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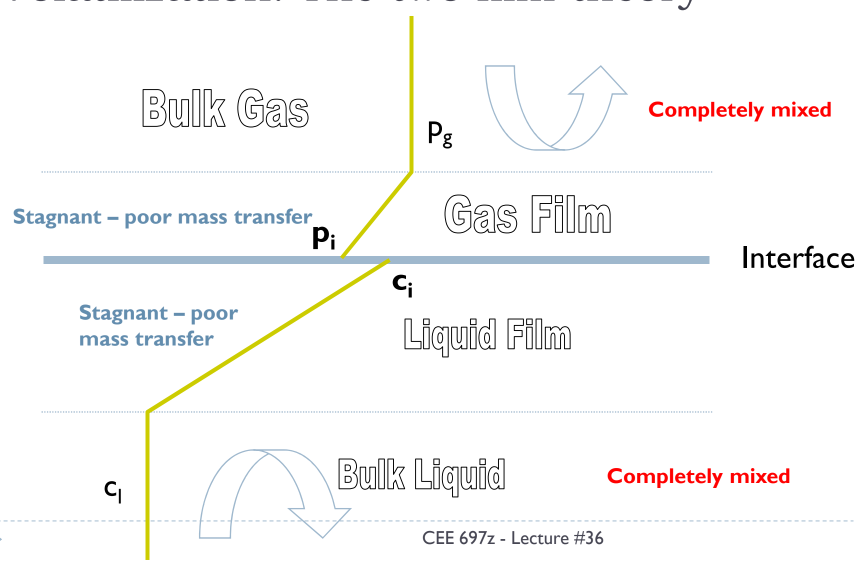
CEE 697z
Organic Compounds in Water and Wastewater

PCBs and other HOCs:
Volatilization & other processes

Lecture #36

Volatilization: The two film theory



Two film model

Universal Gas Law

$$\frac{n}{V} = \frac{P}{RT_a}$$

Molar concentration

- Flux from the bulk liquid to the interface

$$J_l = K_l(c_i - c_l)$$

- Flux from the interface to the bulk gas

Mass transfer velocities (m/d)

$$J_g = \frac{K_g}{RT_a}(p_g - p_i)$$

  - And the K's are related to the molecular diffusion coefficients by:

$$K_l = \frac{D_l}{z_l} \qquad K_g = \frac{D_g}{z_g}$$

Two film theory (cont.)

- We want to be able to relate flux to bulk air and water concentrations
  - interface concentrations cannot be directly measured

$$J = v_v\left(\frac{p_g}{H_e} - c_l\right)$$

- to do this we must substitute expressions for the interface concentrations

Air/Water Equilibrium

- Henry's Law

$$H_e \equiv K_H = \frac{p_i}{x_i}$$

  - or

$$H_e \equiv K_H = \frac{p_i}{c_i}$$

Whitman's 2 film model (cont.)

- According to Henry's law: $p_i = H_e c_i$
- And relating this back to the bulk concentration

$$p_i = H_e\left(\frac{J_l}{K_l} + c_l\right)$$

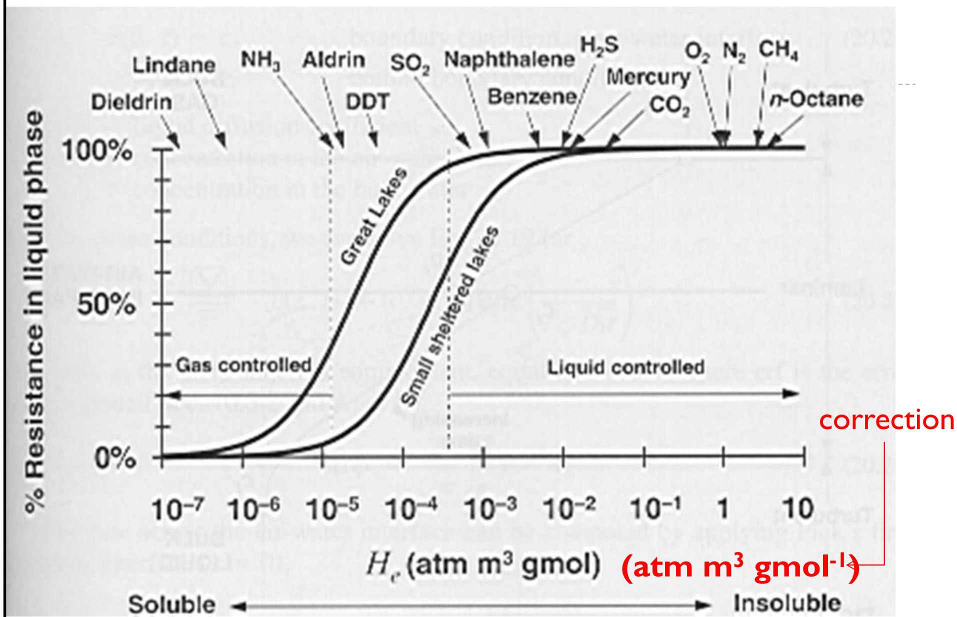
Recall: $J_l = K_l(c_i - c_l)$

So: $c_i = \frac{J_l}{K_l} + c_l$

- now solving and equating the fluxes, we get (pg. 371 in text):

$$\frac{1}{v_v} = \frac{1}{K_l} + \frac{RT_a}{H_e K_g}$$

The net transfer velocity across the air-water interface (m/d) sometimes represented as K_{ol}



