PCBs in Municipal Products

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Contents

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INTRODUCTION

Polychlorinated biphenyls (PCBs) are a toxic manmade chemical found ubiquitously in the environment. Historically, PCBs were primarily used in coolants and lubricants in electrical equipment, such as transformers and capacitors. In the United States, PCBs were largely sold under the trade name Aroclor. Direct production of PCBs was halted in the US in the 1970's due to evidence of human toxicity and persistence in the environment. Since that time, however, PCBs have been incidentally produced in a multitude of manufacturing processes as an unintended byproduct of processes that use heat, chlorine, and carbon.

The Washington State 2008 303(d) list holds 113 Category 5 listings for PCBs, covering 59 waterbodies. Several segments of the Spokane River are included in this list. The City of Spokane has performed stormwater sampling in several of its outfalls that drain to the Spokane River. PCBs were detected in each sample, with a typical sample in the range of 7,000 picograms per liter (pg/L), or parts per quadrillion (ppq).

Once thought to be only a legacy contaminant, PCBs have been found in numerous commercially available products. These PCBs are not intentionally produced, but are rather unintended byproducts of the manufacturing process. Materials containing less than 50 parts per million (ppm) are not considered "PCB-contaminated" under the Toxics Substances Control Act (TSCA) (40 CFR 761.3). For comparison to water quality considerations, 50 ppm is equivalent to 50,000,000,000 ppq. The current Washington State human health surface water quality standard for PCBs is 170 ppq (derived from the National Toxics Rule, 40 CFR 131.36). The Spokane Tribe adopted a water quality standard of 1.3 ppq due to higher fish consumption rates used to derive the standard.

Many products can easily come into contact with rain water and contribute to PCB concentrations in stormwater runoff. Municipalities are concerned about the presence of PCBs in commonly used products such as road paint, asphalt sealers, pesticides, and de-icer, to name a few. However, limited data is available as to the concentration of PCBs in products used for road and facility maintenance.

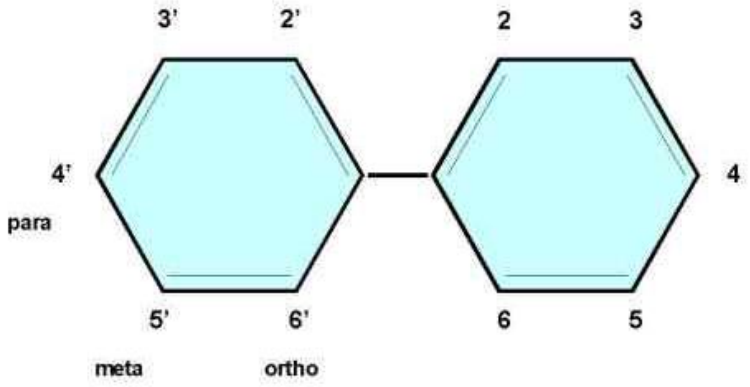
Nearly 50 product samples were collected and analyzed for PCBs using EPA Method 1668C. This method is capable of detecting low concentrations of PCBs for all 209 congeners. The majority of samples were composed of roadway, pipe, and vehicle maintenance products. Because PCBs are also ubiquitously detected in sanitary wastewater samples, five personal care products were sampled as well.

PCB 101

Chemical Structure

PCB molecules are composed of two joined benzene rings with varying degrees of chlorination, as depicted in Figure 1. PCBs can have between one and ten chlorine atoms. There are 209 different arrangements of this molecule, each known as a congener. Congeners are named PCB-1 through PCB-209, with greater numbers corresponding to greater degrees of chlorination. Homologues are the group of PCB molecules having the same degree of chlorination. For example, monochlorobiphenyls (monoCB) is the group of PCBs having one chlorine, dichlorobiphenyls (diCB) are the group of PCBs having two chlorines, etc.

MonoCBs =	1 chlorine
DiCB =	2 chlorines
TriCB =	3 chlorines
TetraCB =	4 chlorines
PentaCB =	5 chlorines
HexaCB =	6 chlorines
HeptaCB =	7 chlorines
OctaCB =	8 chlorines
NonaCB =	9 chlorines
DecaCB =	10 chlorines (PCB-209)



Structure of Polychlorinated Biphenyl (PCB) Molecule

Figure 1. (EPA, 2010b)

During the laboratory analytical process, some congeners cannot be distinguished from one another and are quantified as a complex of more than one congener. These are known as coeluting congeners, and are denoted with a slash in the figures in this report (e.g. 5/8).

Aroclors

Monsanto was the major US manufacturer of PCBs, and sold them under the trade name Aroclor until 1977 (Erickson, 1986). Aroclors were made of standard PCB mixtures to achieve the desired

chemical properties. Each type of Aroclor was given a 4-digit identification number, with the second two digits indicating percentage of chlorine by weight (ASTDR, 2000). For example, Aroclor 1254 contains about 54% chlorine by weight. Homologue patterns for standard Aroclor mixes are shown in Appendix A. Homologue patterns for environmental and product samples can be compared to homologue patterns for Aroclors to give clues as to whether the PCB content may be a legacy Aroclor or not.

METHODOLOGY

Product Selection

Municipalities use numerous products in the roadway environment for construction, traffic safety, and maintenance purposes. Little is known about the PCB content in these products. To help guide product sampling, a literature search was performed to determine the potential for products to contain PCBs. In general, processes that involve chlorine, carbon, and high temperatures have the potential to inadvertently produce PCBs (Munoz, 2007).

Numerous studies have associated pigments with inadvertent PCB production (Christie, 2014; Ecology, 2014; Hu and Hornbuckle, 2010; Rodenburg, 2012). In particular, yellow pigments and white pigments (titanium dioxide) are associated with PCB-11, 206, 208, and 209. Yellow, orange, and red products that are derived from azo pigments (monoazo (Hansa Yellows and azonaphthols) and diarylide yellows) are associated with inadvertent PCB production, as are phthalocyanine blues and greens. Therefore, many items sampled for this study contained colored items. Various yellow and white road paints were sampled as well as hydrant paint and utility locate paint. Personal care products were selected that contain pigments.

Inadvertent PCB production is also associated with the manufacture of a multitude of various other chlorinated chemicals. Table 1 shows chemicals associated with various products that can be exposed to stormwater or enter the wastewater system:

Table 1. Example of Chemicals Associated with Inadvertent PCB Production

Chemical	Associated Products
Ethylenediamine	Surfactants, fungicides, fuel additives, EDTA, hair care products, soaps
Ethylene dichloride	Polyvinyl chloride (PVC), solvents
Phenylchlorosilanes	Silicones: lubricants, adhesives, coatings, hoses
Chlorinated benzidines	Pigments
Chlorinated paraffins	Flame retardants in plastics, paints, adhesives, sealants, and caulks
Glycerol/Glycerin (synthesized by epichlorohydrine)	Toothpaste, numerous personal care products, antifreeze, resins

(Information in this table adapted from Munoz, 2007)

One of the most consistent illicit discharge complaints received by the City of Spokane is vehicles dripping fluids onto the roadway. In 2011, the City sampled various off-the-shelf motor oils and transmission fluid to assess the potential for PCBs to enter stormwater through this pathway. PCBs were detected in appreciable concentrations in each of the samples, as shown in Table 2. Because PCBs are known to be present in these materials, additional motor oils and other petroleum products were sampled for this product sampling study.

Table 2. Oil and Transmission Fluid Sample PCB Concentrations (City of Spokane, 2011)

Sample	Total PCB, micrograms per kilogram (ppb) (EPA Method 1668)
Pennzoil SAE5W-30	37.8
Quaker State SAE5W-30	14
Valvoline Mercon V	49.5
Red Line D4 Automatic Transmission Fluid	8.8
Valvoline Full Synthetic 5W-30	116

One of the objectives of this project is to inform municipalities across the state. To gain a better understanding of which products and brands are most widely used, a survey was distributed across the state to willing participants. Ten jurisdictions responded, 6 from eastern Washington and 4 from western Washington. Results of the survey showed that one traffic paint brand is commonly used on both sides of the state under a state contract with WSDOT. Other product brands varied widely across the region, and the brand names used by the City of Spokane were not uncommon, so the products available at the City of Spokane were sampled.

Quality Assurance Project Plan (QAPP)

A QAPP was prepared for this project and approved by Ecology prior to the collection of samples (LimnoTech, 2014). A copy of the QAPP is available upon request.

Experimental Design

Ultra clean sampling techniques were followed to reduce the chance of sample contamination from ambient sources. Samples were collected August to October, 2014. Products were placed directly into laboratory-prepared sample jars whenever possible. Where equipment was necessary to remove the sample from its container and place it into the sample jar, clean decontaminated equipment was used.

Each product was assigned a three-digit Product ID number. Liquid and gel samples were placed in 40-milliliter glass vials. Solid samples were placed in 4-ounce glass jars. Pipe samples were wrapped in aluminum foil. Spray paint samples were sent to the laboratory in the original spray cans. All readily available product information was recorded at the time of sampling, including product type, brand name, lot number, manufacture date and country of origin in addition to standard sampling information such as time and date, sampler, and sample location.

Four field replicate samples were collected for field sampling quality control purposes. Replicate samples were collected for product ID 001, 003, 008, and 018.

A chain of custody form was filled out for each sample batch. Samples were packed into coolers, chilled to a maximum of four degrees Celsius, and shipped to Pacific Rim Laboratories for analysis. Samples were analyzed using EPA Method 1668C for all 209 PCB congeners.

Laboratory Quality Control

The laboratory maintains internal quality control procedures, including method blanks, laboratory control samples, laboratory duplicates, and labeled compound, cleanup, internal, and injection standards. In addition, data verification was performed by the City's project quality assurance (QA) officer. Data was validated by both the laboratory and the QA officer and was found to be acceptable.

EPA Method 1668 detects PCBs at very low concentrations. PCBs are truly ubiquitous and can be detected in even the most pristine laboratory environment. Therefore, PCBs are frequently detected in blank samples. To account for this, any congener that was detected in a product sample that was within three times the concentration detected in the associated blank sample were removed from the total PCB value. These congeners are also not included in the graphs in this report.

RESULTS AND DISCUSSION

The results of PCB product sampling are summarized in Table B-1 of Appendix B and in more detail in the following sections. PCBs were detected in all but two of the products that were sampled in the parts per trillion to parts per million range. The units reported by the laboratory are in micrograms per kilogram (ug/kg), or parts per billion. Note that Spokane water quality standards are 1.3 picograms per liter, or parts per quadrillion. One part per billion is 1,000,000 times greater than one part per quadrillion. Therefore, products detected at these concentrations are of concern to water quality practitioners.

