tetrachloro-	0.63	0.00197	0.0017	0.073	<i>a</i>	gen col HPLC
	0.47	0.00146			<i>a</i>	gen col GC
1,2,3,7-tetrachloro-	0.42 (20 °C)	0.0013	0.0013	0.0396	31	¹⁴ C-labeled, gen col HPLC, LSC
1,3,6,8-tetrachloro-	0.32 (20 °C)	0.00094	0.000994	0.082	31, 33	¹⁴ C-labeled, gen col HPLC, LSC
2,3,7,8-tetrachloro-	0.2	0.00062			32	GC
	0.317	0.000984			33	¹⁴ C-labeled, gen col HPLC
	0.0193	0.00006	0.00006	0.0353	34	capillary GC/MS
	0.00791	0.0000246			35	¹⁴ C-labeled
1,2,3,4,7-pentachloro-	0.118 (20 °C)	0.000331	0.000331	0.0162	31	¹⁴ C-labeled, gen col HPLC, LSC
1,2,3,4,7,8-hexachloro-	0.00442 (20 °C)	0.0000113	0.000113	0.00321	31	¹⁴ C-labeled, gen col HPLC, LSC
1,2,3,4,6,7,8-heptachloro-	0.0024 (20 °C)	0.00000564	0.00000564	0.00133	31	¹⁴ C-labeled, gen col HPLC, LSC
octachloro-	0.0004 (20 °C)	0.00000087			31, 33	¹⁴ C-labeled, gen col HPLC, LSC
	0.000074	0.000000161	0.00000161	0.00014	<i>a</i>	gen col GC

^aThis work. ^bGen col, generator column; HPLC, high-pressure liquid chromatography; GC, gas chromatography; GC/MS gas chromatography/mass spectrometry; LSC, liquid scintillation counting.

Table III. Temperature Dependence of Aqueous Solubility of Some PCDDs

	solubilities, µg/L					Δ <i>H</i> , kJ/mol
	278 K	288 K	298 K	308 K	318 K	
dibenzo- <i>p</i> -dioxin	205 ± 10	460 ± 14	842 ± 14	1762 ± 35	3262 ± 26	50.68
1-chloro-	136 ± 3.6	233 ± 3.3	417 ± 16	725 ± 24	1240 ± 23	40.85
2-chloro-	63.5 ± 13	137 ± 10	278 ± 10.5	653 ± 34	1109 ± 104	53.55
2,3-dichloro-	3.68 ± 0.1	7.16 ± 0.8	14.9 ± 0.38	30.4 ± 0.8	58.6 ± 3.3	51.30
2,7-dichloro-	1.09 ± 0.05	2.01 ± 0.14	3.75 ± 0.097	7.27 ± 0.35	13.4 ± 0.15	46.32
2,8-dichloro-	4.42 ± 0.14	8.59 ± 0.55	16.74 ± 0.5	27.53 ± 0.9	51.5 ± 2.9	50.04
1,2,4-trichloro-	2.19 ± 0.087	4.77 ± 0.087	8.41 ± 0.16	16.68 ± 1.92	28.22 ± 0.32	46.62
1,2,3,4-tetrachloro-	0.343 ± 0.028	0.451 ± 0.029	0.63 ± 0.025	1.14 ± 0.064	2.085 ± 0.022	33.36

with water, since *K_{OW}* can be viewed not only as the ratio of concentrations but also as the ratio of solubilities. Examination of the magnitudes of *Q* for a homologous series provides a useful check of consistency between solubility and octanol-water partition coefficient.

Data Analysis

Table I lists the properties of 15 dibenzo-*p*-dioxins including chlorine number, molecular weight, melting point, fugacity ratio estimated from an assumed constant entropy of fusion of 56 J/(mol·K), and molar volume calculated by the LeBas method (30) assuming an incremental molar

volume increase of 20.9 cm³/mol for each chlorine atom. The molar volumes (*V*) and chlorine numbers (*N*) are thus linearly related by the expression

$$V = 192 + 20.9N \quad (13)$$

Table II lists the reported and measured solid aqueous solubilities *C_S^S* at 25 °C and the deduced subcooled liquid solubilities *C_L^S*. Table III gives the temperature dependence of these solubilities and the estimated enthalpies of solution. The enthalpies of solution range from 30 to 50 kJ/mol and show no apparent systematic variation with chlorine number.

