

# PCB 101

2016 Pacific Northwest Snowfighters Conference  
June 8, 2016

Dave Hope,  
Pacific Rim Laboratories Inc.



# Outline

- Pacific Rim Laboratories Inc.
- PCB – what is it and why are we still interested in it
- Toxicity
- How do we analyze it – Analytical Methods
- What does PCB have to do with snow fighting?
- Closing thoughts

# Who Am I?

- Analytical Chemist
  - P.Chem. – ACPBC
  - Past-President, Canadian Council of Independent Laboratories
  - Owner, Lab Director, Quality Assurance Officer, Pacific Rim Laboratories
- I am not
  - Toxicologist
  - Consultant



# My Business Partner and co-founder

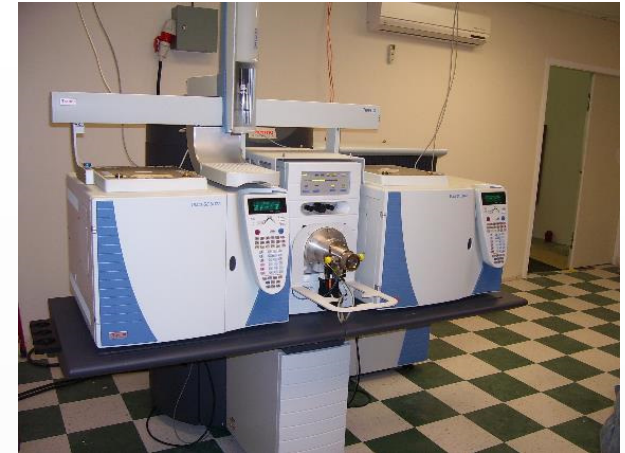
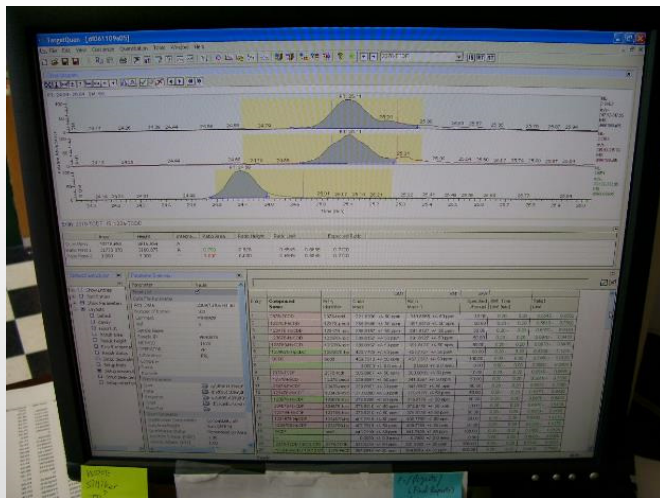


- Patrick Pond
- Chief Technical Officer
- GC and HRMS instrument specialist



# Our Mission Statement

- To be the most diversified (niche) HRMS lab in North America



**PACIFIC RIM**  
LABORATORIES INC

# Pacific Rim Laboratories Inc.

- Small ultra-trace organic laboratory specializing in the analysis of Persistent Organic Pollutants by High Resolution Mass Spectrometry
- Located in Surrey, BC (suburb of Vancouver, Canada)
- Accredited by WDOE and CALA for the analysis of PCB, PCDD/F, PBDE and other persistent organic pollutants (POPs).
- Work in the ppt, ppq and sub-ppq range



# Pacific Rim Laboratories Inc.

## Scientific Research and Experimental Development

- We thrive on innovation
  - PBDE method in 2005
  - 209 congener PCBs in 2005
  - Sub-ppb PAH analysis food in 2006
  - First DFS HRMS in 2008
  - Published 2009 congener PCB by SGE HT8 column (2009)
  - Improved clean-up methods for dioxins/PCB (2014)
  - Single run PAH and alkylated PAH on TSQ8000Evo (2015)



How small is small? mg,  $\mu\text{g}$ , ng, pg, fg, ag  
pg/L or pg/kg = One part per quadrillion ( $10^{-15}$ )

1. Lake Erie (one of the Great Lakes),  $484 \text{ km}^3$
2. Add one pound (454 g)
3. Stir
4. One part per quadrillion



**PACIFIC RIM**  
LABORATORIES INC



How small is small? mg,  $\mu\text{g}$ , ng, pg, fg, ag  
pg/L or pg/kg = One part per quadrillion ( $10^{-15}$ )

- Canada is 10,000,000  $\text{km}^2$
- \$20 bill is 100  $\text{cm}^2$
- Drop the \$20 from an airplane and try to find it
- 1 part per quadrillion



**PACIFIC RIM**  
LABORATORIES INC

# Outline

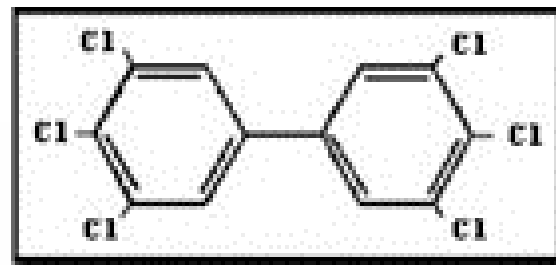
- Pacific Rim Laboratories Inc.
- PCB – what is it and why are we still interested in it
- Toxicity
- How do we analyze it – Analytical Methods
- What does PCB have to do with snow fighting?
- Closing thoughts

# Polychlorinated Biphenyls (PCB)

- Manufactured until early 1970's (1980's in Eastern Europe)
  - Total production 1.3-1.5M Tonnes
  - Aroclor 1016, 1242, 1254, 1260
  - Kanaclor
- Byproduct in the manufacture of other chemicals
  - Copper sulphate from China contaminated with PCB126, 169 and 77.



