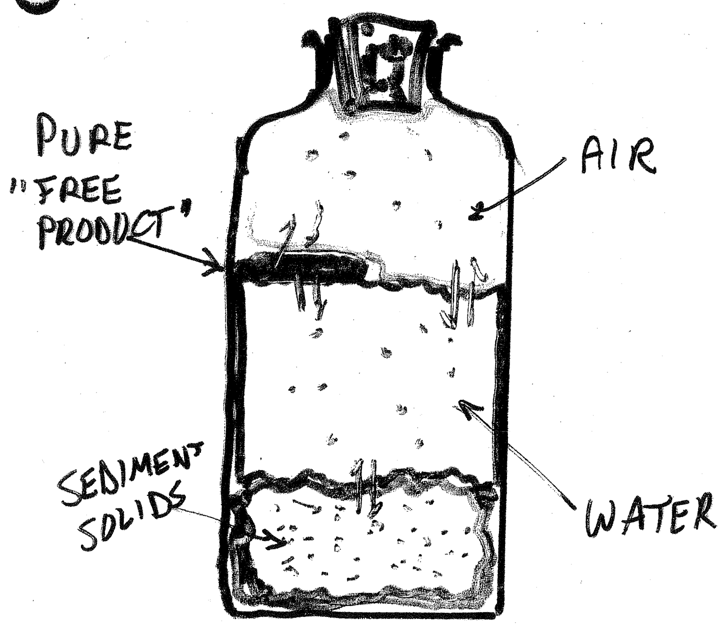
COMMON THREAD AMONG ALL PARTIONING LAWS:

A chemical is trying to achieve its lowest energy state

MORE PRECISELY:

Molecules spontaneously settle into the arrangement that has the lowest free energy



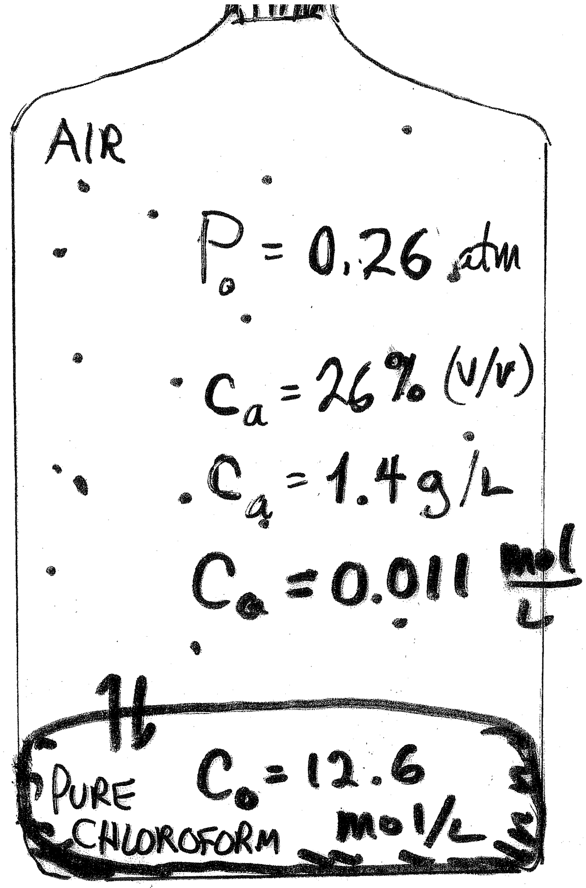
EXAMPLE:

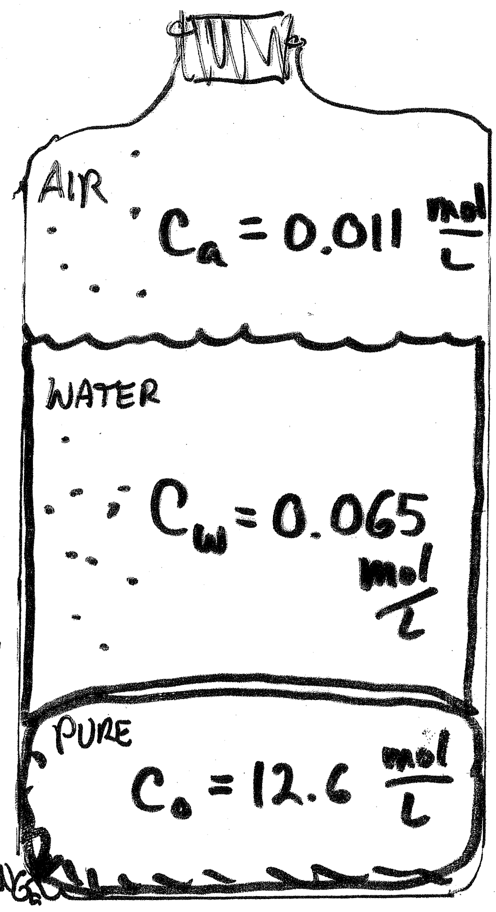
In this bottle at equilibrium we observe <u>very different</u> amounts and concentrations in the four possible phases

