THE HOMEWORK

Show me your nasty molecule

THE HOMEWORK

What makes it environmentally problematic?

THE HOMEWORK

What properties do you remember from organic and p-chem?

If any…

What is a pollutant?

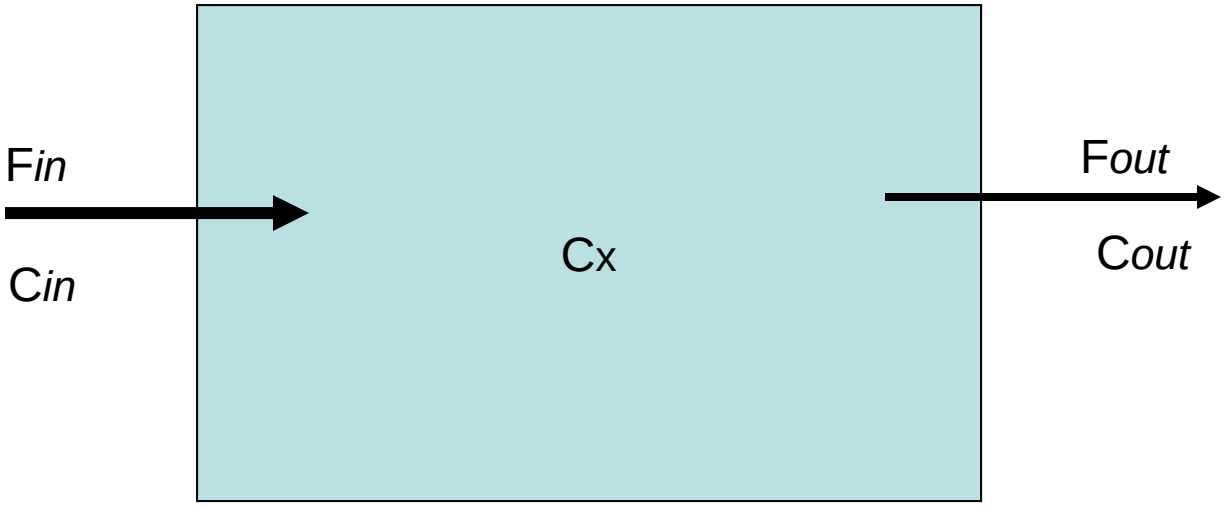
What is a pollutant?

Generally, any substance introduced into the environment that adversely affects the usefulness of a resource or the health of humans, animals, or ecosystems.

What makes a substance a pollutant?

Generally, any substance introduced into the environment that adversely affects the usefulness of a resource or the health of humans, animals, or ecosystems that is persistent, and easily transportable.

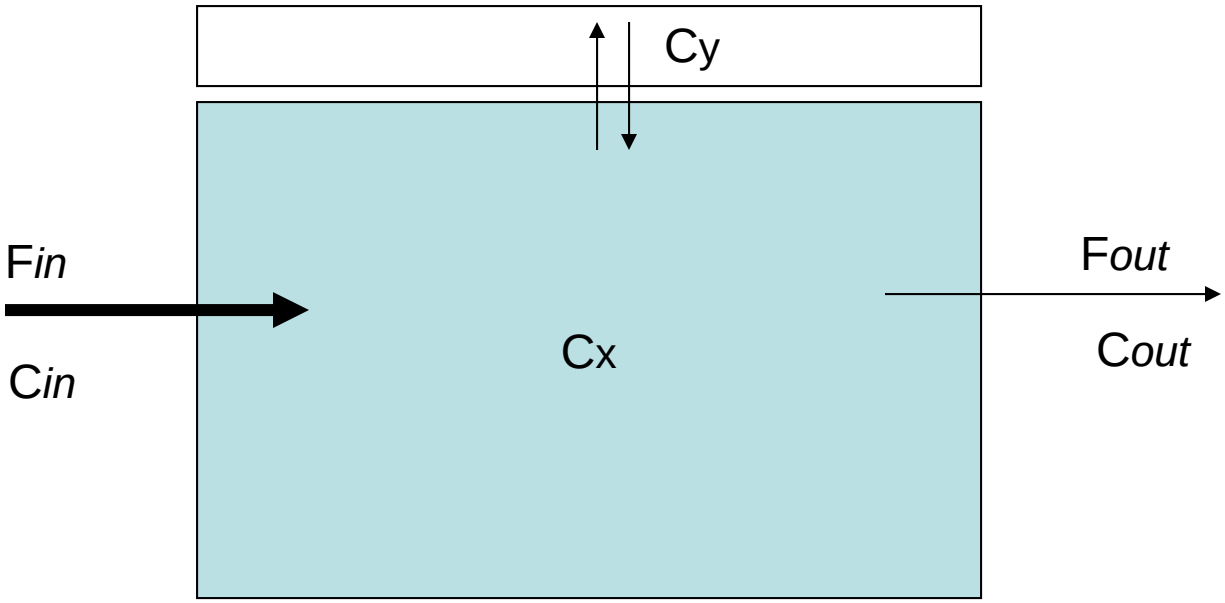
THE BOXES, THE ARROWS, TIME and SPACE



Degradation (chemical)