# Chemical Structure

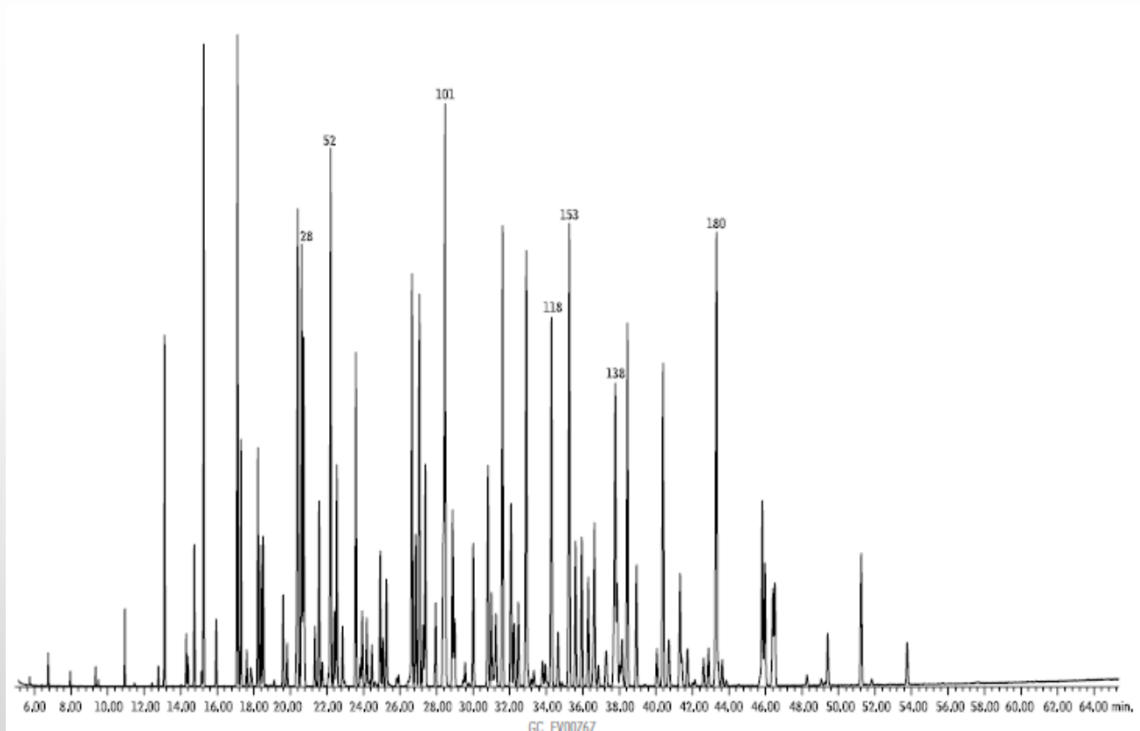


- 209 possible congeners – mono thru decachlorobiphenyl
- Twelve are considered dioxin like and have been assigned Toxic Equivalency Factors (TEF)

- MonoCB 3 congeners
- DiCB 12 congeners
- TriCB 24 congeners
- TetraCB 42 (2) congeners
- PentaCB 46 (5) congeners
- HexaCB 42 (4) congeners
- HeptaCB 24 (1) congeners
- OctaCB 12 congeners
- NonaCB 3 congeners
- DecaCB 1 congeners



# PCBs on ECD – Mix of Aroclor 1242, 1254, 1260



**PACIFIC RIM**  
LABORATORIES INC

# Global Production

**Total global production of PCBs**

| Producer            | Country        | Start       | Stop        | Quantity (tons)  |
|---------------------|----------------|-------------|-------------|------------------|
| Monsanto            | USA            | 1930        | 1977        | 641,246          |
| Geneva Ind.         | USA            | 1971        | 1973        | 454              |
| Kanegafuchi         | Japan          | 1954        | 1972        | 56,326           |
| Mitsubishi          | Japan          | 1969        | 1972        | 2,461            |
| Bayer AG            | West Germany   | 1930        | 1983        | 159,062          |
| Prodelec            | France         | 1930        | 1984        | 134,654          |
| S.A. Cros           | Spain          | 1955        | 1984        | 29,012           |
| Monsanto            | U.K.           | 1954        | 1977        | 66,542           |
| Caffaro             | Italy          | 1958        | 1983        | 31,092           |
| Zakłady Azotowe     | Poland         | 1974        | 1977        | 679              |
| Electrochemical Co. | Poland         | 1966        | 1970        | 1,000            |
| Chemko              | Czechoslovakia | 1959        | 1984        | 21,482           |
| Orgsteklo           | USSR (Russia)  | 1939        | 1990        | 141,800          |
| Orgsintez           | USSR (Russia)  | 1972        | 1993        | 32,000           |
| -Xi'an              | China          | 1960        | 1979        | 8,000            |
| <b>Total</b>        |                | <b>1930</b> | <b>1993</b> | <b>1,325,810</b> |

Source: Breivik, K. et al., "Towards a global historical emission inventory for selected PCB congeners - A mass balance approach", 2007

