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CEE 697z

Organic Compounds in Water and Wastewater

PCBs:
Introduction and Properties

Lecture #33

UMass story: September 2012

UMass, EPA agree on plan to replace contaminated windows at Lederle Graduate Research Center over 15 year period

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The Republican file

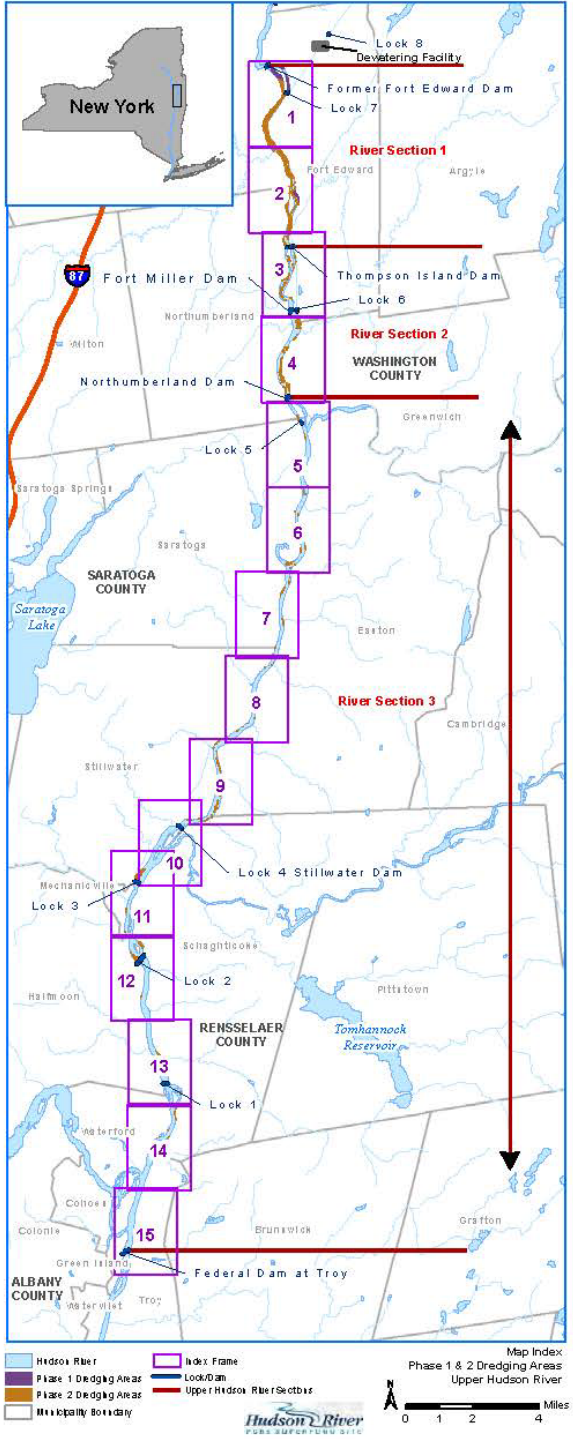
Some of the many window in the John W. Lederle Graduate Research Center on the University of Massachusetts campus in Amherst are seen in this file photo.

AMHERST – Federal environmental officials and the **University of Massachusetts** have entered into a consent agreement for which the university will remove windows contaminated with **polychlorinated biphenyl** at the **John W. Lederle Graduate Research Center** over 15 years.