yet...

The rule above means the molecules must be "equally happy" in each phase (all at lowest G)

CHLOROFORM
$CHCl_3$



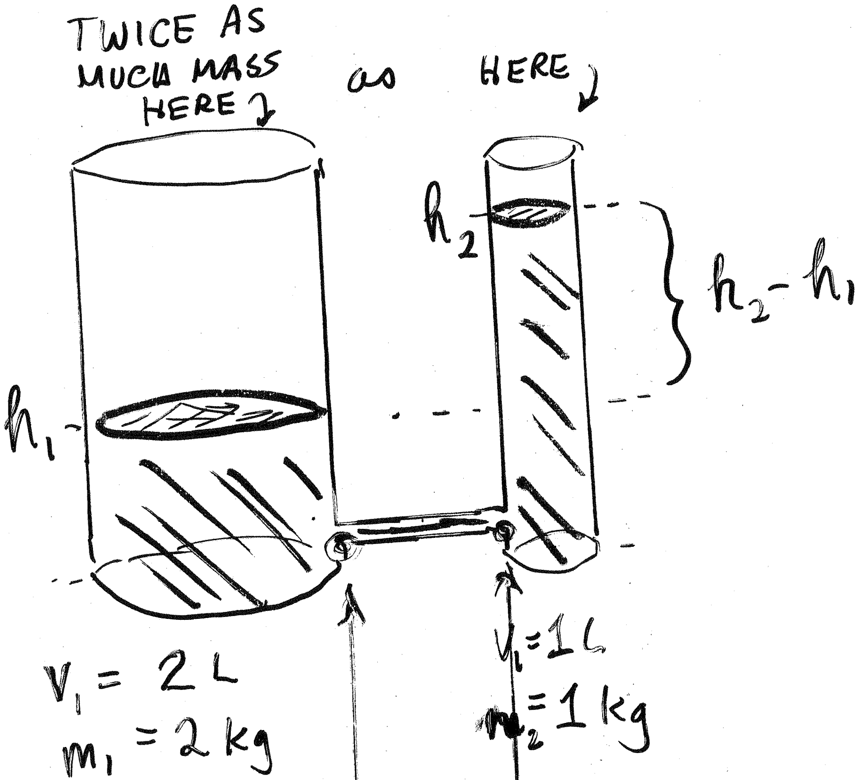


See how different the conc. is in each phase..

yet there is no tendency for these to change

NO DRIVING FORCE FOR CHANGE

OR NO POTENTIAL DRIVING A CHANGE



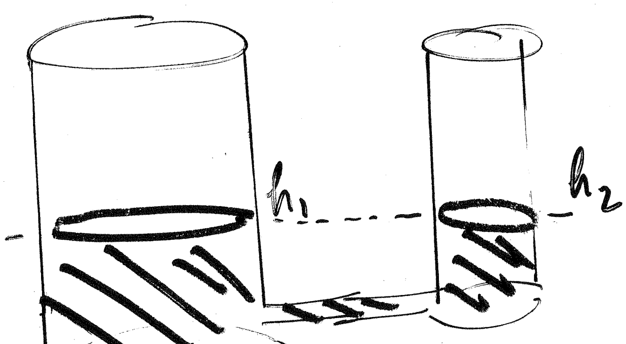
WHICH WAY WILL MASS FLOW TO SPONTANEOUSLY GET TO LOWEST ENERGY LEVEL (EQUILIBRIUM?)

From Greater mass to lesser mass?