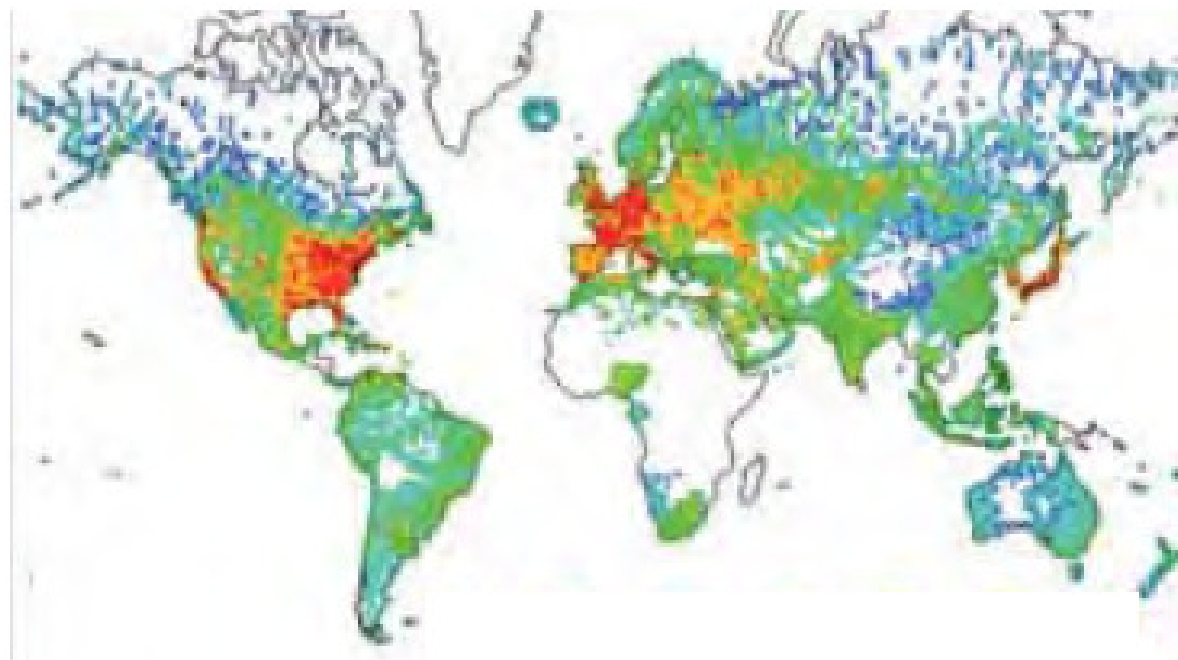
- 48% produced in USA
- 50% of remaining production imported to USA
- 97% in Northern Hemi



**PACIFIC RIM**  
LABORATORIES INC



**Estimated cumulative global usage of PCBs (legends in t) with 1°x1° longitude and latitude resolution**



**< 0.1   0.1-1   1-10   10-50   50-100   100-500   >500**

**Source:** Breivik, K. et al, "Towards a global historical emission inventory for selected PCB congeners - a mass balance approach", 2002



**PACIFIC RIM**  
LABORATORIES INC

# Applications of PCB

- **Closed systems**
- Insulation and/or cooling fluid in transformers (48%)
- Dielectric fluid in capacitors (21%)
- Switches
- **Partially open systems**
- Heat transfer fluids
- Hydraulic fluid in lifting equipment, trucks and high pressure pumps
- Vacuum Pumps
- Voltage Regulators
- Liquid Filled Electrical Cables
- Liquid Filled Circuit Breakers
- **Open systems (21%)**
- Paints
- Lubricating fluid in oils and grease
- Water-repellent impregnating agent and fire retardant for wood, paper, fabric and leather
- Laminating agent in paper production
- Additive in glues, sealants and corrosion protection coatings
- Carrier for insecticides
- Polymerisation catalyst support for petrochemicals
- Immersion oils for microscopy
- Pesticide Formulation
- Cable coatings/casings



**Highest levels of PCBs reported for various open uses.**

| Material                        | Bulk Sample (mg/kg or ppm) | Material                                | Bulk Sample (mg/kg or ppm) |
|---------------------------------|----------------------------|---|----------------------------|
| Adhesive tape                   | 1,400                      | Foam rubber parts                       | 1,092                      |
| Carbonless Copy Paper           | 6,000                      | Grout                                   | 9,100                      |
| Caulking                        | 310,000                    | Insulating materials in electric cable  | 280,000                    |
| Ceiling tiles                   | 53                         | Plastics/plasticisers                   | 13,000                     |
| Cloth/paper insulating material | 12,000                     | Ventilation system cork gasket material | 6,400                      |
| Coal-tar enamel coatings        | 1,264                      | Roofing/siding material                 | 22,000                     |
| Dried paint                     | 97,000                     | Rubber parts                            | 84,000                     |
| Fiberglass insulation           | 39,158                     | Thermal insulation                      | 73,000                     |
| Foam rubber insulation          | 13,100                     | Wool felt gaskets                       | 688,498                    |

**Source:** Use Authorization for and Distribution in Commerce of Non-Liquid Polychlorinated Biphenyls. US Federal Register, 1999



**PACIFIC RIM**  
LABORATORIES INC

# What are POPs – Stockholm Convention

- Ratified in 2001, came into force in 2004
  - Canada was the first country to ratify the treaty on 23 May 2001
- There are 179 parties to the Convention - does not include USA, Italy
- Industrial By-products - Dioxin, Furans, Hexachlorobenzene (HCB)
- Man made - Pesticides – Aldrin, Dieldrin, Endrin, Chlordane, DDT, Heptachlor, Mirex, Toxaphene; **PCB**; HCB
- Added in 2009 -  $\alpha$ -HCH,  $\beta$ -HCH,  $\gamma$ -HCH (Lindane); PBDE (47, 99, 153, 154, 175/183) Flame retardant; Pentachlorobenzene; Chlordecone (similar to Mirex); Hexabromobiphenyl (PBB153); PFOS/PFOA; PCP; PCN; Endosulphan



# Outline

- Pacific Rim Laboratories Inc.
- PCB – what is it and why are we still interested in it
- **Toxicity**
- How do we analyze it – Analytical Methods
- What does PCB have to do with snow fighting?
- Closing thoughts