- Photolysis
- Hydrolysis
- Redox
- Biodegradation

THE BOXES, THE ARROWS, TIME and SPACE

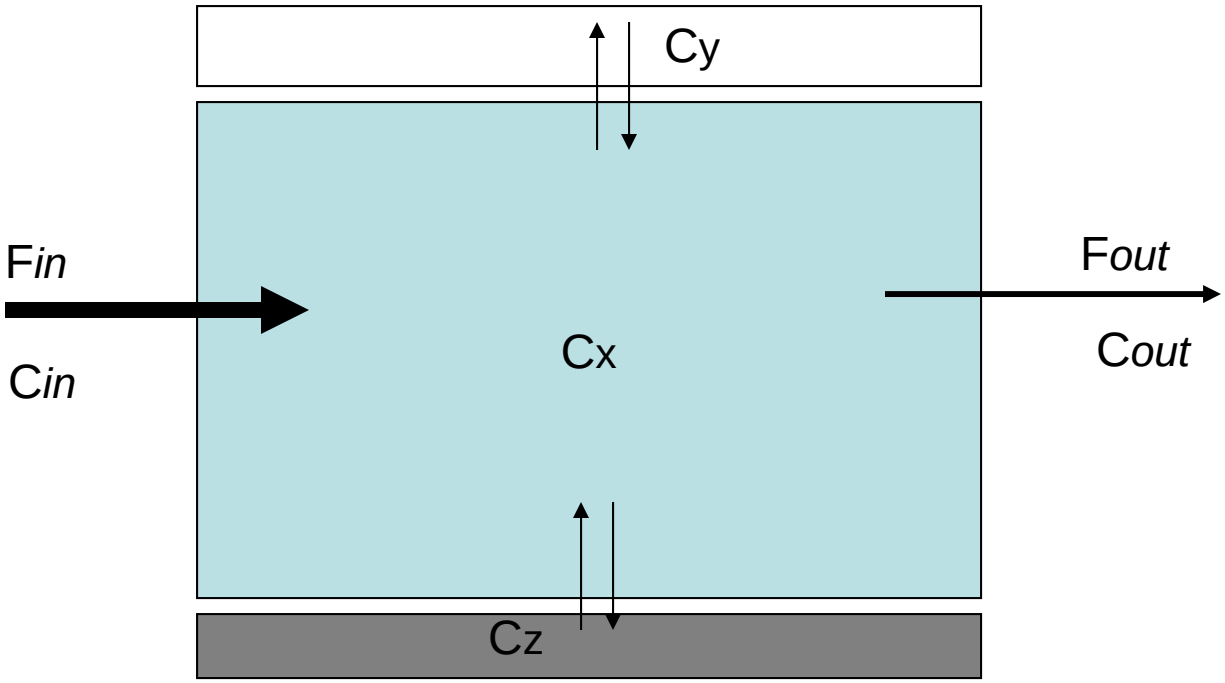


Dissipation (physical) Abiotic

Volatilization

Partitioning

THE BOXES, THE ARROWS, TIME and SPACE



Dissipation (physical) Abiotic

Volatilization

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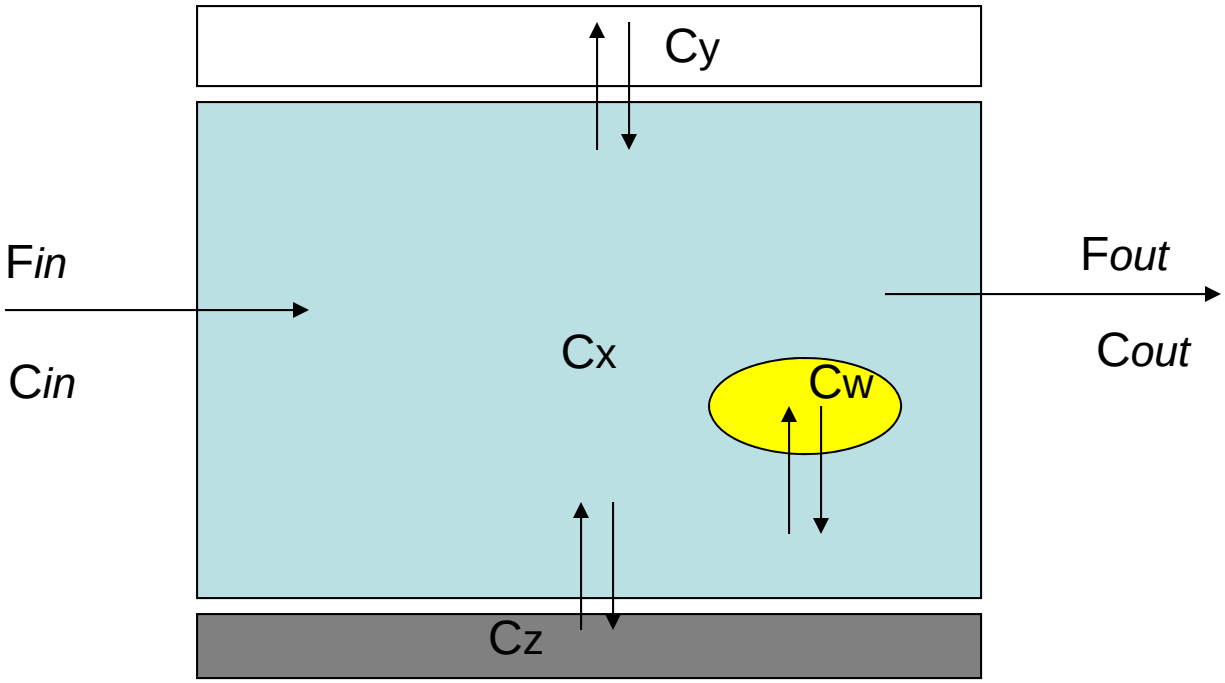
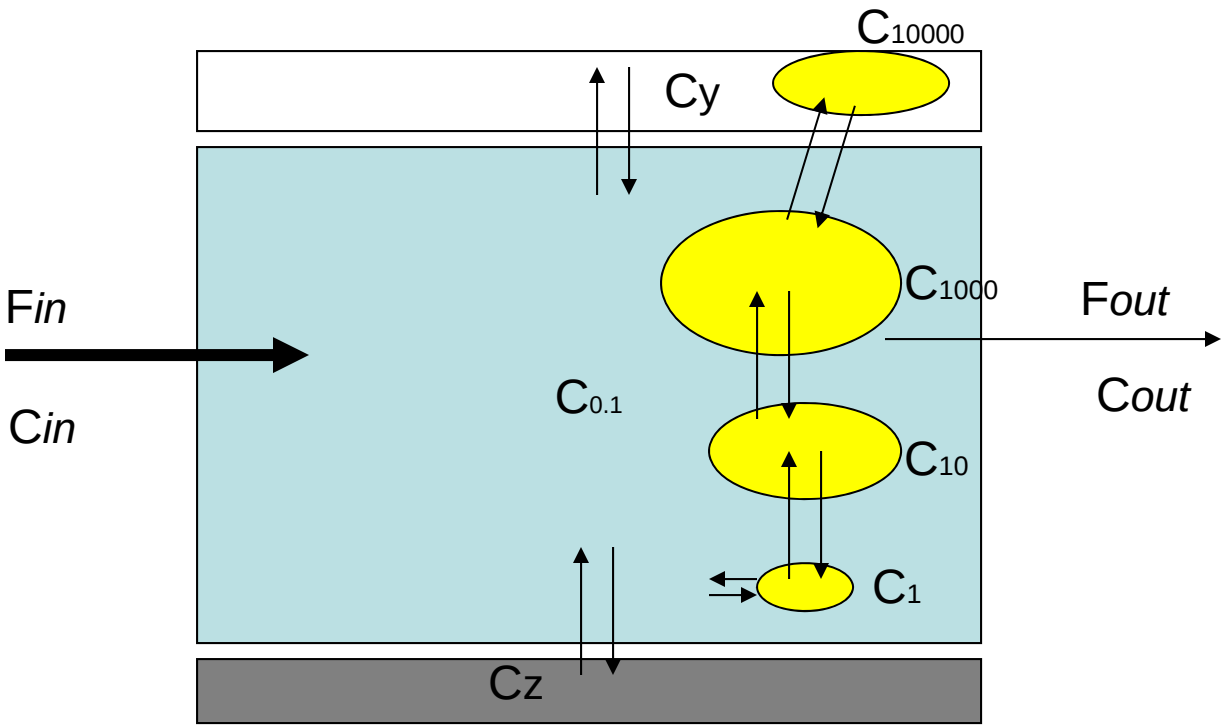
THE BOXES, THE ARROWS, TIME and SPACE