According to a prepared

2012 News Story

- UMass discovered that the window glazing at the research center was contaminated with high levels of contaminants after finishing a window-caulking project in 2009.
- UMass has agreed to replace and dispose of all 900 PCB-contaminated windows over the next 15 years at a cost of about $3 million.
- The university will complete window cleaning, encapsulation, verification and baseline sampling within 24 months, according to the release and to start removing windows in Tower A on floors 3, 7 and 8 by Dec. 31, 2012 according to a UMass statement.
- The cost of these interim measures is about $560,000. The settlement agreement also includes a $75,000 civil penalty that will be waived if both the long-term remediation plan and interim encapsulation plan are completed, according to the release.
- The window-glazing compound was commonly used in construction from the 1950s through the mid-1970s. The Lederle complex at UMass Amherst was constructed in the early 1970s.
- UMass spokesman Edward F. Blaguszewski said "We're obviously concerned with the issue. We want to protect our employees. We've taken steps for an interim plan. This is something that allows for a fairly prompt way to address the exposure," he said. "We really want to partner with the EPA to address the issue."
  He said EPA officials feel that "coming up with a solution such as this is something that could possibly serve as a model" for others with similar issues to follow.



Hudson River Dredging

- GE is dredging the Hudson River in Upstate New York to remove PCBs in one of the largest and most complex environmental cleanups in U.S. history. Dredging is conducted around the clock for six months a year.
- Dredging activities began in 2009 and continued from 2011-2014. The final season of the project will be conducted in 2015. When the six-year project is completed, GE will have removed 100 percent of the PCBs targeted by EPA for removal — more than 2.65 million cubic yards of sediment from a 40-mile stretch of river between Fort Edward and Troy, N.Y.
- EPA's goal for GE is to remove 350,000 cubic yards of sediment from the river each year. Water is squeezed out of the sediment and PCBs are removed from the water at a specialized processing and dewatering facility GE built for the project. The sediment is shipped by train to federally permitted disposal facilities outside of New York State.

Polychlorinated biphenyls (PCBs)

- Properties
  - non-flammability, chemically stabile, high boiling point, and good electrical insulating properties
- Uses:
  - hundreds of industrial and commercial applications including electrical, heat transfer, and hydraulic equipment; and as plasticizers in paints, plastics, rubber products, and building caulk.
- Adverse health effects
  - animal studies, PCBs have been shown to cause cancer as well as serious non-cancer health effects.
  - In humans, PCBs are potentially cancer-causing and can cause other non-cancer effects including immune system suppression, liver damage, endocrine disruption, and damage to the reproductive and nervous systems.

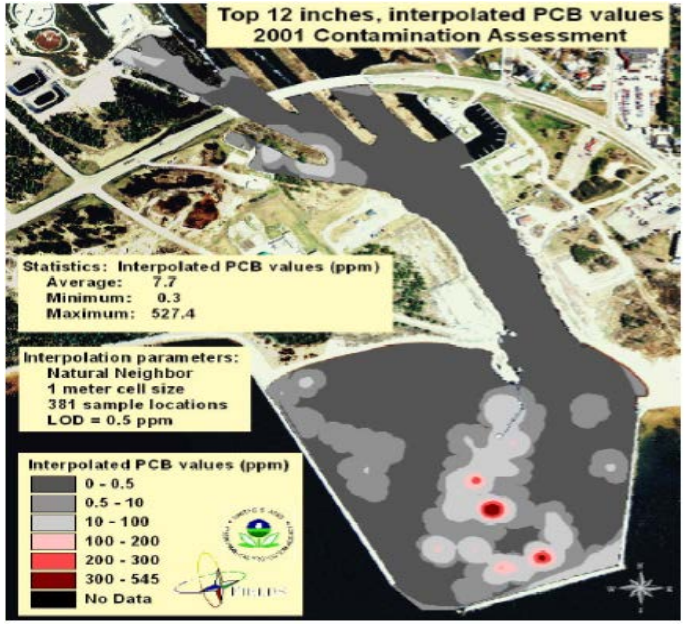
Grad Research Tower

- PCBs were a common additive to caulk because of their water and chemical resistance, durability, and elasticity. PCBs were added as a plasticizer in caulking used to seal joints between masonry units and around windows. Caulk containing PCBs was used in some buildings, including schools, primarily between 1950 and 1980. PCBs were also used in other building materials such as paints, mastics, sealants, adhesives, and specialty coatings.
- If your building was built between 1950 and 1980, you have several options:
  - You can assume you have PCB-containing materials but not remove them. You should renovate with caution however since caulk and surrounding materials may be contaminated with PCB; or
  - You can proceed to test the air to determine if the PCB-containing materials are causing a potential public health problem and therefore should be removed.
  - If you decide to remove the PCB-containing caulk and/or other materials, you are now doing an abatement project, and should refer to Steps to Safe PCB Abatement Activities.