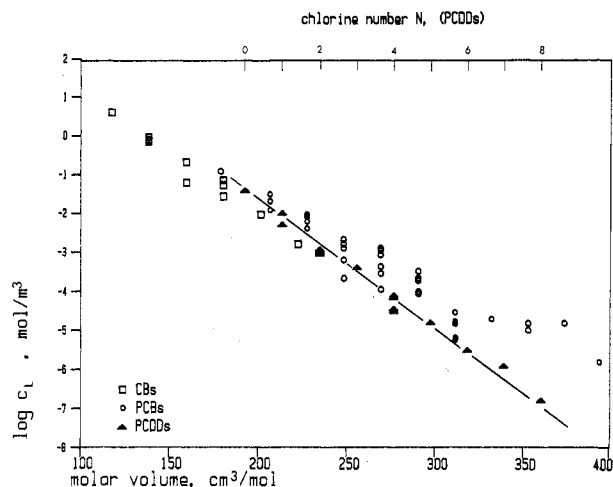


Figure 1. Subcooled liquid solubilities of PCDDs at 25 °C as a function of molar volume and chlorine number. Also shown are solubility-molar volume data for PCBs and chlorobenzenes.

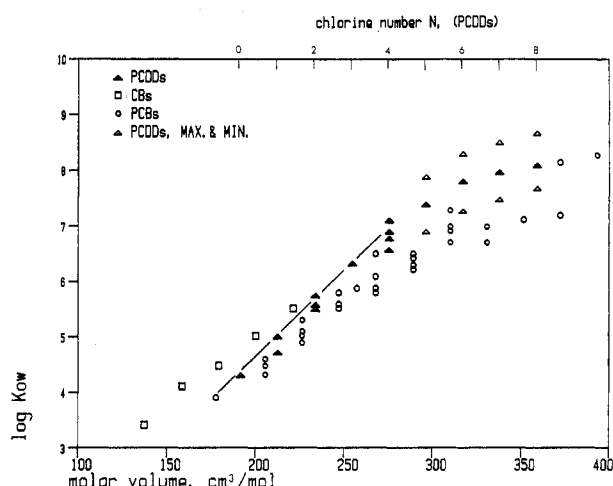


Figure 2. Octanol-water partition coefficients of PCDDs at 25 °C as a function of V and N . Also shown are $K_{OW} - V$ data for PCBs and chlorobenzenes.

The subcooled liquid solubilities are plotted in Figure 1 as a function of molar volume and chlorine number. Also plotted for interest are solubility data for PCBs (22).

It is clear that solubility falls in a consistent near log-linear manner with increasing chlorine number. The correlation line selected by a combination of regression and adjustment taking into account perceived data accuracy is

$$\log C_L^S = 5.03 - V/29.9 \quad (14)$$

where V is molar volume (cm^3/mol) and C_L^S is in mol/m^3 . Each chlorine added decreases the solubility by a factor of 5. Alternatively, each $29.9 \text{ cm}^3/\text{mol}$ increase in molar volume decreases solubility by a factor of 10.

Table IV lists the reported and measured K_{OW} values with the experimental method indicated. Figure 2 is a plot of these data. Likely values and ranges within which the true value is believed to lie were selected for most congeners. When selecting, most weight was placed on the data measured in this study by the generator column technique, and the HPLC-retention time data from Sarna et al. (36) but corrected by Burkhard and Kuehl (26). It is believed that reported calculated K_{OW} data are often in considerable error. Many of the HPLC-retention time derived K_{OW} data are also in error due to difficulties with calibration.

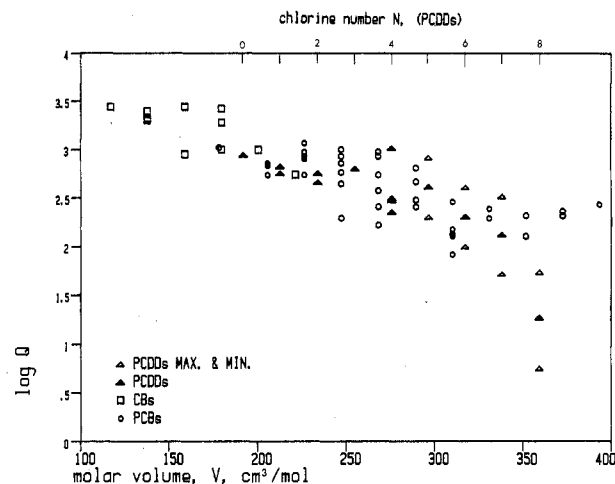


Figure 3. Pseudosolubility in octanol (Q) or $K_{OW}C_L^S$ of PCDDs at 25 °C as a function of V and N . Also shown are $Q - V$ data for PCBs and chlorobenzenes.

