

Northeast Waste Management Officials' Association (NEWMOA)

Introduction to PCB Issues at Waste Site Cleanup Sites

November/December 2012

Agenda

- The problem that never really went away
  (Why are we here?)
- Without chemicals, life itself would be impossible
  (A quick chemistry lesson)
- Exposure and toxicity overview
  (Why do we care?)
- Introduction to characterization
  (A few examples)

PCBs: The Problem that Never Really Went Away

Why are we here?

Mug Shot
(Used Capacitor Oil)

What has brought us all here today?

Durable, long lasting, high performance, and extremely useful compound.

PCBs have a myriad of uses

- Electrical devices
- Paints, adhesives
- Plasticizers
- Carbonless copy paper

Their impact has been huge.

- Over 1.2 trillion pounds produced in the U.S.
- >75-percent used in capacitors/transformers
- Nearly 10-percent (~125 million pounds) used as plasticizers (think building materials).
- Over 3 percent (~45 million pounds) used in carbonless copy paper.

Uses of Aroclor by Type

Current Uses (since 1970)	1221	1232	1242	1248	1254	1260	1268
Capacitors	X		X		X		
Transformers			X			X	
Heat transfer			X				
Hydraulic/lubricants • Hydraulic fluids		X	X	X	X	X	
• Vacuum pumps				X	X		
• Gas-transmission turbines	X		X				
Plasticizers • Rubbers	X	X	X	X	X		X
• Synthetic resins				X	X	X	X
• Carbonless paper	X		X				
Miscellaneous • Adhesives	X	X	X	X	X		X
• Wax extenders			X		X		
• Dedusting agents					X		
• Inks					X	X	
• Cutting oils					X		
• Pesticide extenders					X		
• Sealants and caulking compounds					X		

PCBs are like a Sci-Fi Super Villain with Global Reach

GAPS - Global Atmospheric

Passive Sampling Study*

- ❑ Coordinated air sampling
- ❑ 40 stations / seven continents
- ❑ 13 Persistent Organic Pollutants (POPS)
- ❑ Kalahari Desert – One of the few remote sites where PCBs were not detected in air.
- ❑ The highest PCB air concentrations were detected in urban centers.

* Pozo, et al., *Toward a Global Network for Persistent Organic Pollutants in Air: Results from the GAPS Study*, Vol. 40, No. 16, 2006 / Environmental Science & Technology.