Dissipation (physical) Biotic

Partitioning

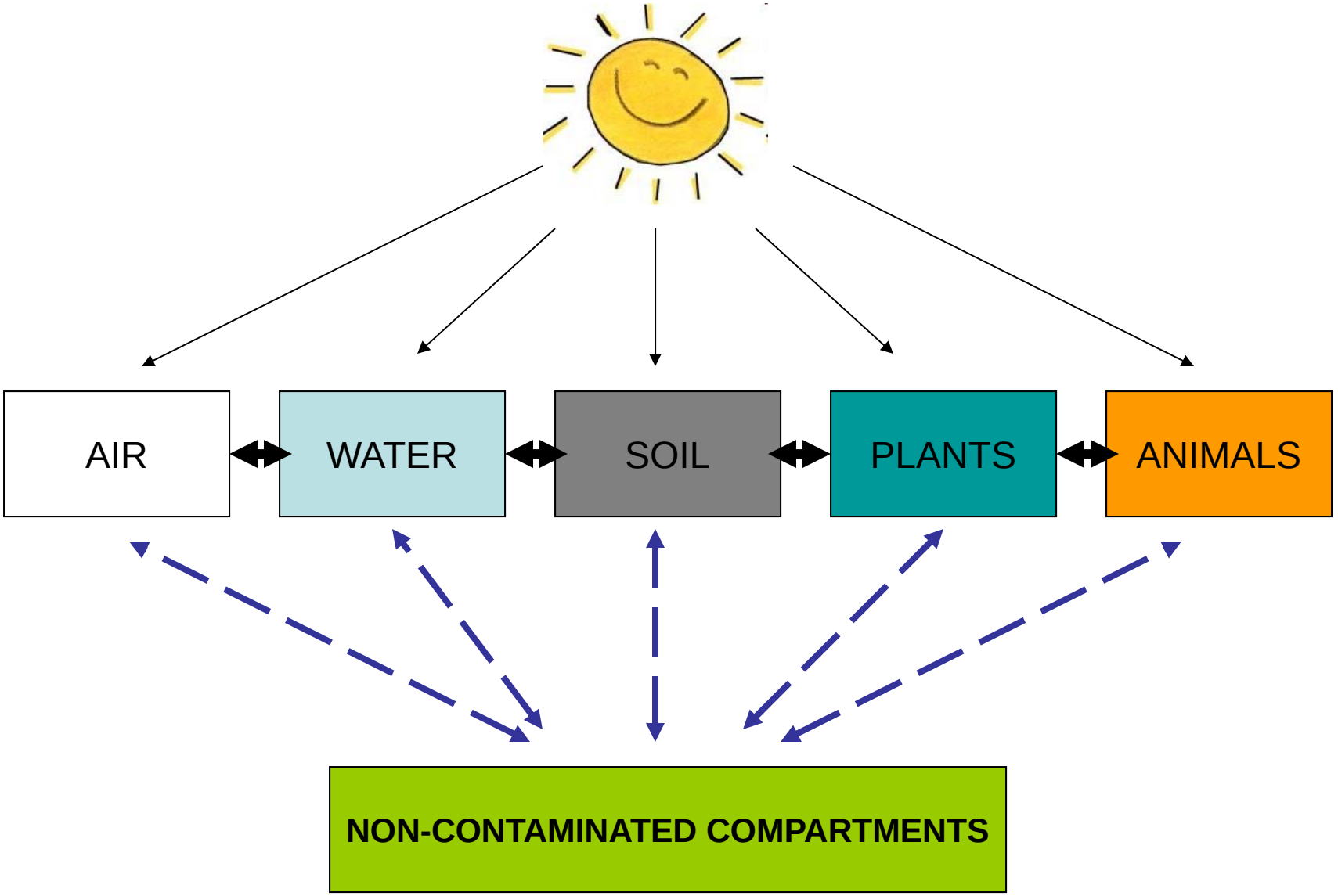
THE BOXES, THE ARROWS, TIME and SPACE



Dissipation (physical) Biotic

- Partitioning
- Bioccumulation
- Bioconcentration
- Biomagnification

A NEVER ENDING CIRCLE



THE BOXES, THE ARROWS, TIME and SPACE

REACTIONS	AIR	WATER	SOILS	PLANTS	ANIMALS
Hydrolysis	Y	Y	Y	Y	Y
Phototransformation	Y	Y	Y	Y	Y
Dissociation	Y	Y	Y	Y	Y
Solubility	Y	Y	Y	Y	Y
Sorption	Y	Y	Y	Y	Y
Biodegradation	Y	Y	Y	Y	Y
Metabolism	N	N	N	Y	Y
Accumulation	N	N	Y	N	N
Bioaccumulation	N	N	N	Y	Y
Volatilization	Y	Y	Y	N	N
Respiration	N	N	N	Y	Y
Excretion	N	N	N	N	Y

The most toxic compound ever known to man

Dioxin

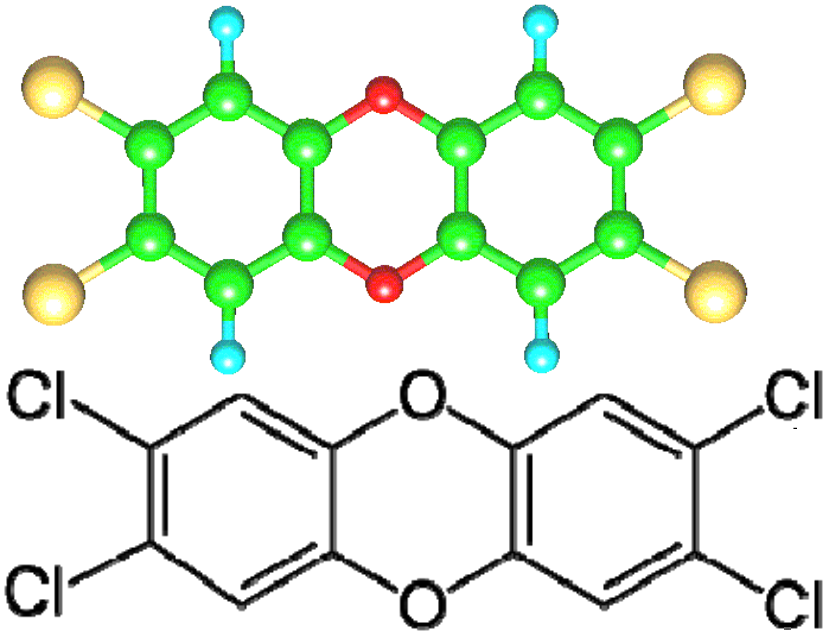
***2,3,7,8-tetrachlorodibenzo[b,e][1,4]dioxin* (TCDD)**

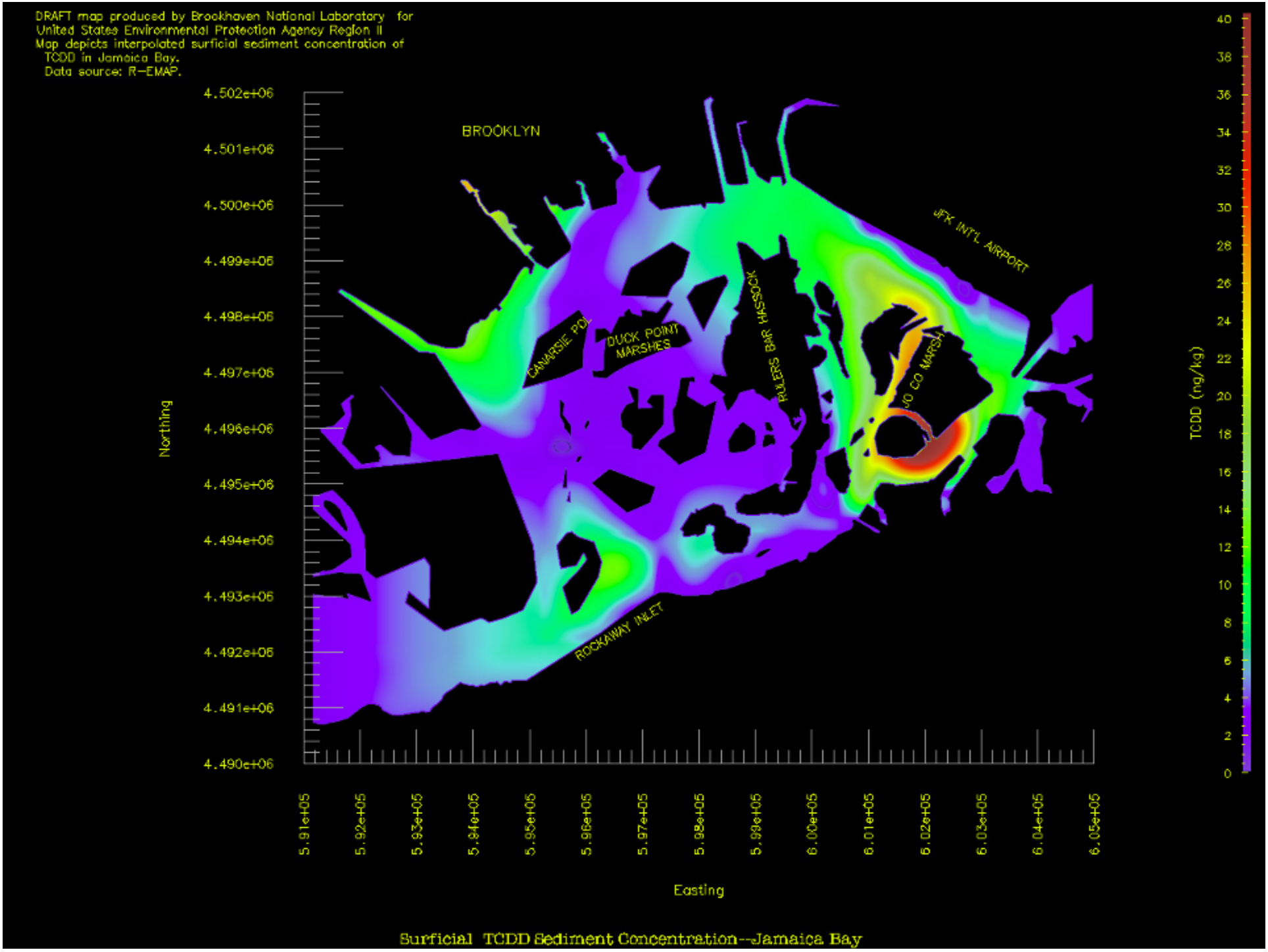
has a reported LD50 of 0.045 mg of dioxin/kg of body mass for rats.