Table IV shows that experimental K_{OW} values for the individual congeners up to tetra-CDD are fairly reliable, the error range being typically 0.3 log unit. For these congeners, $\log K_{OW}$ increases with increasing molar volume in a near linear fashion, comparable to that of PCBs, i.e.

$$\log K_{OW} = -1.63 + V/32.1 \quad N \leq 4 \quad (15)$$

Addition of a chlorine substituent thus results in an increase in K_{OW} by a factor of 4.5. As illustrated in Figure 3, the product of C_L^S and K_{OW} , i.e., Q , the pseudosolubility in octanol, decreases slightly (by a factor of 1.12 per chlorine added) to a similar extent to that observed for PCBs (17).

For the penta- to octa-CDDs there are few experimental values, and variations of 1 log unit are common. This clearly demonstrates the need for more data. As a result, no accurate estimate of the K_{OW} of these congeners can be made, but a range of values, varying not more than 1 log unit, is suggested in Table IV. As can be observed from Figure 2, the higher congener data indicate the presence of a distinct curvature of the $\log K_{OW}$ versus molar volume plot. Also, $\log Q$ for these congeners seems to decrease more rapidly than for the lower chlorinated congeners or PCBs. The apparent curvature in the K_{OW} data and the marked decrease in Q could be due to experimental error, to error in the estimation of the fugacity ratio, to nonlinear behavior of $\log \gamma_{ow}$ with respect to molar volume, to a "solubilizing" effect of octanol in the water phase, or to problems associated with using the mole fraction based Raoult's law instead of a more appropriate volume fraction based expression (47). The quality of the available experimental data does not allow definite conclusions to be reached about the source(s) and extent of this effect.

Table V lists reported vapor pressures and Henry's law constants. Figures 4 and 5 give P_L^S and H as a function of N and V , the correlations at 25 °C being

$$\log P_L^S = 7.97 - V/23.2 \quad (16)$$

$$\log H = 2.94 - V/104 \quad (17)$$

Note that the equations for P_L^S , H , and C_L^S are consistent, i.e., H is P_L^S/C_L^S . A linear relationship between $\log P_L^S$ and N has also been reported by Rordorf (23, 24, 46).

It must be noted that these correlation equations do not discriminate between isomers. An examination of the calculated and selected values shows that in almost all cases C_L^S and K_{OW} are correlated with an accuracy within

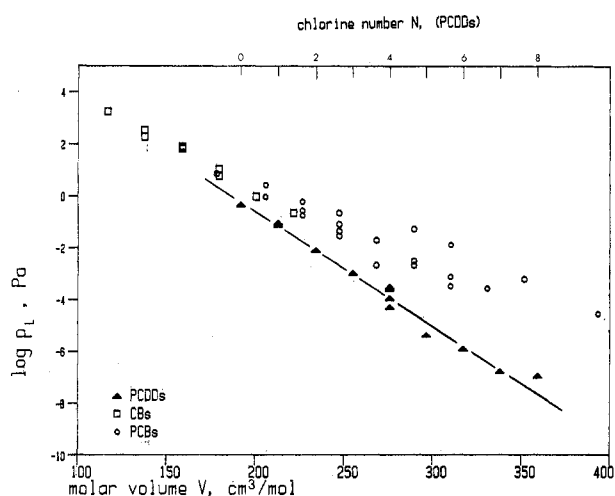
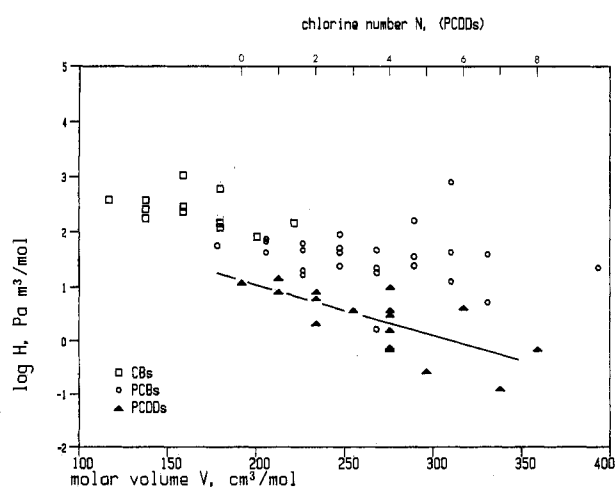
Table IV. Octanol-Water Partition Coefficient of Some PCDDs at 25 °C