Traffic Marking Samples

Several traffic paint samples were collected due to the association between yellow and white pigments and PCBs. One brand of traffic paint is predominantly used by municipalities and agencies throughout the state, sold by Ennis-Flint. Various types of this paint brand are available. Product numbers 983711 and 983712, low VOC, 100% acrylic waterborne traffic line paint, were sampled from the end of a spray nozzle in a City of Spokane shop. A liquid sample, replicate liquid sample, and a dried sample were analyzed (each for white and yellow). The paint was collected in a clean glass beaker and then immediately distributed to each of the sample vials. Dried paint samples were created by City of Spokane staff by pouring a small amount of paint onto a clean Teflon liner and allowing it to dry before sending it to the laboratory for analysis. The purpose of analyzing the dried sample was to determine if some PCB congeners are volatilized after paint application. Ennis-Flint PreMark thermoplastic road striping was also sampled, both in yellow and white.

For comparison, a lesser-used brand of road paint was sampled. Sherwin-Williams Promar solvent based acrylic traffic marking paint is used by some municipalities in southeast Washington. Samples were collected for both yellow and white paint. Replicates of all of the traffic marking samples (except the dried paint) were shipped to Ecology for their own product sampling study. Results of Ecology's analysis will be reported by Ecology. Total PCBs are shown in Tables 3 and 4 along with the percentage of the three most prevalent congeners, PCB-11, 77, and 209.

Table 3. Yellow Traffic Marking

Type	Total PCB (ug/kg)	PCB-11	PCB-77	PCB-209
Ennis	0.73	7%	35%	36%
Ennis (replicate)	2.69	17%	58%	8%
Ennis (dried)	0.565	9%	39%	35%
Promar	64.88	98%	1%	0%
Thermoplastic	10.78	79%	1%	0%

Table 4. White Traffic Marking

Type	Total PCB (ug/kg)	PCB-11	PCB-77	PCB-209
Ennis	0.41	18%	0%	61%
Ennis (replicate)	0.4	23%	0%	57%
Ennis (dried)	0.38	17%	0%	69%
Promar	0.28	41%	1%	0%
Thermoplastic	3.33	22%	0%	0%

Figure 2 shows the congener patterns for both the wet and dried Ennis yellow traffic marking paint samples. Generally the same congeners were detected in each of the samples, with slightly lower concentration in the dried sample than the liquid paint sample. This suggests that some congeners may be volatilizing into the air. However, as the difference in the liquid and duplicate liquid sample show, further study would be warranted to better determine volatilization rates. The Material Safety Data Sheet (MSDS) indicates that the paint composition contains methyl alcohol, titanium dioxide, propylene glycol, 2-butyoxyethanol, and quartz. Pigment content is not listed.

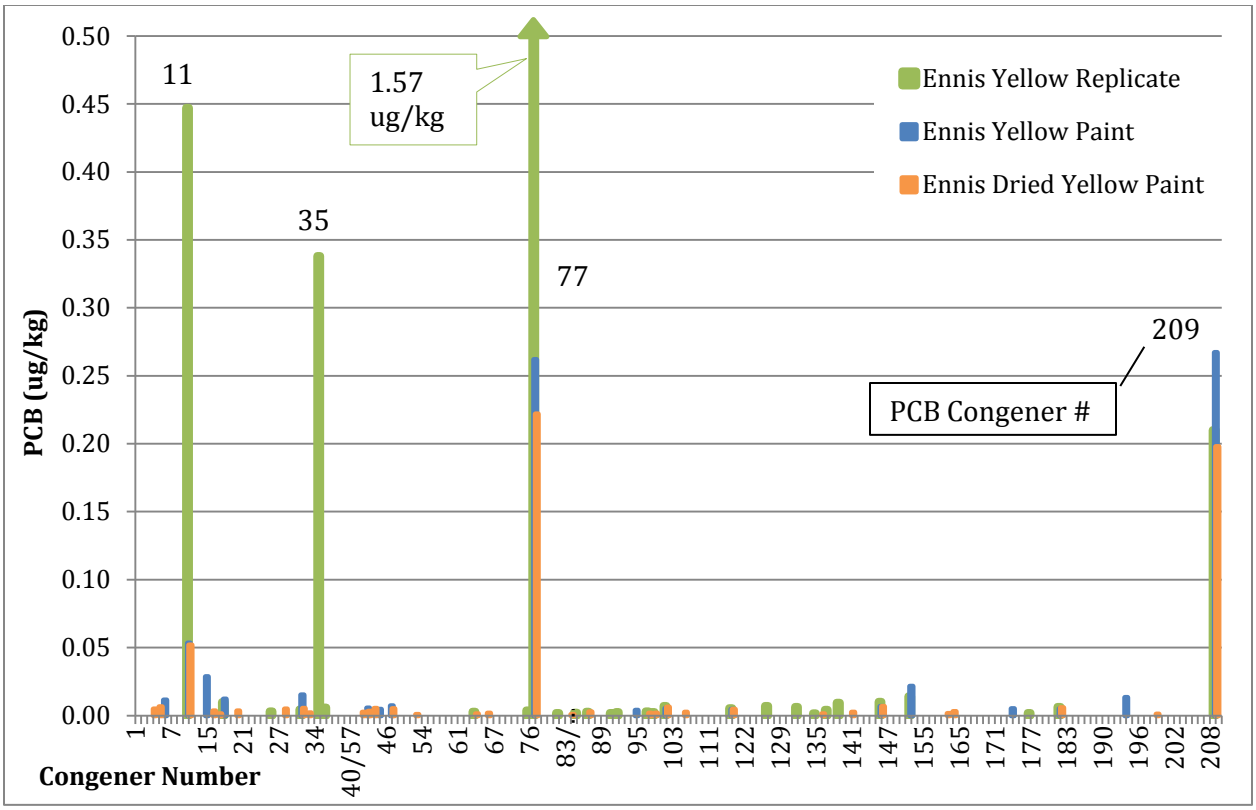


Figure 2. Ennis Wet and Dried Yellow Paint PCB Congeners

Figure 3 shows the congener patterns for the wet and dried Ennis white paint samples. The congener patterns are similar between the three samples. There is no discernible difference between the liquid and dried samples. Interestingly, PCB-11 was detected in the white paint samples in greater concentration than two of the yellow paint samples, although PCB-11 is usually associated with yellow pigment. The concentration of PCB-209 is similar between the yellow and white samples. The MSDS sheets for these products indicate that the yellow paint contains 3-7% titanium dioxide and the white paint contains 7-13% titanium dioxide.

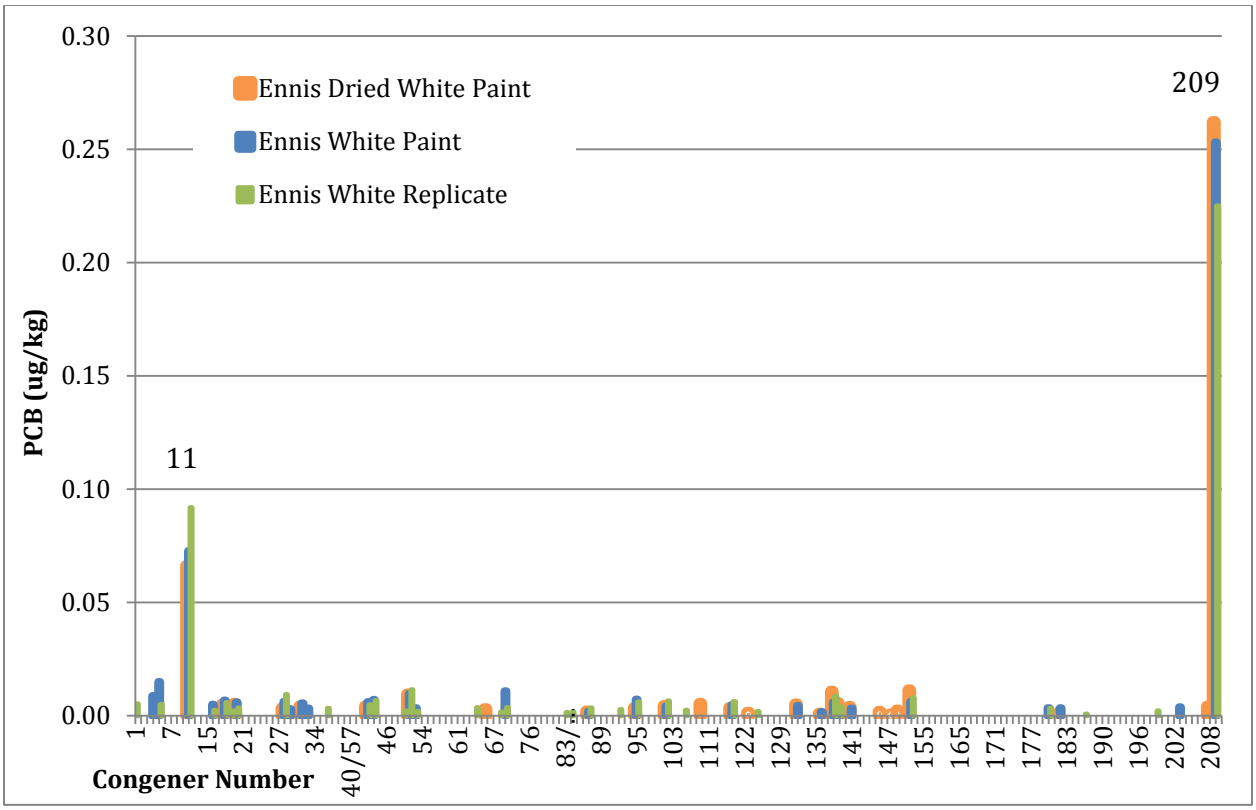


Figure 3. Ennis Wet and Dried W Paint PCB Congeners

Sherwin-Williams Promar yellow and white paint samples are shown in Figure 4. PCB-11 was detected in the yellow paint sample at a significant concentration of 63.8 ug/kg. PCB-35 and 77 were detected similar to the Ennis paint, but PCB-209 was not detected. The MSDS indicates that both white and yellow paints contain ethylbenzene, xylene, acetone, quarts, and titanium dioxide (2% titanium dioxide by weight for yellow and 4% for white). Both yellow and white paints contain approximately 55% pigment by weight.

Figure 5 shows congener patterns for the yellow and white Ennis-Flint PreMark thermoplastic tape samples. Total PCBs are greater than the paint samples (see Table 4 and 5), and there are more congeners detected. Most of the congeners are in the mono-CB through tetra-CB range (having one through four chlorine atoms). The MSDS for this product indicates that it contains the following components in increasing order of concentration: pigments, alkyd resins, polymers, fillers, and glass beads.

