

# PCB Chemistry 101

Presented by Valerie Tillinghast  
O'Reilly, Talbot & Okun Associates, Inc.

# Short History of PCBs

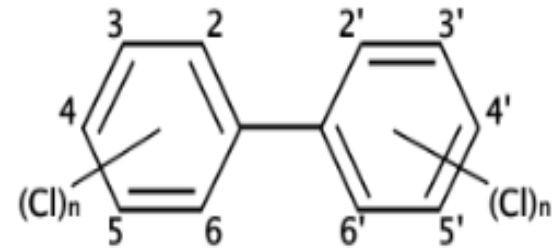
---

- Reports indicate that PCBs were first synthesized by chemists in 1881 but significant commercial development did not begin until the late 1920s.
- Monsanto Chemical Company was the major US manufacturer of PCBs; relatively little PCB was imported to the US.
- PCB commercial use expanded significantly following the end of World War II.
- Other countries (mainly Germany and Japan) also manufactured PCBs, and generally the formulations were similar, but not identical.

# So What are PCBs?

- Simple answer – a mixture of chlorinated biphenyls and a small amount of by-product.
- What's biphenyl?
- It is two phenyl groups (aka benzene rings) that are joined together with a single carbon-carbon bond.

## PCBs (Polychlorinated biphenyl)



Chemical structure of PCBs  
The chemical formula for PCBs is  
 $C_{12}H_{10-x}Cl_x$

# A Little Biphenyl Chemistry

---

- Biphenyl is symmetrical along its horizontal (x) and vertical (y) axis;
- Each of the phenyl groups is flat (all 6 carbons lie in the same plane), but because there is free rotation around the C-C single bond, the biphenyl molecule itself is 3-D.
- Spectroscopic studies show that the preferred angle between the phenyl groups is 44 degrees.
- Substitutions, particularly in the ortho position, restrict rotation around the C-C bond.

# The Hexagon: One of Nature's Perfect Shapes

---



# How Biphenyl turns into PCBs

---

- Biphenyl, like benzene, is a relatively stable organic molecule.
- Also like benzene it is subject to substitution reactions where hydrogen atoms can be replaced by other atoms or groups of atoms.
- To make PCBs, biphenyl is reacted with chlorine gas in the presence of an iron catalyst.
- Chlorine atoms replace the hydrogen atoms.
- Different PCB formulations were made by varying reaction parameters like the duration of the chemical reaction.

# PCB Mixtures

---

- The potentially astronomical number of different PCB molecule types is reduced to 209 because of biphenyl's symmetry.
- This means there are still 209 different possible arrangements of chlorine atoms on the biphenyl molecule.
- Each of these possible PCB molecules is referred to as a "congener"
- Commercial PCB mixtures (e.g. Aroclors) contained 50 or more different congeners.

# Aroclors

---

- Aroclor was the brand name Monsanto used for its PCB mixtures.
- Generally, the last two digits of an Aroclor's number indicates the percent chlorine in the mixture.
- For instance Aroclor 1221 would be 21% chlorine by mass and Aroclor 1260 would be 60% chlorine by mass.
- The physical properties varied significantly between the Aroclors.



# Aroclor Physical Properties

---

- The most important commercial properties of PCBs were their: chemical stability; heat stability; non-flammable; and non-aqueous solvent solubility.
- They do not conduct electricity, and therefore made outstanding dielectric fluids.
- Viscosity and boiling point were two of the most important variables among the Aroclor mixtures.
- Aroclor 1221 had the viscosity of a light machine oil; Aroclor 1254 was as viscous as honey; Aroclor 1268 was a solid at room temperature.
- The most common Aroclors were: 1221, 1232, 1242, 1016 (refined 1242), 1248, 1254, 1260, 1262 and (less commonly) 1268.