	log K _{OW}				method ^b	ref	Q		
	reported	selected	min	max			selected	min	max
dibenzo- <i>p</i> -dioxin	4.37 4.17 4.46 4.20 3.40 4.65 4.26	4.3	4.2	4.4	gen col GC HPLC RT HPLC RT HPLC RT calcd calcd calcd	<i>a</i> 36 36 26 37 28 28	876	696	1103
1-chloro-	5.30 4.91 5.18 4.75 4.20	4.75	4.45	5.05	HPLC RT HPLC RT HPLC RT HPLC RT calcd	<i>a</i> 36 36 36 26 37	671	337	1340
2-chloro-	4.94 5.45 5.64 5.08 4.20 5.47 4.76	5.00	4.80	5.20	gen col GC HPLC RT HPLC RT HPLC RT calcd calcd calcd	<i>a</i> 36 36 26 37 28 28	579	365	918
2,3-dichloro-	4.70	5.60			calcd	37	557		
2,7-dichloro-	6.39 6.62 5.75 4.70	5.75	5.45	6.05	HPLC RT HPLC RT HPLC RT calcd	36 36 26 37	562	282	1122
2,8-dichloro-	4.70	5.60			calcd	37	462		
1,2,4-trichloro-	5.57 7.45 7.76 6.45 5.10	6.35	6.05	6.65	SF HPLC RT HPLC RT HPLC RT calcd	<i>a</i> 36 36 26 37	624	313	1669
1,2,3,4-tetrachloro-	5.77 8.64 8.91 7.18 7.08 5.50 7.70 5.80 6.20	6.60	6.10	7.10	SF HPLC RT HPLC RT HPLC RT HPLC RT calcd calcd calcd calcd	<i>a</i> 36 36 26 26 37 28 28 <i>a</i>	291	92	919
1,2,3,7-tetrachloro-	8.18 8.60 6.91 5.50	6.90	6.40	7.40	gen col GC HPLC RT HPLC RT HPLC RT calcd	36 36 26 26 37	314	99	995
1,3,6,8-tetrachloro-	8.70 9.02 7.20 7.13 5.50	7.10	6.60	7.60	HPLC RT HPLC RT HPLC RT HPLC RT calcd	36 36 26 26 37	1032	326	3264
1,3,7,9-tetrachloro-	7.16 5.50	7.10	6.60	7.60	HPLC RT calcd	26 37	1032		
2,3,7,8-tetrachloro-	7.02 8.93 6.15 7.16 6.84 6.64 5.50	6.80	6.60	7.00	HPLC RT HPLC not reported calcd calcd stirring calcd	26 36 38 39 40 41 37	223	140	1405
1,2,3,4,7-pentachloro-	9.40 9.65 7.44 5.80	7.40	6.90	7.90	HPLC RT HPLC RT HPLC RT calcd	36 36 27 27	407	204	812
1,2,3,4,7,8-hexachloro-	10.22 10.44 7.79	7.80	7.30	8.30	HPLC RT HPLC RT HPLC RT	36 36 26	203	102	404
1,2,3,4,6,7,8-heptachloro-	11.05 11.50 8.20	8.00	7.50	8.50	HPLC RT HPLC RT HPLC RT	36 36 26	133	53	334
octachloro-	11.16 12.72 8.60 7.59 10.56 7.53	8.20	7.70	8.70	HPLC RT HPLC RT HPLC RT gen col GC calcd calcd	36 36 26 <i>a</i> 28 28	17.6	5.6	56

^aThis work. ^bHPLC, high-pressure liquid chromatography; HPLC RT, HPLC retention time; GC, gas chromatography; gen col GC, generator column GC determination; calcd, calculated value.

Table V. Vapor Pressure and Henry's Law Constant for Some Dioxins

	vapor pressure, Pa		ref	Henry's law constant, H , Pa·m ³ /mol	
	P_S^S	P_L^S		exptl (33)	$H = P_L^S/C_L^S$
dibenzo- <i>p</i> -dioxin	0.055	0.514	23, 24, 45, 46		12.29
1-chloro-	0.012	0.1	23, 24, 45, 46		8.38
2-chloro-	0.017	0.0858	23, 24, 45, 46		14.82
2,3-dichloro-	0.00039	0.00926	23, 24, 45, 46		6.61
2,7-dichloro-	0.00012	0.00811	23, 24, 45, 46		8.11
2,8-dichloro-	0.00014	0.00247	23, 24, 45, 46		2.13
1,2,4-trichloro-	0.0001	0.00107	23, 24, 45, 46		3.84
1,2,3,4-tetrachloro-	0.000064	0.000275	23, 24, 45, 46		3.77
1,2,3,7-tetrachloro-	0.000001	0.0000305	23, 24, 45, 46		0.77
1,3,6,8-tetrachloro-	0.000537	0.0136	25	6.9	
	0.0000007	0.0000579	23, 24, 45, 46		0.71
2,3,7,8-tetrachloro-	0.0000045	0.00265	25		
	0.00000151	0.000089	42, 43		
	0.000000098	0.0000581	44		1.63
	0.0000002	0.000118	23, 24, 45, 46		3.34
	0.00000062	0.000365	23, 24, 45, 46		10.34
1,2,3,4,7-pentachloro-	0.00000088	0.0000431	23, 24, 45, 46		0.264
1,2,3,4,7,8-hexachloro-	5.1×10^{-9}	0.00000145	23, 24, 45, 46		4.52
1,2,3,4,6,7,8-heptachloro-	7.5×10^{-10}	1.77×10^{-7}	23, 24, 45, 46		0.133
octachloro-	0.0000087	0.00813	25		
	1.10×10^{-10}	1.19×10^{-7}	23, 24, 45, 46		0.683