Polychlorinated Biphenyls (PCBs)

World production of PCBs since 1930 is estimated at one million tons[2]. Although the manufacture of PCB ceased in 1979 under TSCA, some 750 million pounds remained in use as of the mid-1980s[3], largely in electrical equipment. PCBs enter the environment through effluent discharge, incineration and leakage.

General Electric Corporation, a manufacturer of capacitors, discharged PCBs to the Hudson River under a federal permit for over 20 years. Over a half-million pounds of PCBs remain in the Hudson River, with thousands of pounds migrating downstream each year[3]. Other noteworthy PCB contamination sites include the Fox River at Green Bay (pulping and paper de-inking discharges[4]) and the Manistique River/Harbor (paper and electric industries[5]) in the Upper Peninsula. All of these locations have been the focus of intensive investigation and remediation.

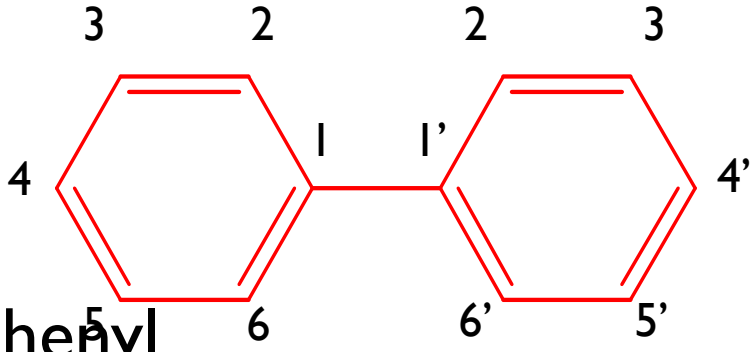


Manistique River Site[6]

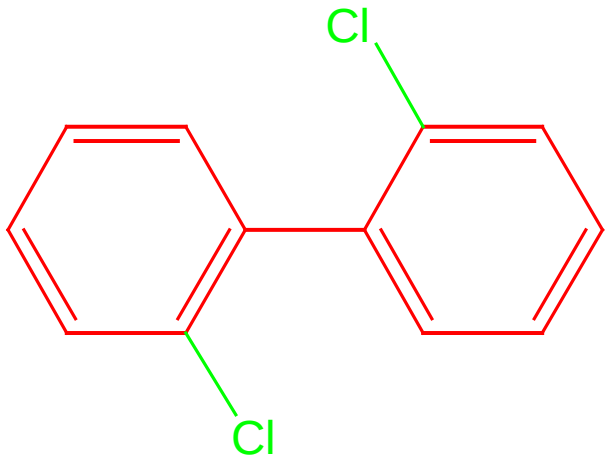
What are the PCBs

Homologs (11)
Isomers (1-46)
Congeners (209)