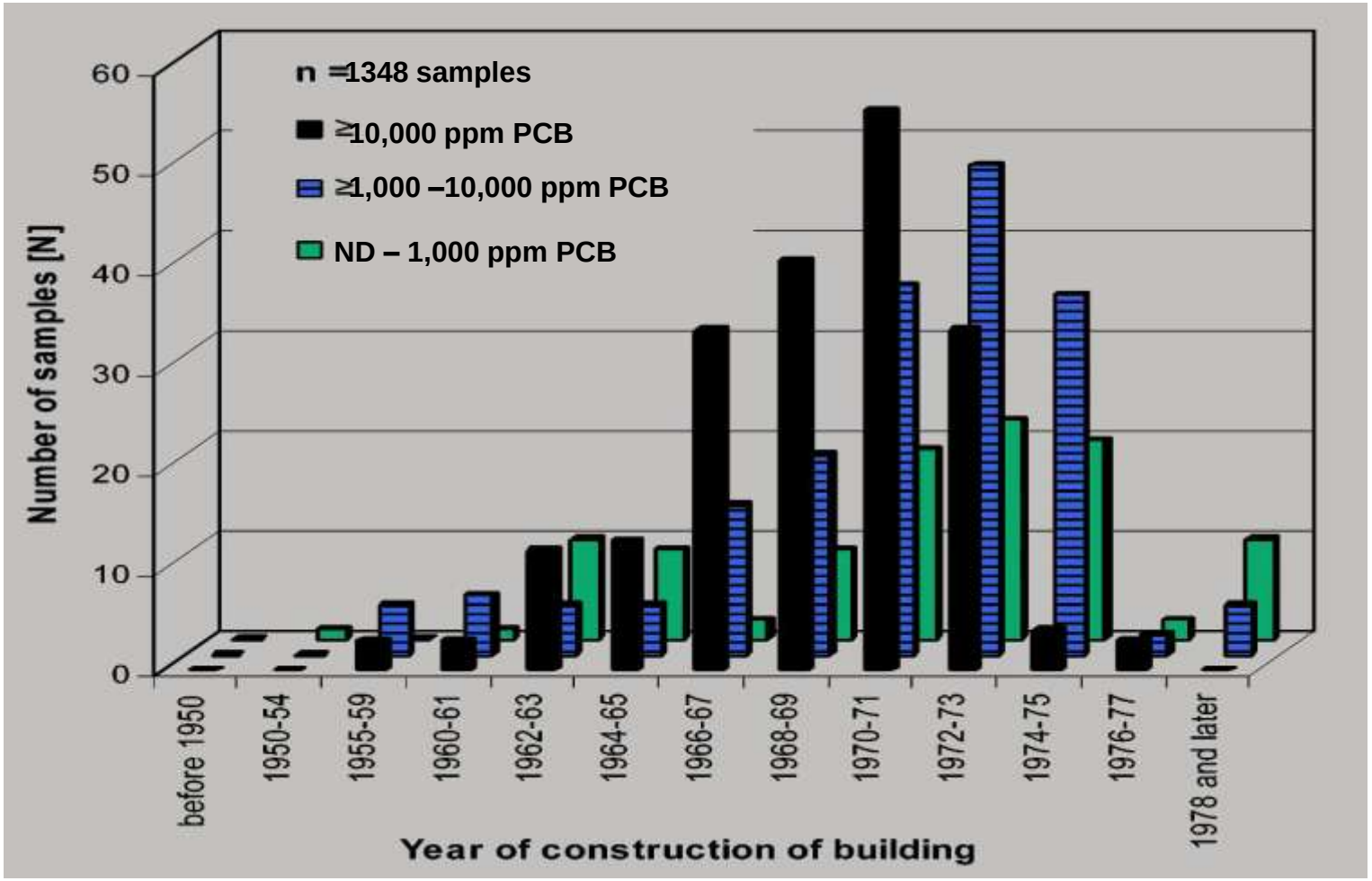
So if Urban Areas are the Hot Spots*….

…then the problem scope is huge!

- Building stock – Over half of the concrete/masonry buildings in the U.S. were built between 1955 and 1975…peak **PCB use timeframe.**
  - Herrick (2010) – "…one-third of the schools constructed from 1950 to 1970 will be found to contain PCBs…"
  - Can we have a quick show of hands?

* Diamond & Hodge. *Urban Contaminant Dynamics: From Source to Effect.* Vol. 41, No. 11, 2007/ Environmental Science & Technology

Importance of Building Age Category

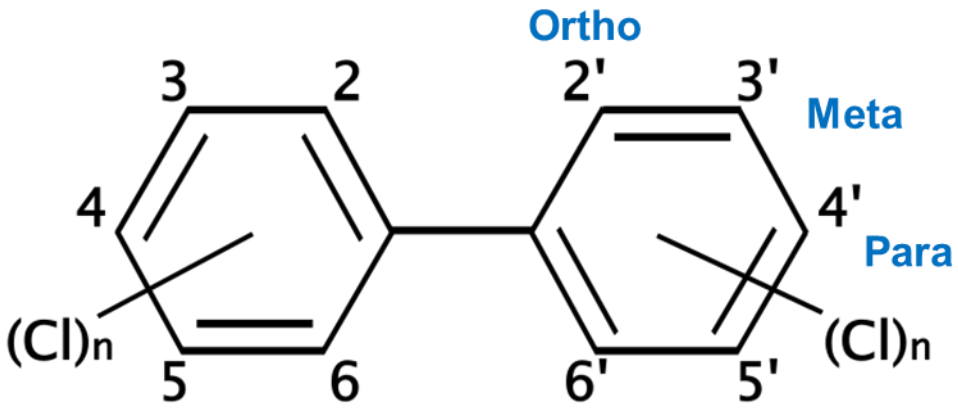


*Source: Kohler et al, 2005 Environmental Science and Technology, 2005, 39, 1967-1973