Figure 4. Vapor pressure of PCDDs at 25 °C as a function of V and N . Also shown are $P_L^S - V$ data for PCBs and chlorobenzenes.Figure 5. Henry's law constants (H) of PCDDs at 25 °C as a function of V and N using selected values of P_L^S and C_L^S to calculate H . Also shown are $H - V$ data for PCBs and chlorobenzenes.

a factor of 2 and P_L^S and H within a factor of 5. This is considered to be satisfactory for most environmental assessment purposes.

Discussion

We believe that the preferred procedure for assessing the physical-chemical properties of a homologous series, such as the PCDDs, is to follow a two-stage process. The first stage considered here is to collect the available data for C^S , P^S , K_{OW} , and H , convert any solid solubilities and vapor pressures to subcooled liquid values, and then plot these data and Q against the simplest available molecular descriptors of chlorine number or molar volume. Regressions can be obtained or lines fitted taking into account perceived accuracy. This gives an initial estimate of properties that may be sufficient for many purposes, but it does not characterize isomer differences.

In a second stage, which is appropriate when more reliable experimental data become available, a more detailed assessment can be conducted to improve the accuracy, including isomer differences and using more sophisticated molecular descriptors such as total surface area and solute-solvent interaction parameters.

The solubility data in Figure 1 show a satisfying log-linear relationship with a drop in solubility by a factor of 5 per chlorine added. Figure 1 also shows that on a molar volume basis, the solubilities of the chlorobenzenes, chlorobiphenyls, and PCDDs are similar, but a deviation apparently occurs at high chlorine numbers. The accuracy in this region however is poor. Molar volume is thus a convenient first estimator of solubility for such series.

The vapor pressure data in Figure 4 show that P_L tends to fall by a factor of 8 per chlorine added, i.e., the line is steeper than that for solubility. It is also steeper than that of the PCBs. These vapor pressure measurements, however, are few, difficult to make, and may have some error, but the effect should be treated as real. This analysis is only possible because of the careful work of Rordorf (45, 46).

The Henry's law constants in Figure 5 apparently fall by a factor of 1.6 per chlorine added as a result of the decrease in vapor pressure (by 8) and solubility (by 5). They lie between 0.1 and 15 Pa·m³/mol, which corresponds to dimensionless air-water partition coefficients in the range of 4×10^{-5} to 6×10^{-3} . Volatilization from water is thus likely to be fairly slow and air-phase resistance controlled, but the process is sufficiently fast that it merits quantification. Burkhard et al. (48) found that H for PCBs

varied from 1.0 to 100 Pa·m³/mol with a mean of approximately 50 and with no systematic variation with chlorine number. A systematic variation does apparently occur with PCDDs. This difference could be attributable to molecular structure, to experimental error, or to congener selection. There is a need to obtain more accurate air-water partition data, preferably by subjecting the same congener to determinations of solubility, vapor pressure, and Henry's law constant until consistency is obtained between these three independent measurements.

Data for the temperature dependence of solubility have also been reported here. These can be combined with Rordorf's data (45) for temperature dependence of vapor pressure to describe the temperature dependence of Henry's law constant. Enthalpies of vaporization typically range from 68 to 88 kJ/mol (mean 80 kJ/mol) while enthalpies of solution range from 33 to 54 kJ/mol (mean 47 kJ/mol), thus Henry's law constants are expected to vary with an enthalpy of vaporization from water of a mean of 33 kJ/mol but with a probable range from 20 to 50 kJ/mol. This mean corresponds to a doubling of *H* by an increase in temperature of 16 °C at ambient conditions. It is thus important to quantify this effect since it has a profound effect on environmental fate.

Octanol-water partition coefficients of PCDDs are generally used to estimate bioaccumulation in aquatic organisms and sorption to organic carbon. Recent studies have, however, shown that the bioaccumulation factor-*K*_{OW} relationship that applies up to log *K*_{OW} of 6 breaks down for more highly hydrophobic chemicals (49-52). This is believed to be the result of a combination of factors such as loss of similarity between octanol and fish lipid solubility, metabolic transformation, and bioavailability phenomena (53). Even if *K*_{OW} is accurately determined for the higher chlorinated congeners, this will not necessarily improve estimates of PCDD body burdens in fish. Clearly there remains a need to obtain reliable *K*_{OW} data, especially for the higher congeners, and to establish more reliable relationships between *K*_{OW} and the extent of bioaccumulation.

