Marine Organic Geochemistry:
Introduction to organic chemicals of environmental concern

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Outline

- Review some of the major organic compounds that have or may have impacted the environment including:
  - -general background on PCBs, DDT, chlorinated dioxins/furans, PBDEs, and PAHs.
  - -structures and physical/chemical properties.
  - -analytical chemistry.
  - -behavior in the environment and animal tissues.

History of industrial chlorination

- Scheele discovered chlorine in 1774.
- Over the past century, chlorine gas has been produced by the chlor-alkali process:

$$2NaCl + 2H_2O \rightarrow 2NaOH + H_2 + Cl_2$$

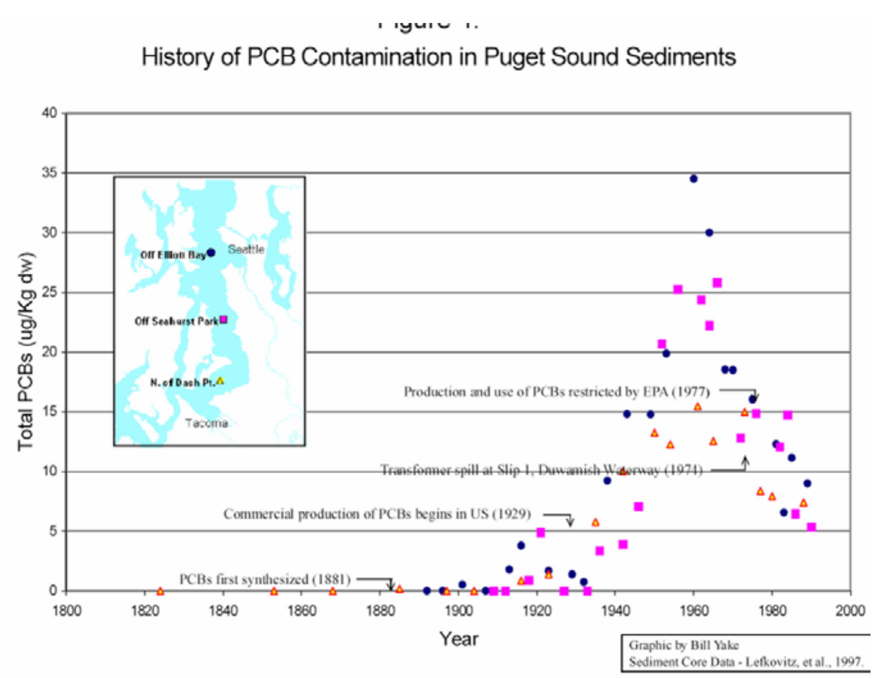
  - Originally, manufacturers were only interested in the NaOH and had to develop uses for the Cl_2 gas produced.
  - Some of the original uses were as chemical weapons. Cl_2 gas was used in World War I as well as dichlorodiethyl sulfide.
  - Later in the later 1920s and 1930s, industry began to manufacture polychlorinated biphenyls (PCBs), chlorofluorocarbons (CFCs or Freons), and *p,p*-dichlorodiphenyltrichloroethane (*p,p*-DDT, generally called DDT). These compounds made a major impact on society, especially DDT.

The United Nations: "Dirty Dozen" Persistent Organic Pollutants (POPs)

Compound	Year of entry	Σ world production (tons)	Usage
Aldrin	1949	240,000	insecticide
Chlordane	1945	70,000	insecticide
DDT	1942	3 million	insecticide
Dieldrin	1948	240,000	insecticide
Endrin	1951	4,000	rodenticide/insecticide
Heptachlor	1948	~1,000	insecticide
Hexachlorobenzene	1945	1 to 2 million	fungicide
Mirex	1959	No data	insecticide
Toxaphene	1948	1.3 million	insecticide
PCBs	1929	1 to 2 million	industrial chemical
Chlorinated dioxins	?	?	never produced purposely
Chlorinated furans	?	?	never produced purposely

General Background on PCBs

- Polychlorinated biphenyls (PCBs) are a class of 209 organic compounds. Each one is often called a congener.
- Only ~140 congeners of the 209 are found in the environment.
- Sold in the U.S. as mixtures called Aroclors (Monsanto) from 1929 to 1978. In other countries, they were sold under the tradenames: Clophens (Germany), Phenoclors (Italy), etc.
- Used as dielectric & heat transfer fluids, in lubricating and cutting oils, pesticides, paints, sealants, and plastics
- Incredibly stable compounds.



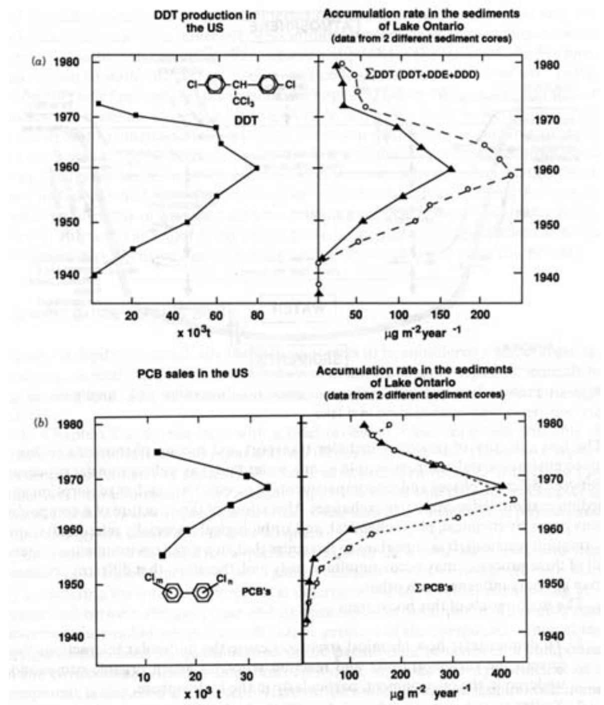
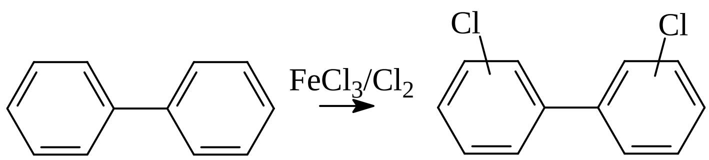