Without Chemicals, Life Itself Would Be Impossible

A Quick PCB Chemistry Lesson

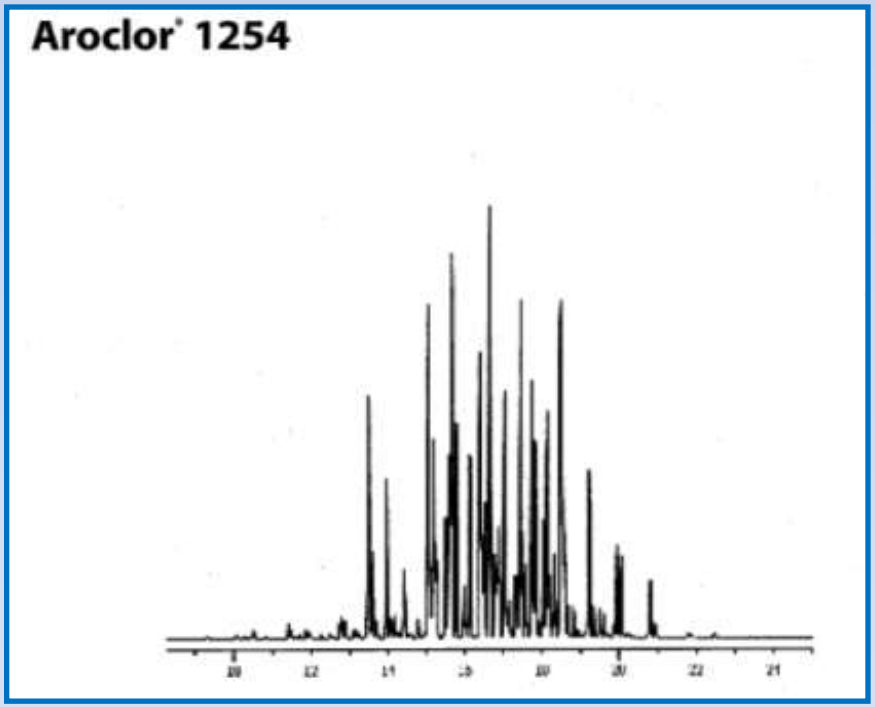
The Basics



- **Polychlorinated biphenyls**
  - Poly prefix meaning “many”
  - Chlorine is an element
  - Biphenyl is the parent molecule
  - Translation - PCBs = biphenyl with many chlorines

PCBs Marketed as Technical Mixtures (Aroclor is essentially a brand name)

- Monsanto was only U.S. producer.
- 1.4 billion pounds produced.
- >50 of 209 different congeners were used in the various complex chemical mixtures.
- Last 2 digits = amount of chlorine on a weight basis.
- Aroclor 1254 = 54% Chlorine by mass.



Technical Mixture –
Think of it like 10W-40 Motor Oil. A chemical mixture composed to meet defined performance criteria.

Let's Add Some Definition (with apologies for the wall of words)

- **PCB Mixtures and Trade Names -** With few exceptions, PCBs were manufactured as a mixture of various PCB congeners, through progressive chlorination of batches of biphenyl until a certain target percentage of chlorine by weight was achieved.

- **Aroclor -** It is one of the most commonly known trade names for PCB mixtures. There are many types of Aroclors and each has a distinguishing suffix number that indicates the degree of chlorination.

Let's Add Some Definition (continued…also with apologies for the wall of words)

- **Congeners -** PCBs are a class of chemical compounds in which 1–10 chlorine atoms are attached to the biphenyl molecule. The 209 possible compounds are called congeners.

- **Homologs -** PCBs can also be categorized by degree of chlorination. The term "homolog" is used to refer to a group of PCB congeners with the same number of chlorines (e.g., trichlorobiphenyls). All the PCB chemicals that have the same number of chlorine atoms are said to belong to the same homolog group.