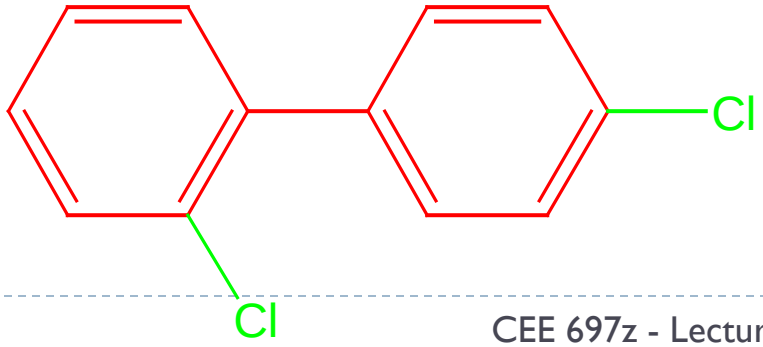
- Biphenyl



- 2,2' - Dichlorobiphenyl



- 2,3' - Dichlorobiphenyl



History

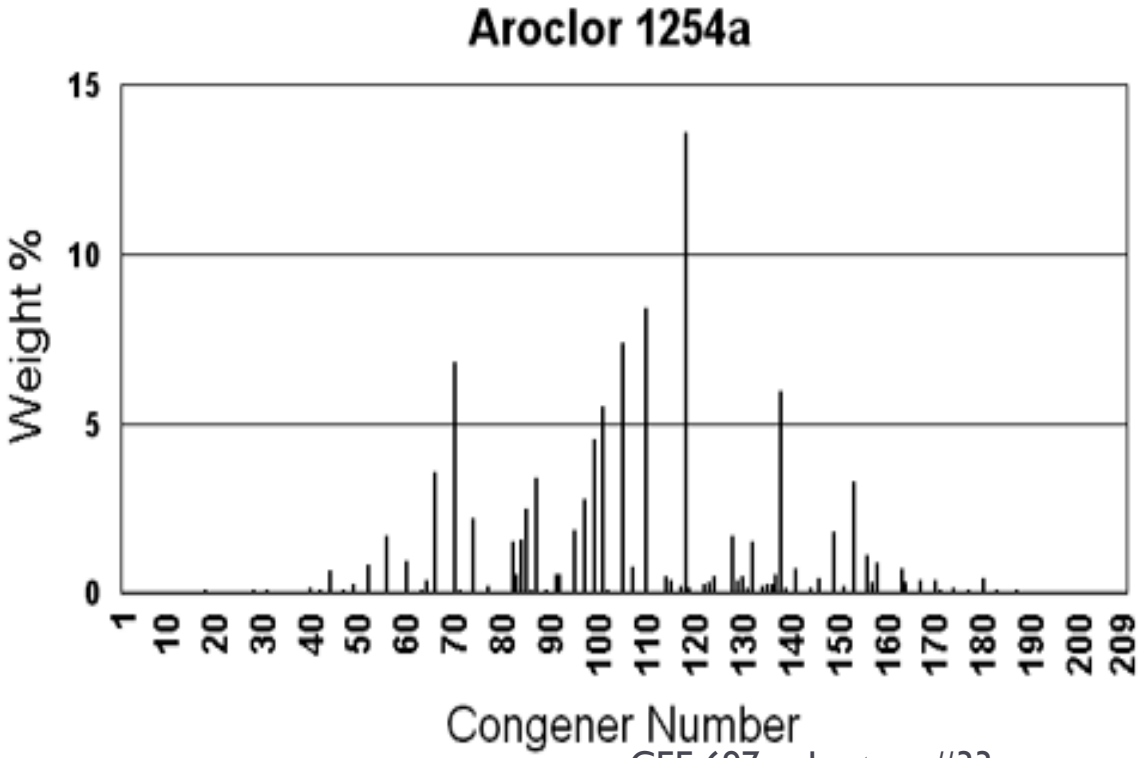
- 1930: Monsanto is major US producer
- 1970: Monsanto decides to sell PCBs only for closed use
- 1975: NY State warns public about salmon and bass in Hudson
- 1979: PCB manufacture banned in US
- 1982: NY State begins dredging "hot spots"
- 1990: all PCB-containing equipment must be removed from US public buildings