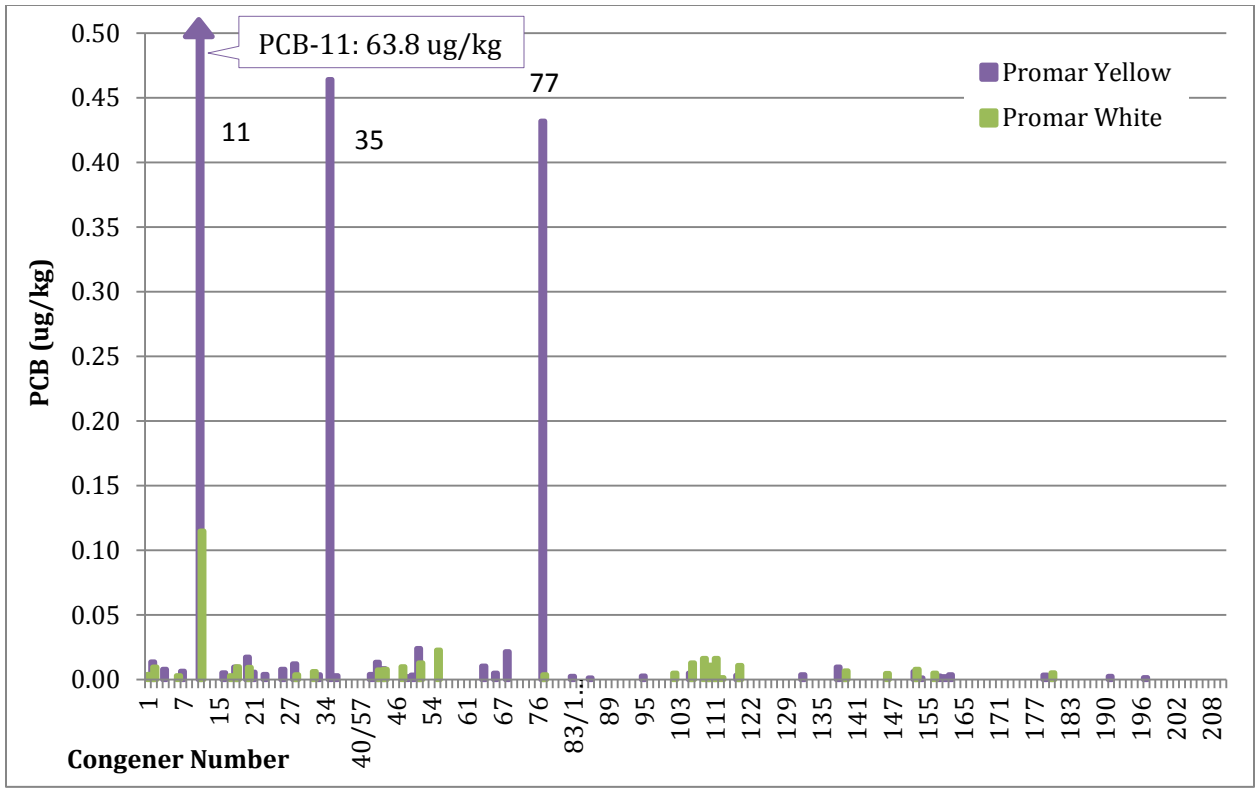


Figure 4. Sherwin-Williams Promar Yellow and White Paint Congeners

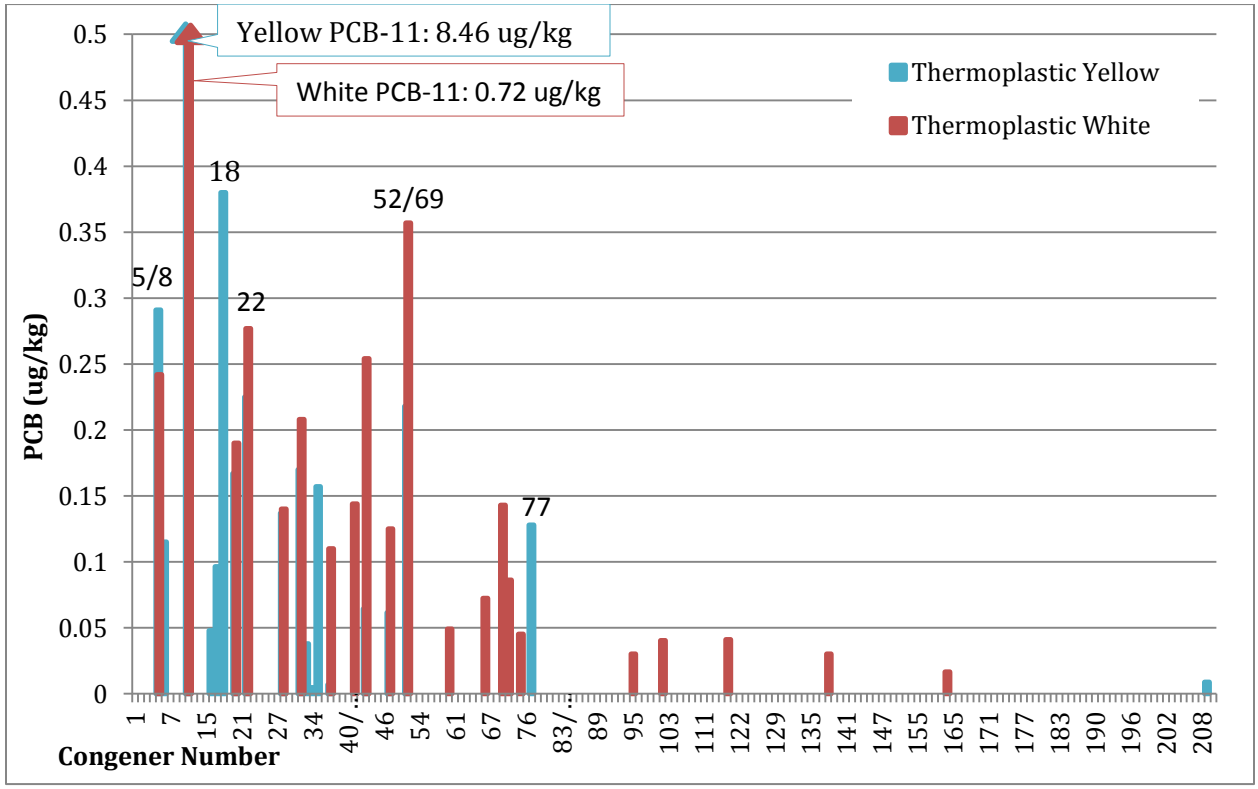


Figure 5. Ennis PreMark Thermoplastic Tape Congners

For samples that have a wide array of PCB congeners, such as the white thermoplastic tape sample, a homologue pattern graph can be a useful tool. These graphs depict the percentage of various homologues that make up the total PCB sample. Figure 6 shows the homologue patterns for both the yellow and white thermoplastic tape samples. The white thermoplastic tape, in particular, has a similar homologue and congener pattern to Aroclor 1016 (Appendix A). Yellow thermoplastic tape also has a similar pattern, but is dominated by PCB-11, a diCB. Aroclor 1016 was one of the lesser used Aroclor mixtures and was used in capacitors.

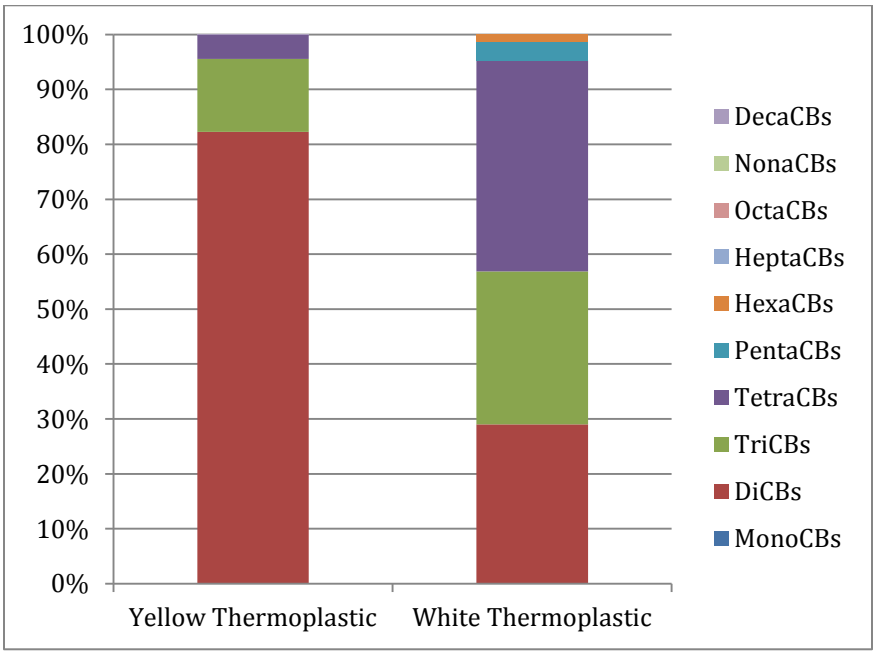


Figure 6. Thermoplastic Tape Homologue Patterns

Hydrant and Utility Locate Paints

Two additional types of paint commonly used on or near roadways were sampled. Fire hydrants are re-painted periodically using spray cans, typically in an aluminum color on the barrel and red on the nozzles. Rustoleum Professional High Performance Enamel Fast-Dry spray paint in Silver Aluminum was sampled. The product contains acetone, liquefied petroleum gas, toluene, xylene, aluminum flake, and ethylbenzene. Total PCBs detected in the sample were **0.0032 ug/kg**, consisting of only the congener PCB-19.

Utility locate paint is sprayed on or near the roadway frequently to mark underground utilities in a variety of colors, including pink, white, green, blue, purple, yellow, orange, and red. The green color denoting sewer utilities was sampled. The product sampled was Rustoleum Industrial Choice Solvent-Based Precision Line inverted marking paint in safety green. The total PCBs detected were **21.527 ug/kg**.

Ingredients listed on the green utility locate paint MSDS include acetone, liquefied petroleum gas, aliphatic hydrocarbon, limestone, xylene, modified alkyd, barium sulfate, talc, naptha (petroleum,

hydrotreated light), titanium dioxide, ethylbenzene, and toluene. Most of the ingredients listed on the MSDS (with the exception of titanium dioxide) are not specifically listed as having the potential to inadvertently produce PCBs in the Munoz (2007) paper, although there may be unlisted intermediate compounds that may produce PCBs. The most likely source of PCB is the pigment, and is most likely a phthalocyanine green based on the presence of PCB-11, 206, 207, 208, and 209. Titanium dioxide may also be contributing to the PCB-206, 208, and 209. On the Rustoleum product website, "phthalo green" is a common pigment used in various paint products, although not specifically listed for this product. The pigments used are proprietary information and would not be shared by the company.