# Why PCBs Became Popular

- PCBs were the Fountain of Youth for many commercial products.
- They lent their own “indestructibility” to the products they were added to
- They prevented fires in electrical equipment.
- Electrical components, paints, caulk etc. all lasted much longer when PCBs were included in their formulations.



"I can't get the childproof cap off."

# PCB Indestructibility

---

- Organic chemicals in the environment are subject to powerful chemical and physical forces that over time break them down.
- Chlorinated molecules are particularly good at resisting attacks by oxygen (oxidation) one of the most powerful mechanisms that degrades organic molecules in the environment.
- The more chlorinated congeners are more resistant to degradation, and more persistent in the environment.

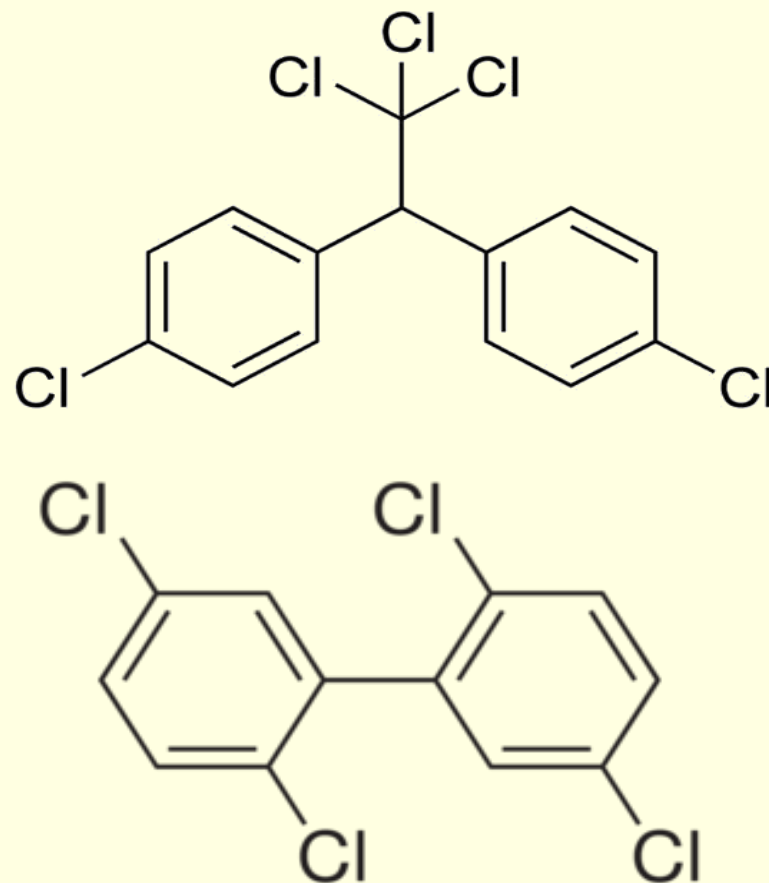
# The Swedes at it Again!

- In the mid 1960s, Swedish environmental chemists began reporting the presence of PCBs in environmental samples, even those collected far from industrial settings.
- Samples of fish and birds taken from the wild were turning up with PCBs concentrated in their fatty tissues.
- Their work was replicated by others; PCBs were turning up everywhere scientists looked.
- PCBs while chemically similar to DDT, were even more resistant to decomposition in the environment.