- Figure 20.4, page 373 in text.

Two Film Volatilization Model

- Jeremiason's equation $$k_{vol} = \frac{K_{ol}}{h} f_w$$
  - Same as Chapra's $$k_v = \frac{v_v}{H_1} f_{d1}$$
- Where:

$$\frac{1}{K_{ol}} = \frac{RT}{k_a H} + \frac{1}{k_w}$$

Estimating 2-film parameters

- The gas film coefficient

$$k_{a,H_2O} = 0.2u_{10} + 0.3$$

$$k_{a,PCB} = k_{a,H_2O}\left(\frac{D_{PCB,air}}{D_{H_2O,air}}\right)^{0.61}$$

- The liquid film coefficient

$$k_{w,CO_2} = 0.45u_{10}^{1.64}$$

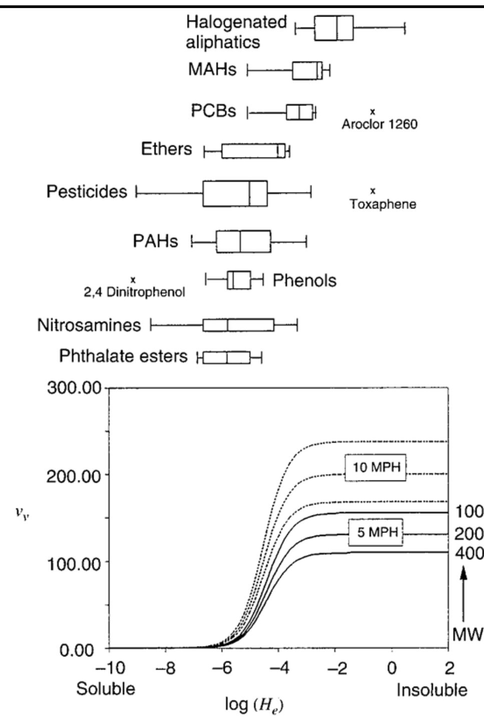
$$k_{w,PCB} = k_{w,CO_2}\left(\frac{Sc_{PCB}}{Sc_{CO_2}}\right)^{-0.5}$$

Kinetic viscosity: molecular diffusivity

- $Sc = \frac{\mu}{\rho . D_v}$ Schmidt Number

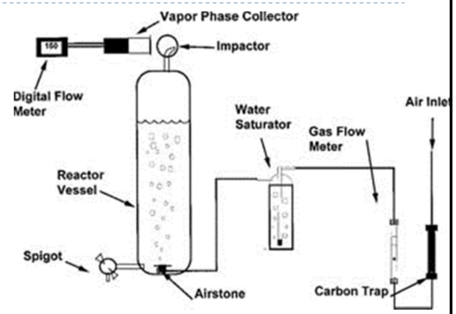
Effect of U_w and H_e

- Chapra, pg. 730



Bamford, H.A., Poster, D.L. and Baker, J.E. (1999) Temperature dependence of Henry's law constants of thirteen polycyclic aromatic hydrocarbons between 4 degrees C and 31 degrees C. Environmental Toxicology and Chemistry 18(9), 1905-1912.

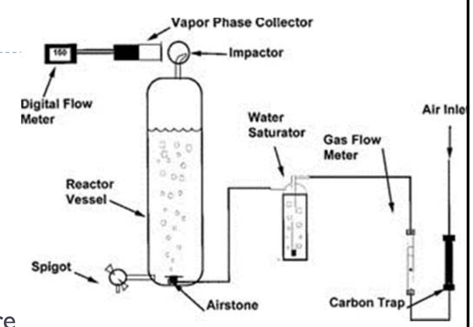
Determination of H_e



- The gas-stripping device:
  - a 122- cm by 15.2-cm diameter glass reactor, a 5-mm glass impactor, a 5-µm pore-size air stone, and a 500-ml glass gas washing bottle.
- Procedure:
  - The apparatus was filled to a depth of 83 cm with 10 L of deionized water.
  - Between 130 ml/min to 200 ml/min of compressed air was passed through a hydrocarbon trap to remove possible contaminants and through a gas washing bottle to saturate the air with water vapor prior to entering the reactor through the air stone mounted at the bottom of the water column.