Arochlor Mixtures

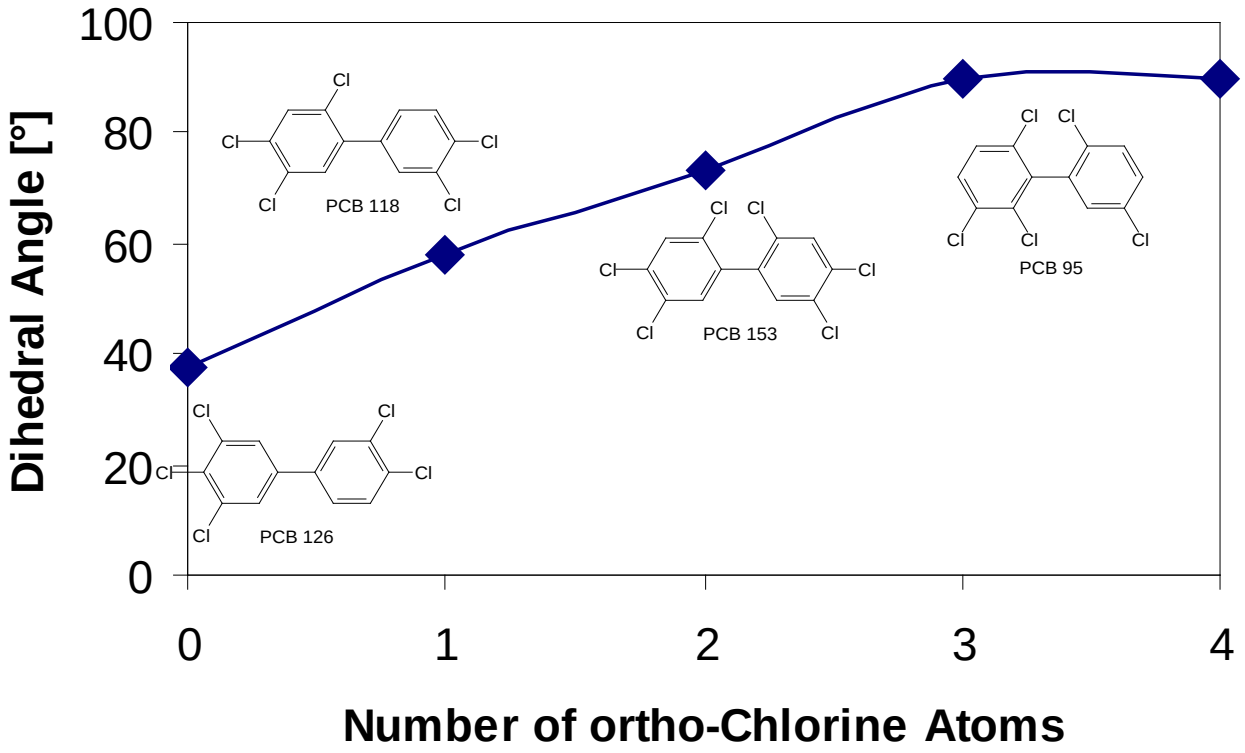
- Arochlor 12xx (xx=% chlorine)
  - 1221: 50% Cl_1, 35% Cl_2
  - 1232: 26% Cl_1, 29% Cl_2, 24% Cl_3
  - 1242: 13% Cl_2, 45% Cl_3, 31% Cl_4
  - 1248: 49% Cl_4, 27% Cl_5
  - 1254: 15% Cl_4, 53% Cl_5, 26% Cl_6
  - 1260: 12% Cl_5, 42% Cl_6, 38% Cl_7
  - 1262: no data
  - 1268: no data

Polychlorinated Biphenyls (PCBs)

PCBs were typically manufactured as a mixture of congeners, created through the progressive chlorination of biphenyl until a target chlorine content (percentage by weight) was obtained and the mixture has characteristic physical-chemical properties. One of the most common mixtures was Arochlor 1254, which contained 54% chlorine by weight. Once released to the environment, mixtures undergo diagenesis, changing the congener balance and making it difficult to determine their origin.