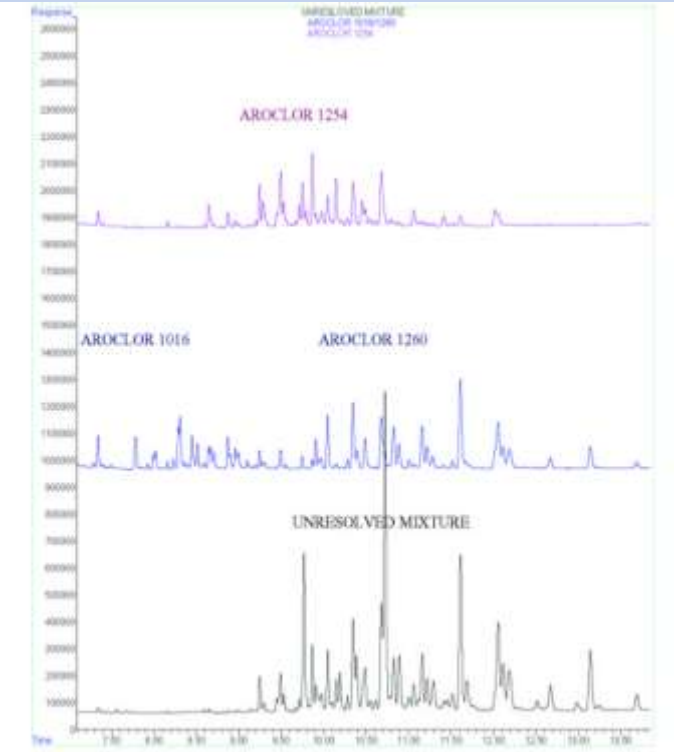
Laboratory Analyses (Extraction and Analysis)

❑ Extraction

- ➢ Waters 3510C (separatory funnel)
- ➢ Solid 3540C (soxhlet)

❑ Analysis

- ➢ EPA SW-846 Method 8082A, (PCB Aroclors), 2007
- ➢ EPA Method 680 (PCB Homologs), 1985
- ➢ EPA Method 1668B (PCB Congeners), 2008



Until the regs change, or unless you apply for a project-specific change under Subpart Q of TSCA, Soxhlet Extraction is a must for solid samples in Region I.

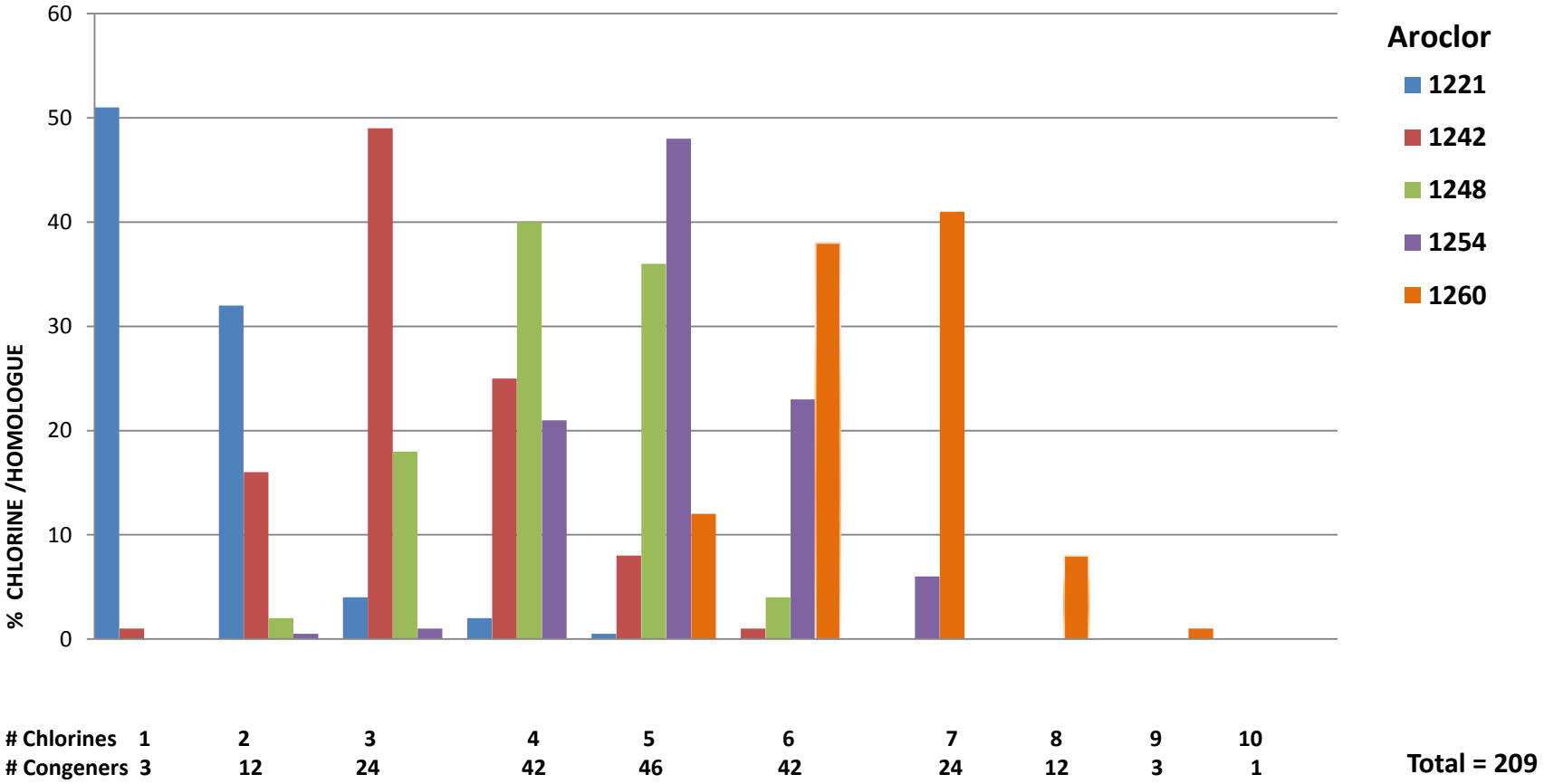
Why should EPA change?