-OR-

From lesser mass to greater mass

BUT $p_1 = \rho g h_1 < p_2 = \rho g h_2$



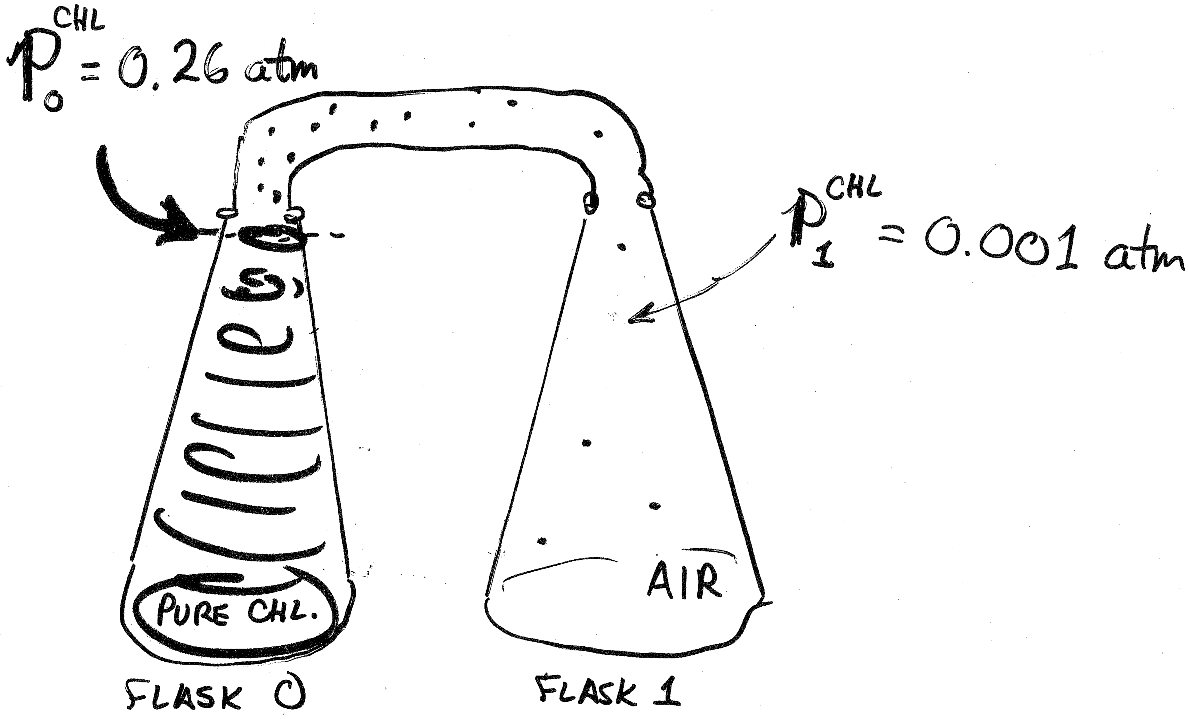
AT EQUILIBRIUM

$$\rho g h_1 = \rho g h_2$$

BUT $m_1 > m_2$

CONCLUSION:

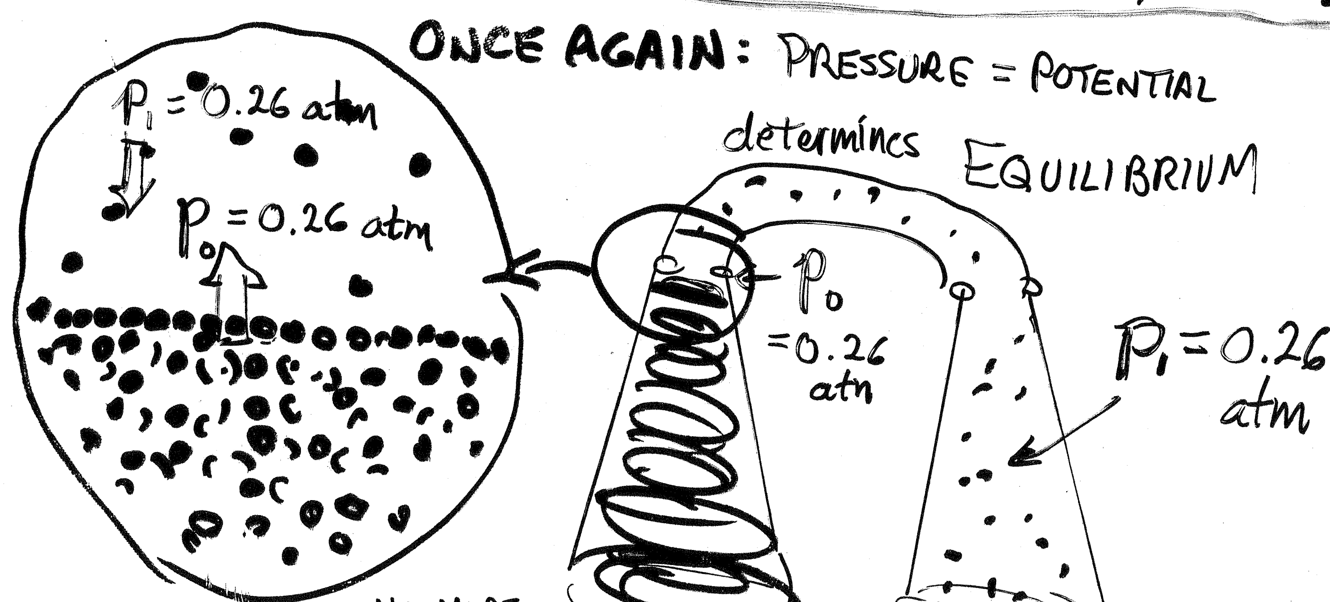
- Mass does not matter
- PRESSURE matters
- PRESSURE IS force driving to EQUILIBRIUM
- PRESSURE = POTENTIAL (ENERGY)



$P_0^{CHL} \gg P_1^{CHL}$

WHICH WAY DOES CHLOROFORM SPONTANEOUSLY FLOW TO GET TO LOWEST ENERGY LEVEL?

ONCE AGAIN: PRESSURE = POTENTIAL determines EQUILIBRIUM



NO MORE FLOW, EVEN THOUGH: $m_0 \gg m_1$

Hence, convenient to express this CHEMICAL POTENTIAL in units of PRESSURE (Atm, Pa, kPa): FUGACITY "TENDENCY TO FLEE"

In vapor phase this is obvious

LESS obvious, but still useful, in aqueous or solid phases.

E.g. "pressure of benzene dissolved in H_2O"

CONCENTRATION = [FUGACITY CAPACITY CONSTANT] x [FUGACITY]

$$C_i = Z_i f$$

Ex: In air $pV = nRT$

$$p = \left(\frac{n}{V}\right)RT = \text{fugacity}$$

↑ c (molar)

$$\left(\frac{n}{V}\right) = C_{air} = \left[\frac{1}{RT}\right] p \qquad Z = \frac{1}{RT}$$

-OR-

$$C_{air} = H C_w$$

↑

Express as PARTIAL PRESSURE

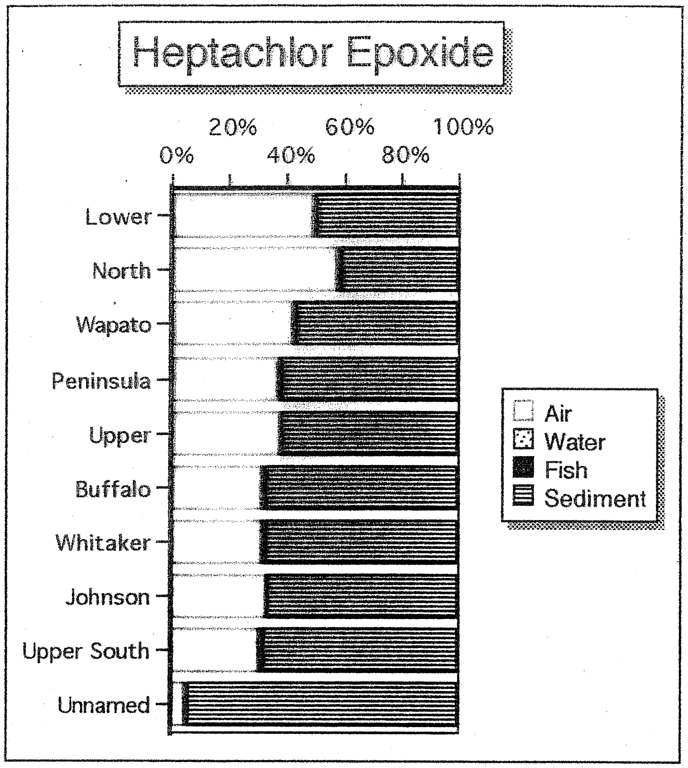
$$C_w = \left(\frac{1}{H}\right) P_{air}$$