# PCB Toxicity

- World Health Organization (WHO) defines twelve toxic congeners
  - Due to positioning of chlorines, the molecule is unable to rotate and forms structure similar to dioxin
- 2,3,7,8-TCDD considered to have a toxicity of 1, all others are relative to TCDD
- Toxic Equivalency Factors (TEF)
  - PCB126 (0.1), PCB169 (0.03), PCB077 (0.0001), PCB081 (0.0003)
  - PCB105, 114, 118, 123, 156, 157, 167, 189 (0.00003)
- PCB TEQ =  $\sum C_x \times TEF_x$  for all PCB congeners



# Regulatory Levels – Food

## Max intake – 2 pg TEQ/kg bw/day

### • European Food Regulations (pg WHO-TEQ/g fat)

|                    | PCDD/F | (&PCB) |
|--------------------|--------|--------|
| • Fish (fresh wt): | 4      | (8)    |
| • Pork:            | 1      | (1.5)  |
| • Poultry          | 2      | (4)    |
| • Beef / mutton:   | 3      | (4.5)  |
| • Liver            | 6      | (12)   |
| • Milk:            | 3      | (6)    |
| • Eggs:            | 3      | (6)    |
| • Vegetable oil:   | 0.75   | (1.5)  |
| • Mix Animal fat:  | 2      | (3)    |
| • Fish oil:        | 2      | (10)   |

### • European Feed Regulations

- Feed\*: 0.75 pg WHO-TEQ/g
- Pet foods: 2.25 pg WHO-TEQ/g
- Animal fat: 2 pg WHO-TEQ/g
- Minerals: 1 pg WHO-TEQ/g
- Fish oil: 6 pg WHO-TEQ/g
- Fish meal: 1.25 pg WHO-TEQ/g
- \* - based on 12% moisture content

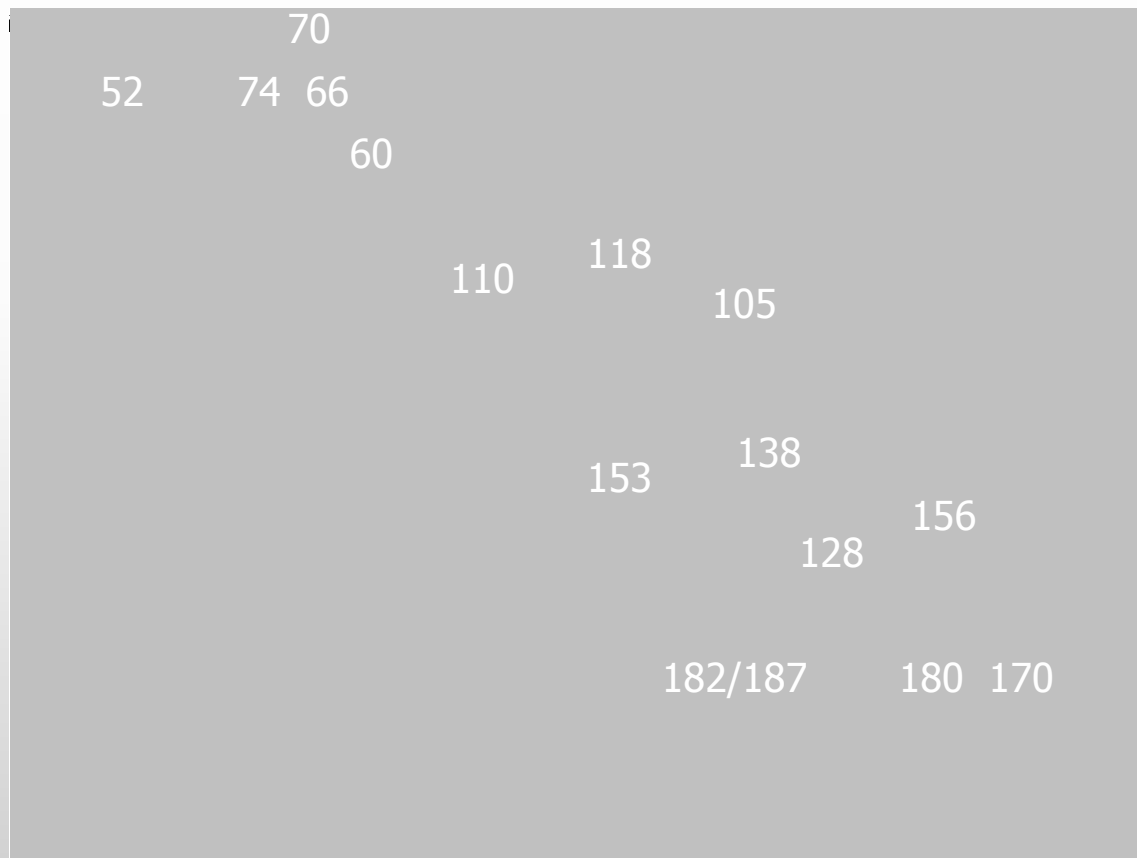


# Food levels

- Eggs – 2.1-38 ug/kg fat
  - 0.11 – 2.86 ng TEQ/kg fat
- Meat – 50 – 1960 ng/kg fat
  - 0.001 – 0.182 ng TEQ/kg fat
- Fish 0.29 – 87 ug/kg
  - 0.1 – 2.4 ng TEQ/kg



