6.4 SORPTION OF HYDROPHOBIC (ORGANIC) COMPOUNDS

1. Low solubility in water eg. CTET Solubility 805 mg/L → 805 ppm
   Drinking H_2O limit 5 ppb.
2. Adsorbed onto • solid surfaces (since hydrophobic)
   • organic matter (important sink)
   exclusively sorbed onto organic if $f_{oc} \geq 0.1\%$
   f_{oc} = organic carbon wt / bulk wt.

Two limits for behavior:

If $f_{oc} \geq 0.1\%$ then $K_{oc} = \frac{K_d}{f_{oc}}$

K_{oc} = organic carbon partition coefficient

If only know wt of organic matter, $K_{oc} = 1.724\, K_{om}$
since organic carbon less wt than organic matter

If $f_{oc} \leq 0.1\%$ then mineral surfaces are an important (relatively) site for the hydrophobic compounds.

∴ $K_d = K_{oc} f_{oc}$ does not apply.

If $f_{oc} \geq 0.1\%$ then

K_{oc} may be estimated from two methods:

1. K_{ow} – octanol-water partition coefficient defines solubility of octanol in water
2. Solubility data specific to the solvent compound.

For example: ($f_{oc} > 0.1\%$)

$$K_d = K_{oc} f_{oc}$$

eg. $K_{oc} = 0.63\ K_{ow}$ Table 3.2, 3.3, 3.4

eg. $\log K_{oc} = 3.64 - 0.55 \log S$

Solubility in mg/L

see table 3.5, 3.6

TABLE 3.5 Empirical equations by which K_{oc} can be estimated from S.

Equation Number	Equation	Reference
(T13)	$\log K_{oc} = 0.44 - 0.54 \log S$ S in mole fraction, $r^2 = 0.94$	Karickhoff, Brown, and Scott 1979
(T14)	$\log K_{oc} = 3.64 - 0.55 \log S$ S in mg/L	Kenaga 1980
(T15)	$\log K_{oc} = 4.273 - 0.686 \log S$ S in mg/L	Means et al. 1980
(T16)	$\log K_{oc} = 3.95 - 0.62 \log S$ S in mg/L	Hassett et al. 1983
(T17)	$\log K_{om} = 0.001 - 0.729 \log S$ S in moles/L, $r^2 = 0.996$	Chiou, Porter, and Schmedding 1983

$\log K_{oc} = 3.64 - 0.55 \log S$

$S_{\text{ETHYL BENZENE}} = 140 \text{ mg/L}$

$\log S = 2.15$

$\log K_{oc} = 3.64 - 0.55(2.15) = 2.46$

$\therefore K_{oc} = 288 \text{ L/kg} \approx (\text{mL/g})$

TABLE 3.6 K_{oc} values estimated from the aqueous solubility.

Compound:	Dichloroethane	Benzene	Trichloroethene	Ethyl Benzene	Tetrachloroethene	Napthalene	2,2'-Dichlorobiphenyl	Pyrene
Molecular weight:	98.96	78.12	131.38	165.82	106.18	128.18	223.10	202.26
				Solubility (mg/L)				
	5500	1780	1100	140	150	31	1.86	0.032
Log S:	3.74	3.25	3.04	2.15	2.18	1.49	0.269	−1.50
				Solubility (moles/L)				
	5.56×10^{-2}	2.28×10^{-2}	8.37×10^{-3}	8.44×10^{-4}	1.41×10^{-3}	2.42×10^{-4}	8.32×10^{-6}	1.58×10^{-7}
Log S:	−1.25	−1.64	−2.08	−3.07	−2.85	−3.62	−5.08	−6.80
				Solubility (Mole Fraction)				
	1.00×10^{-3}	4.10×10^{-4}	1.51×10^{-4}	1.52×10^{-5}	2.54×10^{-5}	4.35×10^{-6}	1.49×10^{-7}	2.84×10^{-9}
Log S:	−3.00	−3.39	−3.82	−4.82	−4.60	−5.36	−6.83	−8.55
Equation Number*				Estimated log K_{oc}				
(T13)	2.06	2.27	2.50	3.04	2.87	3.33	4.13	5.06
(T14)	1.58	1.85	1.97	2.46	2.44	2.82	3.79	4.47
(T15)	1.67	2.01	2.15	2.76	2.74	3.21	4.46	5.27
(T16)	1.63	1.94	2.07	2.62	2.60	3.03	4.12	4.88
(T17)	1.15	1.43	1.75	2.47	2.31	2.88	3.93	5.19
Range	1.15–2.06	1.43–2.27	1.75–1.50	1.80–3.04	2.31–2.87	2.82–3.33	3.79–4.46	4.47–5.27
Mean	1.62	1.90	2.09	2.67	2.59	3.05	4.09	4.97
St. dev.	0.32	0.31	0.27	0.24	0.22	0.22	0.25	0.32
Coef. var	0.08	0.07	0.06	0.05	0.04	0.04	0.05	0.08

* The equation numbers in his table refer to Table 3.5.