Table 1
Total PCB production in t as reported in the literature

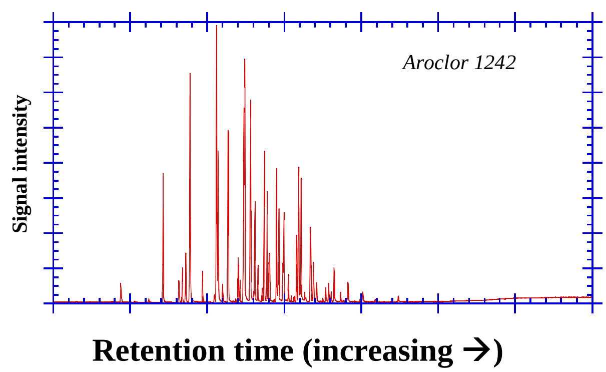
Producer	Country	Start	Stop	Amount	Reference
Monsanto	USA	1930	1977	641 246	de Voogt and Brinkman (1989)
Geneva Ind.	USA	1971	1973	454	de Voogt and Brinkman (1989)
Kanegafuchi	Japan	1954	1972	56 326	Tatsukawa (1976)
Mitsubishi	Japan	1969	1972	2461	Tatsukawa (1976)
Bayer AG	West Germany	1930	1983	159 062	de Voogt and Brinkman (1989)
Prodelec	France	1930	1984	134 654	de Voogt and Brinkman (1989)
S.A. Cros	Spain	1955	1984	29 012	de Voogt and Brinkman (1989)
Monsanto	U.K.	1954	1977	66 542	de Voogt and Brinkman (1989)
Caffaro	Italy	1958	1983	31 092	de Voogt and Brinkman (1989)
Chemko	Czechoslovakia	1959	1984	21 482	Schlosserová (1994)
Orgsteklo	USSR (Russia)	1939	1990	141 800	AMAP (2000)
Orgsintez	USSR (Russia)	1972	1993	32 000	AMAP (2000)
Xi'an	China	1960	1979	8000	Jiang et al. (1997)
Total		1930	1993	1 324 131	

Synthesis of PCBs



Degree of chlorination depended on the length of the reaction.
The longer the reaction, the more chlorines were added to the biphenyl.
Key point is that this reaction did not create one congener but complex mixtures of PCBs.

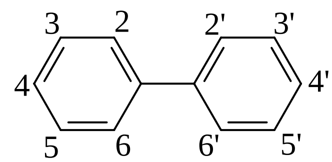
Gas chromatogram (capillary) of Aroclor 1242



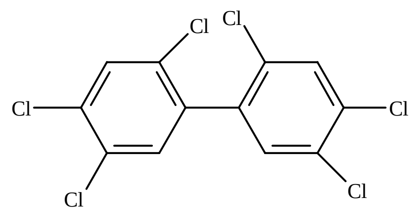
---Many congeners in an Aroclor mixture.

PCBs nomenclature

- In the US, mixtures of PCBs were sold as Aroclors by Monsanto. The main products were Aroclor 1242, 1254, and 1260.
- The "12" comes for the number of carbons on the biphenyl. The last two numbers indicate the mass percentage of Cl in the PCB mixtures. Hence, Aroclor 1260 is 60% chlorine by mass and it contains more chlorinated congeners than Aroclor 1242, etc.
- Individual congeners are numbered after a simple system, which is also used for other contaminants (dioxins, PBDEs, etc).



General numbering system



2,2',4,4',5,5'-hexachlorobiphenyl
(Shorthand CB-153; PCB-153, or 153)

Key Point on PCBs and many other halogenated organic hydrocarbons

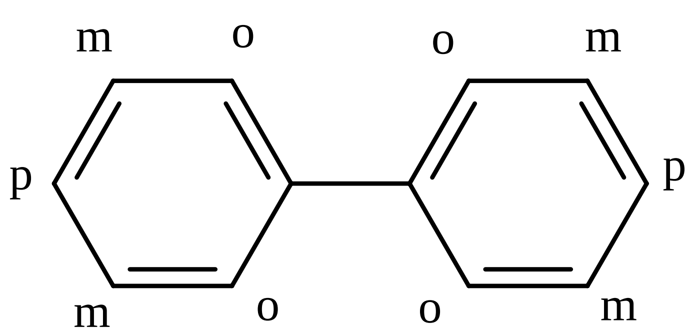
- While PCBs are one distinct group, all 209 congeners have wide ranging physical and chemical properties, which in turn can affect environmental fate and biological activity. Very subtle differences in the placement of a chlorine on the biphenyl structure can be dramatic in effects.
- It is essential that we think about these compounds on a congener-specific basis!!!

Table 1. IUPAC numbers and chlorine atom positions of all PCB congeners *(1)* [a]