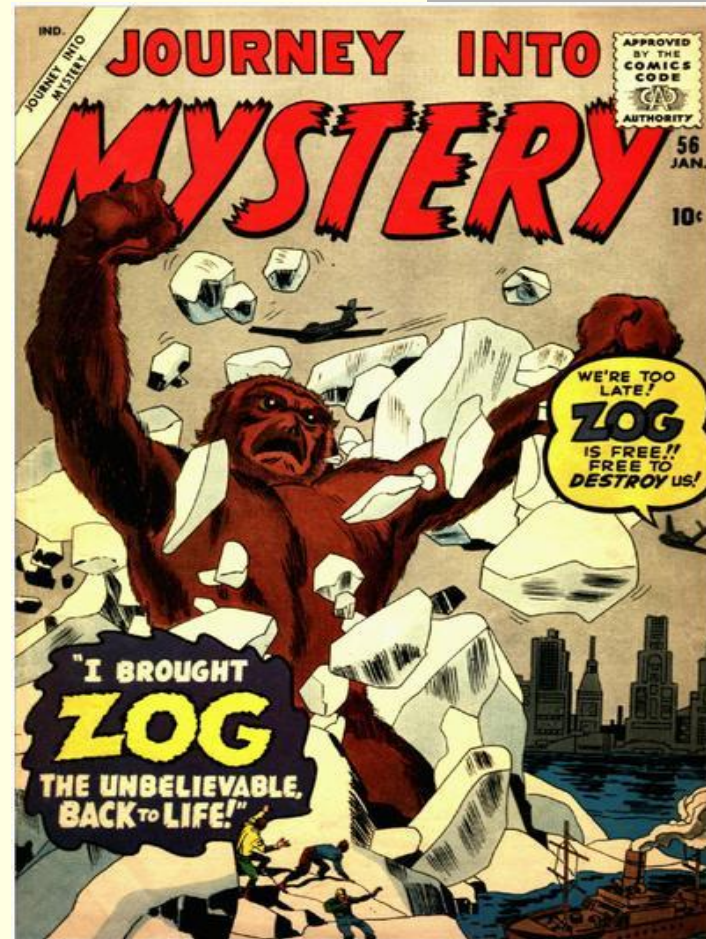
# PCBs compared to DDT

- DDT is on the top, PCB 52 (2,2',5,5'-TCB) is on the bottom.
- Each is a chlorinated partially aromatic hydrocarbon.
- Each is relatively insoluble in water and highly soluble in most organic solvents.
- Each is persistent in the environment.



# PCBs in the Environment

- With the realization that PCBs were now present throughout the globe, scientists began research projects to better understand their significance.
- Developing better analytical chemistry methods to measure PCBs was high on the to-do list.
- Because of previous work on the chlorinated pesticides, chemists had a head-start in being able to measure PCBs.





# Limitations of Early Analytical Methods

- The chromatograms to the right are typical of what a PCB analysis looked like in the 1970s-early 80s.
- Each peak represented dozens of different congeners.
- Further resolution came with the use of capillary GC columns and MS detectors.

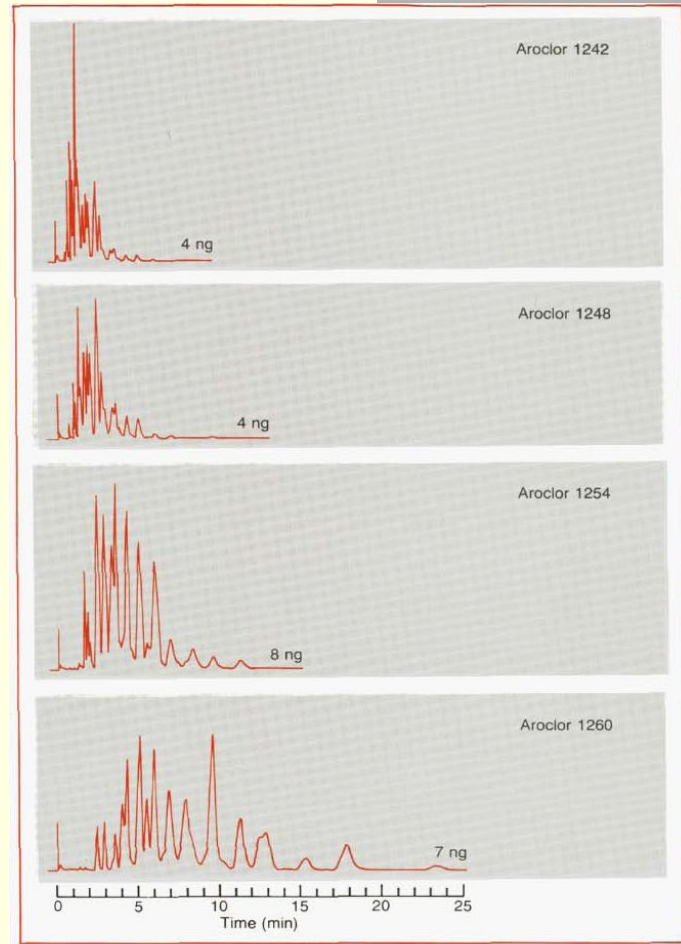
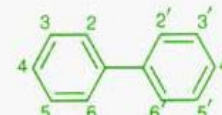