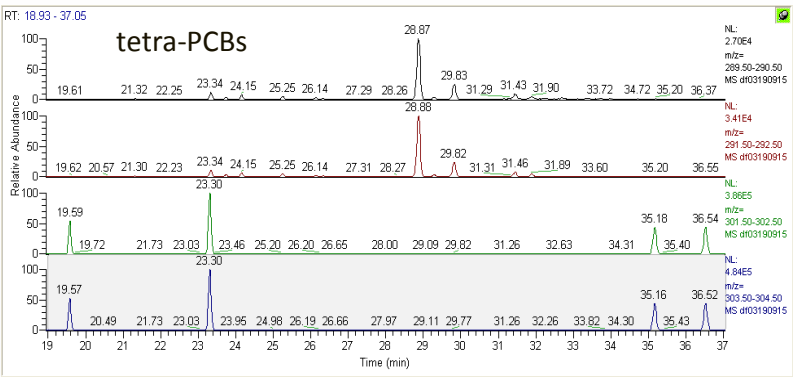
# Fish sample – Cl<sub>4</sub>-Cl<sub>7</sub>



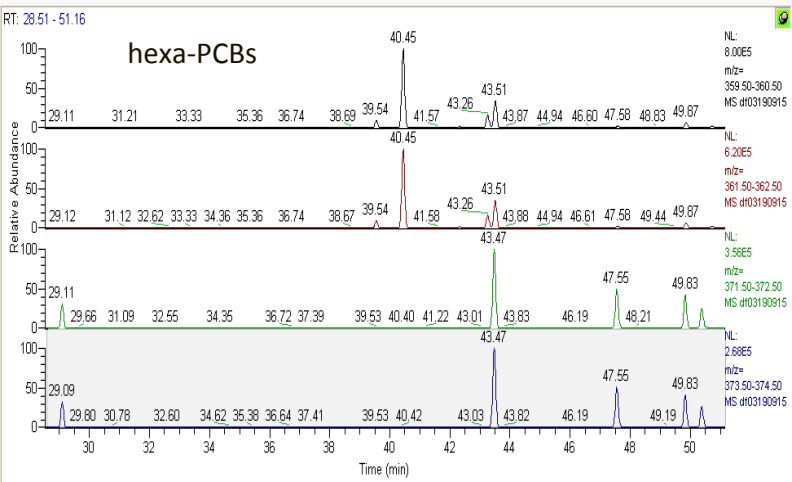
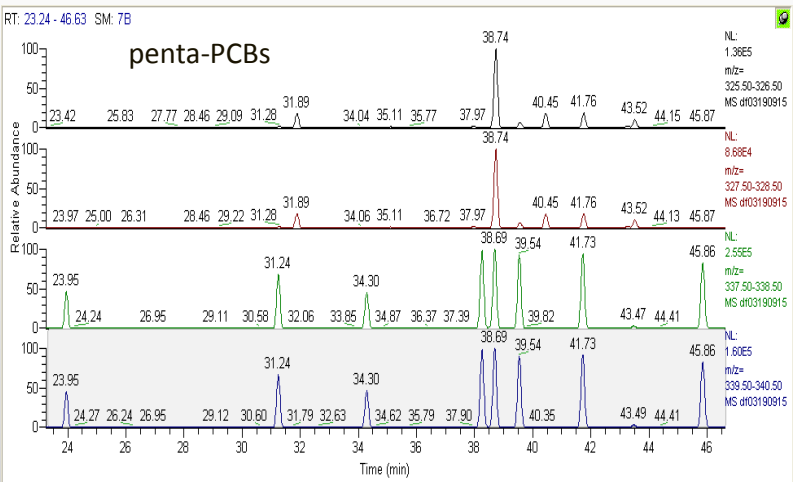
# Fish sample – Cl<sub>7</sub>-Cl<sub>10</sub>



# PCB Analysis in Blood



- PCBs in blood
  - 200-800 ug /kg lipid
  - PCB153 > 138 > 180 > 187 > 118 > 170 > 99



# Outline

- Pacific Rim Laboratories Inc.
- PCB – what is it and why are we still interested in it
- Toxicity
- **How do we analyze it – Analytical Methods**
- What does PCB have to do with snow fighting?
- Closing thoughts



# Analytical Methods

Good – Better - Best

- GC/ECD Methods
  - EPA 8081, 8082, 608, 508
- GC/MS Methods
  - EPA 8270
- GC/HRMS Methods
  - EPA 1668



**PACIFIC RIM**  
LABORATORIES INC

# Analytes

Good – Better - Best

- Total PCB – Aroclor equivalents
- Homolog Totals
  - 10 levels of chlorination
- Congener specific (209)