Bamford, H.A., Poster, D.L. and Baker, J.E. (1999) Temperature dependence of Henry's law constants of thirteen polycyclic aromatic hydrocarbons between 4 degrees C and 31 degrees C. Environmental Toxicology and Chemistry 18(9), 1905-1912.

Det. of H_e (cont.)



- Procedure (cont.):
  - Air exiting the reactor passed through the impactor to remove aerosols created by breaking bubbles, then through a cylindrical polyurethane foam plug (PUF) housed in a glass column to capture vapor-phase compounds.
    - The efficiency and application of PUF to absorb hydrophobic organic contaminants (HOCs) have been evaluated in several studies
  - Water samples (50 ml) were drawn through a Teflon stopcock located at the base of the reactor.
  - During each experiment, simultaneous air and water samples were collected every 24 to 48 h for 6 to 12 d.

Det. of H_e (cont.) with QC

- The entire system was located in a controlled environment room, where the lights remained off during each experiment to minimize any loss of compounds to photodegradation.
- Compound mass balances were determined to insure analytes were not lost to degradation or to leaks in the system
  - Mass recoveries for the compounds ranged between 85% and 112% of the initial mass added.

Bamford, H.A., Poster, D.L. and Baker, J.E. (1999) Temperature dependence of Henry's law constants of thirteen polycyclic aromatic hydrocarbons between 4 degrees C and 31 degrees C. Environmental Toxicology and Chemistry 18(9), 1905-1912.

Bamford, H.A., Poster, D.L. and Baker, J.E. (1999) Temperature dependence of Henry's law constants of thirteen polycyclic aromatic hydrocarbons between 4 degrees C and 31 degrees C. Environmental Toxicology and Chemistry 18(9), 1905-1912.

Det. of H_e - Chemical Analysis

- **Extraction**: The PUF samples were Soxhlet extracted for 24 h with ~150 ml of chromatographic grade petroleum ether. Extracts were reduced to <3 ml by rotary evaporation, switched to hexane, and further concentrated under a gentle stream of clean N_2 to a final volume of ~1 ml. Each water sample was solvent extracted three times with 10 ml of hexane in a separatory funnel, and combined extracts were dried with Na_2SO_4 and reduced by rotary evaporation to ~1 ml in hexane. The concentrated samples were transferred to amber autosampler vials and sealed with Teflon caps and stored in the dark at 4°C until analysis.
- **Analysis**: All compounds were analyzed by GC/MS (HP 5890 GC and HP 5972 Mass Selective Detector) operated in selective ion monitoring (SIM) mode. The column was 30 m in length, 0.25 mm i.d. with a cross linked 5% phenyl-methyl silicone film thickness of 0.25 µm.
  - Identification of individual compounds was based on the retention times of the parent ion of each compound relative to the retention time of a calibration standard. Internal standards, consisting of deuterated compounds were added to the calibration standard and each sample prior to GC/MS analysis. Internal standards were used to calculate relative response factors for each analyte by comparing a known mass of analyte in the calibration standard to the known mass of a particular internal standard.

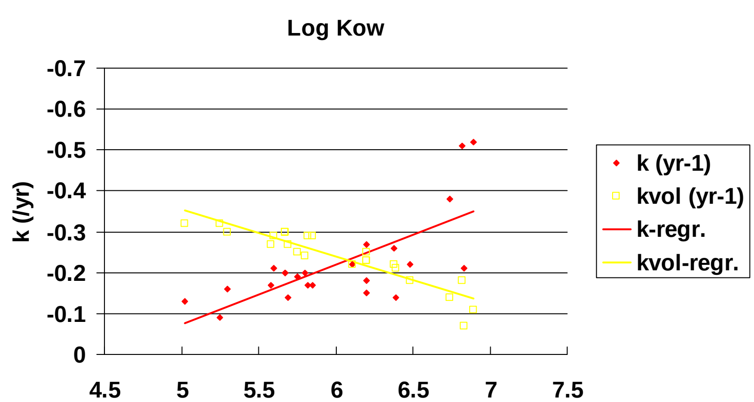
Det. of H_e - Results

Table 1. Henry's Law Constants (K_H) at Different Temperatures in the Range between (4 and 31) °C[a,b] (K_H/Pa·m³·mol⁻¹)