No.	Structure	No.	Structure	No.	Structure	No.	Structure
1	2	56	2,3,3',4'	111	2,3,3',5,5'	166	2,3,4,4',5,6
2	3	57	2,3,3',5	112	2,3,3',5,6	167**	2,3',4,4',5,5'
3	4	58	2,3,3',5'	113	2,3,3',5',6	168	2,3',4,4',5',6
4	2,2'	59	2,3,3',6	114**	2,3,4,4',5	169*	3,3',4,4',5,5'
5	2,3	60	2,3,4,4'	115	2,3,4,4',6	170***	2,2',3,3',4,4',5
6	2,3'	61	2,3,4,5	116	2,3,4,5,6	171	2,2',3,3',4,4',6
7	2,4	62	2,3,4,6	117	2,3,4',5,6	172	2,2',3,3',4,5,5'
8	2,4'	63	2,3,4',5	118**	2,3',4,4',5	173	2,2',3,3',4,5,6
9	2,5	64	2,3,4',6	119	2,3',4,4',6	174	2,2',3,3',4,5,6'
10	2,6	65	2,3,5,6	120	2,3',4,5,5'	175	2,2',3,3',4,5',6
11	3,3'	66	2,3',4,4'	121	2,3',4,5',6	176	2,2',3,3',4,6,6'
12	3,4	67	2,3',4,5	122	2',3,3',4,5	177	2,2',3,3',4',5,6
13	3,4'	68	2,3',4,5'	123**	2',3,4,4',5	178	2,2',3,3',5,5',6
14	3,5	69	2,3',4,6	124	2',3,4,5,5'	179	2,2',3,3',5,6,6'
15	4,4'	70	2,3',4',5	125	2',3,4,5,6'	180***	2,2',3,4,4',5,5'
16	2,2',3	71	2,3',4',6	126*	3,3',4,4',5	181	2,2',3,4,4',5,6
17	2,2',4	72	2,3',5,5'	127	3,3',4,5,5'	182	2,2',3,4,4',5,6'
18	2,2',5	73	2,3',5',6	128	2,2',3,3',4,4'	183	2,2',3,4,4',5',6
19	2,2',6	74	2,4,4',5	129	2,2',3,3',4,5	184	2,2',3,4,4',6,6'
20	2,3,3'	75	2,4,4',6	130	2,2',3,3',4,5'	185	2,2',3,4,5,5',6
21	2,3,4	76	2',3,4,5	131	2,2',3,3',4,6	186	2,2',3,4,5,6,6'
22	2,3,4'	77*	3,3',4,4'	132	2,2',3,3',4,6'	187	2,2',3,4',5,5',6
23	2,3,5	78	3,3',4,5	133	2,2',3,3',5,5'	188	2,2',3,4',5,6,6'
24	2,3,6	79	3,3',4,5'	134	2,2',3,3',5,6	189**	2,3,3',4,4',5,5'
25	2,3',4	80	3,3',5,5'	135	2,2',3,3',5,6'	190	2,3,3',4,4',5,6
26	2,3',5	81	3,4,4',5	136	2,2',3,3',6,6'	191	2,3,3',4,4',5',6
27	2,3',6	82	2,2',3,3',4	137	2,2',3,4,4',5	192	2,3,3',4,5,5',6
28	2,4,4'	83	2,2',3,3',5	138	2,2',3,4,4',5'	193	2,3,3',4',5,5',6
29	2,4,5	84	2,2',3,3',6	139	2,2',3,4,4',6	194	2,2',3,3',4,4',5,5'
30	2,4,6	85	2,2',3,4,4'	140	2,2',3,4,4',6'	195	2,2',3,3',4,4',5,6
31	2,4',5	86	2,2',3,4,5	141	2,2',3,4,5,5'	196	2,2',3,3',4,4',5,6'
32	2,4',6	87	2,2',3,4,5'	142	2,2',3,4,5,6	197	2,2',3,3',4,4',6,6'
33	2',3,4	88	2,2',3,4,6	143	2,2',3,4,5,6'	198	2,2',3,3',4,5,5',6
34	2',3,5	89	2,2',3,4,6'	144	2,2',3,4,5',6	199	2,2',3,3',4,5,6,6'
35	3,3',4	90	2,2',3,4',5	145	2,2',3,4,6,6'	200	2,2',3,3',4,5',6,6'
36	3,3',5	91	2,2',3,4',6	146	2,2',3,4',5,5'	201	2,2',3,3',4',5,5',6
37	3,4,4'	92	2,2',3,5,5'	147	2,2',3,4',5,6	202	2,2',3,3',5,5',6,6'
38	3,4,5	93	2,2',3,5,6	148	2,2',3,4',5,6'	203	2,2',3,4,4',5,5',6
39	3,4',5	94	2,2',3,5,6'	149	2,2',3,4',5',6	204	2,2',3,4,4',5,6,6'
40	2,2',3,3'	95	2,2',3,5',6	150	2,2',3,4',6,6'	205	2,3,3',4,4',5,5',6
41	2,2',3,4	96	2,2',3,6,6'	151	2,2',3,5,5',6	206	2,2',3,3',4,4',5,5',6
42	2,2',3,4'	97	2,2',3',4,5	152	2,2',3,5,6,6'	207	2,2',3,3',4,4',5,6,6'
43	2,2',3,5	98	2,2',3',4,6	153	2,2',4,4',5,5'	208	2,2',3,3',4,5,5',6,6'
44	2,2',3,5'	99	2,2',4,4',5	154	2,2',4,4',5,6'	209	2,2',3,3',4,4',5,5',6,6'
45	2,2',3,6	100	2,2',4,4',6	155	2,2',4,4',6,6'		
46	2,2',3,6'	101	2,2',4,5,5'	156**	2,3,3',4,4',5		
47	2,2',4,4'	102	2,2',4,5,6'	157**	2,3,3',4,4',5'		
48	2,2',4,5	103	2,2',4,5',6	158	2,3,3',4,4',6		
49	2,2',4,5'	104	2,2',4,6,6'	159	2,3,3',4,5,5'		
50	2,2',4,6	105**	2,3,3',4,4'	160	2,3,3',4,5,6		
51	2,2',4,6'	106	2,3,3',4,5	161	2,3,3',4,5',6		
52	2,2',5,5'	107	2,3,3',4',5	162	2,3,3',4',5,5'		
53	2,2',5,6'	108	2,3,3',4,5'	163	2,3,3',4',5,6		
54	2,2',6,6'	109	2,3,3',4,6	164	2,3,3',4',5',6		
55	2,3,3',4	110	2,3,3',4',6	165	2,3,3',5,5',6		

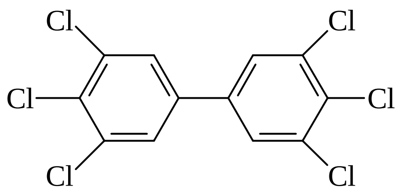
[a] Marked congeners have been assigned "toxic equivalency factors" (TEFs): * non-ortho congener; ** mono-ortho congener; *** di-ortho congener. These congeners are also chlorinated in both *para* and at least two *meta* positions.

Old school nomenclature

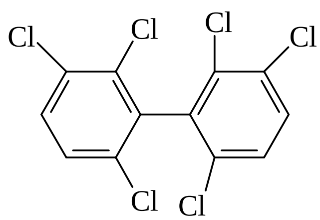


Ortho (o), meta (m), and para (p) positions. Often used to group different congeners.

Structural placement of chlorines affects biological activity



3,3'4,4',5,5'-hexachlorobiphenyl
CB-169; non-ortho PCB
Non-ortho allows two rings to rotate. Generally more bioactive.