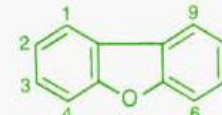
Figure 2. Electron capture responses of various Aroclor standards: 2% OV101, 6 ft X 2 mm, 200 °C

# Advanced Analytical Methods Lead to Improved Understanding

- With new methods, chemists could begin to identify major congeners.
- They also discovered a class of highly toxic contaminants, the PCDFs, that can form when PCBs are heated above 250° C for extended periods of time.
- More on PCDFs in the toxicology session.



Polychlorinated  
Biphenyls  
(PCBs)



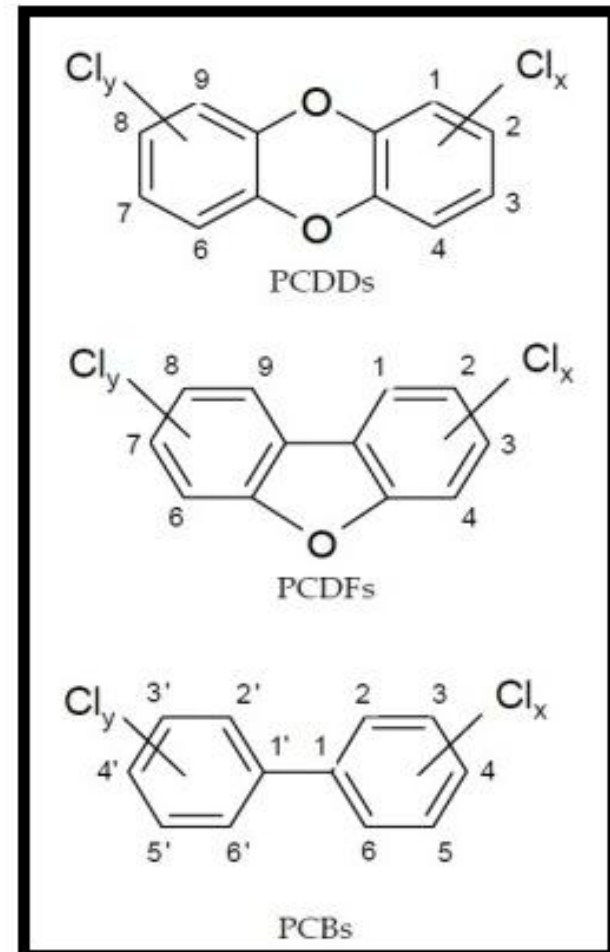
Polychlorinated  
Dibenzofurans  
(PCDFs)

Chlorine Substitution	PCBs	PCDFs
Mono-	3	4
Di-	12	16
Tri-	24	28
Tetra-	42	38
Penta-	46	28
Hexa-	42	16
Hepta-	24	4
Octa-	12	1
Nona-	3	—
Deca-	1	—
<b>Totals =</b>	<b>209</b>	<b>135</b>



# Coplanar (aka Dioxin-Like) PCBs

- PCBs with no Cl in the 2, 2',6 or 6' (the ortho positions) are called coplanar PCBs because they are able to become flatter than other PCB congeners
- PCBs with only one Cl in an ortho position are sometimes also referred to coplanar, although these are not able to get as flat as congeners with no ortho substitutions.
- More on coplanars in the toxicology session.