(LD50 is the concentration expected to kill half a given population.)

Byproduct of synthesis of chlorophenols


C&EN
CHEMICAL & ENGINEERING NEWS
OLYMPIC CHALLENGE
Lab to work 24/7 to detect banned drugs P.25
HEART-HEALTHY FAT
Advances in synthesizing omega-3 fatty acids P.39
CONTAMINATION ADVISORY
POLLUTION AND POLITICS
Dow Chemical, dioxins, and cleaning up P.15


Cl
O
Cl
Cl
O
Cl

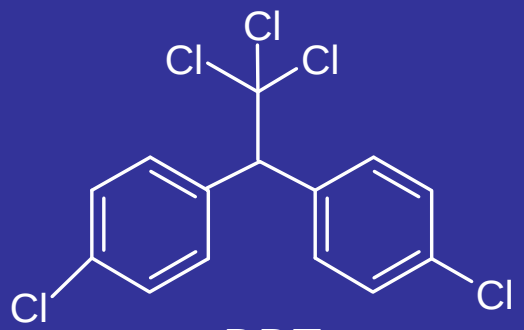

DRAFT map produced by Brookhaven National Laboratory for
United States Environmental Protection Agency Region II
Map depicts interpolated surficial sediment concentration of
TCDD in Jamaica Bay.
Data source: R-EMAP.
BROOKLYN
JFK INT'L AIRPORT
CANARSIE PO
DUCK POINT MARSHES
RULERS BAR HASSOCK
JO CO MARSH
ROCKAWAY INLET
Northing
4.502e+06
4.501e+06
4.500e+06
4.499e+06
4.498e+06
4.497e+06
4.496e+06
4.495e+06
4.494e+06
4.493e+06
4.492e+06
4.491e+06
4.490e+06
5.91e+05
5.92e+05
5.93e+05
5.94e+05
5.95e+05
5.96e+05
5.97e+05
5.98e+05
5.99e+05
6.00e+05
6.01e+05
6.02e+05
6.03e+05
6.04e+05
6.05e+05
Easting
TCDD (ng/kg)
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
32
34
36
38
40
Surficial TCDD Sediment Concentration--Jamaica Bay

Some compounds were better!

DDT, DDD and DDE: environmental legacy

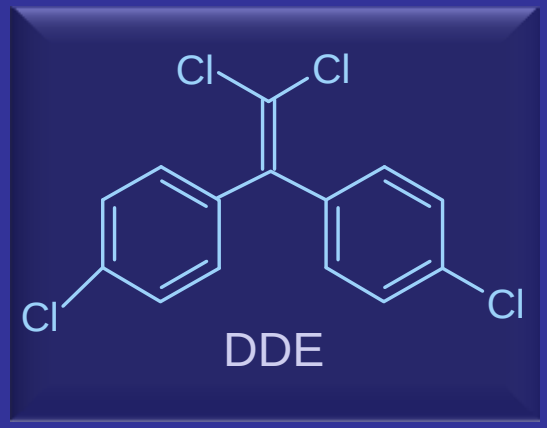
Paul Hermann Müller won the 1948 Nobel Prize in Physiology or Medicine for his 1939 discovery of DDT as an insecticide useful in the control of malaria, yellow fever and many other insect-vector diseases.

p,p’-DDT
+
o,p-DDT

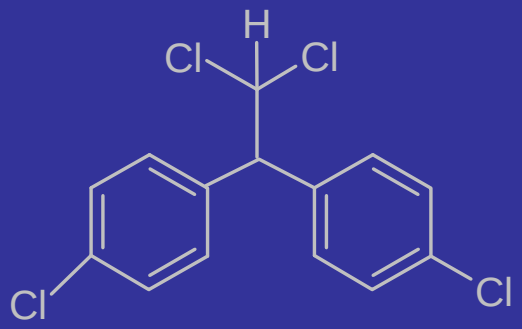


DDT

- SOIL
- SEDIMENT
- ORGANISMS



DDE



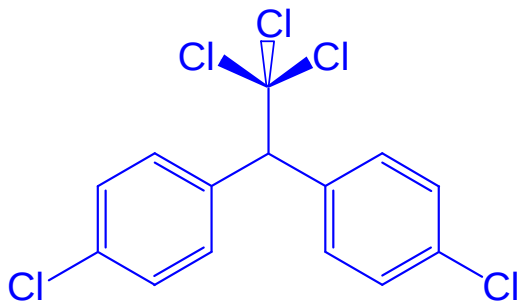
DDD

DDMU, DDA, DBP…

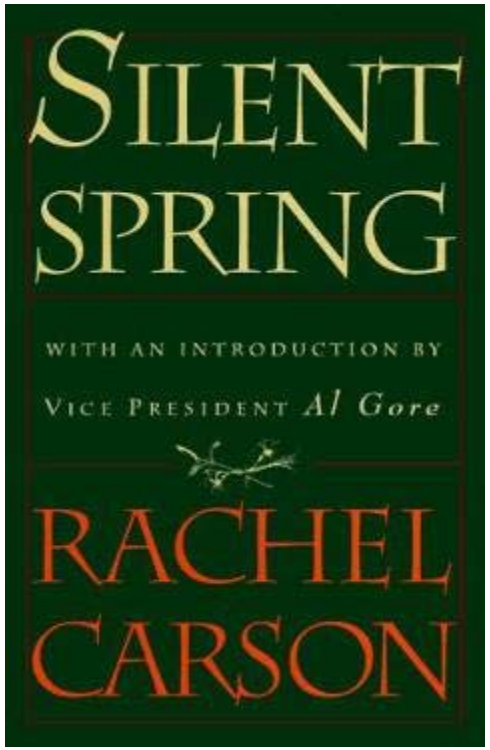
Rappolt, RT (1973). "Use of oral DDT in three human barbiturate intoxications: hepatic enzyme induction by reciprocal detoxicants". Clin Toxicol 6 (2): 147-51