3D Structure of PCBs: Calculated Dihedral Angle



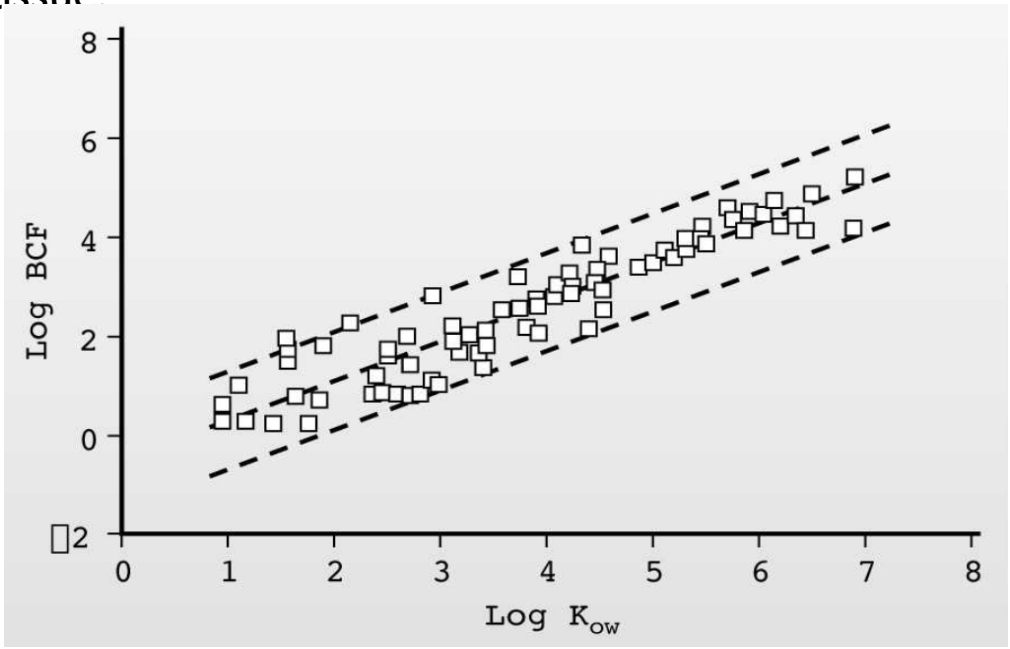
Mechanisms of toxicity of PCBs and their metabolites

Congener/metabolite	Molecular Target	Action
non-ortho and mono-ortho-PCBs	aryl hydrocarbon receptor (AHR)	altered gene expression (CYP1A and others); oxidative stress?
di-ortho PCBs (PCB-95: 2,2',3,5,6-PCB)	ryanodine receptor	altered calcium homeostasis, neurotoxicity?
di-ortho PCBs	??	altered neurotransmitter metabolism (dopamine & serotonin)
ortho PCBs (PCB-164: 2,3,3',4',5',6-HCB)	constitutive androstane receptor (CAR)	induction of CYP2B
highly chlorinated PCBs (PCB-184, -196, -153)	rodent PXR (agonists) human SXR (antagonists)	induction of CYP3A; varies by species
OH-PCB	transthyretin (TTR)	inhibition of thyroid hormone transport and retinoid homeostasis (rodents > humans; TTR vs TBG)
OH-PCB	sulfotransferase, glucuronosyl transferase	inhibition of sulfotransferase (E2 and T4 , 3-OH-BaP)
PCB and OH-PCB	estrogen receptor (ER)	ER agonist or antagonist
methylSO$_2$-PCB	uteroglobin	displacement of progesterone??
methylSO$_2$-PCB	glucocorticoid receptor	GR antagonist

Polychlorinated Biphenyls (PCBs)

PCBs have been demonstrated to cause a variety of adverse health effects, including cancer and disruption of the endocrine, nervous, and reproductive systems[1]. It has a potency factor for toxicity more than 4 times that of arsenic[7].

PCBs have a very high bioconcentration factor and are regularly found present in fish tissue.



$$BCF = \frac{C_{fish}}{C_{water}} = \frac{\frac{mg\ chemical}{kg\ fish}}{\frac{mg\ chemical}{L\ water}} = \frac{L}{kg}$$

The BCF has been empirically correlated with K_{ow}, and thus a tendency to partition into the fatty tissue of fish or humans. PCBs have a BCF of 100,000 L/kg, compared with 4 for chloroform and 44 for arsenic[7].

- To next lecture