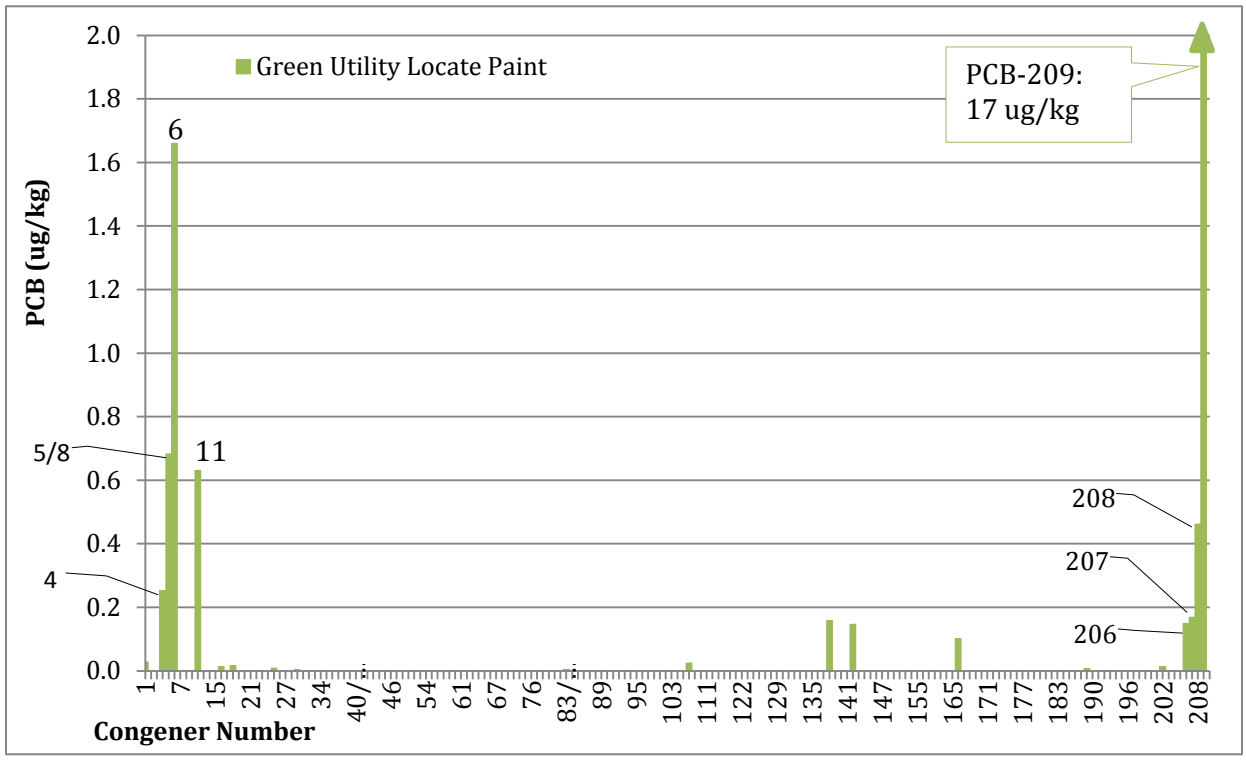


Figure 7. Green Utility Locate Paint Congeners

Deicer

The City of Spokane uses FreezeGard magnesium chloride for roadway deicing. Of the municipalities surveyed, most in eastern Washington use magnesium chloride while most in western Washington use calcium chloride. The Washington State Department of Transportation (WSDOT) Eastern Region uses an enhanced salt brine with sugar beet boost. Both the City of Spokane and WSDOT deicers were sampled. Total PCBs are shown in Table 5.

Table 5. Deicer Total PCB

Sample	Total PCB (ug/kg)
Magnesium Chloride	1.332
Magnesium Chloride Replicate	1.952
SB Boost	0.038

The magnesium chloride is sourced from naturally occurring minerals in the Great Salt Lake.

The magnesium chloride samples were dominated by tetraCBs, while the SB Boost sample congeners were distributed between the triCB to heptaCB range. Homologue patterns are shown in Figure 8 and congener patterns are shown in Figure 9.

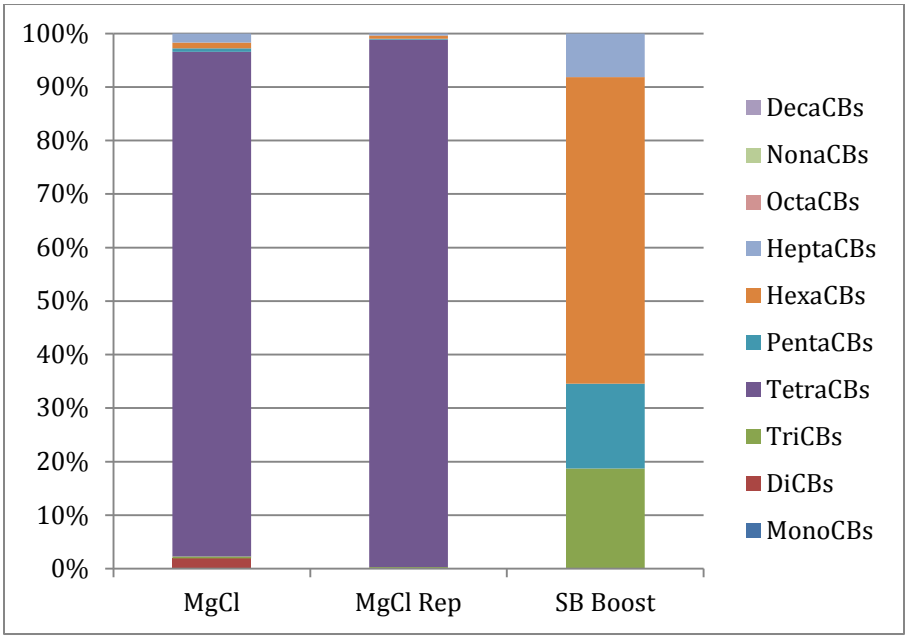


Figure 8. Deicer Homologue Patterns

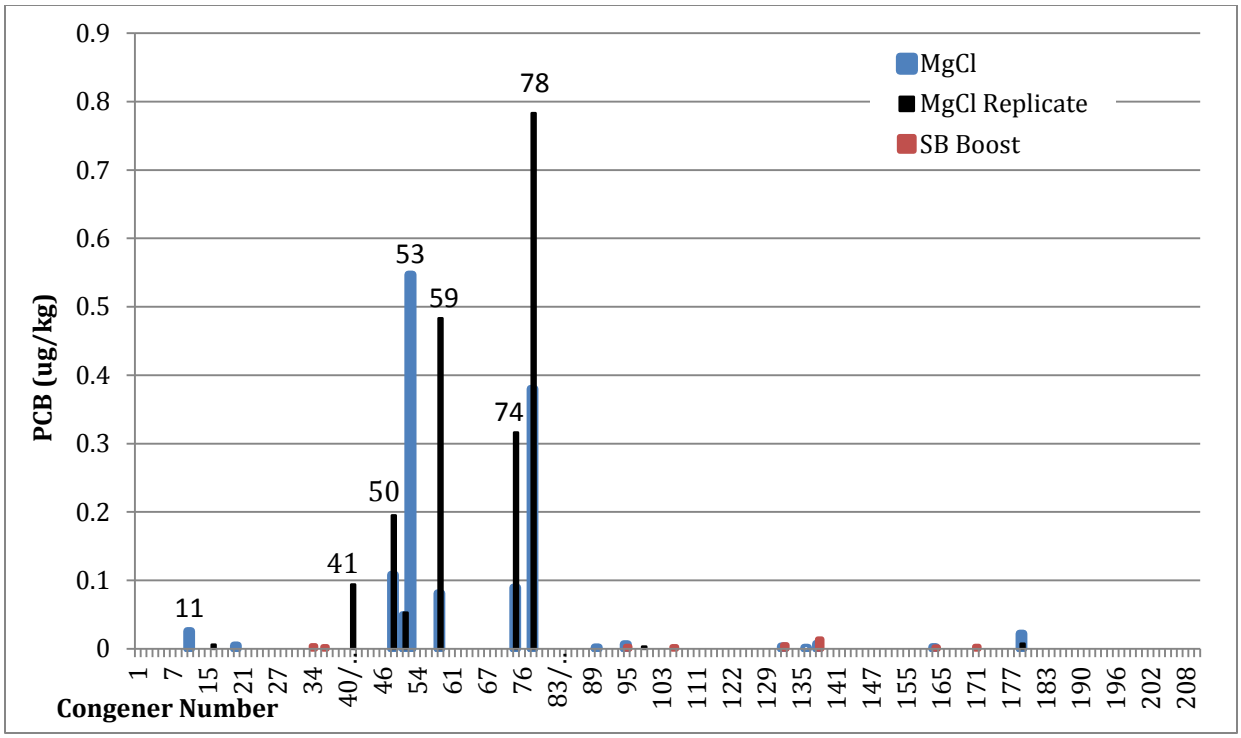


Figure 9. Deicer PCB Congeners

Antifreeze

Antifreeze mixtures may contain inadvertently generated PCBs, particularly those made with glycerol (also known as glycerin) synthesized from epichlorohydrine (Munoz, 2007). Kool Green Extended Life antifreeze was sampled, which contains a yellow color. The MSDS indicates that it contains ethylene glycol, diethylene glycol, and proprietary additives, inhibitors, and dye. The ethylene and diethylene glycols and glycerol have a similar chemical structure, but are not the same compound. Total PCB detected in the sample was **0.018 ug/kg**. Despite its yellow color, PCB-11 was not detected in the sample.

