

Note to students:

This presentation received a 50/50 as graded by me and their fellow students. Keep in mind the grade also reflects things you didn't see (delivery, presentation, etc.). The content was very good, the chemistry concepts were explained very well, and the delivery was great. The students really rated this one high and were impressed that this person chose to do it alone.

Greg

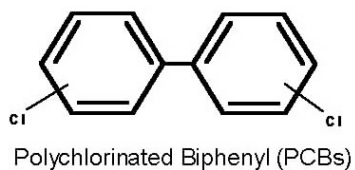
PCBs and the Great Lakes

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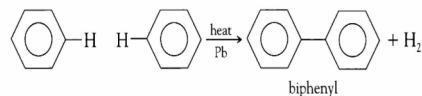
- 📄 Introduction
- 📄 Toxicology
- 📄 Regulation
- 📄 Impact on the Great Lakes
- 📄 Current Debates

Introduction

PCBs General Structure



Synthesis of PCBs



Biphenyl + Cl₂ + FeCl₃ (catalyst) → 209 possible PCB congeners

Physiochemical Properties

- Individual PCBs are solids at room temp.
- Mixtures are liquids/low melting-point solids
- High boiling point
- Low conductivity
- Flame retardant

Physiochemical properties (continued)

- Low vapor pressure
- Very low solubility in water
- Soluble in hydrophobic substances
 - ◆ Lipids
 - ◆ Oils
 - ◆ Suspended particles in water
- Chemical stability
 - ◆ Resistant to chemical & biological degradation

Physiochemical properties (continued)

- Degree of chloride substitution determines:
 - ◆ Molar mass
 - ◆ Boiling point
 - ◆ Vapor pressure
 - ◆ Fugacity
 - ◆ Molecule polarity
 - ◆ Solubility in water
 - ◆ Solubility in lipids
 - ◆ Toxicology

Sample Congener Properties

Table 23.4 Physicochemical Properties and Model Parameters for Two Selected PCB Congeners

IUPAC No.			2,3,4-Trichlorobiphenyl PCB33	2,2',3,4,5,5',6-Heptachlorobiphenyl PCB185
Molar mass	M_i	(g mol ⁻¹)	257.5	395.4
Air-water partition constant at 15°C ^a	$K_{aw} = K_H / RT$	(-)	0.003	0.007
Air-water transfer velocity				
Air ^b	v_a	(m d ⁻¹)	450	390
Water ^b	v_w	(m d ⁻¹)	0.67	0.58
Total, Eq. 20-3	v_{aw}	(m d ⁻¹)	0.45	0.48
Air-water exchange rate	$k_{aw} = v_{aw} / h$	(yr ⁻¹)	1.10	1.17
Atmospheric concentration ^d	C_a	(mol m ⁻³)	1.8×10^{-13}	1.2×10^{-14}
Octanol-water partition constant	K_{ow}	(-)	6.0×10^5	2.0×10^7
Natural organic matter-water partition coefficient	K_{oc}	(m ³ kg _{oc} ⁻¹)	27	360
Distribution coefficient				
Suspended solids ^c	K_d	(m ³ kg _s ⁻¹)	5	70
Settled solids ^c	K_{ds}	(m ³ kg _s ⁻¹)	0.8	10
Fraction dissolved in the water column, Eq. 9-12	f_w	(-)	0.998	0.973
Total input rate of PCB congener ^e	I_i	(mol yr ⁻¹)	100	30

Persistence in aqueous environments

- Low water solubility
- High lipid solubility (hydrophobic)
- Low vapor pressure
- High boiling point
- Low fugacity
- PCBs are persistent organic pollutants (POPs)

Sources of PCBs

- Exclusively anthropogenic
 - ◆ No natural sources
- Intentional Production
 - ◆ 700,000 tons of PCBs produced (1929-1977)
- Unintentional Production
 - ◆ Byproducts of chemical processes

Past uses of PCBs

- Insulation of electrical equipment
- Synthetic resins
- Epoxy paints
- Inks and carbonless copy paper
- Hydraulic and heat transfer fluids
- Pesticides
- Other unknown/undisclosed uses