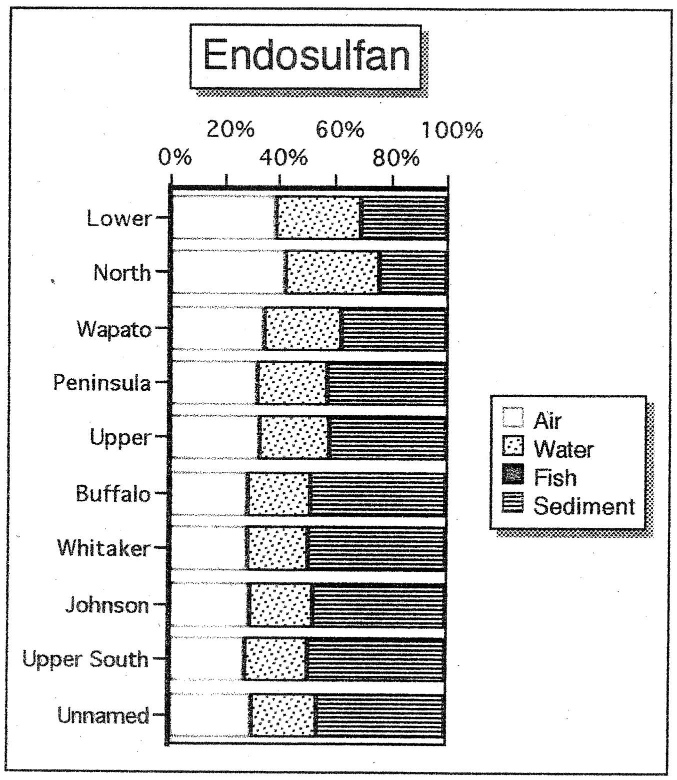
$$\therefore Z_w = \frac{1}{H}$$

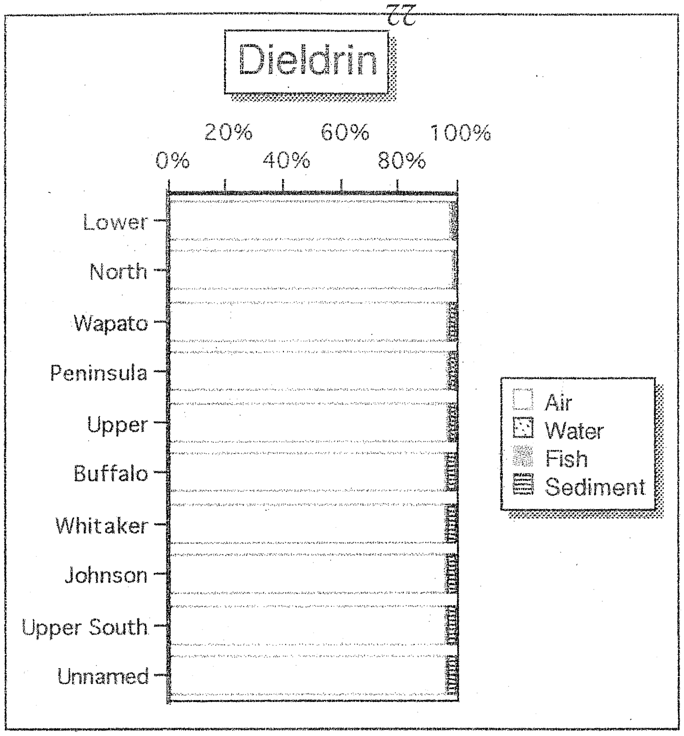
etc...
(p. 55, text)