# Yusho

---

- The tipping point for PCBs came with the 1968 Yusho rice oil poisoning in Japan (more on this in the toxicology session).
- The same indestructibility that made them so commercially popular was their ultimate undoing; PCBs don't go away, they just accumulate over time.
- Within 4 years of Yusho, PCBs were banned in Japan, in another 6 years the US followed Japan's lead. Most of the rest of the world also agreed to abandon PCBs.

# Aroclor 1016

---

- Following Yusho, Monsanto developed a new less toxic PCB formulation named Aroclor 1016.
- Aroclor 1016 was a refined version of Aroclor 1242 that contained a lower percentage of higher and lower chlorinated congeners.
- The new Aroclor 1016 was made by distilling Aroclor 1242. The by-product of this distillation was subjected to an additional chlorination step and sold as Aroclor 1254.
- Subsequent testing showed Aroclor 1254 produced by this new process contained higher amounts of coplanar PCBs and PCDFs than the original formulation. Less than 1% of total Aroclor 1254 was produced by the new method.

# Methods for Measuring PCBs in the Environment

---

- Other presenters will cover this in more detail.
- As an LSP you need to think about what type of PCB analytical results you need for your projects.
- The main options are measuring PCBs as Aroclors, homologs or congeners.
- Most of the time measuring for Aroclors will be the right answer, but sometimes it's not, like when there may have been changes in the PCB congener composition in the environment.

# Measuring PCB Homologs

- Homologs are a way of grouping congeners by the number of chlorine substitutions.
- Analysis of PCB homologs can be a very useful tool for assessing PCBs that have been subjected to attenuation.

PCB Homolog	Cl Substituents	Number of Congeners
Monochlorobiphenyl	1	3
Dichlorobiphenyl	2	12
Trichlorobiphenyl	3	24
Tetrachlorobiphenyl	4	42
Pentachlorobiphenyl	5	46
Hexachlorobiphenyl	6	42
Heptachlorobiphenyl	7	24
Octachlorobiphenyl	8	12
Nonachlorobiphenyl	9	3
Decachlorobiphenyl	10	1

# How PCBs can Change

---

- While it is convenient to think of PCBs as a single analytical parameter, it's also important to remember that it is really a mixture of many different chemicals.
- Some congeners are more water soluble, some are more volatile and some are more susceptible to biodegradation. Generally, the less chlorinated congeners are more labile.
- When these attenuating mechanisms have acted on PCBs, the makeup of the mixture can change.
- When these changes occur measuring PCBs as Aroclors may not give an accurate results.

# Measuring PCB Congeners

---

- Analysis of all 209 possible congeners is still research level analytical chemistry.
- There are a number of congener analytical packages that laboratories offer that tie into regulatory requirements.
- The NOAA PCB congener method cites 20 congeners to be reported, this is often used for sediment analysis.
- The USACE PCB congener method cites 18 congeners to be reported.
- The World Health Organization (WHO) list includes 12 congeners.
- Each agency selects its list based on its own regulatory or research agenda.
- Congener data is useful for forensic purposes, but the guidance available for interpreting the data is fairly limited. Having 20+ data points for each PCB analysis does not always help you to understand what is happening.

# PCB Chemistry 101 Questions

---

- 1) What is a PCB Congener? And how many of them are there?
- 2) How do PCB congeners differ from homologs?
- 3) How did the different Aroclors vary?
- 4) Which chemical properties most distinguish PCBs?
- 5) What are the advantages of measuring PCBs as Aroclors? Homologs? Congeners?
- 6) What makes coplanar congeners different?
- 7) What are PCDFs?
- 8) Which congeners are most likely to degrade in the environment?