Conclusions

PCDD property data have been measured and gathered, analyzed, and suggested regressions obtained versus chlorine numbers and molar volume at 25 °C. Estimates have been made of temperature dependence. It is striking that the reported data vary by several orders of magnitude, thus considerable errors can be made when estimating environmental fate by inappropriate selection of data from the literature. It is hoped that this analysis will reduce such errors. There remains a need to obtain more data, covering the entire range of environmental temperatures. The fugacity ratio calculation should be improved to include measured enthalpies of fusion and heat capacities. Better molecular descriptors could be used, especially total surface area.

If the environmental fate and effects of the PCDDs are to be better elucidated, more fundamental physical property data should be obtained, by more laboratories, and subjected to more detailed critical review.

In any calculations of environmental fate it is essential to consider the error limits suggested in this analysis.

Registry No. Dibenzo-*p*-dioxin, 262-12-4; 1-chlorodibenzo-*p*-dioxin, 39227-53-7; 2-chlorodibenzo-*p*-dioxin, 39227-54-8; 2,3-dichlorodibenzo-*p*-dioxin, 29446-15-9; 2,7-dichlorodibenzo-*p*-dioxin, 33857-26-0; 2,8-dichlorodibenzo-*p*-dioxin, 38964-22-6; 1,2,4-trichlorodibenzo-*p*-dioxin, 39227-58-2; 1,2,3,4-tetrachlorodibenzo-*p*-dioxin, 30746-58-8; 1,2,3,7-tetrachlorodibenzo-*p*-dioxin,

67028-18-6; 1,2,3,4,6,7,8-heptachlorodibenzo-*p*-dioxin, 35822-46-9; octachlorodibenzo-*p*-dioxin, 3268-87-9; chlorodibenzo-*p*-dioxin, 35656-51-0.