Equation Number	Equation	Chemicals Used	Reference
(T1)	$\log K_{oc} = 0.52 \log K_{ow} + 0.62$	72 substituted benzene pesticides	Briggs, 1981
(T2)	$\log K_{oc} = 1.00 \log K_{ow} - 0.21$	10 polyaromatic hydrocarbons	Karickhoff, Brown, and Scott 1979
(T3)	$K_{oc} = 0.63 K_{ow}$	Miscellaneous organics	Karickhoff, Brown, and Scott 1979
(T4)	$\log K_{oc} = 0.544 \log K_{ow} + 1.377$	45 organics, mostly pesticides	Kenaga and Goring 1980
(T5)	$\log K_{oc} = 1.029 \log K_{ow} - 0.18$ $r^2 = 0.91$; $n = 13$	13 pesticides	Rao and Davidson 1980
(T6)	$\log K_{oc} = 0.94 \log K_{ow} + 0.22$	s-trizines and dinitroanalines	Rao and Davidson 1980
(T7)	$\log K_{oc} = 0.989 \log K_{ow} - 0.346$ $r^2 = 0.991$; $n = 5$	5 polyaromatic hydrocarbons	Karickhoff 1981
(T8)	$\log K_{oc} = 0.937 \log K_{ow} - 0.006$	Aromatics, polyaromatics, triazines	Lyman 1982
(T9)	$\ln K_{oc} = \ln K_{ow} - 0.7301$	DDT, tetrachlorobiphenyl, lindane, 2,4-D, and dichloropropane	McCall, Swann, and Laskowski 1983
(T10)	$\log K_{oc} = 0.904 \log K_{ow} - 0.779$ $r^2 = 0.989$; $n = 12$	Benzene, chlorinated benzenes, PCBs	Chiou, Porter, and Schmedding 1983
(T11)	$\log K_{oc} = 0.72 \log K_{ow} + 0.49$ $r^2 = 0.95$; $n = 13$	Methylated and chlorinated benzenes	Schwarzenbach and Westall 1981
(T12)	$\log K_{oc} = 1.00 \log K_{ow} - 0.317$ $r^2 = 0.98$; $n = 22$	22 polynuclear aromatics	Hassett et al. 1980

log Koc

TABLE 3.4 Experimentally derived (K_{oc}) values.

Compound	log(K_{oc})	Reference
Benzene	1.50	Chiou, Porter, and Schmedding 1983
	1.92	Karickhoff, Brown, and Scott 1979
	1.98	Rogers, McFarlane, and Cross 1980
Ethylbenzene	2.22	Chiou, Porter, and Schmedding 1983
2,2'-Dichlorobiphenyl	3.92	Chiou, Porter, and Schmedding 1983
Tetrachloroethene	2.32	Chiou, Peters, and Freed 1979
Napthalene	3.11	Karickhoff, Brown, and Scott 1979
Pyrene	4.92	Karickhoff, Brown, and Scott 1979
	4.80	Means et al. 1980

EXPERIMENTAL VALUES

COMPARE?

TABLE 3.3 Estimated values of K_{oc} based on published K_{ow} values.

	Dichloroethane	Benzene	Trichloroethene	Ethyl Benzene	Tetrachloroethene	Napthalene	2,2'-Dichlorobiphenyl	Pyrene
Log K_{ow}	1.79	2.13	2.29	3.14	3.40	3.37	4.80	5.32
Equation Number*	Estimated log K_{oc}							
(T1)	1.79	1.96	2.05	2.49	2.62	2.61	3.35	3.62
(T2)	1.58	1.92	2.10	2.93	3.19	3.16	4.59	5.11
(T3)	1.13	1.34	1.44	1.98	2.14	2.16	3.07	3.35
(T4)	2.35	2.54	2.62	3.09	3.23	3.21	3.99	4.27
(T5)	1.66	2.01	2.18	3.05	3.32	3.29	4.76	5.29
(T6)	1.90	2.22	2.37	3.17	3.42	3.39	4.73	5.22
(T7)	1.42	1.76	1.92	2.76	3.02	2.99	4.40	4.92
(T8)	1.67	1.99	2.14	2.94	3.18	3.15	4.49	4.98
(T9)	1.06	1.40	1.56	2.41	2.67	2.64	4.07	4.59
(T10)	1.08	1.39	1.53	2.06	2.30	2.51	3.80	4.27
(T11)	1.78	2.02	2.14	2.75	2.94	2.92	3.95	4.32
(T12)	1.47	1.81	1.97	2.82	3.08	3.05	4.48	5.00
Range	1.06–2.35	1.34–2.54	1.44–2.62	1.98–3.17	2.14–3.42	2.16–3.39	3.07–4.76	3.35–5.29
Mean	1.57	1.86	2.00	2.70	2.93	2.92	4.14	4.58
St. dev.	0.38	0.35	0.33	0.39	0.41	0.37	0.54	0.63
Coef. var.	0.24	0.19	0.17	0.14	0.15	0.13	0.13	0.14

* The equation numbers in this table refer to Table 3.2

log Kow = 2.13

10^x it !!