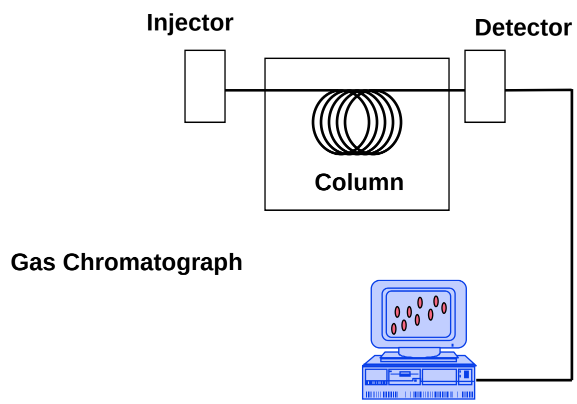


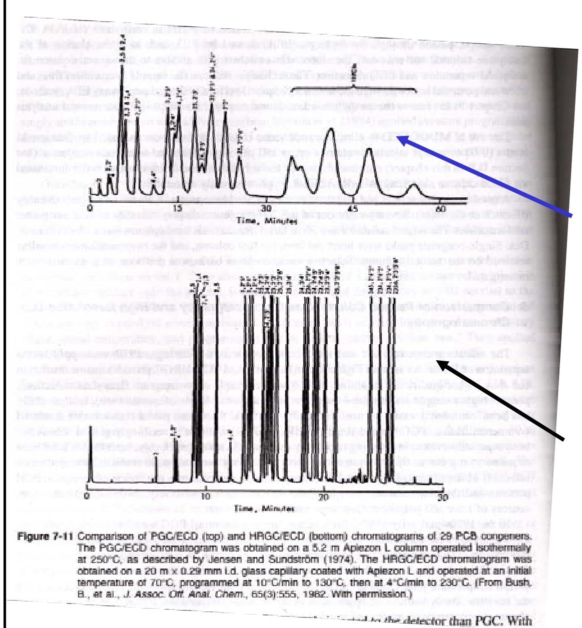
2,2',3,3',6,6'-hexachlorobiphenyl
CB-136; all ortho positions filled. Structurally rigid. Generally less bioactive.

Distribution of PCB congeners by chlorine content

Molecular formula	Name:	Number of congeners	IUPAC-No.	Molecular mass	% of Cl	
$C_{12}H_9Cl$	Mono	3	1-3	188.65	18.79	
$C_{12}H_8Cl_2$	Di	12	4-15	233.10	31.77	
$C_{12}H_7Cl_3$	Tri	24	16-39	257.54	41.30	
$C_{12}H_6Cl_4$	Tetra	42	40-81	291.99	48.65	
$C_{12}H_5Cl_5$	Penta	46	82-127	326.43	54.30	
$C_{12}H_4Cl_6$	Hexa	42	128-169	360.88	58.93	
$C_{12}H_3Cl_7$	Hepta	24	170-193	395.32	62.77	
$C_{12}H_2Cl_8$	Octa	12	194-205	429.77	65.98	
$C_{12}HCl_9$	Nona	3	206-208	464.21	68.73	
$C_{12}Cl_{10}$	Deca	1	209	498.66	71.10	

Gas chromatography





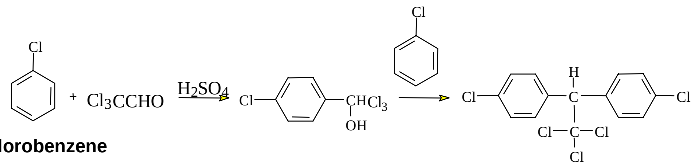
Packed column
gas chromatography
(*less resolution,
less congener-specific
data*)

Capillary column
Gas chromatography
(*sometimes called
high resolution gas
chromatography…
more resolution, more
congener-specific data.*)

Background on DDT

- First of the modern chemical pesticides.
- Originally synthesized in late 1800s.
- Paul Mueller observed biological activities in late 1930s and won the Nobel Prize in 1948 for this effort.
- Banned since about 1970 in many countries, including US and Canada because of its effect on wildlife, particularly fish-eating birds.
- May still be used today in countries where malaria is endemic. Usage in 3rd world countries is a hot topic. Very cheap and surprisingly effective.
- Interesting geochemistry as it transforms to DDE, which is more bioactive and more persistent.

Synthesis of DDT



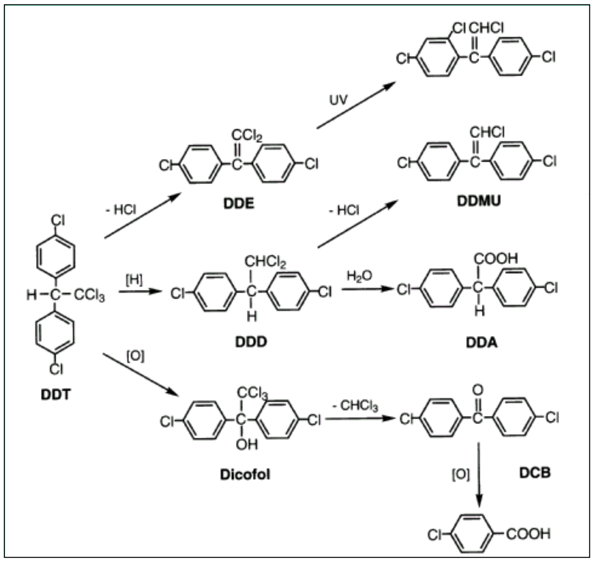
chlorobenzene

trichloroacetaldehyde

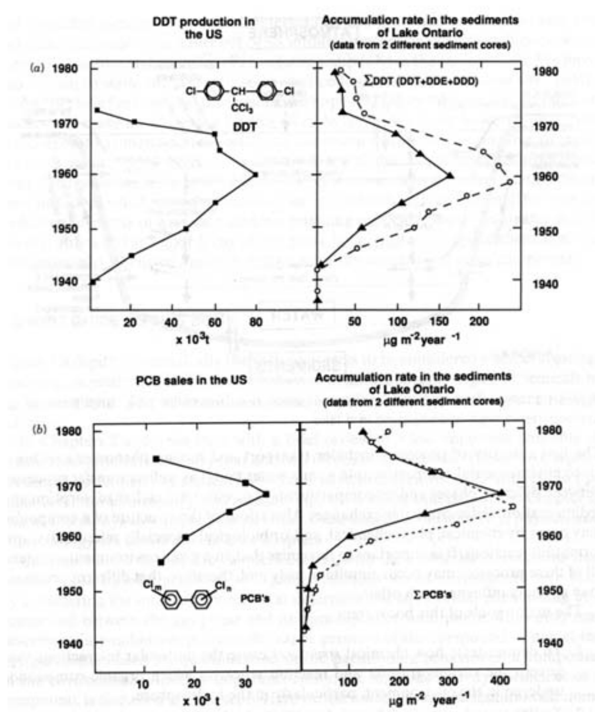
p,p-DDT (70%)

The other main product of this reaction was o,p-DDT (~25%).