Literature Cited

- (1) Hutzinger, O.; Blumich, M. J.; van den Berg, M.; Olle, K. *Chemosphere* 1985, 14, 581.
- (2) Hutzinger, O.; Choudry, G. G.; Chittim, B. G.; Johnston, L. E. *EHP, Environ. Health Perspect.* 1985, 60, 3.
- (3) Kociba, R. J.; Cabey, O. *Chemosphere* 1985, 14, 649.
- (4) Goldstein, J. A. In *Halogenated Biphenyls, Terphenyls, Naphthalenes, Dibenzodioxins and Related Compounds*; Kimbrough, R. E., Ed.; Elsevier/North Holland Biomedical: Amsterdam, 1980; pp 151-190.
- (5) Safe, S. *CRC Crit. Rev. Toxicol.* 1984, 13, 319.
- (6) Safe, S.; Mason, G.; Keys, B.; Farrell, K.; Zmudzka, B.; Sawyer, T.; Piskorska-Pliszczyńska, J.; Safe, L.; Romkes, M.; Bandiera, S. *Chemosphere* 1986, 15, 9-12.
- (7) May, W. E.; Wasik, S. P.; Freeman, D. H. *Anal. Chem.* 1978, 50, 175.
- (8) May, W. E.; Wasik, S. P.; Freeman, D. H. *Anal. Chem.* 1978, 50, 977.
- (9) Stolzenburg, T. R.; Andren, A. W. *Anal. Chim. Acta* 1983, 151, 271.
- (10) Woodburn, K. B.; Doucette, W. J.; Andren, A. W. *Environ. Sci. Technol.* 1984, 18, 457.
- (11) Mackay, D.; Shiu, W. Y. In *Gas Transfer at Water Surface*; Brutsaert, W., Jirka, G. H., Eds.; Reidel: Dordrecht, Holland, 1984; pp 3-16.
- (12) Mackay, D.; Shiu, W. Y. In *QSAR in Environmental Toxicology*; Kaiser, K. L. E., Ed.; Reidel: Dordrecht, Holland, 1984; pp 261-278.
- (13) Prausnitz, J. M. *Molecular Thermodynamics of Fluid Phase Equilibria*; Prentice-Hall, Englewood Cliffs, NJ, 1969.
- (14) Miller, M. M.; Ghodbane, S.; Wasik, S. P.; Tewari, Y. B.; Martire, D. E. *J. Chem. Eng. Data* 1984, 29, 184.
- (15) Yalkowsky, S. H. *Ind. Eng. Chem. Fundam.* 1979, 18, 108.
- (16) Mackay, D.; Shiu, W. Y. *J. Phys. Chem. Ref. Data* 1981, 10, 1175.
- (17) Miller, M. M.; Wasik, S. P.; Haung, G. L.; Shiu, W. Y.; Mackay, D. *Environ. Sci. Technol.* 1985, 19, 522.
- (18) Banerjee, S.; Yalkowsky, S. H.; Valvani, S. C. *Environ. Sci. Technol.* 1980, 14, 1227.
- (19) Chiou, C. T.; Schmedding, D. W.; Manes, W. *Environ. Sci. Technol.* 1982, 16, 4.
- (20) Yalkowsky, S. H.; Valvani, S. C.; Mackay, D. *Residue Rev.* 1983, 85, 43.
- (21) Mackay, D.; Bobra, A. M.; Shiu, W. Y.; Yalkowsky, S. H. *Chemosphere* 1980, 9, 701.
- (22) Shiu, W. Y.; Mackay, D. *J. Phys. Chem. Ref. Data* 1986, 15, 911.
- (23) Rordorf, B. F. *Chemosphere* 1985, 14, 885.
- (24) Rordorf, B. F. *Thermochim. Acta* 1985, 85, 435.
- (25) Webster, G. R. B.; Friesen, K. J.; Sarna, L. P.; Muir, D. C. G. *Chemosphere* 1985, 14, 609.
- (26) Burkhard, L. P.; Kuehl, D. W. *Chemosphere* 1986, 15, 163.
- (27) DeVoe, H.; Miller, M. M.; Wasik, S. P. *J. Res. Natl. Bur. Stand. (U.S.)* 1981, 86, 361.
- (28) Doucette, W. J. Ph.D. Thesis, University of Wisconsin-Madison, 1985.
- (29) Poland, A. E.; Yang, G. C. *J. Agr. Food Chem.* 1972, 20, 1093.
- (30) Reid, R. C.; Prausnitz, J. M.; Sherwood, T. K. *The Properties of Gases and Liquids*, 3rd ed.; McGraw-Hill: New York, 1977.
- (31) Friesen, K. J.; Sarna, L. P.; Webster, G. R. B. *Chemosphere* 1985, 14, 1267.
- (32) Crummett, W. F.; Stehl, R. H. *EHP, Environ. Health Perspect.* 1973, 5, 15.
- (33) Webster, G. R. B.; Sarna, L. P.; Muir, D. C. G. Presented at the ACS National Meeting, Washington, DC, 1983.
- (34) Marple, L.; Brunck, R.; Throop, L. *Environ. Sci. Technol.* 1986, 20, 180.
- (35) Adams, W. J.; Blaine, K. A. *Chemosphere* 1986, 15, 1397.
- (36) Sarna, L. P.; Hodge, P. E.; Webster, G. R. B. *Chemosphere* 1985, 13, 975.

- (37) Kaiser, K. L. E. *Chemosphere* 1983, 12, 1159.
- (38) Kenaga, E. *Environ. Sci. Technol.* 1980, 14, 553.
- (39) Perkow, J.; Eschenroeder, A.; Goyer, M.; Stevens, J.; Wechsler, A. "An Exposure and Risk Assessment for 2,3,7,8-Tetrachlorodibenzo-*p*-dioxin"; Office of Water Regulations and Standards, U.S. EPA: Washington, DC, 1980.
- (40) Johnson, H. *Aquatic Fate Process Data for Organic Priority Pollutants*; Mabey, W. R., Ed.; EPA Final Report on Contract 68-01-3867; U.S. Government Printing Office: Washington, DC, 1982.
- (41) Marple, L.; Berridge, B.; Throop, L. *Environ. Sci. Technol.* 1986, 20, 397.
- (42) Schroy, J. M.; Hileman, F. D.; Chang, S. C. *Chemosphere* 1985, 14, 877.
- (43) Schroy, J. M.; Hileman, F. D.; Chang, S. C. In *Aquatic Toxicology and Hazard Assessment*, 8th Symposium; Bahner, R. C., Hansen, D. J., Eds.; ASTM STP 891, American Society for Testing and Materials: Philadelphia, 1985; pp 409-421.
- (44) Podoll, R. T.; Jaber, H. M.; Mill, T. *Environ. Sci. Technol.* 1986, 20, 490.
- (45) Rordorf, B. F., Ciba Geigy Ltd., Switzerland, private communication, 1986.
- (46) Rordorf, B. F. *Chemosphere* 1986, 15, 1325-1332.
- (47) Chiou, C. T.; Manes, M. J. *J. Chem. Soc., Faraday Trans. 1* 1986, 82, 243.
- (48) Burkhard, L. P.; Armstrong, D. E.; Andren, A. W. *Environ. Sci. Technol.* 1985, 19, 590.
- (49) Gobas, F. A. C.; Shiu, W. Y.; Mackay, D.; Opperhuizen, A. *Chemosphere* 1986, 15, 1985.
- (50) Opperhuizen, A.; Wahenaar, W. J.; Van der Wielen, F. W. M.; Van der Berg, M.; Olie, K.; Gobas, F. A. P. C. *Chemosphere* 1986, 15, 2049.
- (51) Kuehl, D. W.; Cook, P. W.; Batterman, A. R. *Chemosphere* 1985, 14, 871.
- (52) Muir, D. C. G.; Marshall, W. K.; Webster, G. R. B. *Chemosphere* 1985, 14, 829.
- (53) Gobas, F. A. P. C.; Shiu, W. Y.; Mackay, D. In *QSAR in Environmental Toxicology—II*; Kaiser, K. L. E., Ed.; Reidel: Dordrecht, Holland, 1987; pp 107-123.