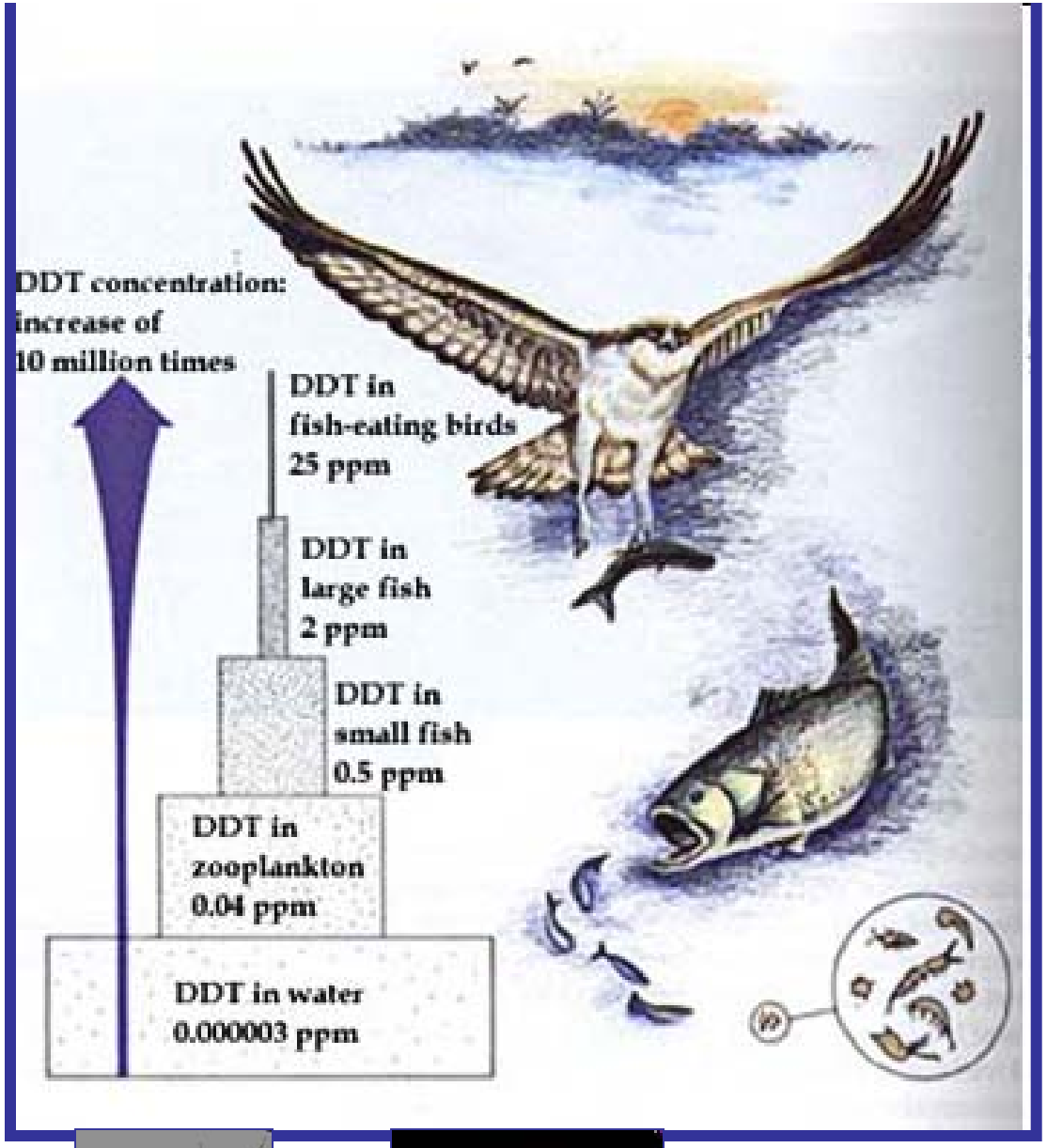
DDT, DDD and DDE: environmental legacy

- Rachel Carson (1962)
  - ***Silent Spring***
  - DDT
  - world-wide distribution
  - accumulating in organisms



2,2-Bis(*p*-chlorophenyl)-1,1,1-trichloroethane



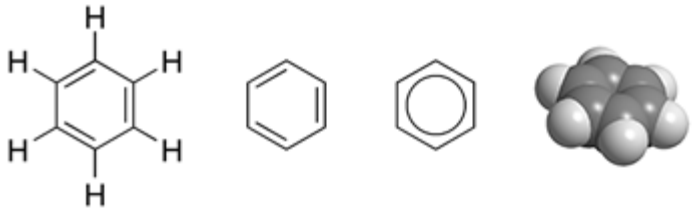

DDT concentration:
increase of
10 million times
DDT in
fish-eating birds
25 ppm
DDT in
large fish
2 ppm
DDT in
small fish
0.5 ppm
DDT in
zooplankton
0.04 ppm
DDT in water
0.000003 ppm

k


1896
1969

Organic Contaminants: environmental legacy

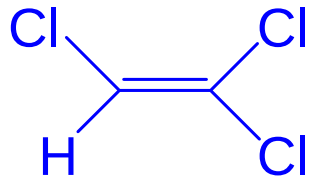
- Love Canal (1976)
  - Hooker Chemical buried wastes in canal
  - residential construction on site
  - chlorinated hydrocarbons seeping into homes, schools
  - first large-scale EPA intervention
  - led to CERCLA (Superfund)



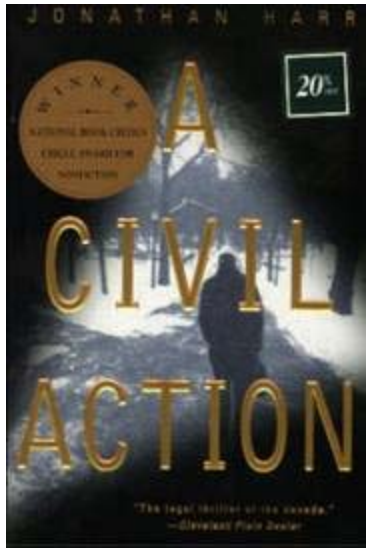
Organic Contaminants: environmental legacy

TETRACHLOROETHYLENE

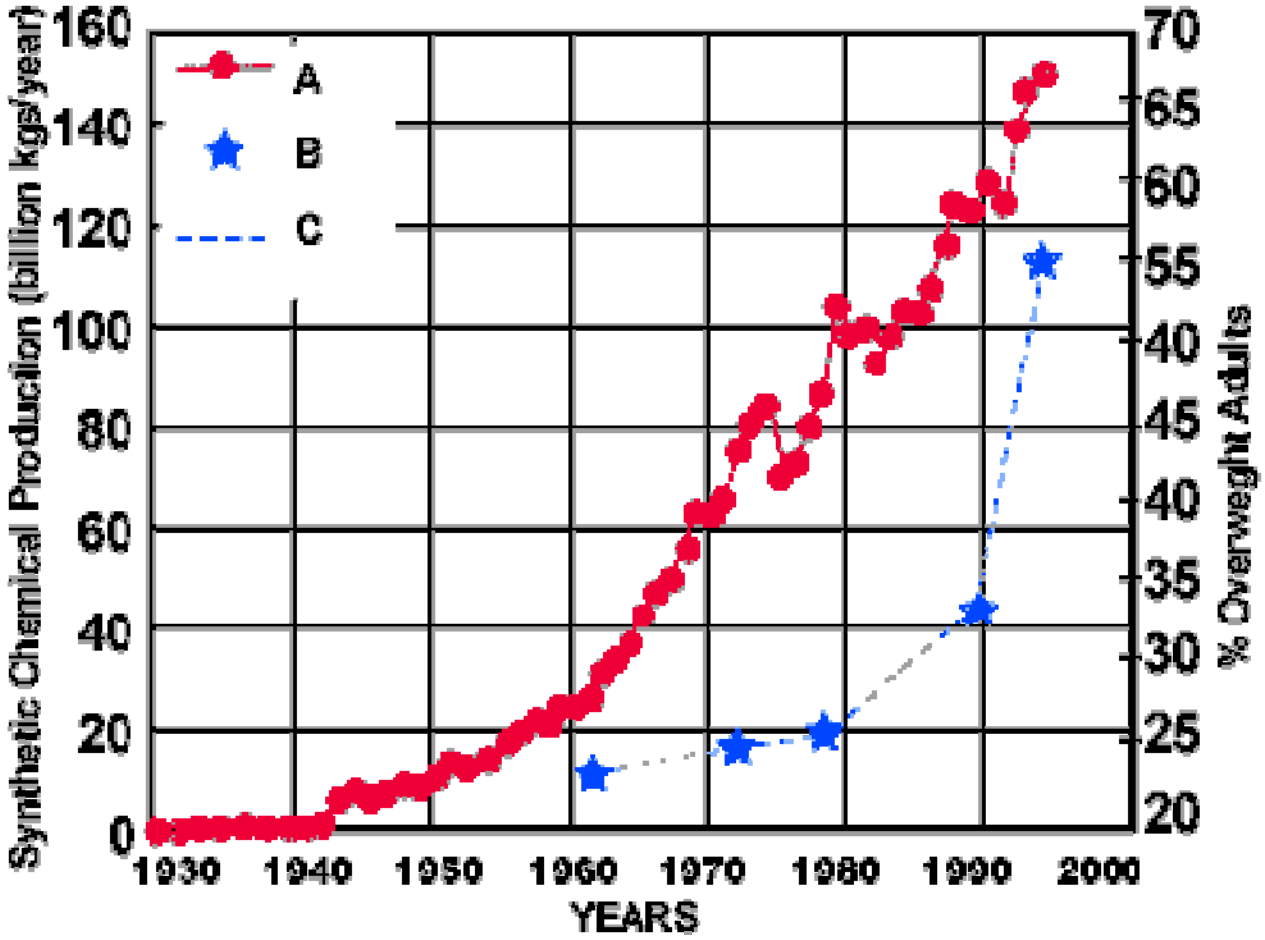
- Woburn, MA (1980s)
  - TCE



  - wide-spread in groundwater
  - disputed source
  - suspected to cause cancer (leukemia)
  - ***A Civil Action***
    - Jonathan Harr (1995)



Organic Chemicals and YOU!