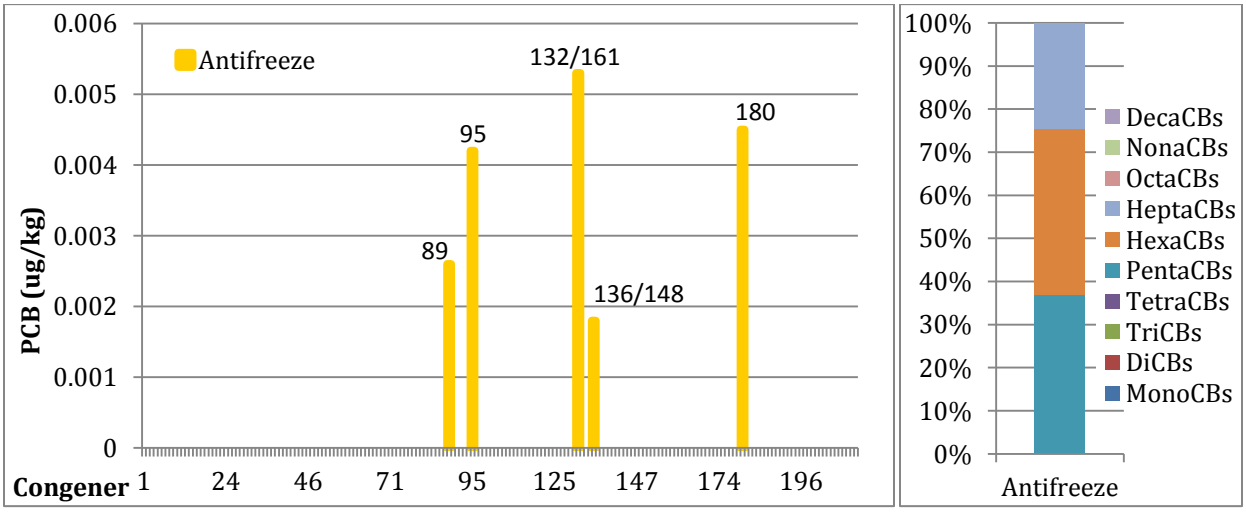


Figure 10. Antifreeze PCB Congeners and Homologue Patterns

Pesticides

Three types of pesticide and one adjuvant were sampled, including Weedar 64 (2,4-D formula), Portfolio 4F, Roundup Pro Max, and the adjuvant Crosshair. The chemical processes that make up chlorinated pesticides have been broadly determined by EPA to have a high potential for inadvertent PCB generation (Munoz, 2007).

PCBs were **non-detect** in the Weedar 64 sample and laboratory duplicate. None of the congeners were flagged for blank contamination. The main ingredients listed on the MSDS are 2,4-dichlorophenoxy acetic acid (2,4-D), dimethylamine salt, and trade secret inert ingredients. Interestingly, chemicals with similar structures to 2,4-D, including trichlorophenoxy acetic acid and dichlorophenyl acetic acid are listed as having the potential for inadvertent PCB generation, but 2,4-D is not (Munoz, 2007).

The total PCBs detected in the Portfolio 4F sample were **6.89 ug/kg**. The majority of this sample was composed of the coeluting congeners PCB-64 and 72. Sulfentrazone is the active ingredient in Portfolio 4F, making up about 40% of the product. Its chemical name is N-[2,4-dichloro-5-[4-(difluoromethyl)-4,5-dihydro-3-methyl-5-oxo-1H-1,2,4-triazol-1-yl]phenyl]methanesulfonamide. Other ingredients include toluene and propylene glycol.

Total PCBs detected in the Roundup Pro Max sample were **0.012 ug/kg**. The active ingredient, making up about 49% of the product, is potassium salt of N-(phosphonomethyl) glycine (potassium salt of glyphosate). Glycine is listed as a chemical product having the potential to contain inadvertently generated PCBs (Munoz, 2007).

The sample of the adjuvant Crosshair contained **0.316 ug/kg** total PCBs. It is composed of methyl ester, modified soybean oil. Soybean oil can be modified through a number of different processes. One option is to synthesize it from epoxidised soybean oil using methylene chloride (Xu et al., 2011). If this process was used, it could possibly be the pathway for inadvertent PCB generation because chlorine is introduced in the process. Glycerine is also a byproduct of this process, which is also listed as a potential inadvertent PCB generating substance when a chlorinated compound is used (Munoz, 2007). Figure 11 shows the congeners detected in the pesticide and adjuvant samples.

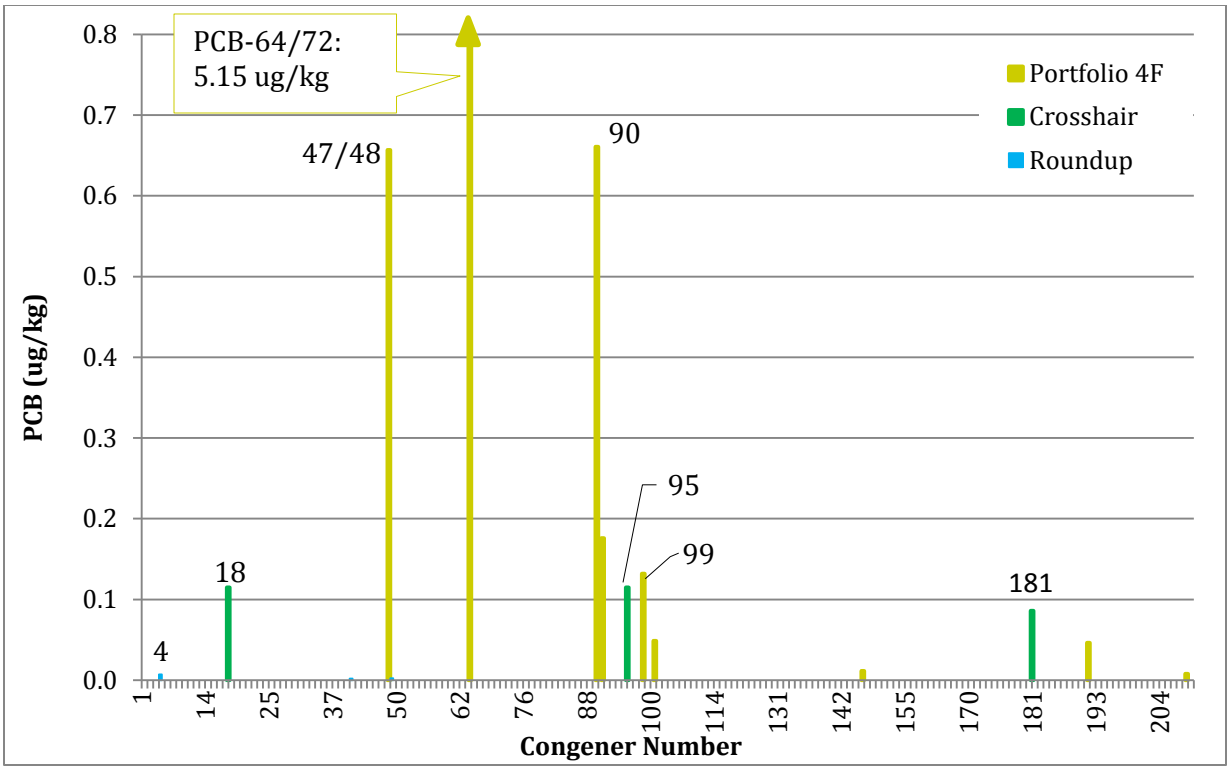


Figure 11. Pesticide and Adjuvant Congeners

Motor Oil and Lubricant

The Fleet Maintenance department primarily uses ConocoPhillips Firebird SAE 15W-40 Heavy Duty EC oil to maintain the City's vehicle fleets. This oil is made from greater than 50% re-refined base stocks. Because this same oil is used in many vehicles and serviced at the same shop, there was an opportunity to sample the same type of oil both before use and after an oil change for comparison. Additionally, Valvoline Full Synthetic SAE 5W-30 was sampled off-the-shelf from a local automotive store. This oil was sampled by the City in 2011 and contained the greatest concentration of PCBs of the oils sampled (see Table 2). A lubricant, MP Gear Lube SAE 85W-140 by Phillips 66 was also sampled. Total motor oil and lubricant PCB concentrations sampled in 2014 are shown in Table 6.

Table 6. Motor Oil and Lubricant Total PCBs

Sample	Total PCB (ug/kg)
Firebird 15-40 Bulk	0.856
Used Firebird 15-40 Bulk	0.502
Used Firebird 15-40 Bulk Replicate	2.375
Valvoline Full Synthetic 5-30	0.969
Gear Lube	0.623

There was a wide range of PCB congener distribution for the various oil and lubricant samples. Most of the congeners were in the low to mid chlorinated range. The used Firebird motor oil sample and its duplicate were not similar to each other in total PCB concentration or congener distribution as a result of its heterogeneity.