1. ***It's slow….18 hour extraction.***
2. ***It's not green….it's labor intensive and uses a lot of solvent (methylene chloride).***
3. ***Other methods (pressurized fluid extraction [3545A], microwave extraction [3546]) are faster and just as efficient, rigorous, and robust…but EPA differs for high concentrations***

Analytical Output

Aroclors (8082A)	Homologs (680)	Congeners (1668B)
Aroclor 1016 Aroclor 1221 Aroclor 1232 Aroclor 1242 Aroclor 1248 Aroclor 1254 Aroclor 1260 Aroclor 1262 Aroclor 1268 Total PCB Output is organized and summed by Aroclor pattern.	Monochlorobiphenyls Dichlorobiphenyls Trichlorobiphenyls Tetrachlorobiphenyls Pentachlorobiphenyls Hexachlorobiphenyls Heptachlorobiphenyls Octachlorobiphenyls Nonachlorobiphenyls Decachlorobiphenyl Total PCBs Output organized by homolog group (by number of chlorine atoms) and summed.	A snipit from a wetland sediment sample round from a project. 81-TeCB - 3,4,4',5-Tetrachlorobiphenyl 77-TeCB - 3,3',4,4'-Tetrachlorobiphenyl 123-PeCB - 2',3,4,4',5-Pentachlorobiphenyl 118-PeCB - 2,3',4,4',5-Pentachlorobiphenyl 114-PeCB - 2,3,4,4',5-Pentachlorobiphenyl 105-PeCB - 2,3,3',4,4'-Pentachlorobiphenyl 126-PeCB - 3,3',4,4',5-Pentachlorobiphenyl 167-HxCB - 2,3',4,4',5,5'-Hexachlorobiphenyl 156,157-HxCB 2,3,3',4,4',5-Hexachlorobiphenyl + 2,3,3',4,4',5'-Hexachlorobiphenyl 169-HxCB - 3,3',4,4',5,5'-Hexachlorobiphenyl 189-HpCB - 2,3,3',4,4',5,5'-Heptachlorobiphenyl Individual congeners reported, except that some congeners co-elute...so the output will not cover all 209 possible congeners individually (see 156/157 above for example).

Composition of PCB Aroclor Mixtures (% Chlorine by Homologue Substitution Number)



For Aroclor by Aroclor congener plots, visit this EPA website: http://www.epa.gov/osw/hazard/tsd/pcbs/pubs/aroclorplots.pdf

Some Pros and Cons of the Analytical Methods

Method	Pro	Con
Aroclors (8082A)	▪ Relatively inexpensive (<$100/sample) ▪ Widely available analytical service	▪ Affected by weathering ▪ Although still used, it is not the best for air sampling
Homologs (680)	▪ Good estimate of total PCBs ▪ Overcomes weathering of Aroclors ▪ Good option for air analysis (Aroclors may not evaporate as tech. mixtures) ▪ More accurate-no human interpretation	▪ Expensive (~$300/sample) ▪ A service not offered by all laboratories
Congeners (1668B)	▪ Provides a breakout of all the individual PCB chemicals present ▪ Provides quantitation of the dioxin-like congeners ▪ Provides added flexibility in a risk assessment. More accurate (not dependent on human interpretation)	▪ Expensive (~$800/sample) ▪ Few laboratories offer the analysis (less than with homologs) ▪ Not all of the laboratories do it well (engage your QC chemist)
Screening kits (various)	▪ Cheap ▪ May help with faster delineation	▪ Subject to interferences ▪ Generally higher detection limits ▪ No standing under the Compendium of Analytical Methods (CAM) in Massachusetts (not applicable to CT). ▪ Not an option for risk assessment