Reactions involving DDT

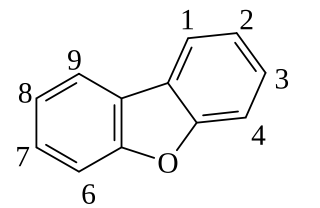


Data is often presented as ΣDDT metabolites (sometimes called DDX).

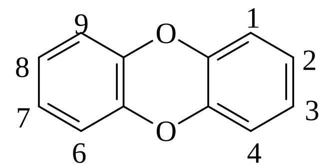


Chlorinated dioxins and furans

- Very different background than PCBs or DDT.
- They were never intentionally produced but rather were by-products of industrial synthesis (often found in trace quantities in Aroclors, Agent Orange, pentachlorophenol).
- Also formed during combustion of organic matter in the presence of chloride, etc.
- Natural sources possible, too.
- 75 possible structures for chlorinated dioxins.
- 135 possible structures for chlorinated furans.

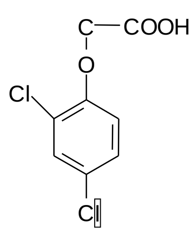


dibenzofuran

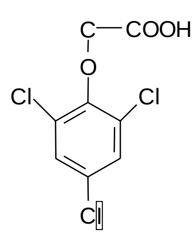


dibenzo-p-dioxin

Inadvertent industrial source (Agent Orange)

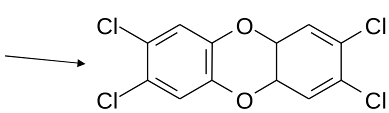


2,4-D
(50%)



2,4,5-T
(50%)

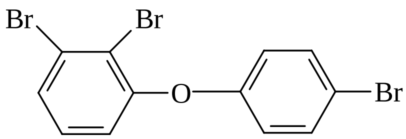
trace
impurity



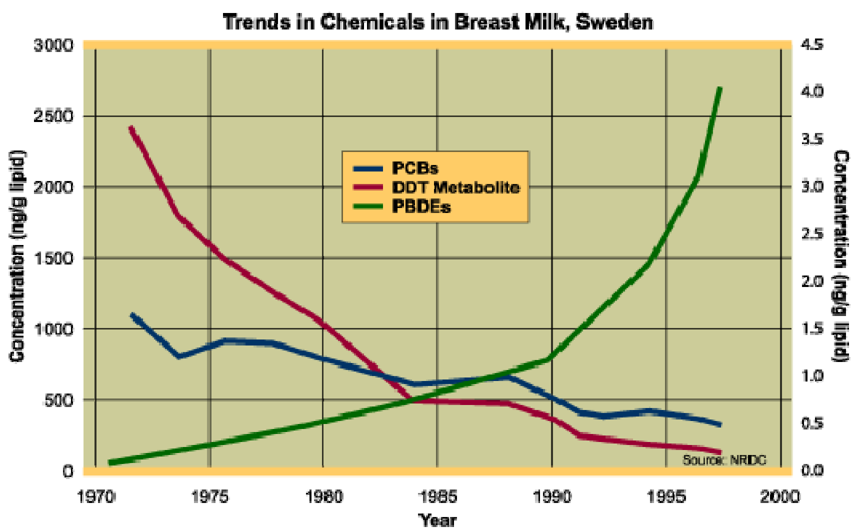
2,3,7,8-tetrachlorodibenzodioxin (2,3,7,8-TCDD)

Background on PBDEs

- Polybrominated diphenyl ethers (PBDEs) are used as flame retardants.
- They are added to materials to decrease the likelihood and intensity of fire in a wide variety of products, including vehicles, furniture, textiles, carpets, building materials, electronic circuit boards and cases… just about anywhere that plastics are used.
- Synthesized mainly as mixtures (similar to PCBs).
- Production started in the 1960s.
- Gained a lot of attention lately.



2,3,4'-tribromodiphenylether (PBDE-22)



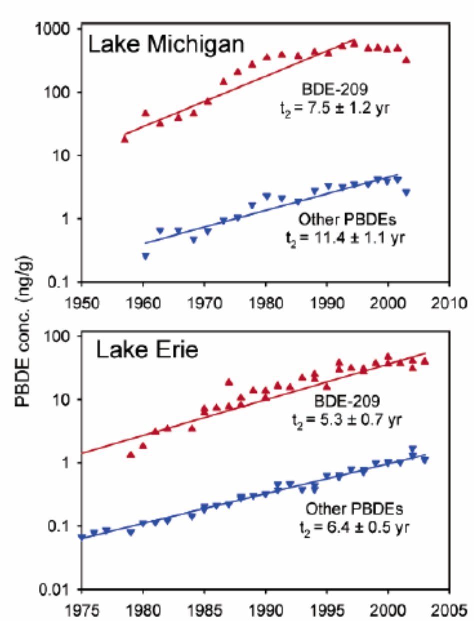
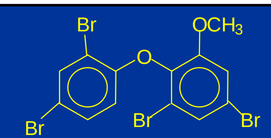
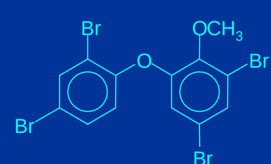


FIGURE 3. Concentrations of BDE-209 and other PBDEs (∑PBDE′) as a function of deposition year in Lakes Michigan and Erie. Note the logarithmic scale for the concentrations.