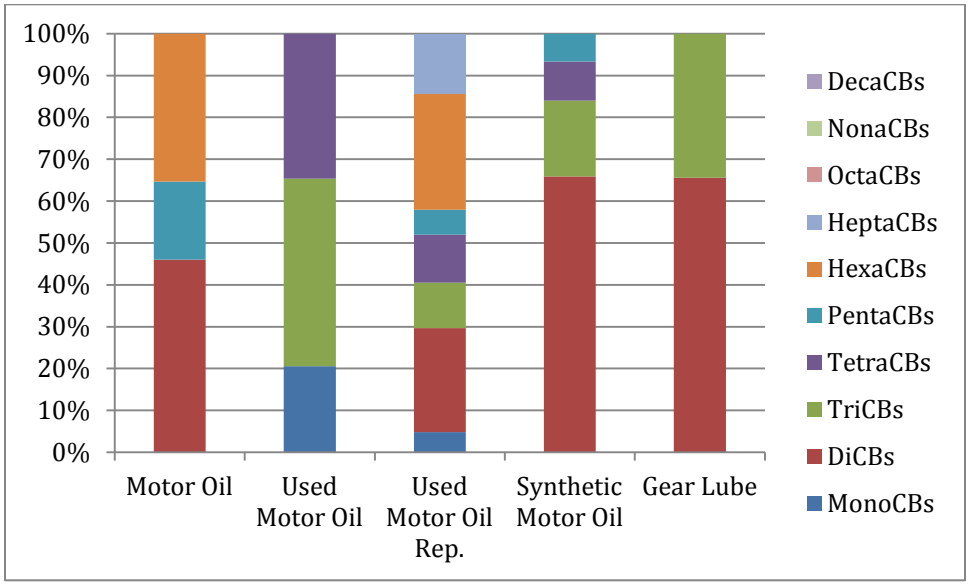


Figure 12. Motor Oil and Lubricant PCB Homologue Patterns

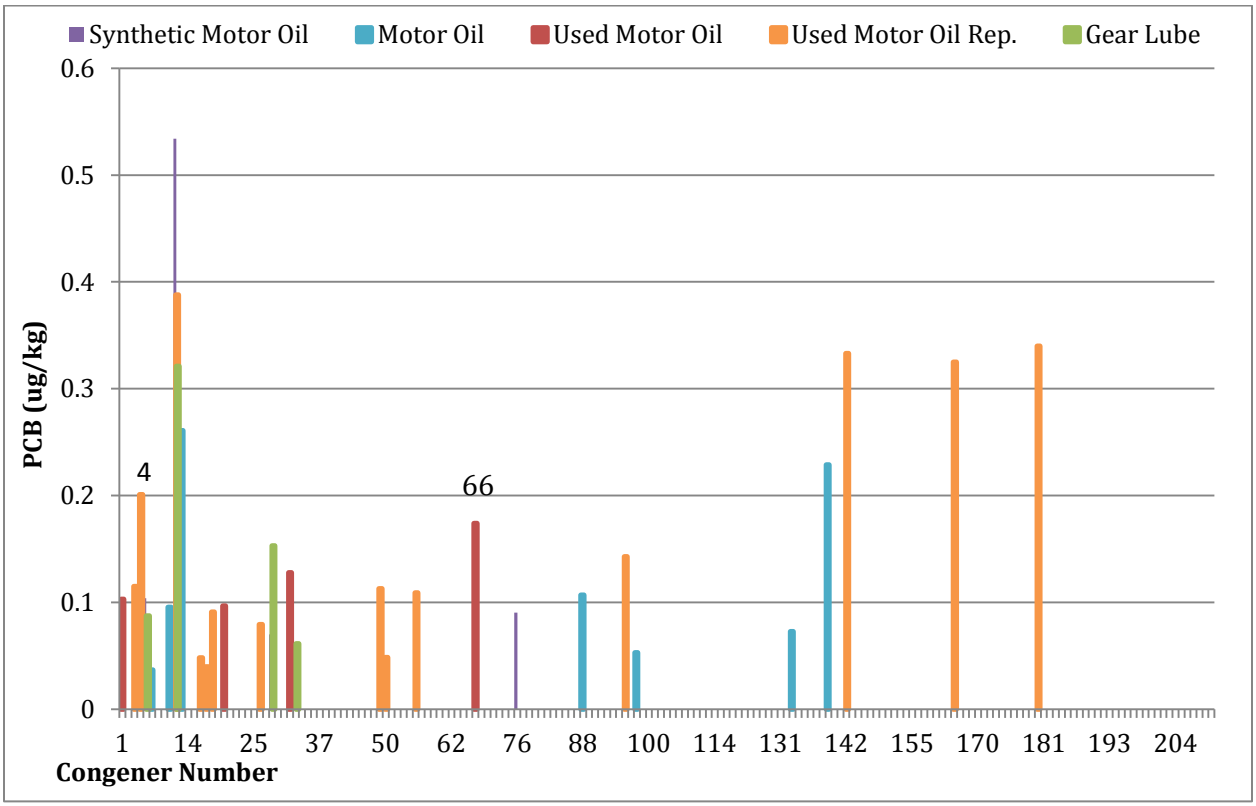


Figure 13. Motor Oil and Lubricant PCB Congeners

Gasoline and Diesel

Regular unleaded gasoline and #2 dyed diesel were sampled from the fuel tanks at the City's Riverside Park Water Reclamation Facility. The diesel sample was non-detect. During laboratory analysis, coextracting interferences resulted in the detection limits being raised to 2 ug/kg for each of the monoCB, diCB, and triCB congeners. Therefore, PCBs may still be present in diesel at less than 2 ug/kg per congener, but were unable to be detected due to interferences.

The total PCBs for the gasoline sample was **0.935 ug/kg**. Nearly all of the sample was composed of PCB-2 (0.93 ug/kg). The remainder was the coeluting congeners PCB-138 and 160.

Dust Suppressant

The City of Spokane has some unimproved roads that have not been paved and require dust control. Three forms of dust control approved for use in the City are magnesium chloride (at a different concentration than the deicer), emulsified asphalt dust abatement (EADA), and lignosulfonate. Samples were collected from each of these three dust suppressants.

The magnesium chloride dust suppressant brand is DustGard, made from naturally occurring minerals from the Great Salt Lake. EADA is a petroleum-based product, containing primarily petroleum asphalt and petroleum bitumen with water and a proprietary mix of petroleum distillates, polymer modifier, surfactants, emulsifier, and other additives. Ligno Road Binder lignosulfonate is derived from natural polymers in wood, and contains sucrose, plant fiber, and an aquatic solution according to its MSDS.

Table 7. Dust Suppressant Total PCBs

Sample	Total PCB (ug/kg)
EADA	0.091
Lignosulfonate	0.086
Magnesium Chloride	3.574