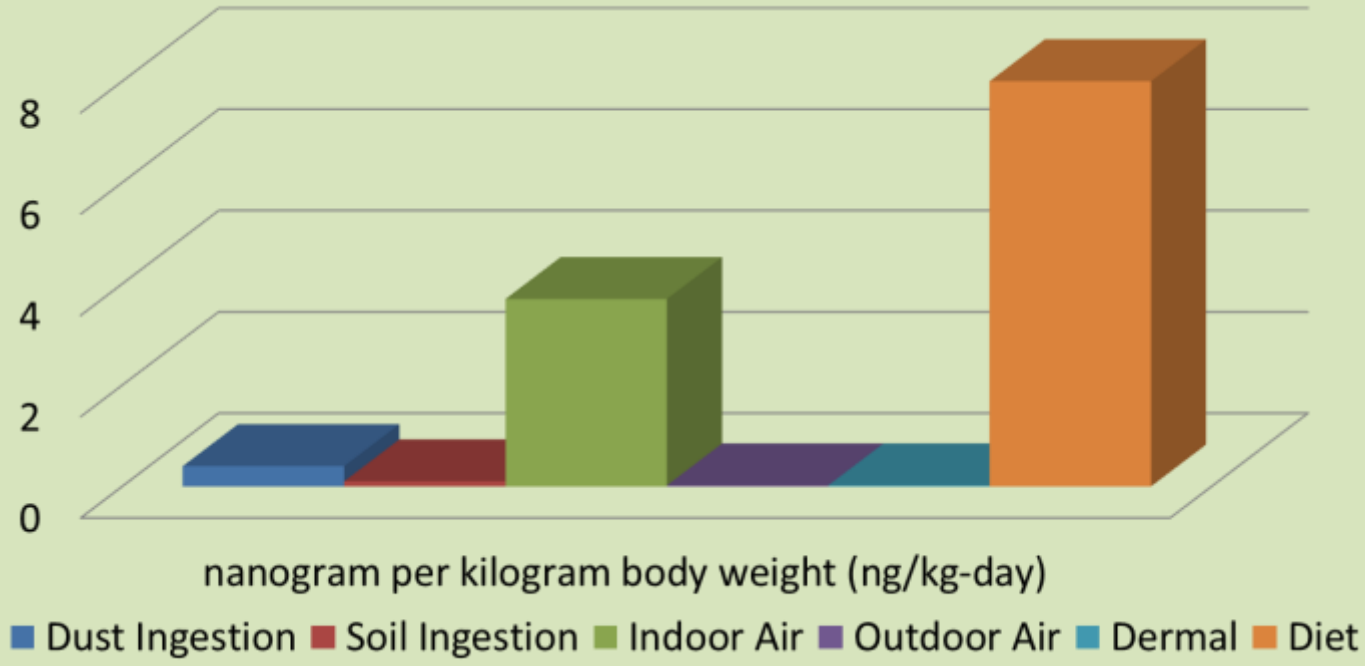
PCBs: Real World Considerations

Exposure and Toxicity
(Why do we care?)

Adapted from Diane M. Silverman, PhD, TRC Environmental Corporation.