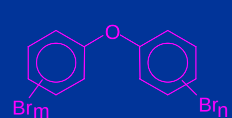
Zhu and Hites (2005)



Unknown source? (found in animals from coastal Australia, Japan, Norway, and US; Med. Sea; Baltic Sea; Detroit River)



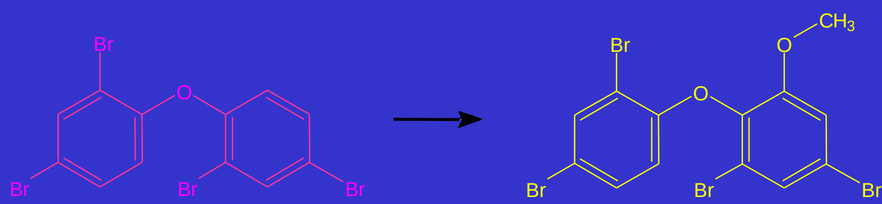
Isolated from the marine sponge, *Dysidea herbacea*, in the Indian Ocean (8°N, 73°E)



m+n = 1 to 10

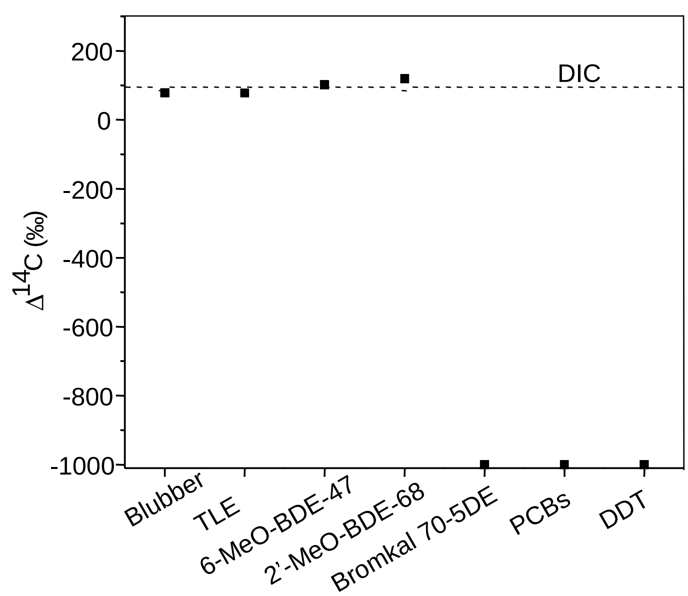
PBDEs
Industrial flame retardants

Transformation from flame retardant to unknown compound
(*possible but not yet directly shown*)

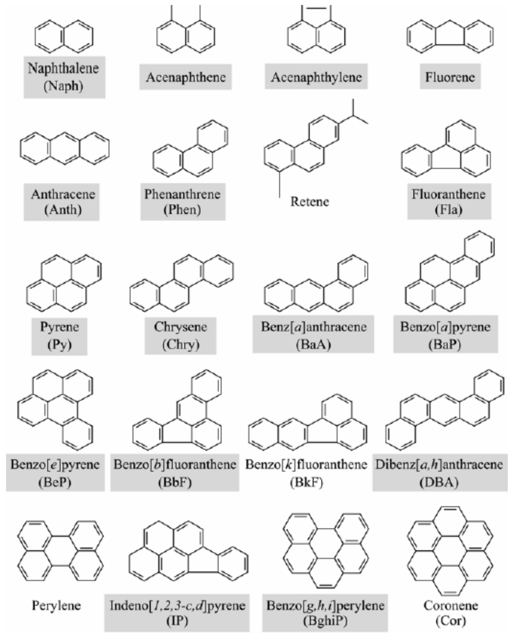


BDE-47
(flame retardant)

6-MeO-BDE-47
(unknown source?)



Polycyclic aromatic hydrocarbons (PAHs)



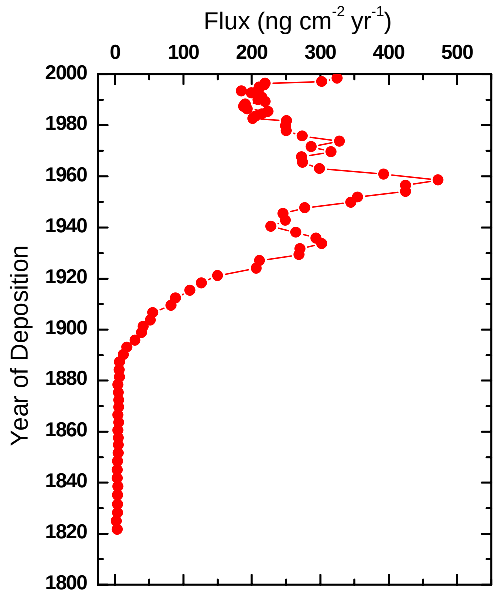
Sources of PAHs

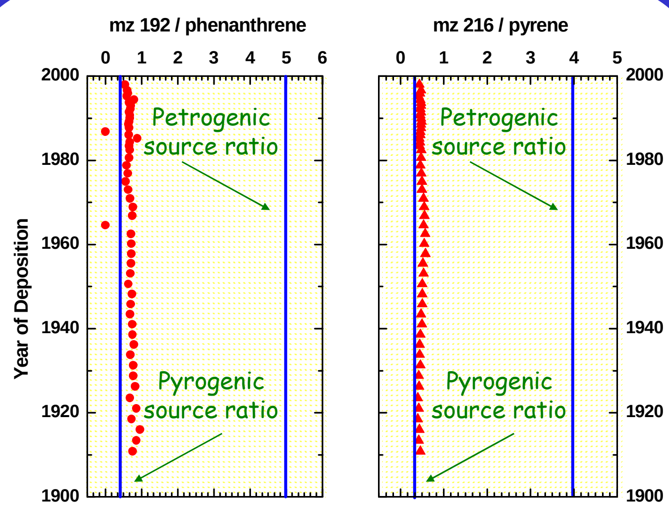
Combustion-Derived (pyrogenic): Wildfires and prescribed burnings, residential wood stoves, burning of scrap tires, open trash burning, on-road vehicles, industrial boilers, cigarette smoking, and meat charbroilers.

Petroleum-Derived (petrogenic): oil spills (acute or chronic), natural seeps.

Natural sources: retene (plant resins) and perylene (anaerobic sediments).