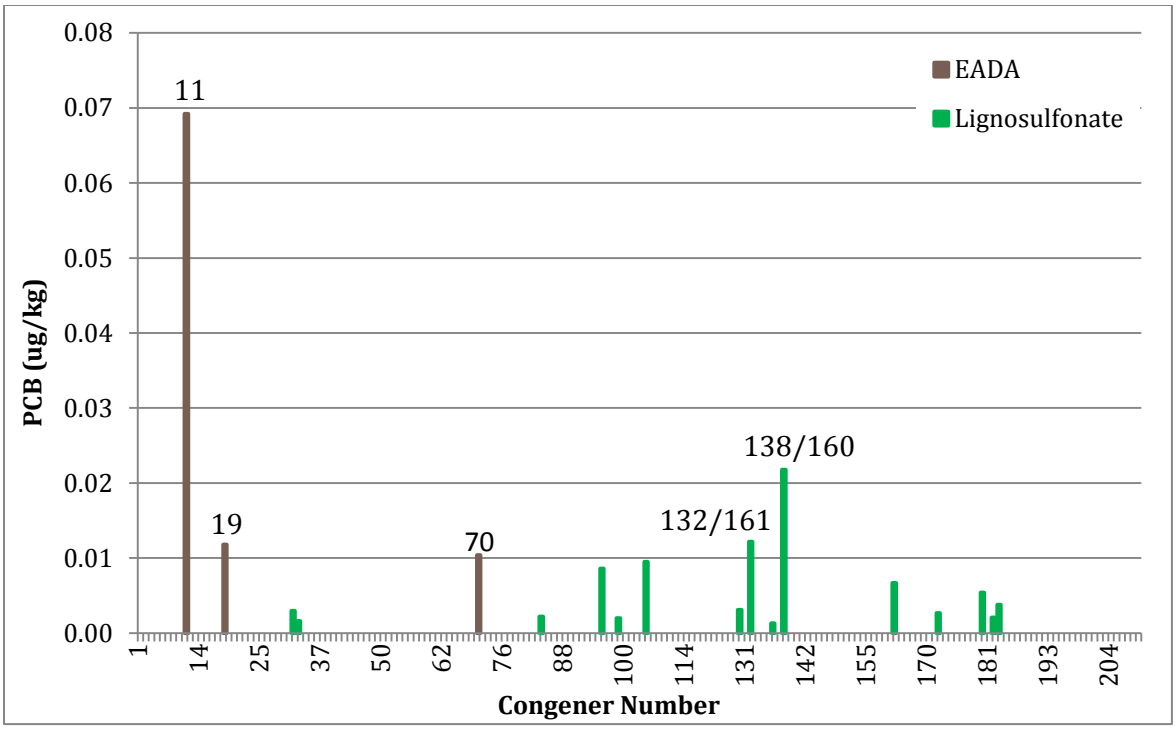


Figure 14. EADA and Lignosulfonate Congeners

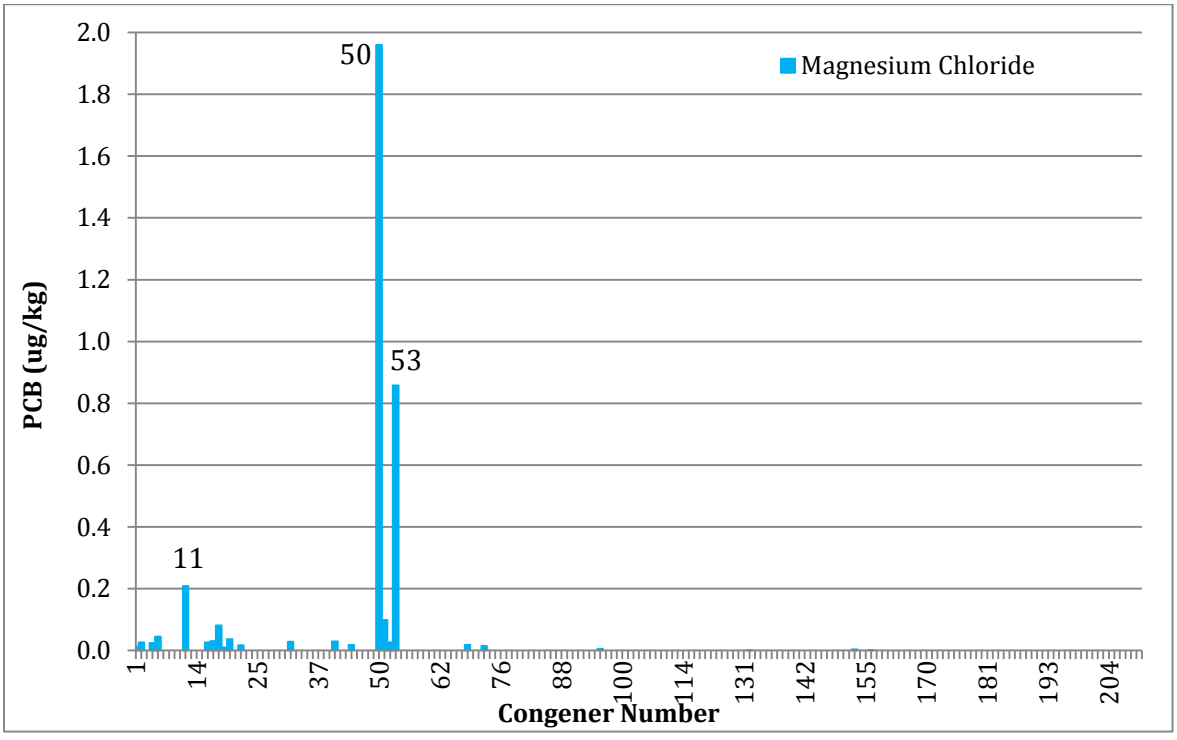


Figure 15. DustGard Magnesium Chloride Congeners

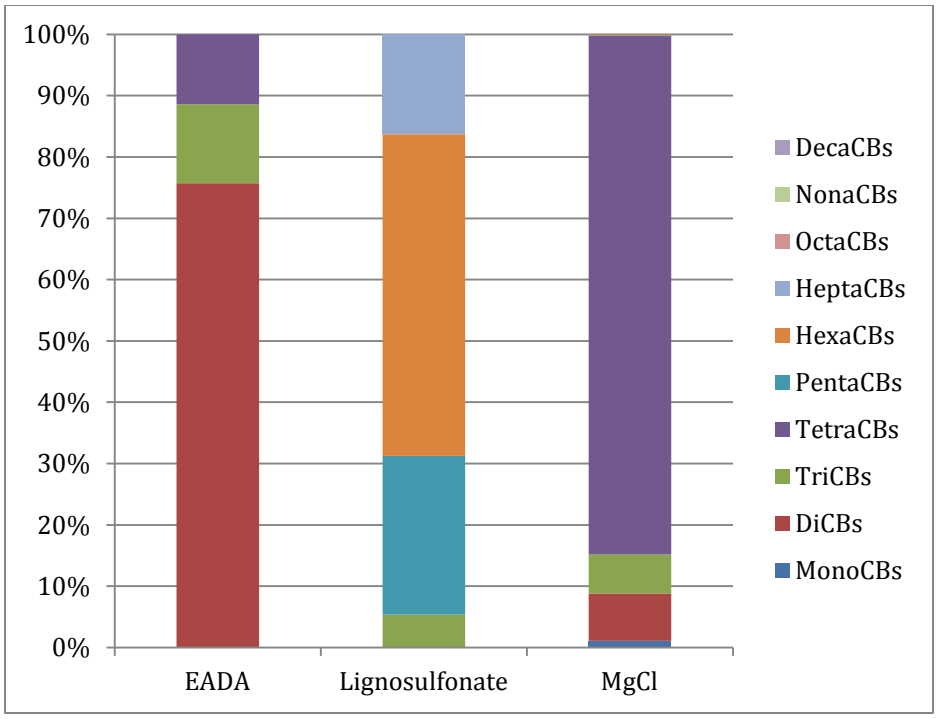


Figure 16. Dust Suppressant Homologue Patterns

The homololgue pattern for EADA is similar to synthetic oil (Figure 12), dominated by diCBs with lesser percentages of triCBs and tetraCBs. Lignosulfonate has a somewhat similar homologue pattern to Aroclor 1260, but the individual congener patterns don't match up well (see Appendix A).

Asphalt Related Products

The asphalt products that were sampled include asphalt tack, crack sealer, and an asphalt release agent. Asphalt tack is made of an asphalt emulsion, and is placed between old and new asphalt layers to adhere them to one another. The crack sealer, SA Premier, is made of asphalt, vacuum distillate, petroleum distillate, styrene-butadiene block copolymer, vulcanized rubber compound, mineral filler, methyl methacrylate, and linear low density polyethylene. The asphalt release agent brand is Soy What by TechniChem, and is "crafted from a by-product that is extracted from soybeans," according to the technichemcorp.com website. Total PCBs and congener and homologue patterns are shown in the following table and figures.

Table 8. Asphalt Related Product Total PCBs

Sample	Total PCB (ug/kg)
Asphalt Tack	0.085
Crack Sealer	7.975
Asphalt Release Agent	0.558

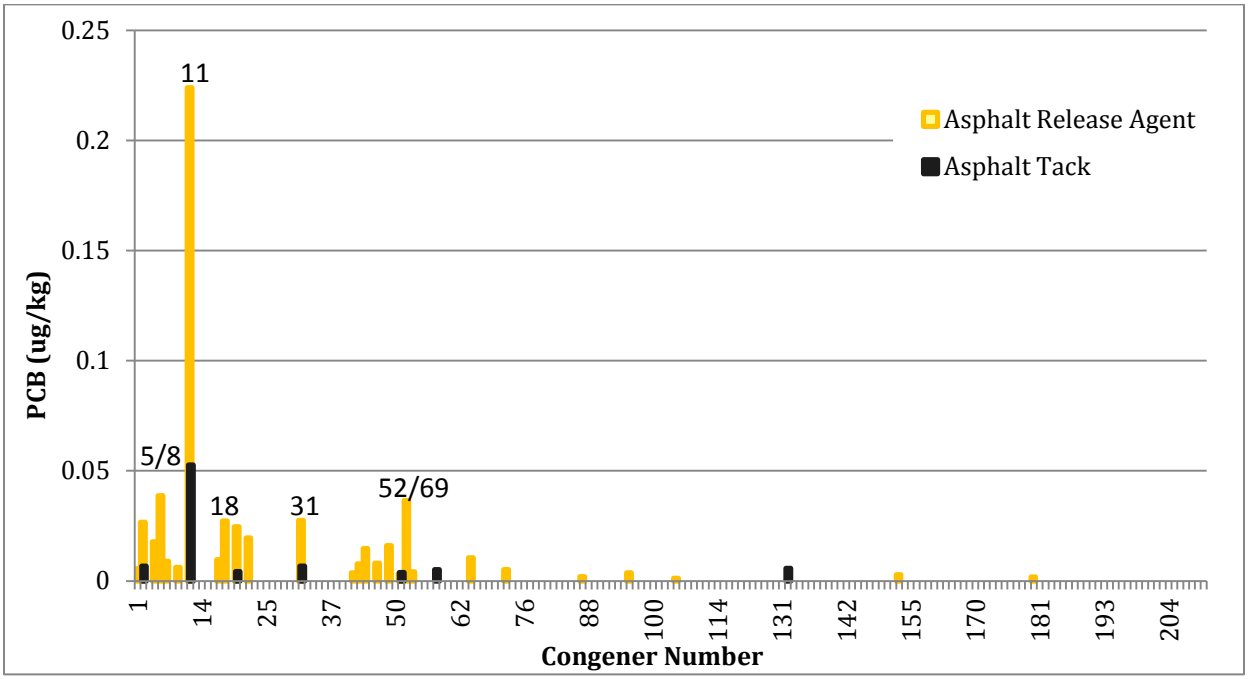


Figure 17. Asphalt Release Agent and Tack Congener Patterns

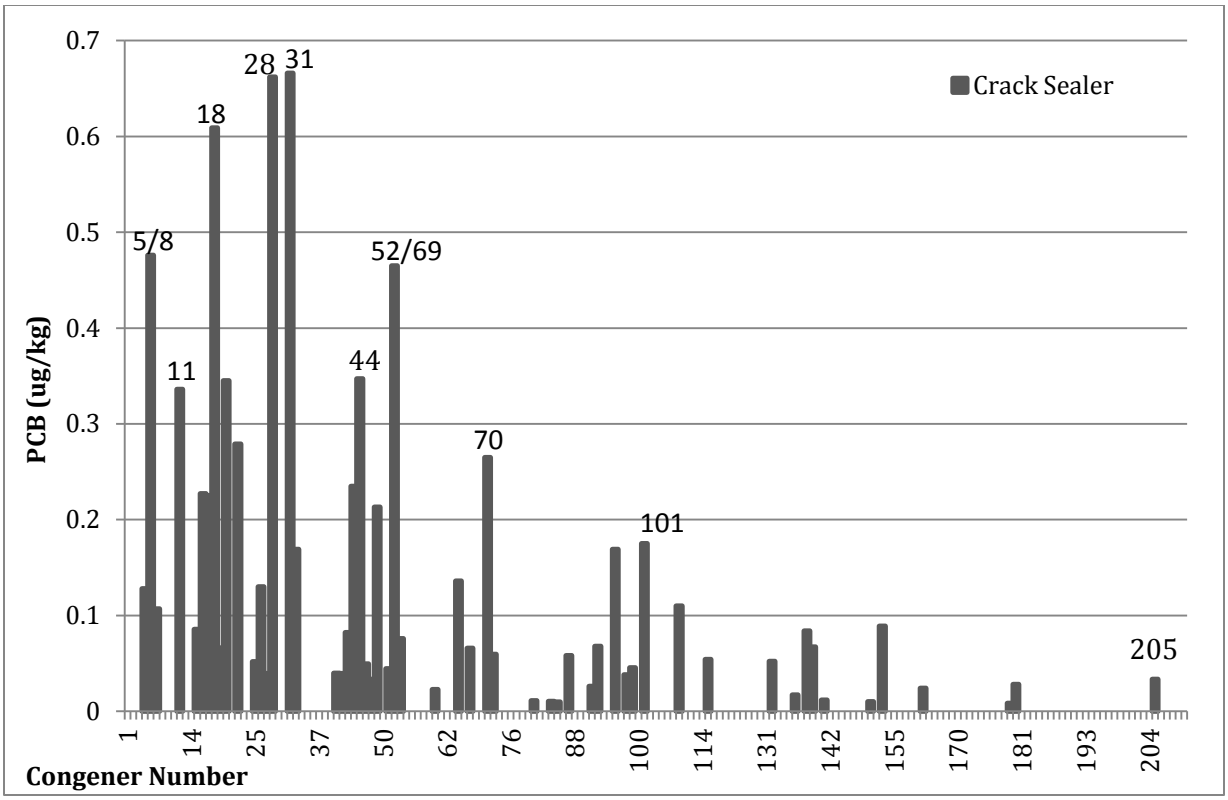


Figure 18. Crack Sealer Congener Pattern

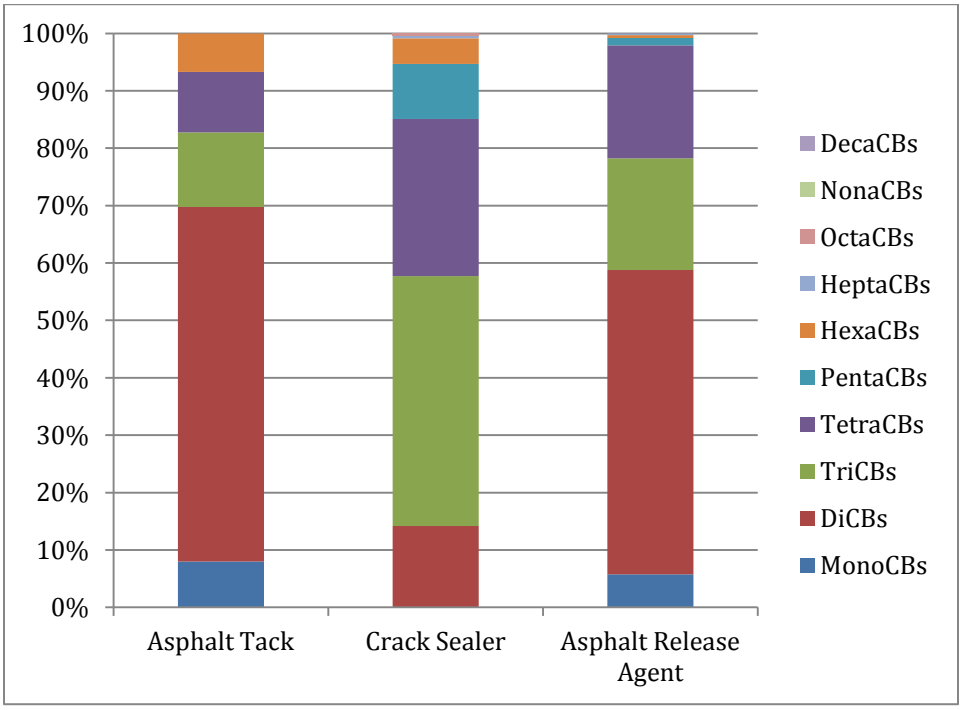


Figure 19. Asphalt Product Homologue Patterns

The crack sealer has a similar congener and homologue pattern to Aroclor 1242. The congeners from the crack sealer sample were converted to percent of total PCB by weight and are plotted against Aroclor 1242 in the same units in Figure 20. Aroclor 1242 had a wide variety of end uses, one of them being in rubbers. One of the ingredients in the crack sealer is vulcanized rubber compound. PCB-11 was detected at over 4% of the crack sealer PCB composition, but is not present in most Aroclor mixes.