Kow = 135

Koc = 0.63 Kow

= 84.98

log Koc = 1.92

1.92

TAKE CARE IN APPLYING $f_{oc} \geq 0.1\%$ where $f_{oc} < 0.1\%$.

eg. Border results: $f_{oc} = 0.02\%$

$K_d = K_{oc} f_{oc}$

For Carbon Tetra Chloride (CTET) Solubility, $S = 805$ mg/L

Using (T14) $\log K_{oc} = 3.64 - 0.55 \log S$

$= 3.64 - 0.55(2.9) = 2.04$

$K_{oc} = 110$ mg/L mL/g

From calculator $f_{oc} > 0.1\%$ $K_d = 110(0.0002) = 0.02$ ~~mg/L~~ mL/g

From plume $R = 2.42$; $K_d = 0.213$ ~~mg/L~~ mL/g

1. Estimated value is too low — neglects the significant of the mineral surfaces.
2. Reasonable correspondence.

This table sheds some insight into the foc contents of typical sands and gravels

TABLE 4.1 Field Studies that Have Yielded Reliable Estimates Of Organic Contaminant Retardation in Sand/Gravel Aquifers

Site Location and Test Type (reference)[a]	Retardation Factors Determined For Listed Contaminants		Organic Carbon Content Of Solids (reference)
	Contaminant	Factor	
Palo Alto, California			nr[c]
Forced gradient (1)	Chloroform	2.5-3.5	
	Bromoform	6.0	
	1,1,1-Trichloroethane	12.0	
	Chlorobenzene	23.0	
R. Aare, Switzerland			nr
River infiltration (2)	Tetrachloroethene	5.0	
Gloucester, Ontario			0.1-0.25% (4, 5)
Forced gradient (3, 4)	1,4-Dioxane	1.4	
	Tetrahydrofuran	2.2	
	Diethyl ether	3.0	
Plume interpretation (4, 5)	1,4-Dioxane	1.6	
	Tetrahydrofuran	2.2	
	Diethyl ether	3.3	
	1,3 Dichlorobenzene	7.6	
	Benzene	8.8	
	Carbon tetrachloride	22.0	
Borden, Ontario			0.02% (6, 11)
Natural gradient (6, 7)	Bromoform	1.9-2.7	
	Carbon tetrachloride	1.8-2.5	
	Tetrachloroethene	2.7-5.9	
	1,3-Dichlorobenzene	3.9-9.0	
	Hexachloroethane	6.0-7.9	
Moffett Naval Air Station, California			0.11% (8)
Forced gradient (8)	Trichloroethene	6-9	
	1,1,1-Trichloroethane	1.4-2.0	
Otis Air Force Base, Massachusetts			0.01-0.75% (9)
Plume interpretation (9)	Trichloroethene	1.0	
	Tetrachloroethene	1.0	
	Dichlorobenzene	1.0-1.1	
	DTBB[b]	2.4-2.6	
	P-Nonylphenol	1.1-2.3	
Rocky Mountain Arsenal, Colorado			0.005% (12)
Forced gradient (10)	Trichloroethene	1-2	
	1,1,1-Trichloroethane	1-2	

[a] References: (1) Roberts et al., 1982; (2) Schwarzenbach et al., 1982; (3) Whiffin and Bahr, 1985; (4) Patterson et al., 1985; (5) Jackson et al., 1985; (6) Mackay et al., 1986; (7) Roberts et al., 1986; (8) Semprini et al., 1987; (9) Barber et al., 1988; (10) Mackay et al., 1988; (11) Ball et al., 1989; (12) Mackay et al., unpublished results.

[b] DTBB is 2,6-di-tert-butyl-p-benzoquinone.

[c] nr: not reported.

1985 b

1986a

Source: Mackay, D. Characterization of the Distribution and Behavior of Organic Contaminants in the Subsurface. In Proceedings of a National Research Council Symposium. National Academy Press (in press 1990)

Rocky Mtn Arsenal ⇒ f_{oc} > 0.005% ⇒ $S \cdot K_d C > 10^{-3}$ gms TCE / gm solid i.e. $f_{oc} f_{om}$ TCE > 10^{-3} i.e. no appreciable contribution of TCE to the organic carbon content.

TCE @ sat'n g/l

K_d TCE = 0.2 cm³/g

4-18