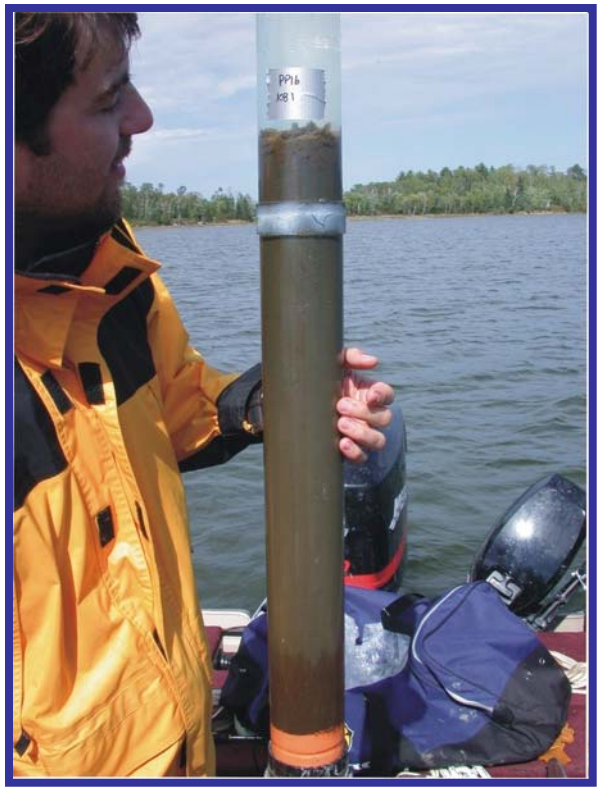
A = Synthetic chemical production

B = % Overweight adults, based on survey points

C = % Overweight adults, interpolated

From The Body Restoration Plan: Eliminate Chemical Calories™ and Repair Your Body's Natural Slimming System" by Dr. Paula Baillie-Hamilton © 2003 by Dr. Paula Baillie-Hamilton 200

Organic Contaminants: how do we know we did it?



biology.queensu.ca/~pearl/taste/tpics/core.jpg

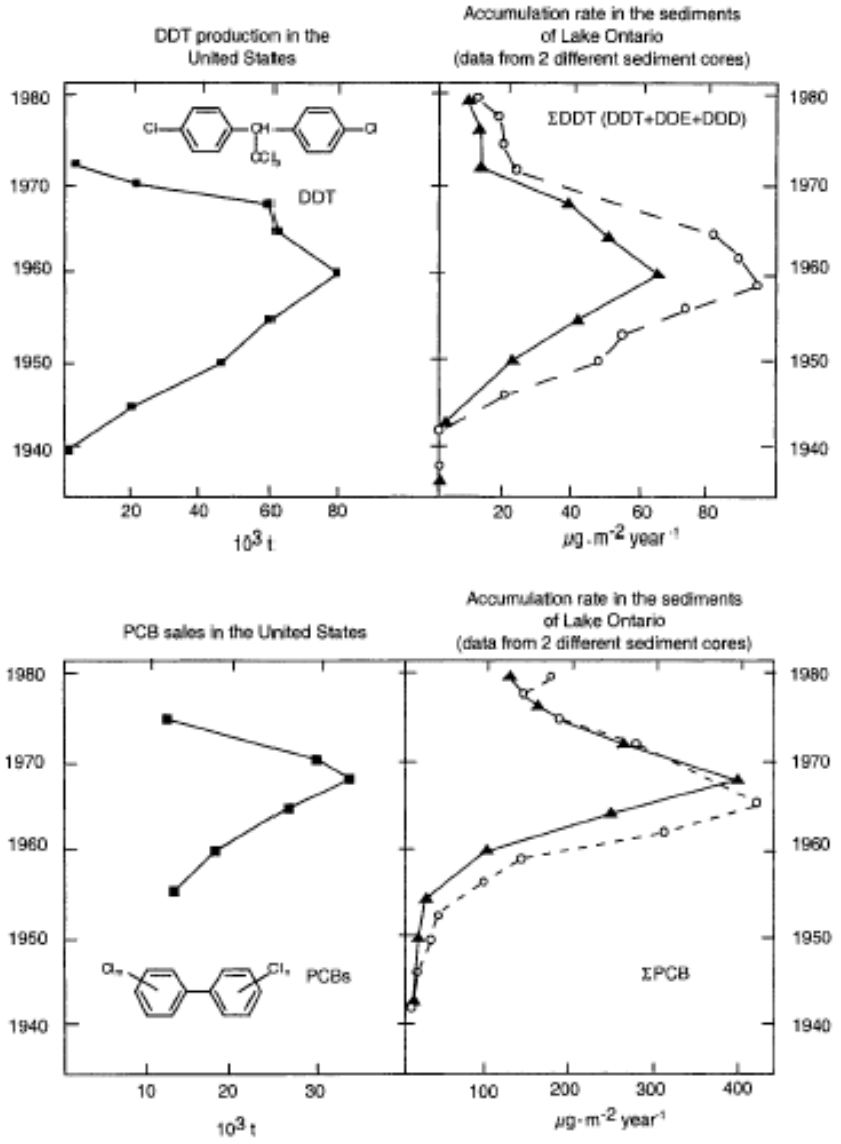


Figure 1.1 Historical records of the sales/production volumes of (*a*) DDT and (*b*) PCBs, and the similarity of these time-varying trends to the accumulation rates of these chemicals in the sediments of Lake Ontario (from Eisenreich et al., 1989).