Why do we care about PCBs? #1

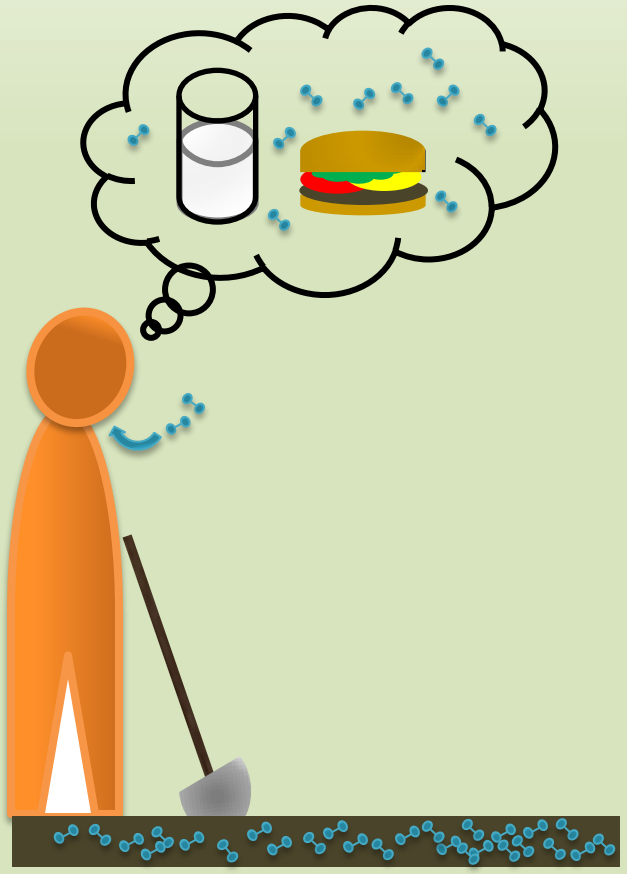
- **There is significant background exposure**
  - **Sources of daily exposure for pre-school children** (3-6 years old)



Total background exposure is ~12 ng/kg-day

Why do we care about PCBs? #2

- **They are persistent in the body**
  - **Easily absorbed**
  - **Stored in fat**
  - **Slowly excreted**
  - **Lead to high "body burdens"**
  - **Produce long-lasting effects**



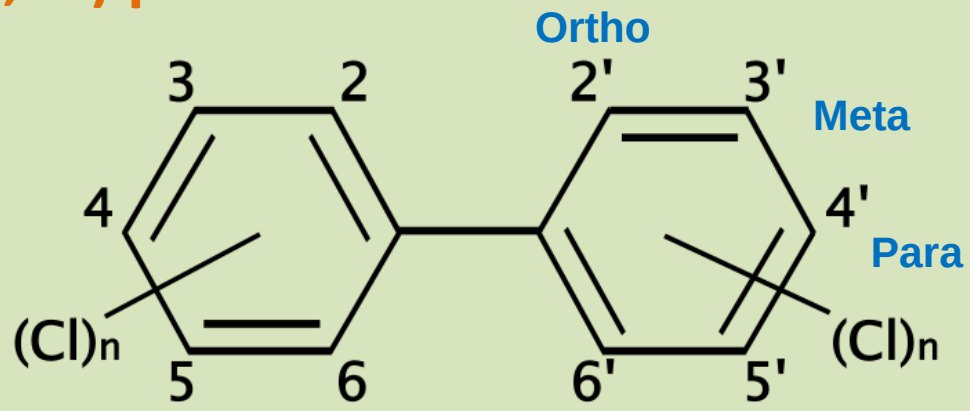
Why do we care about PCBs? #3

- **The "Safe" level of exposure is low and uncertain.**
  - **20 ng/kg-day**
    - **> 10-fold lower than a "safe" level for arsenic**
    - **Total "background" exposure ranges from 3-14 ng/kg-day**
  - **Based on immune system/nail effects in monkeys (Aroclor 1254)**
    - **300-fold uncertainty factor**
    - **Environmental mixtures may be more or less toxic**
  - **Toxicity assessment is circa 1996 – Reassessment began 2012**
    - **Larger body of scientific data gathered over the last 15 years**
    - **More sensitive endpoints studied – "safe" level may decrease**
    - **EPA began reassessment in 2012**

The Bottom Line – Difficult to characterize toxicity due to chemical variability and complexity

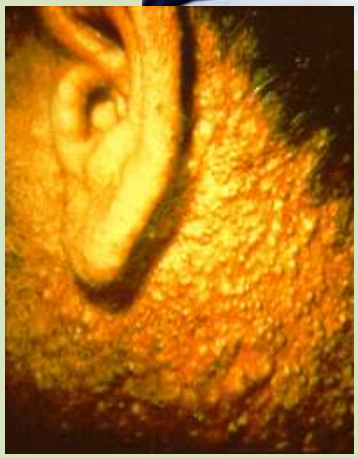
Toxicity vs. Chemical Structure

- **Number and position of chlorines dictates toxicity**
  - Chlorinated meta (3, 3’, 5, 5’) and para (4, 4’) positions
  - Planar configuration, greater cellular response, higher order of toxicity
- **Chlorinated ortho (2, 2’, 6, 6’) positions**
  - Inversely related to toxicity
- **12 Coplanar PCBs**
  - At least 4 chlorines
  - Both para positions occupied
  - At least 2 meta positions occupied
  - 0 or 1 ortho positions occupied
  - “Dioxin-like” toxicity