congener[c]	4 °C	11 °C	18 °C	25 °C	31 °C	lit. 25 °C
1	5.13 ± 0.15	8.32 ± 0.18	13.17 ± 0.25	20.43 ± 0.52	29.3 ± 1.1	28.9,[d] 30.2[e]
8	6.010 ± 0.086	9.87 ± 0.10	15.85 ± 0.14	24.89 ± 0.29	36.07 ± 0.60	20.3,[f] 24.9,[d] 30.7[e]
18	8.11 ± 0.14	12.07 ± 0.15	17.64 ± 0.18	25.35 ± 0.34	34.14 ± 0.65	58.1,[d] 25.3,[h] 38.5,[g] 32.0[e]
28	13.13 ± 0.15	19.06 ± 0.15	27.18 ± 0.19	38.14 ± 0.37	50.39 ± 0.71	22.8,[d] 32.0,[g] 29.0,[e] 20.3[h]
29	12.12 ± 0.19	18.04 ± 0.21	26.37 ± 0.27	37.89 ± 0.53	51.03 ± 1.0	25.3,[d] 30.0,[e] 20.3[h]
44	11.86 ± 0.14	16.02 ± 0.13	21.33 ± 0.15	28.05 ± 0.27	35.13 ± 0.48	24.3,[f] 32.8,[d] 23.3[e]
50	28.86 ± 0.72	38.18 ± 0.67	49.84 ± 0.78	64.3 ± 1.4	79.3 ± 2.4	138,[d] 61.8[e]
52	11.34 ± 0.19	16.13 ± 0.19	22.56 ± 0.23	31.07 ± 0.42	40.43 ± 0.77	22.3,[f] 53.2,[d] 34.7,[g] 32.3[e]
66	14.17 ± 0.22	19.80 ± 0.22	27.25 ± 0.26	36.97 ± 0.48	47.51 ± 0.87	84.2,[f] 13.7,[d] 20.5[e]
77	4.46 ± 0.14	6.99 ± 0.16	10.75 ± 0.21	16.20 ± 0.41	22.69 ± 0.81	4.37,[d] 9.52,[g] 10.4[e]
87	12.97 ± 0.29	18.83 ± 0.30	26.86 ± 0.37	37.71 ± 0.69	49.8 ± 1.3	33.4,[f] 19.9,[d] 18.6[e]
101	15.75 ± 0.31	22.20 ± 0.31	30.78 ± 0.34	42.07 ± 0.70	54.4 ± 1.3	32.7,[d] 25.4,[g] 24.9,[e] 9.1[h]
104	39.4 ± 1.0	47.17 ± 0.88	56.00 ± 0.88	66.0 ± 1.4	75.5 ± 2.1	185,[d] 90.9,[g] 75.1[e]
105	3.09 ± 0.12	7.10 ± 0.22	15.73 ± 0.44	33.6 ± 1.3	62.5 ± 3.9	10.1,[e] 5.68[d]
118	7.34 ± 0.23	12.81 ± 0.30	21.79 ± 0.44	36.2 ± 1.0	54.8 ± 2.3	40.5,[f] 12.7,[e] 9.35[d]
126	0.958 ± 0.038	2.82 ± 0.087	7.88 ± 0.22	21.02 ± 0.83	47.0 ± 3.0	8.29,[e] 2.78[d]
128	0.890 ± 0.031	3.224 ± 0.091	10.99 ± 0.30	35.4 ± 1.5	92.3 ± 6.6	50.7,[f] 6.85,[d] 1.3,[h] 3.04,[g] 10.5[e]
138	2.88 ± 0.11	7.50 ± 0.22	18.68 ± 0.49	44.6 ± 1.7	91.1 ± 5.6	48.6,[f] 11.0,[d] 13.2,[e] 2.1[h]
153	6.50 ± 0.19	13.52 ± 0.31	27.2 ± 0.58	52.8 ± 1.6	91.2 ± 4.3	35.5,[f] 17.9,[d] 2.3,[h] 13.4,[g] 16.7[e]
154	17.34 ± 0.50	29.18 ± 0.63	47.85 ± 0.96	76.7 ± 2.2	113.1 ± 4.8	72.1,[e] 58.5[d]
170	0.128 ± 0.004	0.760 ± 0.018	4.139 ± 0.096	20.84 ± 0.80	78.5 ± 5.5	19.3,[d] 8.85,[e] 0.91[h]
180	0.425 ± 0.012	2.025 ± 0.046	8.96 ± 0.20	37.0 ± 1.3	118.5 ± 7.8	30.4,[d] 10.9,[e] 1.01[h]
187	3.034 ± 0.099	8.72 ± 0.23	23.84 ± 0.57	62.2 ± 2.2	136.7 ± 8.2	42.2,[d] 20.5[e]
188	15.77 ± 0.47	31.39 ± 0.74	60.5 ± 1.4	113.1 ± 4.0	188.6 ± 10.4	44.9,[e] 113[d]
195	0.079 ± 0.003	0.485 ± 0.015	2.724 ± 0.088	14.13 ± 0.78	54.5 ± 5.5	12.0,[e] 12.8,[d] 1.1[h]
201	1.069 ± 0.032	5.14 ± 0.13	22.98 ± 0.59	95.8 ± 4.4	308 ± 29	13.2,[e] 64.5,[d] 1.7[h]