Organic Contaminants: BOXES AND ARROWS

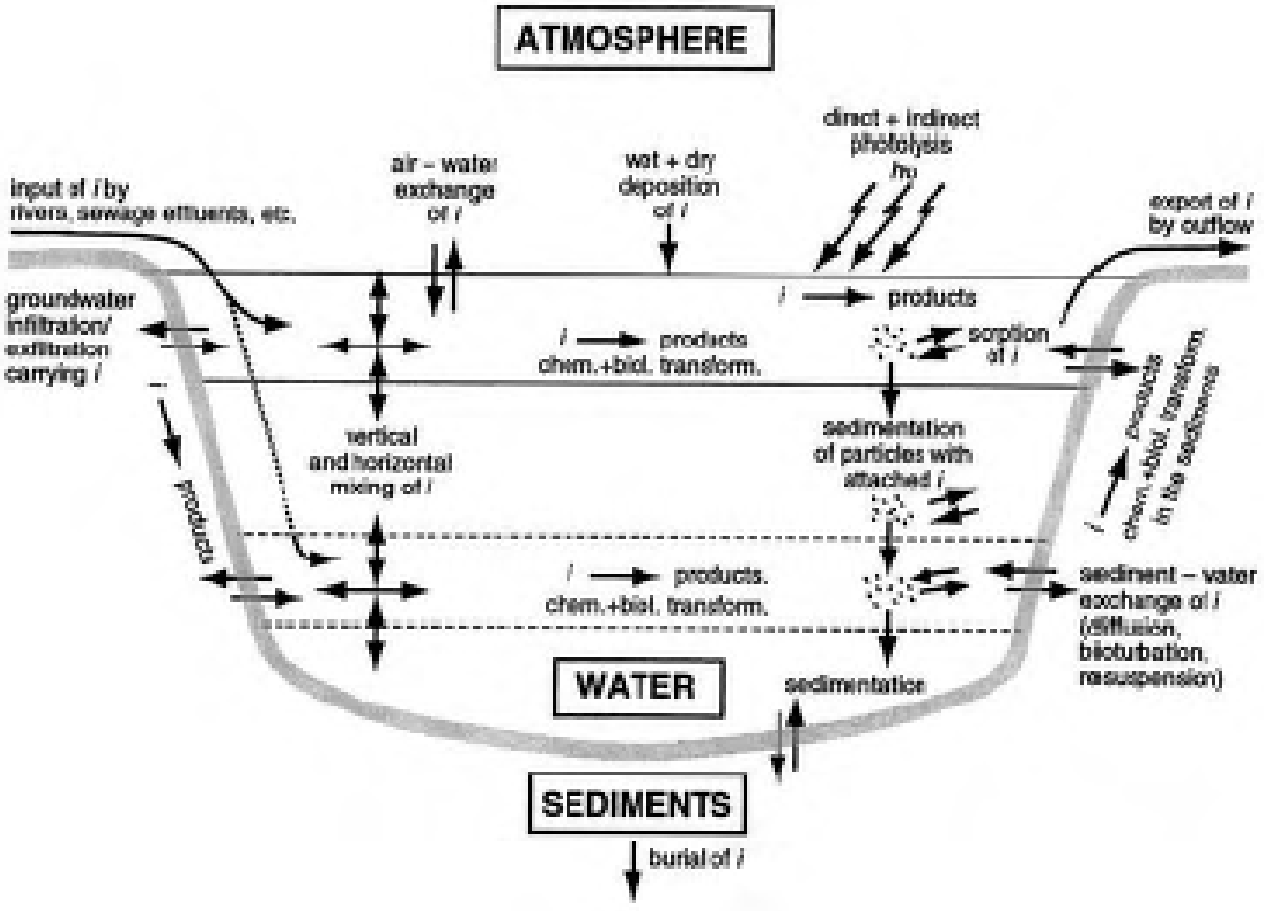


Figure 1.2 Processes that determine the distribution, residence time, and sinks of an organic chemical *i* in a lake. This example illustrates the various physical, chemical, and biological processes that a compound is subjected to in the environment.

Organic Contaminants: BOXES AND ARROWS

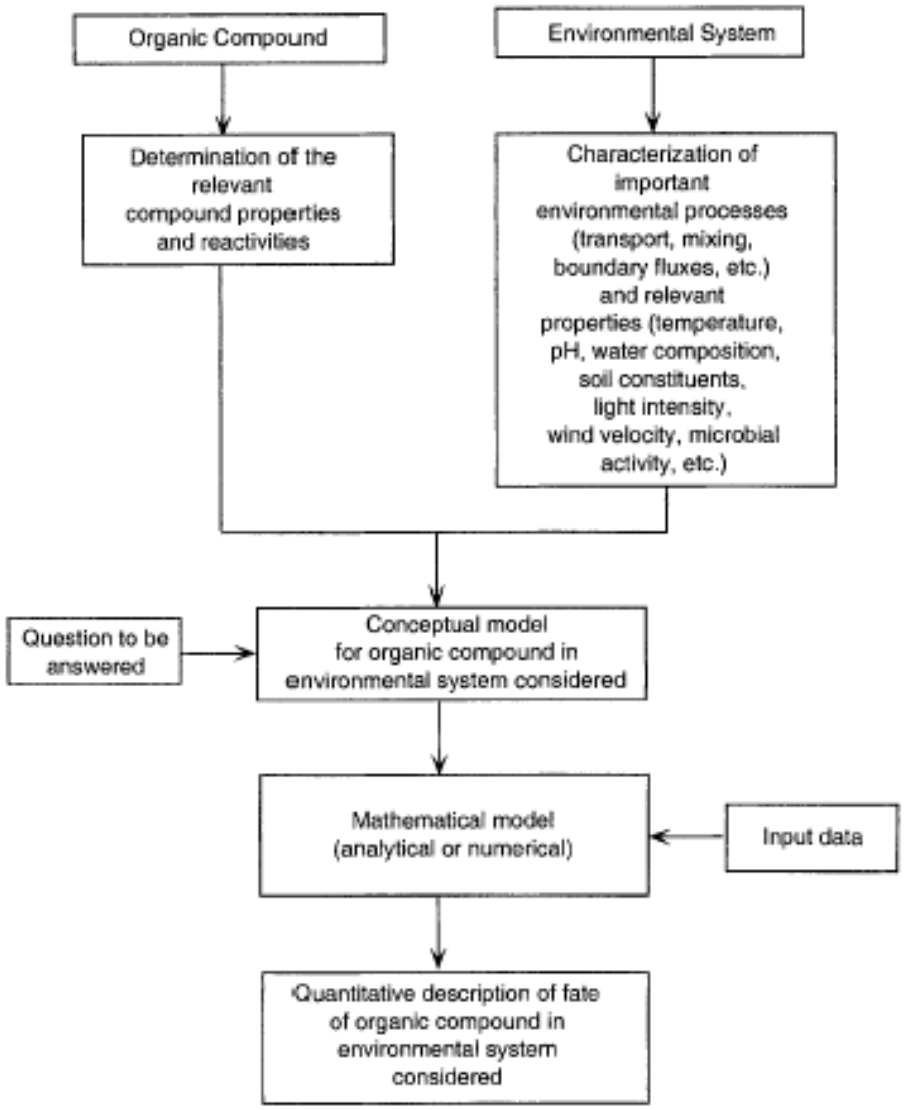


Figure 1.3 General scheme for evaluation of the environmental behavior of anthropogenic organic compounds.

OUR GOALS?

Can we evaluate every compound for every compartment???

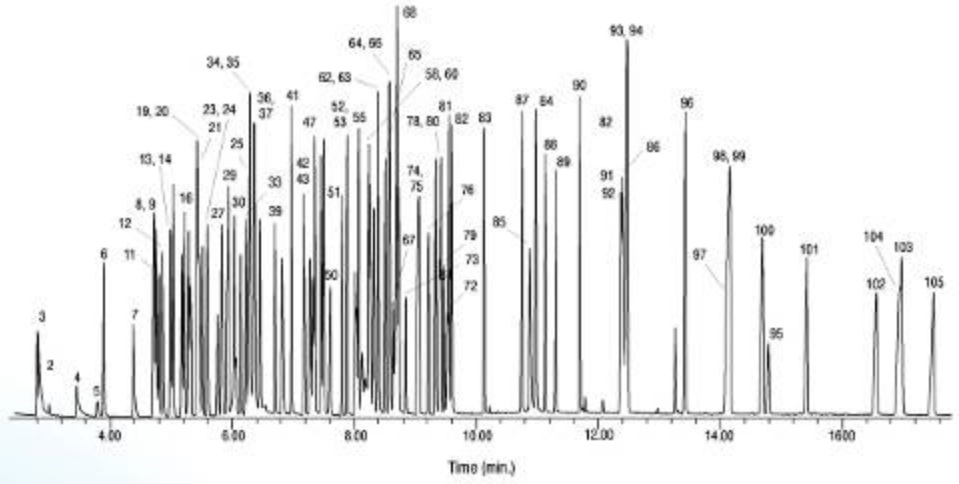
The book is 1313 pages long!

Lessons from the past: almost everything at the same time

- Analytical capabilities
  - Low concentrations
  - Specific compounds
  - Positive identification
  - No metabolites