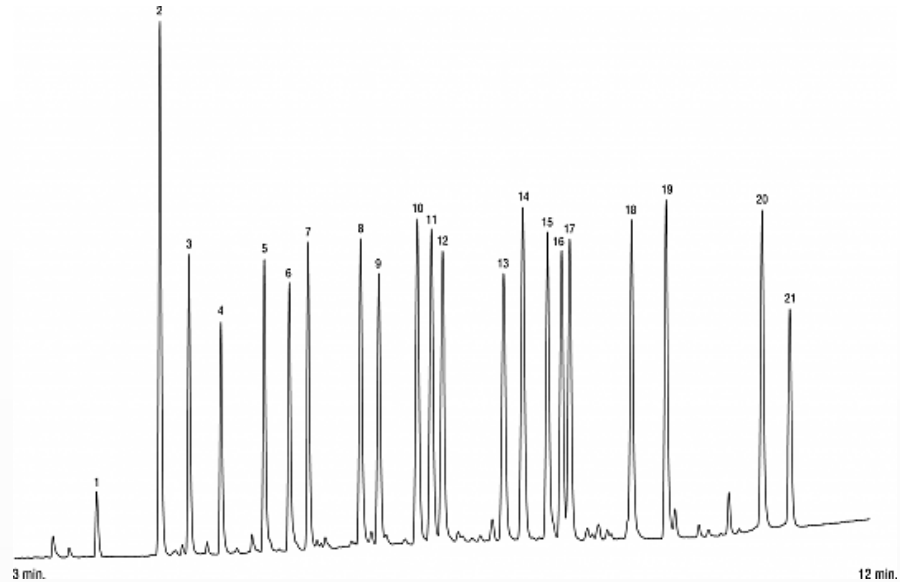
**PACIFIC RIM**  
LABORATORIES INC

# Quantitation Methods

## Good – Better - Best

- External standard
  - compare with calibration curve
  - Requires known final volume and amount injected
- Internal Standard
  - Add standard just before analysis
  - Relative response factors determined from calibration curve
  - With area of IS peak and RRF, can calculate concentration
- Isotope dilution
  - Stable isotopes added before extraction used to quantify results
  - Corrects for losses during work-up

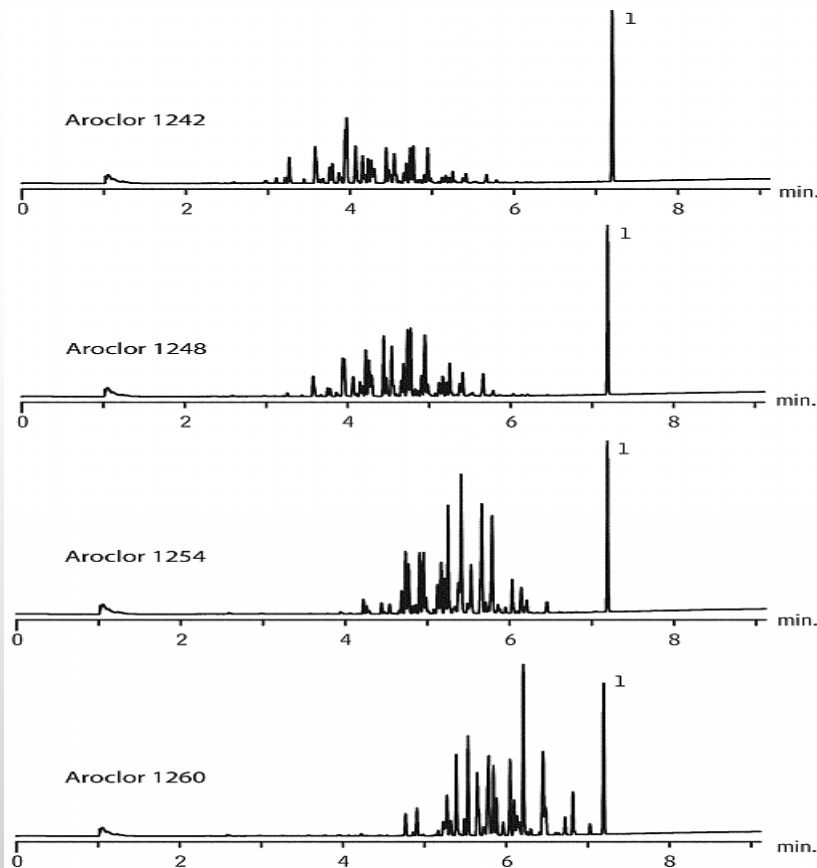
# EPA 8082



- Can be used to identify Aroclors or congeners
- 19 congeners – MonoCB – NonaCB
- PCB1, 15, 18, 31, 44, 52, 66, 87, 101, 110, 138, 141, 151, 153, 170, 180, 183, 187, 206
- IS Method: One internal standard and one surrogate standard



# Pattern Recognition



- Must match the pattern in the sample with one of 7 Aroclor standards
- Use 3-5 peaks in the standard to quantify sample (External Std)
- Detection limits 0.05 ug/L
- Problems with pattern recognition in weathered samples

# GC/MS Methods

- EPA 8270
  - Generic catch-all method
  - Uses GC/MS for ultimate identification, but causes a greatly reduced sensitivity (increased detection limit)
  - Detection limits 10 ug/L (Aroclor equivalents)
- Homolog Total Methods
  - Uses GC/MS in SIM for greater sensitivity and selectivity
  - Internal Standard for each level of chlorination
  - PCB defined as having peaks in QM and RM channels and being within 15% of theoretical mass ratio
  - Quantifies on congener basis but not identified
  - Detection limits 0.001 ug/L on a congener basis





# EPA Method 1668

- HRGC-HRMS congener specific method (first written 1999, revised in November 2008, June 2010)
- Uses 27 internal standards ( $^{13}\text{C}_{12}$ -labeled congeners)
  - All twelve dioxin-like PCBs
  - First and last eluters in each level of chlorination (LOC)
  - Three  $^{13}\text{C}_{12}$ -clean-up standards and five  $^{13}\text{C}_{12}$ -recovery standards
- Five (1-2000 ng/mL) or six point (0.2-2000 ng/mL) calibration for dlPCBs and LOC PCBs
- Single point calibration for all remaining PCBs
- Two methods of quantification
  - Isotope dilution (for 27 congeners with labeled standards)
  - Internal standard – everything else



# HRMS analysis - Issues

- Coelutions for TeCB, PeCB and HxCB
  - M-Cl gives significant peak, therefore cannot have coelutions with significant peaks of higher LOC
- Each LOC requires four ions
  - PeCB, HxCB, HpCB and OcCB overlap
  - Requires 16 ion channels
- Need to maximize sensitivity, therefore typical collection rates of 1 hz (no 10-100 hz that can be found with ECDs or MSDs)