[a] Predicted Henry's law constants from the linear regression analysis of measured ln $K_{H'}$ versus the reciprocal temperature. [b] 95% Working–Hotelling simultaneous confidence bounds[27] for linearly predicted Henry's law constants. [c] Congeners are listed in order of IUPAC number. [d] Burkhard et al., 1985.[17] [e] Dunnivant et al., 1992.[32] [f] Murphy et al., 1983.[31] [g] Dunnivant et al., 1988.[34] [h] Brunner et al., 1990.[33]

Volatilization vs overall loss rate



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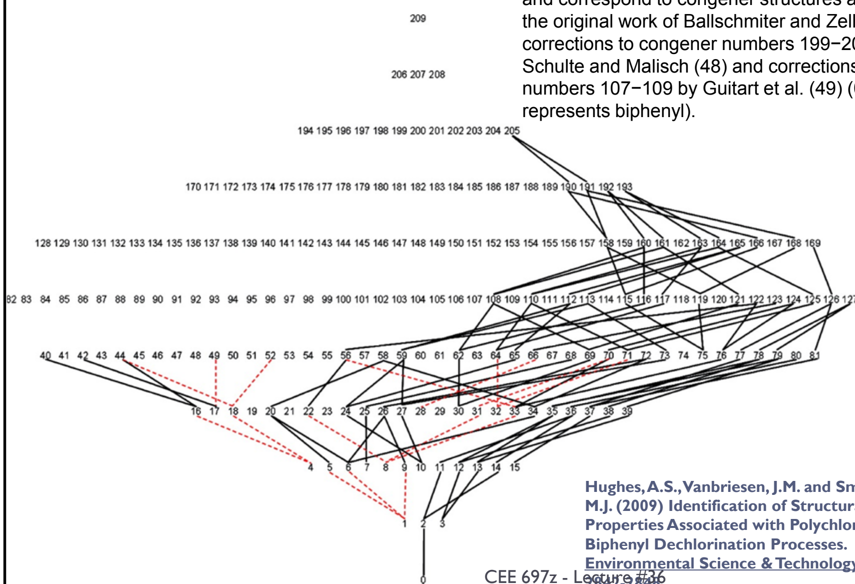
Explicitly reported pathways (dashed lines) and pathways added to dechlorination process M through the classification tree analysis (solid lines). Note that the numbers are arranged by homologue and correspond to congener structures assigned in the original work of Ballschmiter and Zell (47) with corrections to congener numbers 199−201 by Schulte and Malisch (48) and corrections to numbers 107−109 by Guitart et al. (49) (0 represents biphenyl).



Hughes, A.S., Vanbriesen, J.M. and Small, M.J. (2009) Identification of Structural Properties Associated with Polychlorinated Biphenyl Dechlorination Processes. Environmental Science & Technology 44(8), 2842-2848.

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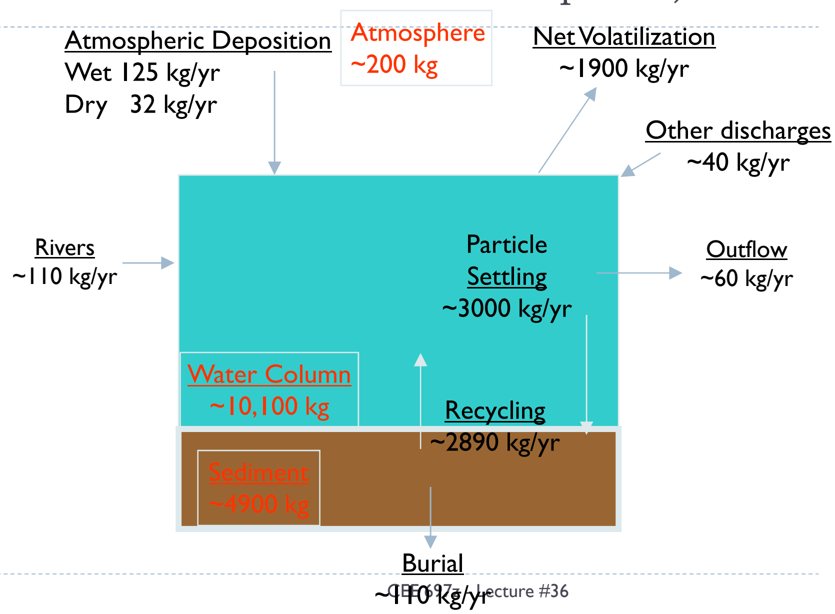
PCB Mass Balance in Lake Superior, 1986