Semivolatiles—Solid Waste Analysis, GC/MS

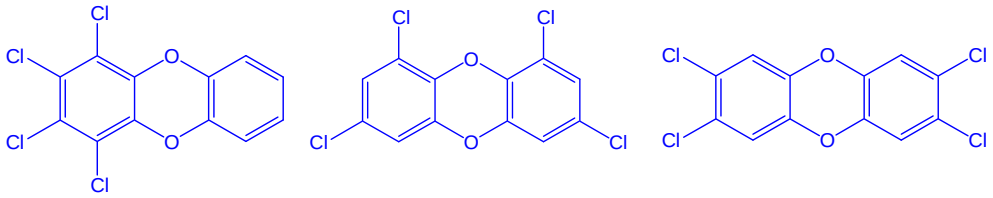
1. 1,4-Dichlorobenzene-d4	23. Nitrobenzene-d5	44. Acenaphthene-d10	65. Diethylphthalate	86. Chrysene-d12
2. Pyridine	24. Nitrobenzene	45. 2,4,6-Trichlorophenol	66. 4-Chlorophenyl-phenylether	87. Pyrene
3. N-Nitrosodimethylamine	25. Naphthalene-d8	46. 2,4,5-Trichlorophenol	67. 4-Nitroaniline	88. Terphenyl-d14
4. 2-Picoline	26. N-Nitrosopiperidine	47. 2-Fluorobiphenyl	68. Diphenylamine	89. p-Dimethylaminoazobenzene
5. Methyl methanesulfonate	27. Isophorone	48. 2-Chloronaphthalene	69. n-Nitrosodiphenylamine	90. Butylbenzyl phthalate
6. 2-Fluorophenol	28. 2-Nitrophenol	49. 1-Chloronaphthalene	70. Diphenylhydrazine	91. Benzo[a]anthracene
7. Ethyl methanesulfonate	29. 2,4-Dimethylphenol	50. 2-Nitroaniline	71. 4,6-Dinitro-2-methylphenol	92. 3,3'-Dichlorobenzidine
8. Phenol-d5	30. bis(2-Chloroethoxy)methane	51. Dimethylphthalate	72. Phenanthrene-d10	93. Chrysene
9. Phenol	31. 2,4-Dichlorophenol	52. Acenaphthylene	73. 2,4,6-Tribromophenol	94. bis(2-Ethylhexyl)phthalate
10. Aniline	32. Benzoic acid	53. 2,6-Dinitrotoluene	74. 4-Bromophenyl-phenyl ether	95. Perylene-d12
11. bis(2-Chloroethyl)ether	33. 1,2,4-Trichlorobenzene	54. 3-Nitroaniline	75. Phenacetin	96. Di-n-octylphthalate
12. 2-Chlorophenol	34. a-,a-Dimethylphenethylamine	55. Acenaphthene	76. Hexachlorobenzene	97. Benzo(b)fluoranthene
13. 1,3-Dichlorobenzene	35. Naphthalene	56. 2,4-Dinitrophenol	77. 4-Aminobiphenyl	98. 7,12-Dimethylbenz(a) anthracene
14. 1,4-Dichlorobenzene	36. 4-Chloroaniline	57. Dibenzofuran	78. Pentachlorophenol	99. Benzo (k) fluoranthene
15. Benzyl alcohol	37. 2,6-Dichlorophenol	58. Pentachlorobenzene	79. Pentachloronitrobenzene	100. Benzo[a]pyrene
16. 1,2-Dichlorobenzene	38. Hexachlorobutadiene	59. 4-Nitrophenol	80. Pronamide	101. 3-Methylcholanthrene
17. 2-Methylphenol	39. N-Nitroso-di-n-butylamine	60. 2,4-Dinitrotoluene	81. Phenanthrene	102. Dibenz[a,j]acridine
18. bis(2-chloro-isopropyl)ether	40. 4-Chloro-3-methylphenol	61. 1-Napthylamine	82. Anthracene	103. Dibenz[a,h]anthracene
19. 4-Methylphenol	41. 2-Methylnaphthalene	62. 2-Napthylamine	83. Di-n-butylphthalate	104. Indeno (1,2,3-cd) pyrene
20. Acetophenone	42. 1,2,4,5-Tetrachlorobenzene	63. 2,3,4,6-Tetrachlorophenol	84. Fluoranthene	105. Benzo[g,h,i]perylene
21. n-Nitroso-di-n-propylamine	43. Hexachlorocyclopentadiene	64. Fluorene	85. Benzidine	
22. Hexachloroethane				



Conditions:
Column: HP-5MS, 30 m x 0.25 mm x 0.25 µm (Part No. 140915-433)
Carrier: Helium, pressure program 0.1 psi (0.1 min) at 99 psi/min to 7.4 psi
Injection: 0.1 µl, 250°C
Oven: Temperature program listed above
Detector: MSD, 280°C

Same family different isomers?

- Different structure causes different
  - **toxicity**
  - reactivity
  - Partitioning
- If you are not planar or larger than 10A not that bad!
- Quantitative structure-activity relationship (QSAR) is the process by which chemical structure is quantitatively correlated with a well defined process, such as biological activity or chemical reactivity

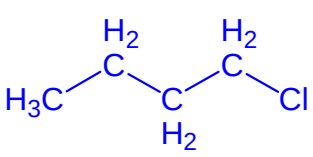


> 1 g kg^{-1} >0.1 g kg^{-1} 0.00004 g kg^{-1}

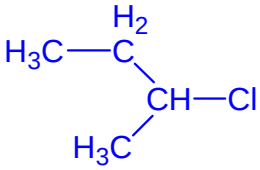
acute toxicity (LD_{50} for rats)

Same family different isomers?

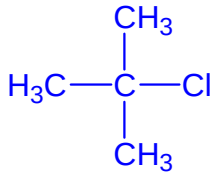
- Different structure causes different
  - toxicity
  - **reactivity**
  - partitioning



~ 1 yr



~ 40 d

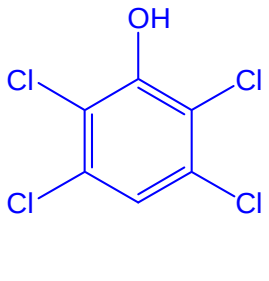


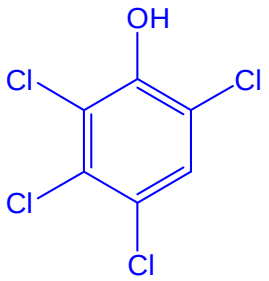
~ 30 s

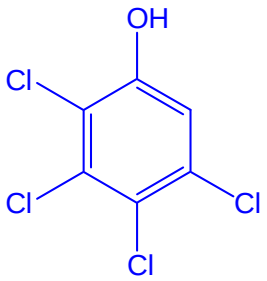
degradation (hydrolysis half-life, pH 7)

Same family different isomers?

- Different structure causes different
  - toxicity
  - reactivity
  - **partitioning**





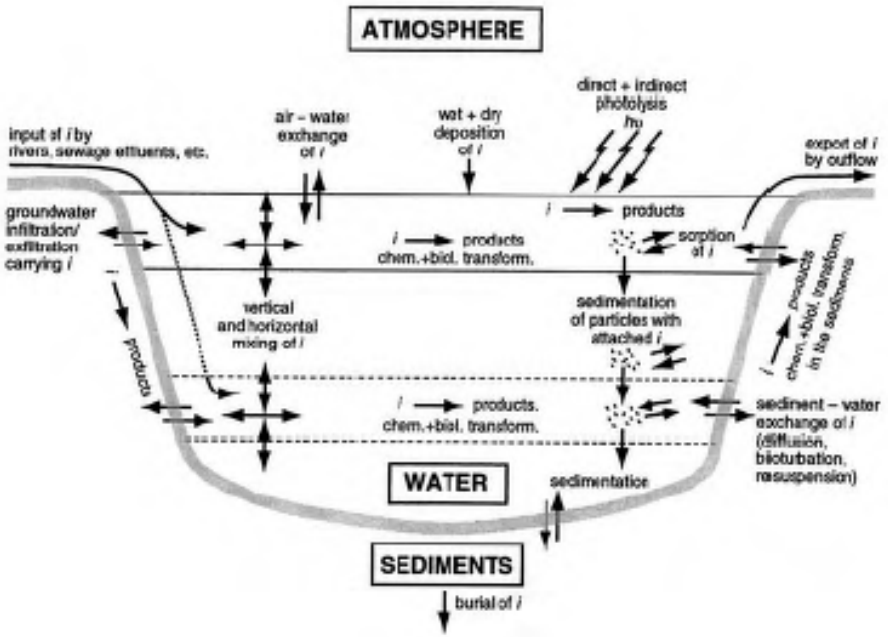


pK_a:	5.04	5.40	6.35
K_p:	10 L kg^{-1}	20 L kg^{-1}	180 L kg^{-1}

sorption to river sediments at pH 7

Value Engineering → make your life easier

- Simplify to box models
  - air
  - water
  - suspended matter
  - soil and sediment
  - organisms
  - etc.
- Remember the details
  - don't simplify if simplification underestimates an important process



PUTTING YOUR NECK ON THE LINE

http://www.youtube.com/watch?v=z4lijvIjpRw