PAHs in Rhode Island (Lima et al 2003)



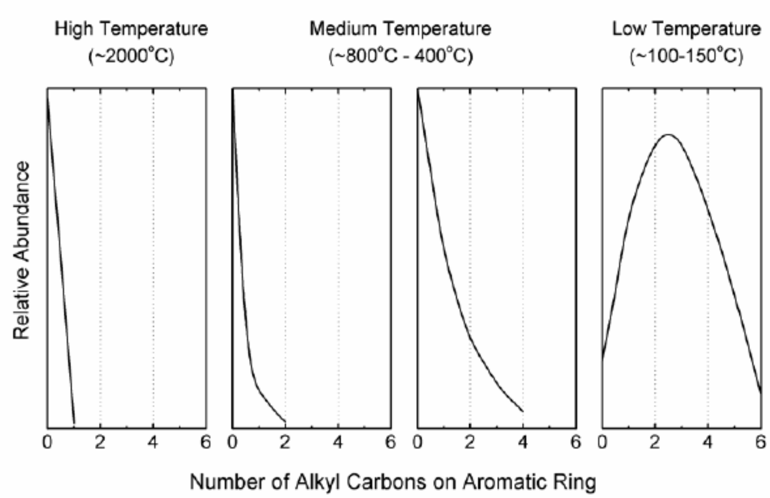


Gustafsson & Gschwend (1997)

C1-phenanthrenes (molecular weight 192 g/mole)

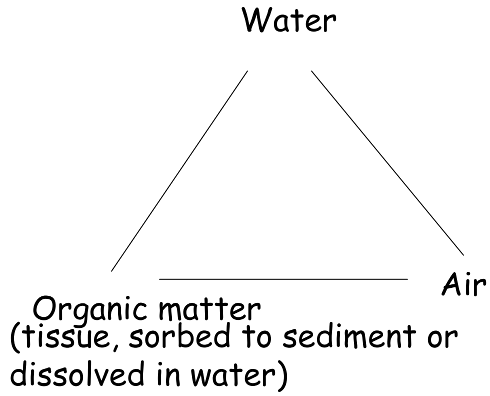
phenanthrene (molecular weight 178 g/mole)

PAHs: Effect of T on formation and alkylation



pyrogenic ——————————— petrogenic

Three phases in the environment



Chemical/Physical Properties That Control Fate

- Water solubility (S)
- Vapor pressure (VP)
- Octanol-water partition coefficient (Kow)
- Organic matter-water partition coefficient (Kom)
- Henry's Law Constant (H)

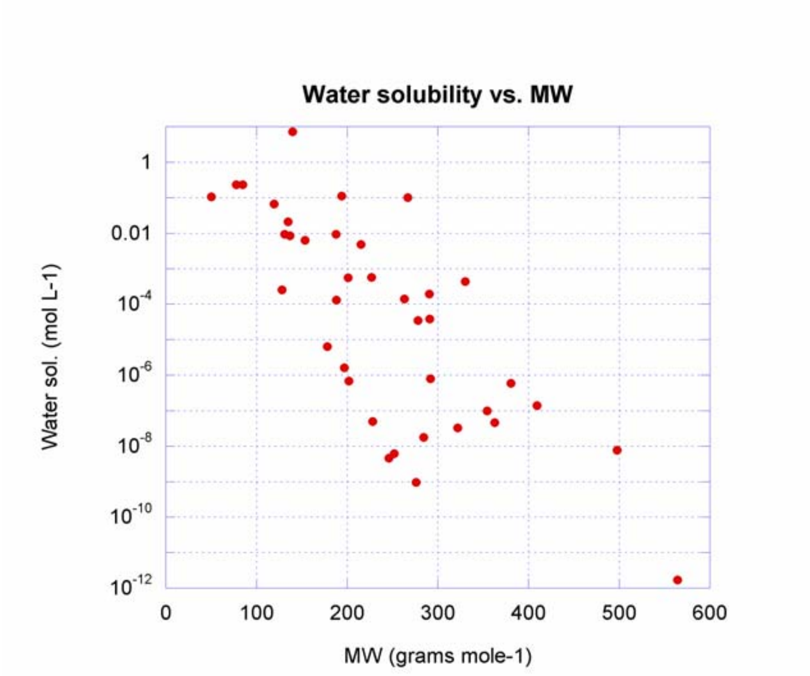
Organic matter

- Fish tissue (mainly fat)
- Sediments or particles have a film of organic matter (slime).
- Dissolved organic matter

Water solubility (S)

- Water solubility (S): the maximum concentration of a chemical in water at a specific temperature and pressure, usually 25°C and 1 atm. Possibly the most important property concerning the fate of organic contaminants. Units are in mole per liter.

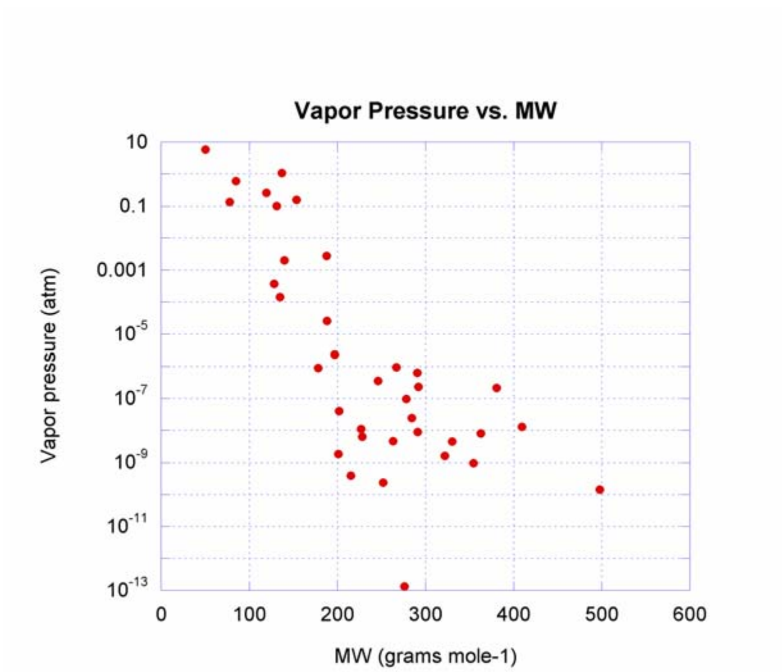
-The larger the value, the more likely a compound will stay in water and not go into air, sediment, and or tissue.



Vapor Pressure (VP)

- Vapor pressure (VP): the pressure of a vapor exerted from a liquid or solid compound. Units are in atmospheres. This term indicates how "volatile" a compound is and is important in understanding whether it will evaporate.