Current allowable uses

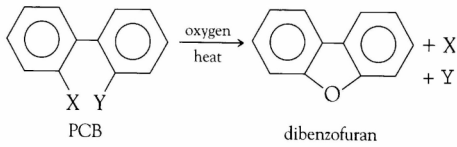
- Transformers
- Capacitors

Toxicology

Acute Toxicology

- Coplanar PCBs of greatest concern
- Most toxic PCB:
 - ◆ 3,3',4,4',5'-pentachlorobiphenyl
 - ◆ Similar in size and shape as 2,3,7,8-TCDD
 - ◆ ~ 1/10th as toxic as TCDD
- PCBs can oxidize to give the potentially more toxic polychlorodibenzofurans (PCDFs)

Polychlorodibenzofuran (PCDF) formation



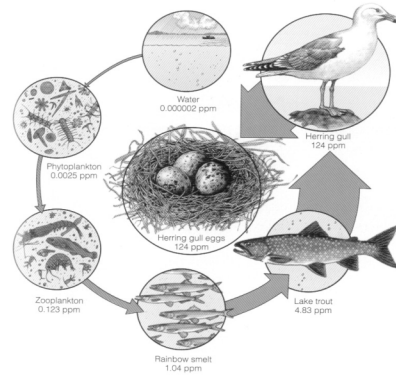
Acute Toxicology (continued)

- Greatest exposure risk:
 - ◆ Electrical industry workers
 - ◆ Chemical processing plant personnel

Chronic Toxicology

- Nonplanar PCBs
 - ◆ Higher abundance relative to coplanar PCBs
- Greatest human exposure source:
 - ◆ Fish and shellfish consumption
 - ◆ A consequence of bioaccumulation

Bioaccumulation of PCBs



Fish Toxicology

- 4 ppm PCBs in trout and salmon:
 - ◆ Goiter
 - ◆ Impaired metabolism
 - ◆ Reproduction problems
 - ◆ Tumors

Fish lip tumor



Laboratory animal tests

- PCB exposure can cause:
 - ◆ Cancers/tumors
 - ◆ Birth defects
 - ◆ Reproductive deficiencies
 - ◆ Liver and gastric tract disorders
 - ◆ Eye/vision degeneration

Human health effects

- PCBs stored in lipid tissues
 - ◆ Minimal excretion or metabolism
- Effects on laboratory animals may correlate to humans.
- Primary concerns:
 - ◆ Carcinogenic effects
 - ◆ Reproductive effects
 - ◆ Cognitive development in children

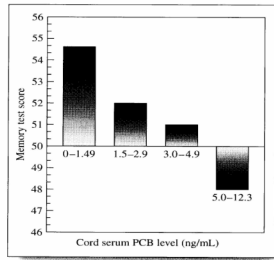


Figure 1-1
 Test outcomes (McCarthy verbal test scores) of the 1990 Lake Michigan case study of four-year-old children. The children's scores are graphed versus the PCB concentrations in the umbilical cord serum at birth. (Source: Redrawn from J. L. Jacobson, S. W. Jacobson, and H. E. B. Humphrey, 1990. Effects of in utero exposure to polychlorinated biphenyls and related contaminants on cognitive functioning in young children. *Journal of Pediatrics* 116(1): 38-44.)

Regulation

Regulation of PCBs

- Toxic Substances Control Act (TSCA)
- Clean Air Act
 - ◆ PCBs are Hazardous Air Pollutants (HAPs)
- Clean Water Act
- Safe Drinking Water Act
 - ◆ Maximum concentration of 0.5 ppb
- Department of Agriculture
 - ◆ Protection of food products

Impact on the Great Lakes

Loading of PCBs

- **Loading** = the modes by which a chemical enters a system.
- **Chemical of Interest** = PCBs
- **System of Interest** = The Great Lakes
 - ◆ All five lakes are connected
 - ◆ Loading of PCBs is not isolated for any one lake
- **Main loading mechanism:**
 - ◆ atmospheric deposition (~50%)

Great Lakes box model

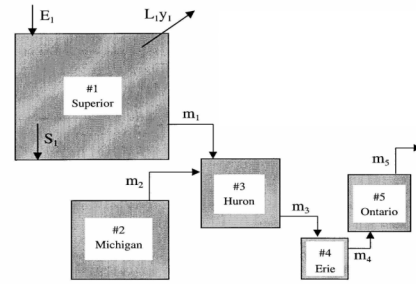


FIGURE 1
Integrated Atmospheric Deposition Network sites

Master stations (red squares) are the main sites in the network and the first to be established for each lake. Satellite stations (purple diamonds) have been added to augment the master stations.