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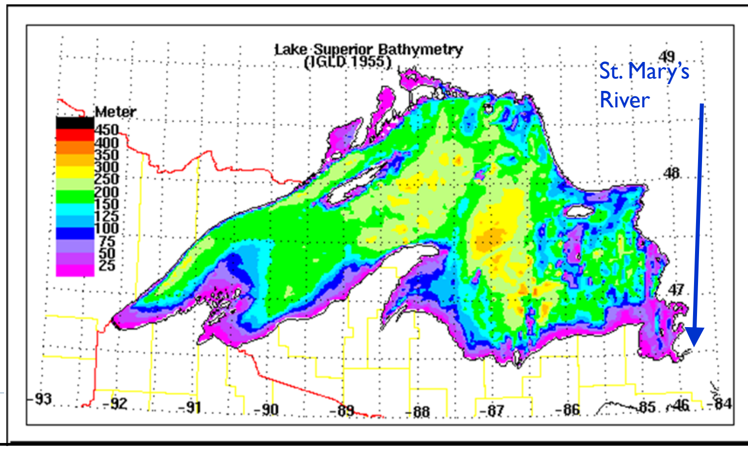
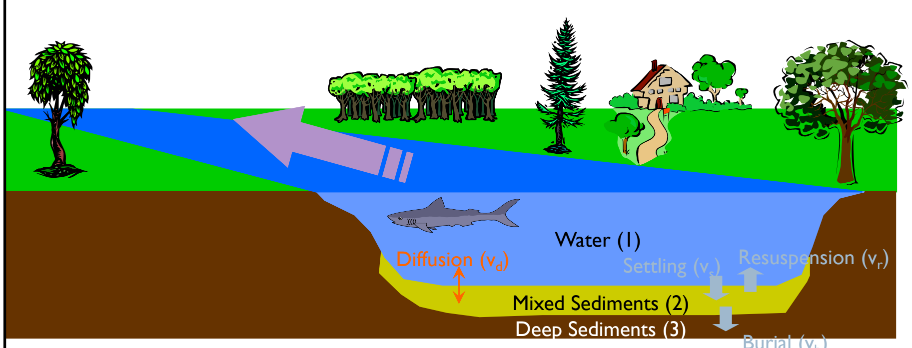
PCBs in the Lake Superior

- Reference: "PCBs in Lake Superior, 1978-1992: Decrease in Water Concentrations Reflect Loss by Volatilization," by Jeremiason, Hornbuckle and Eisenreich, Environmental Science and Technology, 28:903 (1994)

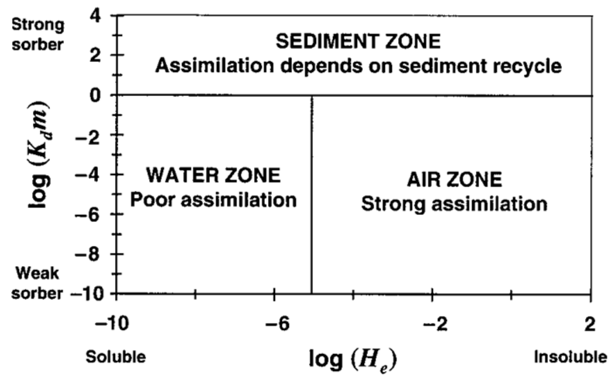


Full 1, 2 or 3-d mechanistic model

- Combine with advective flow



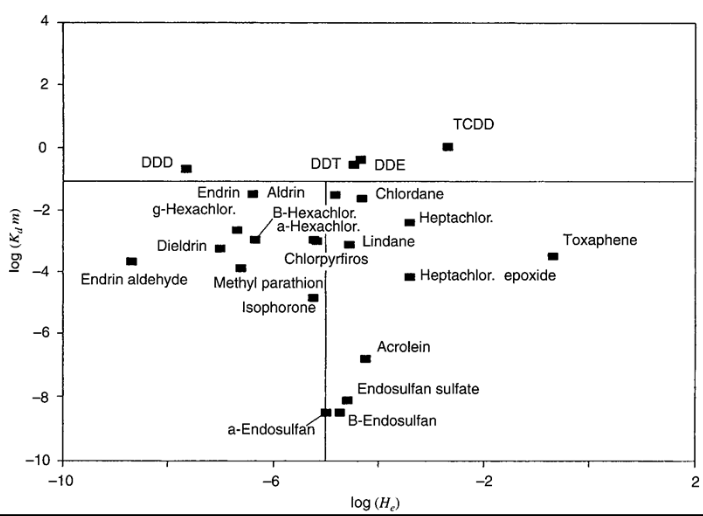
Summary of sorption & volatilization effects



- Assume
  - T_a=283 K
  - M=200 g/mole
  - U_w = 5 mph
  - v_s =91 m/yr
- Assimilation refers to general rate of removal