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Effect of a Subsurface Sediment on Hydrolysis of Haloalkanes and Epoxides

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■ Neutral and base-catalyzed hydrolyses of isopropyl bromide, 1,1,2,2-tetrachloroethane, 1,1,1-trichloroethane, and ethylene dibromide were studied in pure water and in barely saturated subsurface sediment at 25–60 °C. Half-lives in sediment at 25 °C were 2.1, 29, 450 (measured), and 1500 days (calculated), respectively. No significant differences in the kinetics or products were observed in the sediment pores compared to those in water at the same pH, indicating that the effects of ionic strength, surface catalysis, and adsorption are unimportant for the low-carbon sediment studied. Thus, kinetic and product data for haloalkanes obtained in pure water are applicable to such groundwater systems. On the other hand, epoxide hydrolysis can be affected by the presence of sediments; styrene oxide (acid catalyzed below pH 7) hydrolyzed 4 times faster in sediment than in buffered water and also formed benzaldehyde by oxidation.

Introduction

Contamination of groundwater from landfills, hazardous waste dumps, septic systems, and underground storage tanks, etc. continues to be a major environmental problem. Although knowledge about the chemical and microbiological effects of (organic-rich) soils and surface sediments on the transport and transformation of chemicals is considerable (1–3), much less is known about such effects in low-carbon, subsurface sediments, which often represent the largest fraction of aquifer material. The purpose of this study was to evaluate whether or not these types of sediments substantially alter hydrolysis kinetics and pathways from those observed in surface waters. Such information will provide a basis for predicting hydrolysis rate constants and products in groundwater systems for a variety of hydrolyzable structures for use in fate and exposure models and will help develop generalizations about structure, reactivity, and the effect of varying sediment properties.

Hydrolysis rates and products can be affected by such factors as ionic strength, acid or base catalysis, surface

catalysis, and partitioning into nonaqueous regimes (3–5). Recent work (6, 7) has shown that rates of acid-catalyzed hydrolysis of compounds in unsaturated clays can be orders of magnitude higher than rates in distilled water having the same bulk pH. This effect was attributed to an enhanced acidity at the clay surface. A potential for altered rates and products in such systems exists due to catalysis at the sediment surface and to ionic strength effects or general acid or base catalysis by the inorganic solutes present.

Other physical, chemical, and biological processes compete in the transport and transformation of compounds in surface water or groundwater. Microbial processes are often important, and oxidizing or reducing agents in sediments such as transition metals or sulfides may introduce alternate chemical pathways (8). However, hydrolysis of leached chemicals can be a significant transformation process in sediments even when hydrolysis rates are low, if competing processes are slow or absent. This can be true particularly for small halogenated compounds that are often not readily biotransformed (9). In this study, experiments were specifically designed to minimize intervention in hydrolysis by volatilization, biotransformation, or chemical reduction by using sealed, sterile sediments under aerated conditions; oxidation processes could occur, but with one exception, products indicated that losses were due entirely to hydrolysis.

We have chosen for study four halogenated organic compounds, isopropyl bromide (IPB), 1,1,1-trichloroethane (TrCE), 1,1,2,2-tetrachloroethane (TeCE), and 1,2-dibromoethane (ethylene dibromide, EDB) as examples of solvents or pesticides entering groundwaters. TrCE has come into widespread use as a solvent, particularly as a degreaser in the semiconductor industry, since trichloroethane was banned for this use in 1979 as a potential carcinogen (10). In general, such compounds exhibit no specific acid catalysis, but reaction may occur with OH[−] (4). Hydrolyses of haloalkanes typically are slow ($t_{1/2} \approx$ weeks to years) and can proceed either by elimination of hydrohalide to yield relatively stable haloolefins or by