Health Effects

- **Developmental effects**
  - Impaired learning and motor function
  - Delays in organ system development
  - Possible related to endocrine disruption
- **Reproductive effects**
  - Increase in spontaneous abortion
  - Low birth weight/increased infant mortality
- **Immune system suppression**
  - Decreased antibody production
  - Increased susceptibility to disease
- **Liver damage**
  - Microscopic changes
  - Not strongly correlated with changes in function
- **Skin effects**
  - Chloracne rash/nail deformities



Public Health Levels for School Indoor Air

Developed by EPA to provide guidance when indoor air is sampled

Age group	Public Health Level (ug/m^3)	Total Background Exposure (ng/kg-day)
Daycare/Pre-School	0.07 to 0.1	12 to 14
Elementary	0.3	6
Middle School	0.45	5
High School	0.6	4
Adult Staff	0.45	3

- Factor in "background" exposure to PCBs so a "safe" level of exposure is unlikely to be exceeded considering total PCB exposure
- Assumes that PCB dust concentrations inside school are at "background" levels
- Building-specific information can be used to "refine" Public Health Levels

So what about cancer?

PCBs are classified as "probable" human carcinogens

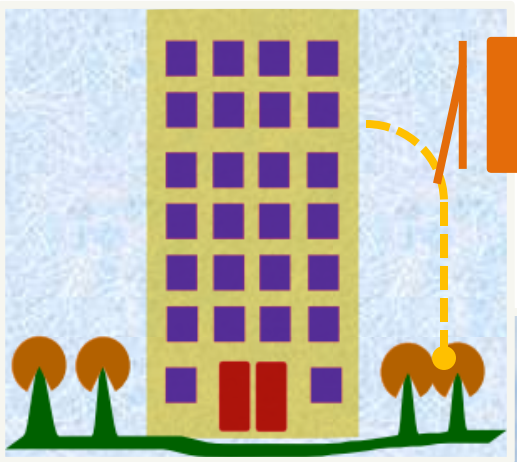
- **Cancer risk is thought about differently**
  - Defined as the "incremental" risk above background (1 in 10 to 1 in 100)
  - Acceptable "incremental" cancer risk varies (e.g., 1 in 100,000)
  - Cancer risk increases as years of exposure increases, i.e., cumulative
- **Non-cancer effects dominate for school/work situations**
  - Cancer dominates for residential exposures
- **Uncertain relationship to human exposure and cancer**
  - Conclusive evidence of liver tumors in rats exposed to various Aroclors
  - Inconclusive evidence of tumors of digestive system and blood in humans

Introduction to Characterization

Some examples

PCB Bulk Product Waste ¤ 761.3 ¤ 761.50(b)(4)	PCB Remediation Waste ¤ 761.3 ¤ 761.50(b)(3)	Excluded PCB Product ¤ 761.3
≥ 50 ppm total PCBs ▪ One valid sample will do to gain entry. ▪ Obligations begin.	**Any concentration material w/PCBs total > 1 ppm when associated with BPW over 50 ppm.** ▪ Unauthorized source (typical in building context) ▪ Example - PCB Bulk Product Waste source	**< 50 ppm total PCBs** ▪ Lines of evidence. ▪ Origin, dilution, coverage.
▪ Unauthorized use ▪ ***Must be removed*** ▪ **Note Oct. 24, 2012 reinterpretation**	▪ Unauthorized disposal ▪ ***Investigate/remediate***	▪ Not regulated for removal. ▪ Management plan?
Applies to primarily to unauthorized materials.	**Applies to impacted substatrates (like brick) and environmental media.**	**Building materials below the threshold backed by other evidence.**

Illustration of Concepts – Characterization Examples



inter-media transfer

homogeneous paint areas

non-porous

porous

Looks consistent, but is it?

multiple layers

If the paint is dirty, what of the brick?

direct/indirect vent system impacts

Thank you

Questions?

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