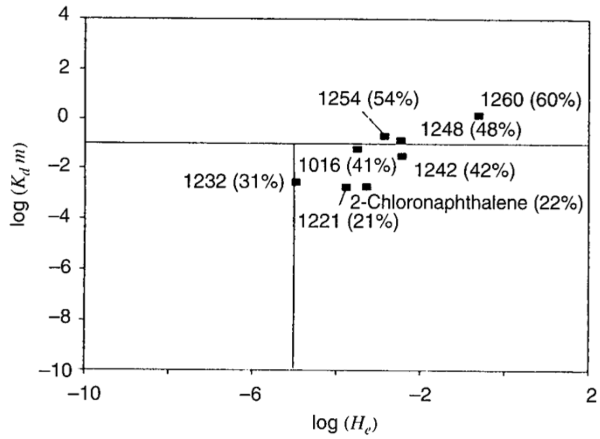
Summary: pesticides

- Chapra, pg.735



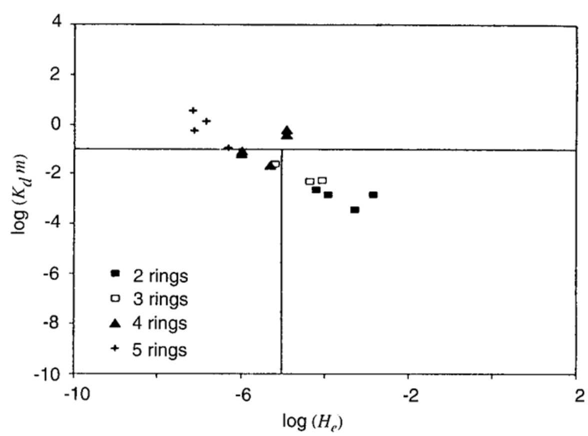
Summary: PCBs

- Chapra, pg.736



Summary: PAHs

- Chapra, pg.736



Conclusions on PCB fate

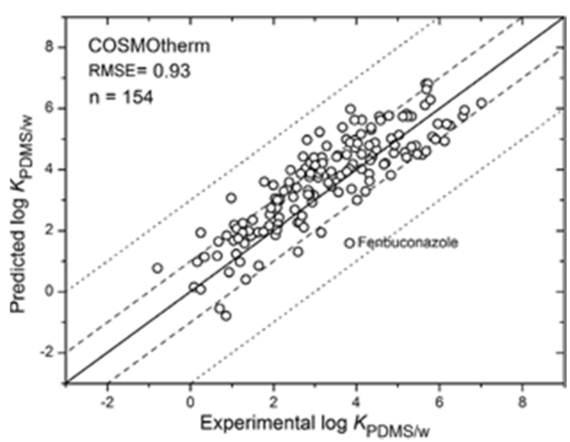
The environmental fate and transport of PCBs is largely governed by their physical-chemical characteristics, properties which vary considerable across the spectrum of species included in this family of chemicals. Chief among these properties are the octanol-water partition coefficient, a measure of the potential to associate with particles, and the Henry's Law constant, a reflection of the partitioning of the chemical between air and water. In general, high MW PCBs are strongly associated with particles and low MW PCBs are more strongly partitioned to the atmosphere.

As a result, fish consumption advisories are common in Michigan and other states.

▲ Unlimited consumption.
● One meal per month.
▼ One meal per week.
■ Six meals per year.
◆ Do not eat these fish.

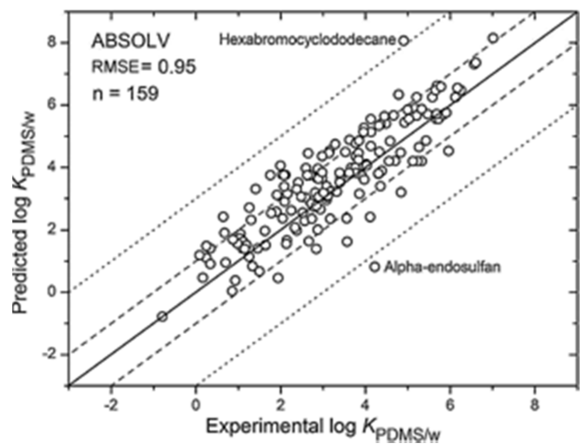
Water body	Species	Contaminant(s)	General Population – Length (inches) 6-8	8-10	10-12	12-14	14-18	18-22	22-26	26-30	30 +	Women & Children – Length (inches) 6-8	8-10	10-12	12-14	14-18	18-22	22-26	26-30	30 +
Detroit River	Carp	PCBs, Dioxin	◆	◆	◆	◆	◆	◆	◆	◆	◆	◆	◆	◆	◆	◆	◆	◆	◆	◆
	Freshwater Drum	Mercury, PCBs	▲	▲	▲	▲	▼	▼	▼	▼	▼	●	●	●	●	●	●	●	●	●
	Northern Pike	PCBs							▲	▲	▲							●	●	●
	Redhorse Sucker	PCBs	▲	▲	▲	▲	▲	▲	▲	▲		●	●	●	●	■	■	■	■	
	Walleye	PCBs				▲	▲	▲	▲	▲	▲				●	●	●	●	●	●
	Yellow Perch	PCBs	▲	▲	▲	▲	▲					▼	▼	▼	▼	▼				