**PACIFIC RIM**  
LABORATORIES INC

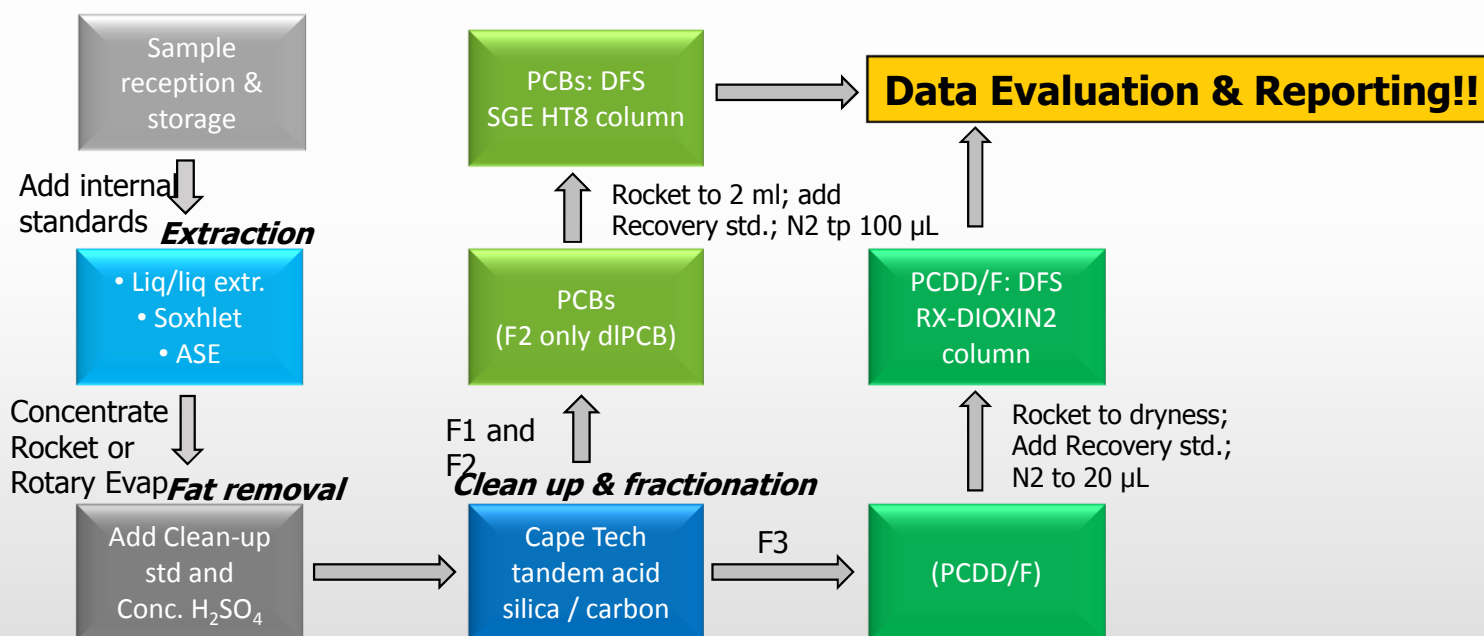
# Results

- 209 resolvable by ECD @ 100 hz
- 189 resolvable peak tops by HRMS
- 37/42 TeCB
- 37/46 PeCB
- 40/42 HxCB





# Analytical Workflow – Dioxin/PCB



# What is the Detection Limit?

- Standard methods for MDL determination
  - 7-10 blank samples spiked at low level with analytes of interest
  - $MDL = 3 * SD$  (approximately)
  - Better precision leads to low MDLs
  - Our MDLs are 1-13 pg/L
- Isotope dilution allows for lower theoretical MDLs due to lower SD
- Many isotope dilution methods call for the reporting of Instrument Detection Limits based on  $2.5 * SN$
- Can give IDLs  $<1$  pg/L



# What is Total PCB?

- Sounds simple, add up individual results for all 209 congeners
- How do you handle different detection limits? Co-elutions? Low level concentrations?
- Should data be reported below EQL?





# Total PCB when DL set to 10 pg/L

| PCB #                | A          | B          | C           | D          | E           | Blank       |
|----------------------|------------|------------|-------------|------------|-------------|-------------|
| Homologs             | pg/L       | pg/L       | pg/L        | pg/L       | pg/L        | pg/L        |
| Monochlorobiphenyls  | 10.8       | 10         | 12.3        | 10.7       | 11          | 0           |
| Dichlorobiphenyls    | 19.6       | 74.6       | 50.5        | 52         | 14.4        | 0           |
| Trichlorobiphenyls   | 63         | 12.6       | 0           | 11.3       | 0           | 0           |
| Tetrachlorobiphenyls | 101        | 0          | 10.4        | 0          | 0           | 0           |
| Pentachlorobiphenyls | 152        | 23.2       | 15.5        | 27.6       | 0           | 29.9        |
| Hexachlorobiphenyls  | 69.2       | 0          | 0           | 0          | 0           | 0           |
| Heptachlorobiphenyls | 0          | 0          | 0           | 0          | 0           | 0           |
| Octachlorobiphenyls  | 0          | 0          | 0           | 0          | 0           | 0           |
| Nonachlorobiphenyls  | 0          | 0          | 0           | 0          | 0           | 0           |
| Decachlorobiphenyl   | 0          | 0          | 0           | 0          | 0           | 0           |
| <b>Total PCB</b>     | <b>415</b> | <b>110</b> | <b>88.7</b> | <b>102</b> | <b>25.4</b> | <b>29.9</b> |