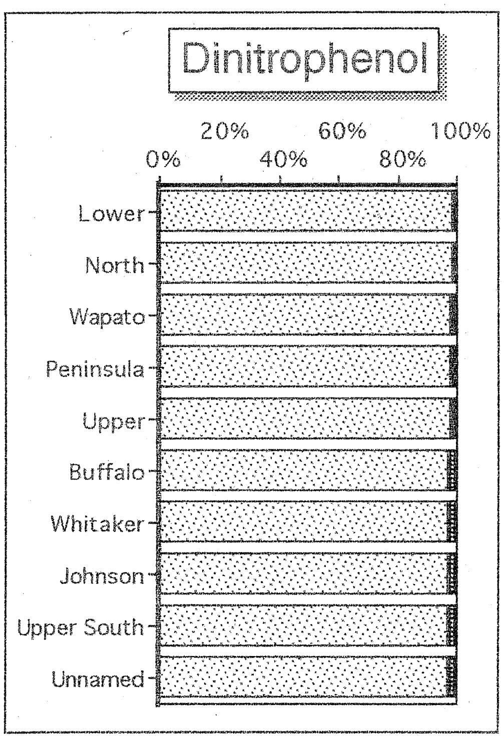
"FUGACITY", per se, tells us nothing new

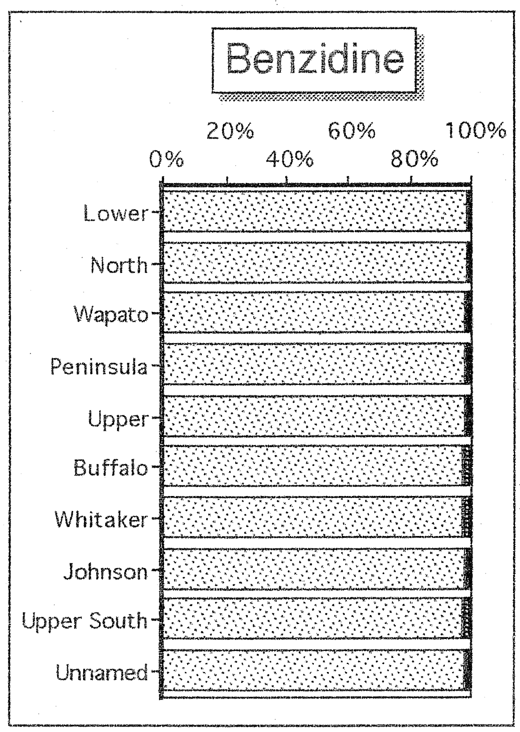
BUT CAN BE USEFUL CONCEPTUAL FRAMEWORK for thinking about partitioning

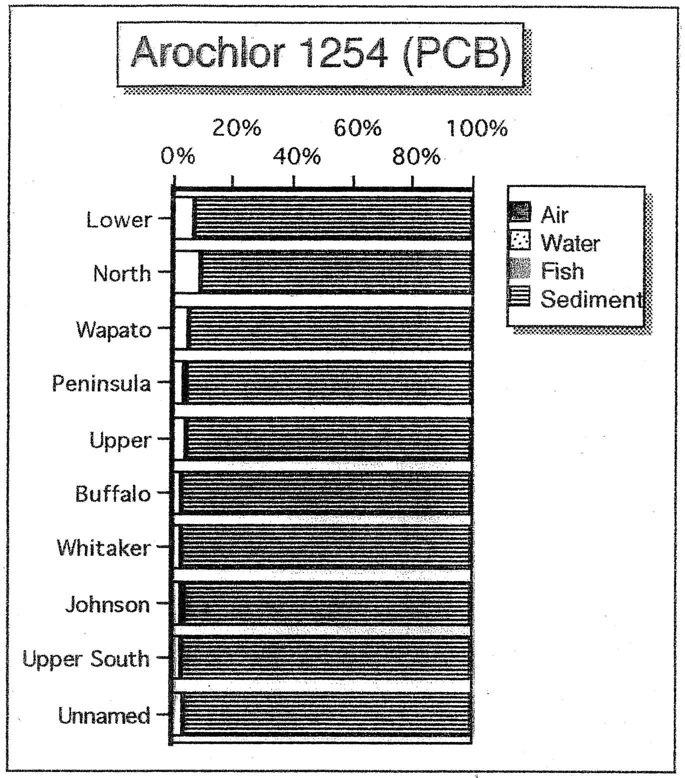

Heptachlor Epoxide
0%
20%
40%
60%
80%
100%
Lower
North
Wapato
Peninsula
Upper
Buffalo
Whitaker
Johnson
Upper South
Unnamed
Air
Water
Fish
Sediment