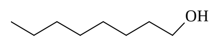
Example: moth balls→naphthalene



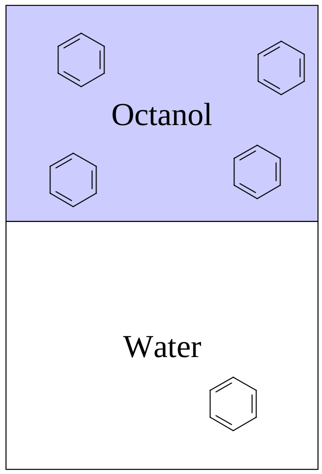
Octanol-water partition coefficient (Kow)

- Octanol-water partition coefficient (Kow): the ratio of the concentration of a water to the concentration in octanol. Units are (mole per liter of water) per (moles per liter of water). This term is inversely proportion to the water solubility and indicates how "hydrophobic" a compound is. Very important for determining whether a compound will bioaccumulate.
- Example, salad dressing (oil and vinegar)

Kow



Octanol

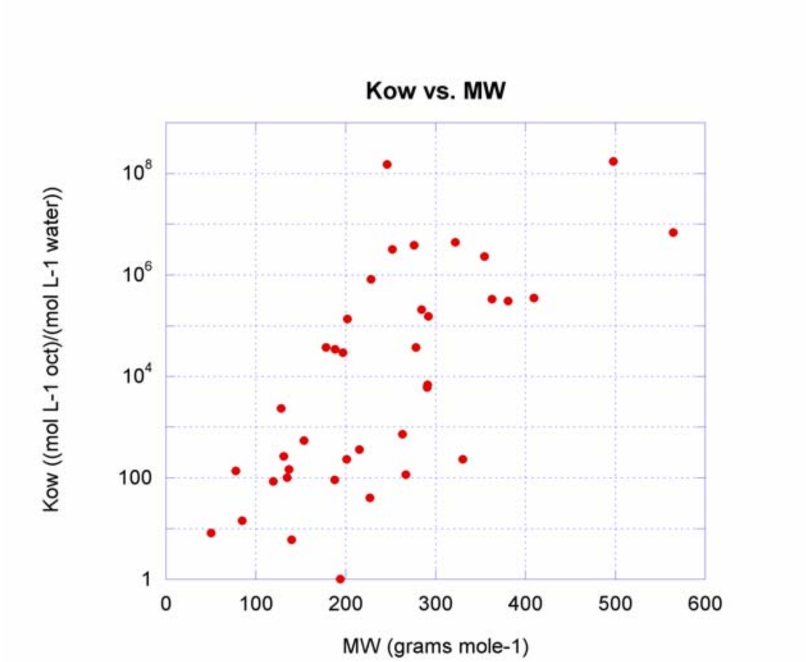


$$K_{ow} = \frac{\text{CONC oct}}{\text{CONCwater}}$$

Benzene's Kow is 135

Log Kow is 2.13

10^2.13=135



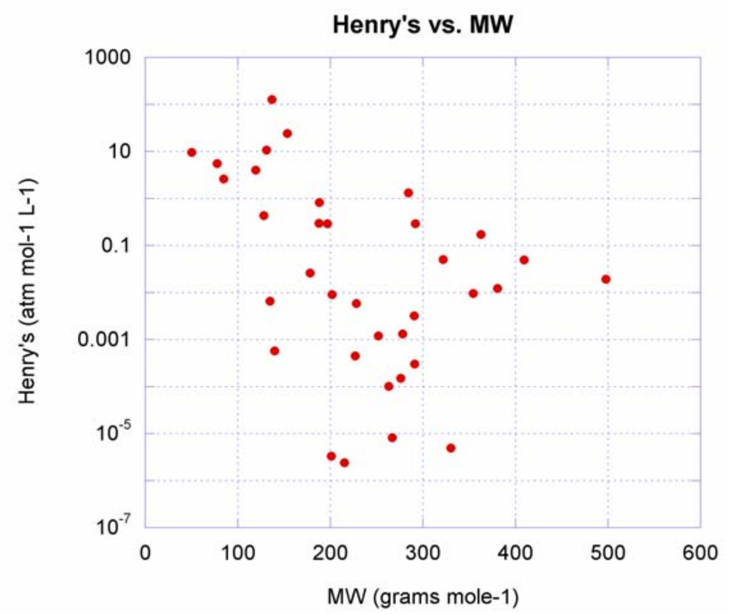
Kom

- Octanol-water partition coefficient (Kom): the ratio of the concentration of a compound in sediment organic matter to the concentration of water surrounding it. Units are (mole per kg of organic carbon) per (moles per liter of water).

This term is very similar to Kow. Used to determine the extent of sorption to sediment or dissolved organic matter.

Henry's Law constant (H)

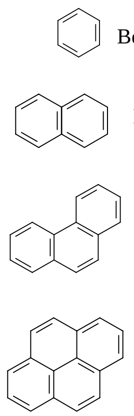
- Henry's Law constant (H): the ratio of the vapor pressure of a compound to its water solubility. Units atm L/mole
- H=VP/water solubility (estimate)
- It describes the willingness of a compound to go into the air from water or vice versa.
- The larger the value, the more likely the compound will partition into air.



General trends

- The larger the compound,
  - -smaller water solubility
  - -smaller vapor pressure
  - -larger Kow
  - -smaller Henry’s Law Constant

Where do these compounds go?

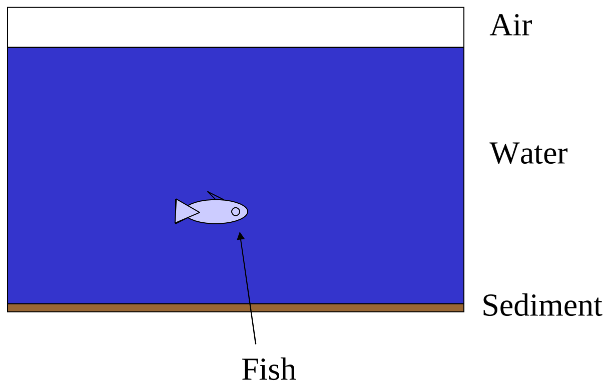


Benzene

Naphthalene

Phenanthrene

Pyrene



795 L of water; 200 L of air

15 kg of sediment; 0.5 kg of fish

Fishbowl results at equilibrium

	Benzene	Naphthalene	Phenanthrene	Pyrene
Water	0.41	0.49	0.06	0.02
Fish	0.00	0.08	0.17	0.18
Sediment	0.02	0.38	0.77	0.80
Air	0.57	0.05	0.00	0.00