| PCB #                | A          | B            | C            | D          | E            | Blank       |
|----------------------|------------|--------------|--------------|------------|--------------|-------------|
| Homologs             | pg/L       | pg/L         | pg/L         | pg/L       | pg/L         | pg/L        |
| Monochlorobiphenyls  | 14.5       | 18.7         | 18.5         | 20.1       | 17.6         | 9.3         |
| Dichlorobiphenyls    | 19.6       | 86.1         | 50.5         | 52         | 14.4         | 0           |
| Trichlorobiphenyls   | 88.2       | 42.5         | 31.5         | 36         | 34.7         | 0           |
| Tetrachlorobiphenyls | 132.8      | 29.5         | 33.6         | 37.7       | 24.4         | 0           |
| Pentachlorobiphenyls | 173.4      | 40.2         | 24           | 27.6       | 15.5         | 29.9        |
| Hexachlorobiphenyls  | 119.3      | 9.2          | 14.5         | 4.6        | 5.6          | 1.8         |
| Heptachlorobiphenyls | 30.2       | 0            | 0            | 0          | 2.3          | 0           |
| Octachlorobiphenyls  | 11.6       | 0            | 2.5          | 0          | 1.4          | 0           |
| Nonachlorobiphenyls  | 0          | 0            | 0            | 0          | 0            | 0           |
| Decachlorobiphenyl   | 4.4        | 0            | 0            | 0          | 0            | 0           |
| <b>Total PCB</b>     | <b>594</b> | <b>226.2</b> | <b>175.1</b> | <b>178</b> | <b>115.9</b> | <b>41</b>   |
|                      |            |              |              |            |              |             |
|                      |            |              |              |            |              |             |
|                      |            |              |              |            |              |             |
| PCB #                | A          | B            | C            | D          | E            | Blank       |
| Homologs             | pg/L       | pg/L         | pg/L         | pg/L       | pg/L         | pg/L        |
| Monochlorobiphenyls  | 10.8       | 10           | 12.3         | 10.7       | 11           | 0           |
| Dichlorobiphenyls    | 19.6       | 74.6         | 50.5         | 52         | 14.4         | 0           |
| Trichlorobiphenyls   | 63         | 12.6         | 0            | 11.3       | 0            | 0           |
| Tetrachlorobiphenyls | 101        | 0            | 10.4         | 0          | 0            | 0           |
| Pentachlorobiphenyls | 152        | 23.2         | 15.5         | 27.6       | 0            | 29.9        |
| Hexachlorobiphenyls  | 69.2       | 0            | 0            | 0          | 0            | 0           |
| Heptachlorobiphenyls | 0          | 0            | 0            | 0          | 0            | 0           |
| Octachlorobiphenyls  | 0          | 0            | 0            | 0          | 0            | 0           |
| Nonachlorobiphenyls  | 0          | 0            | 0            | 0          | 0            | 0           |
| Decachlorobiphenyl   | 0          | 0            | 0            | 0          | 0            | 0           |
| <b>Total PCB</b>     | <b>415</b> | <b>110</b>   | <b>88.7</b>  | <b>102</b> | <b>25.4</b>  | <b>29.9</b> |

Now the results have been reported when IDLs have been used

# What is Blank?

- PCB is omnipresent
- Almost impossible to achieve a complete blank in the lab
- Every sample we analyze has detectable PCB levels.
- In order to reduce blank levels in the lab
  - Use carbon filtered water
  - Disposable glassware (not always possible)
  - Keep food samples away!
- <20 pg/L per congener is excellent

# Outline

- Pacific Rim Laboratories Inc.
- PCB – what is it and why are we still interested in it
- Toxicity
- How do we analyze it – Analytical Methods
- **What does PCB have to do with snow fighting?**
- Closing thoughts

# City of Spokane – unique or just the leading edge?

- Current WA water quality regulations
  - PCB concentrations <170 pg/L
  - Based on fish consumption of 1-2 meals per month
- Spokane River major source of food for native Americans
  - Daily consumption for many therefore increased potential harm from fish
- Recommend acceptable levels <6 pg/L
- Spokane City passed an ordinance restricting purchasing to PCB free products.
  - Is this even possible



**PACIFIC RIM**  
LABORATORIES INC

# How does PCB get into De-Icer Fluids?

- Not naturally abundant in  $\text{MgCl}_2$  or  $\text{NaCl}$ .
- Possible source is from storage in plastics
  - Plastics contain trace levels of PCBs
  - These can be transferred to brine during storage
- Additional chemicals need to be checked to make sure they are PCB free
- Are PCBs present or are they artifacts of the analysis?



# Present in sample or lab contamination?

- What is the detection limit of the method?
- What are the concentrations found in the method blank?
- Concentrations below the EQL are suspect.
  - EQL is based on the lowest standard in the calibration curve (0.2 pg/ $\mu$ L injected)
  - For 1 L sample with 100  $\mu$ L final volume
    - $\text{EQL} = 0.2 \text{ pg}/\mu\text{L} \times 100 \mu\text{L} / 1 \text{ L} = 20 \text{ pg/L}$  or 0.02 ng/L
- Most confidence when results are 5-10 x EQL



# What is being found?

- Most results for brine solutions are  $<1$  ng/L and within a factor of 5 of blank concentrations
- If you are testing product, discuss it with your testing lab first.
  - Will help you with clean sample containers and advice on how to sample
- Data interpretation is not straight forward.
  - Blank contamination
  - Detection limits
  - Methodology used





# What is achievable?

- Less than 20 labs in North America can run EPA 1668C and only a few will give detection limits  $<10$  pg/L
- No analytical confidence at 6 pg/L for Total PCB in water let alone brine solutions



**PACIFIC RIM**  
LABORATORIES INC

# Thank you

[dave@pacificrimlabs.com](mailto:dave@pacificrimlabs.com)

[www.pacificrimlabs.com](http://www.pacificrimlabs.com)



**PACIFIC RIM**  
LABORATORIES INC