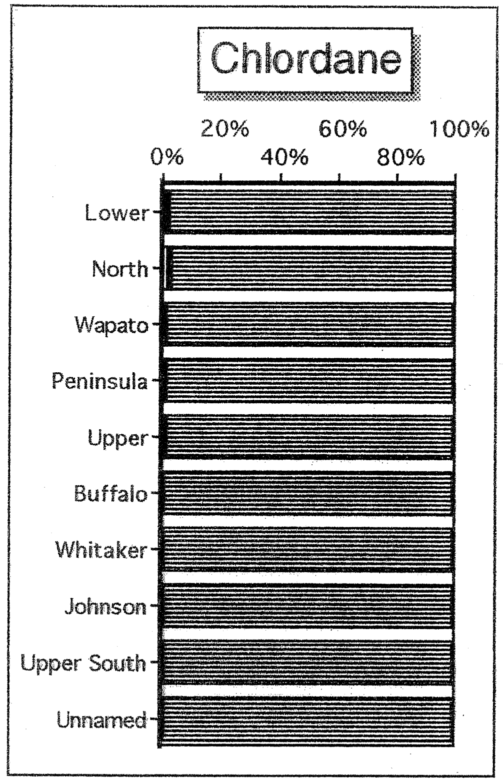

Endosulfan
0%
20%
40%
60%
80%
100%
Lower
North
Wapato
Peninsula
Upper
Buffalo
Whitaker
Johnson
Upper South
Unnamed
Air
Water
Fish
Sediment

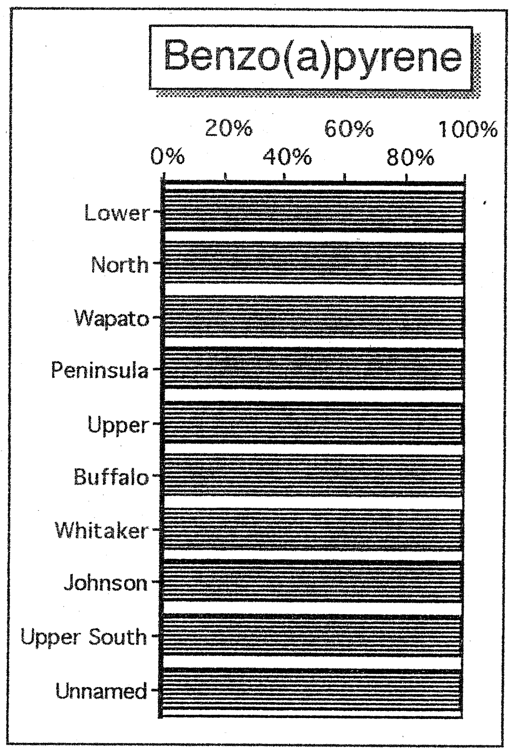

Dieldrin
0%
20%
40%
60%
80%
100%
Lower
North
Wapato
Peninsula
Upper
Buffalo
Whitaker
Johnson
Upper South
Unnamed
Air
Water
Fish
Sediment


Dinitrophenol
0%
20%
40%
60%
80%
100%
Lower
North
Wapato
Peninsula
Upper
Buffalo
Whitaker
Johnson
Upper South
Unnamed


Benzidine
0%
20%
40%
60%
80%
100%
Lower
North
Wapato
Peninsula
Upper
Buffalo
Whitaker
Johnson
Upper South
Unnamed


Arochlor 1254 (PCB)
0%
20%
40%
60%
80%
100%
Lower
North
Wapato
Peninsula
Upper
Buffalo
Whitaker
Johnson
Upper South
Unnamed
Air
Water
Fish
Sediment


Chlordane
0%
20%
40%
60%
80%
100%
Lower
North
Wapato
Peninsula
Upper
Buffalo
Whitaker
Johnson
Upper South
Unnamed


Benzo(a)pyrene
0%
20%
40%
60%
80%
100%
Lower
North
Wapato
Peninsula
Upper
Buffalo
Whitaker
Johnson
Upper South
Unnamed