Prediction of partition coefficients for complex environmental contaminants: Validation of COSMOtherm, ABSOLV, and SPARC



Stenzel, A., Goss, K.U. and Endo, S. (2014) Prediction of Partition Coefficients for Complex Environmental Contaminants: Validation of COSMOTHERM, ABSOLV, and SPARC. Environmental Toxicology and Chemistry 33(7), 1537-1543.

Prediction of partition coefficients for complex environmental contaminants: Validation of COSMOtherm, ABSOLV, and SPARC



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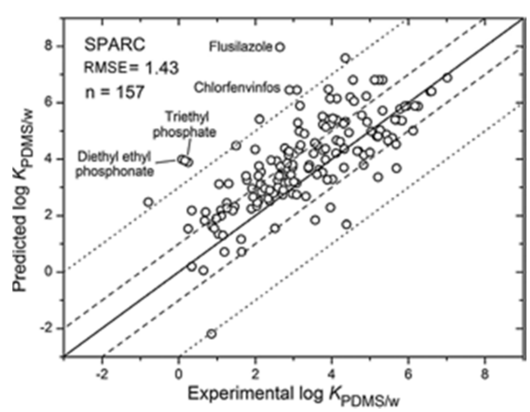
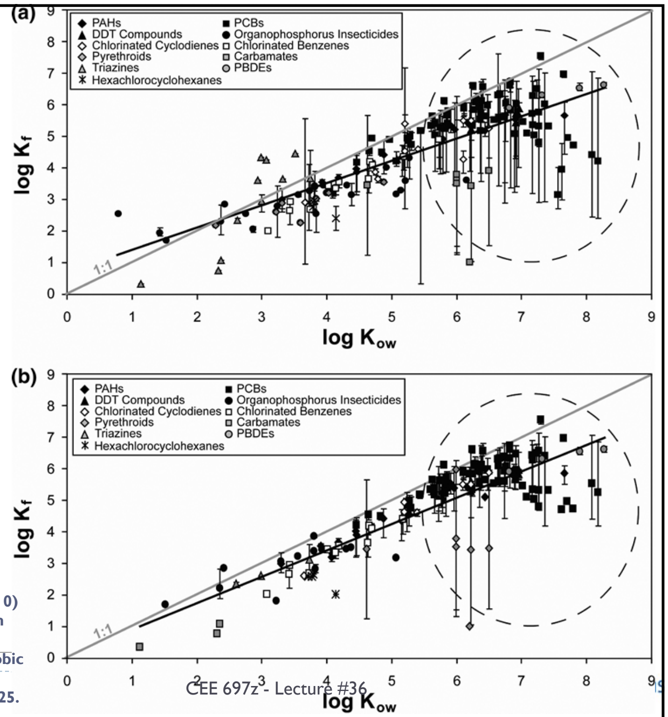


Stenzel, A., Goss, K.U. and Endo, S. (2014) Prediction of Partition Coefficients for Complex Environmental Contaminants: Validation of COSMOTHERM, ABSOLV, and SPARC. Environmental Toxicology and Chemistry 33(7), 1537-1543.

(a) Plot of log *Kow* versus log *Kf* for all data. The plotted log *Kf* values are the average of all published data for compounds listed in Table SI-1. Bars indicate the range in data. The black line is the linear regression between log *Kf* and log *Kow* for all of the data (log*Kf* = 0.70log*Kow* + 0.70; *R*2 = 0.65). The dashed circle illustrates the region with the highest range in log *Kf* values (log *Kow* ≥ 5.5). (b) Plot of log *Kow* versus log *Kf* for all passing data. The plotted log *Kf* values are the average of all passing published data for the compounds listed in Table SI-1. Bars indicate the range in data. The black line is the linear regression between log *Kf* and log *Kow* for all of the passing data (log*Kf* = 0.83log*Kow* + 0.07; *R*2 = 0.73). The dashed circle illustrates the region with the highest range in log *Kf* values (log *Kow* ≥ 5.5).



Difilippo, E.L. and Eganhouse, R.P. (2010) Assessment of PDMS-Water Partition Coefficients: Implications for Passive Environmental Sampling of Hydrophobic Organic Compounds. Environmental Science & Technology 44(18), 6917-6925.

- The End