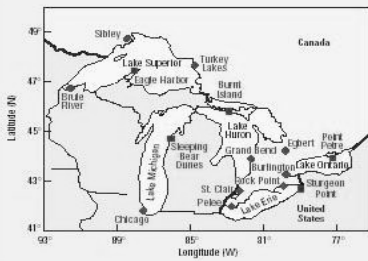
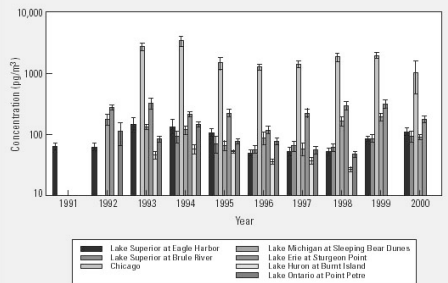
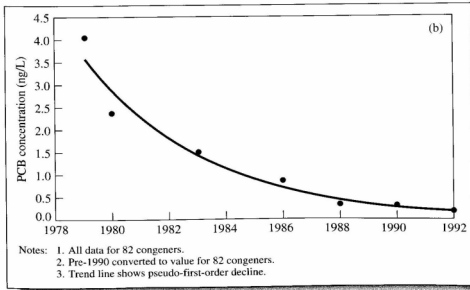


FIGURE 3
Annual average atmospheric gas-phase total PCB concentrations for IADN master stations and two U.S. satellite sites

Polychlorinated biphenyl (PCB) concentrations are in picograms per cubic meter and error bars represent the standard error for each average. (Data for 1999 and 2000 are not yet available for Lakes Huron and Ontario.)



PCBs trend in Lake Superior



PCBs trend in Lake Ontario gull eggs

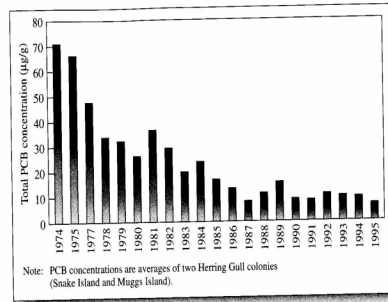
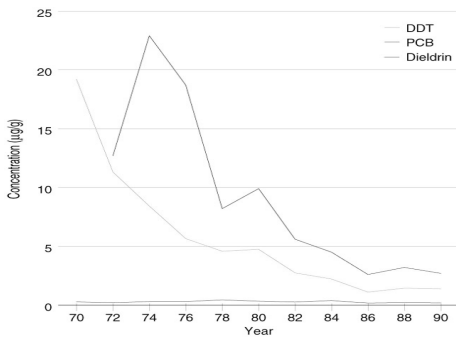
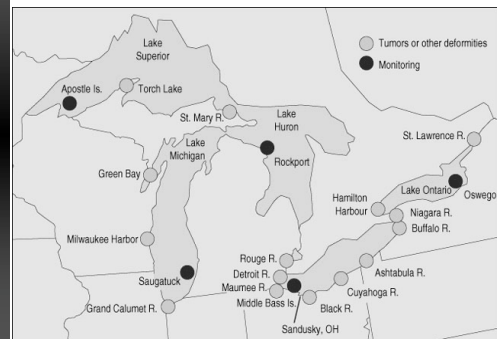


Figure 6-8
Trends in total PCB concentrations in herring gull eggs in Lake Ontario, 1974-95. (Source: The State of Canada's Environment 1996, Ottawa: Government of Canada.)

Trends in Lake Michigan Lake Trout



Priority observation sites



Current Debates

Current Debates over PCBs

- Opinion 1:
 - ◆ The dangers of PCBs are wildly overstated
 - ◆ No human deaths directly linked to PCBs
 - ◆ Regulation and monitoring is expensive
- Opinion 2:
 - ◆ Biomagnification is a problem
 - ◆ High relative toxicity per molecule
 - ◆ Ubiquitous distribution impacts nearly all environments

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