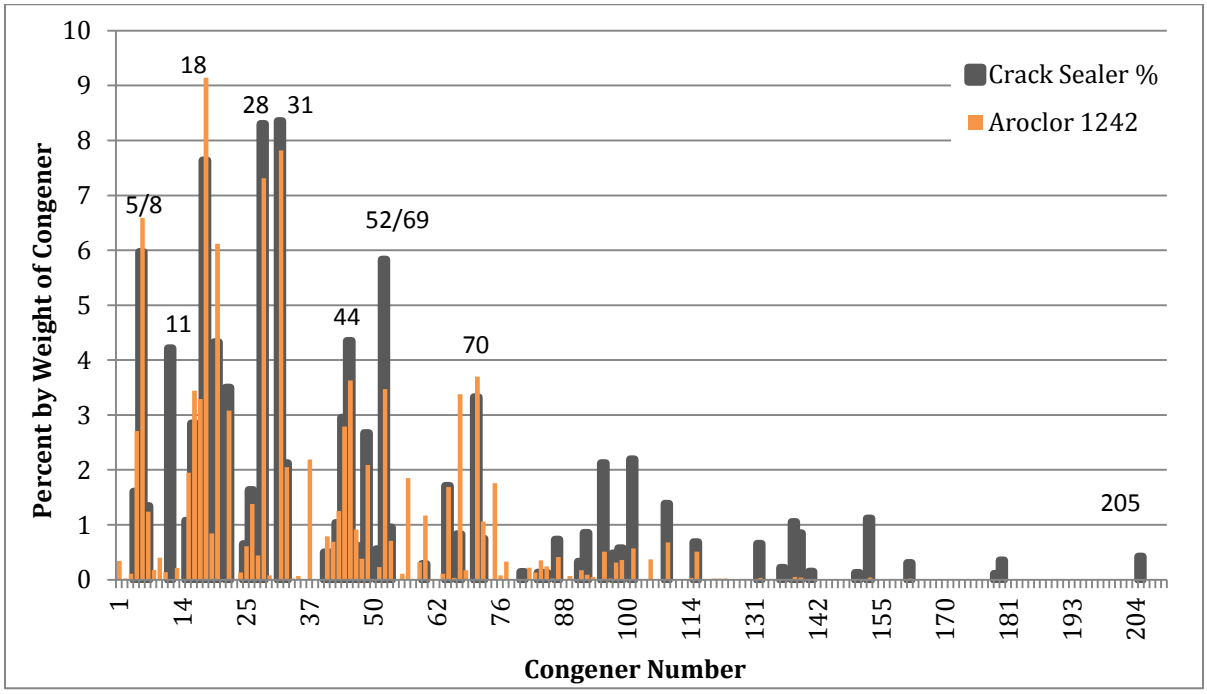


Figure 20. Crack Sealer and Aroclor 1242 Congener Distributions

Hydroseed

A hydroseed mix was sampled due to the prevalent use of hydroseed in roadside projects and its typical green coloring. The sample was collected from a new 50 pound bag of Nature's Own Hydromulch, which was not yet mixed with seed, fertilizer, or other additive. The Nature's Own Hydromulch MSDS indicates that it is composed of primarily wood fiber material with green liquid and a surfactant. The sample contained shredded colored newspaper cellulose. Total PCBs detected in the sample was **2,509 ug/kg**. The following figures show the congeners detected and homologue patterns for the sample.

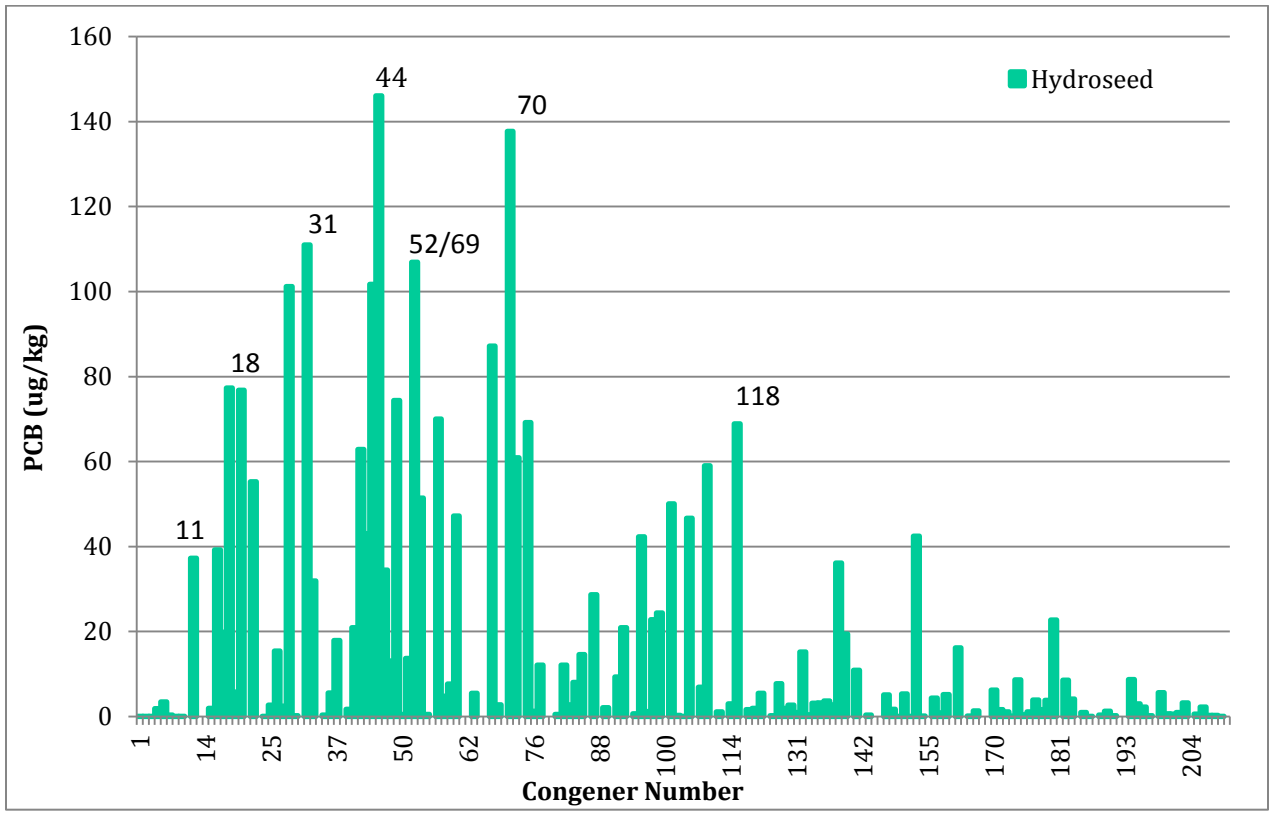


Figure 21. Hydroseed Congeners

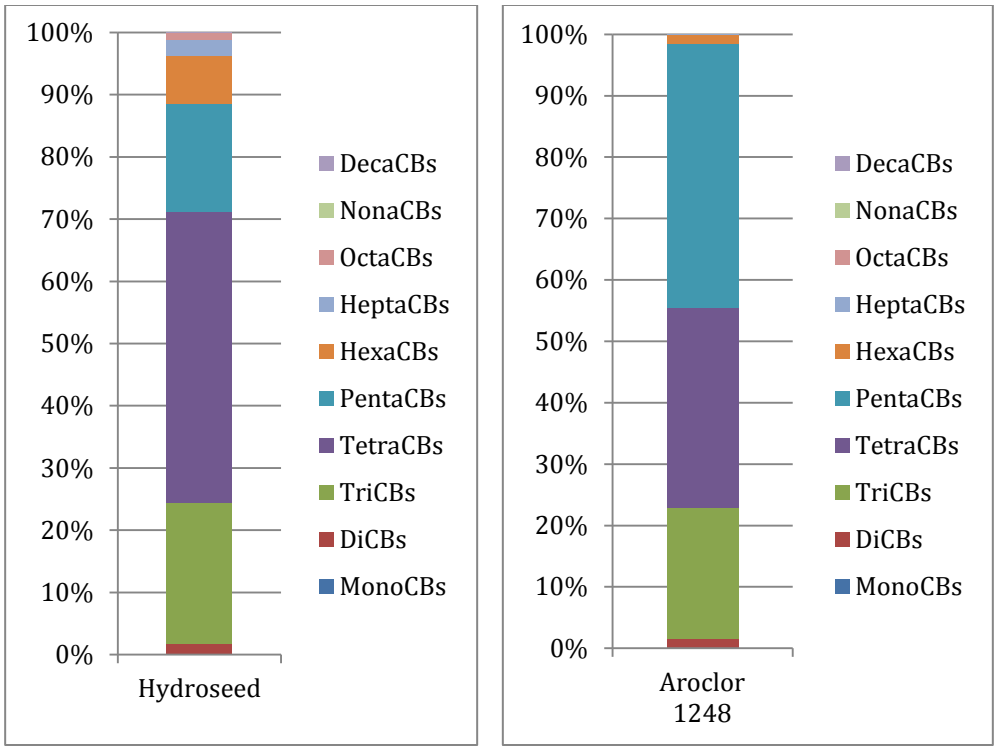


Figure 22. Hydroseed and Aroclor 1248 Homologue Patterns

In an unrelated incident, a landscape contractor received a penalty from the State of Iowa for illegally discharging a hydroseed mixture on the bank of a creek (Scriven-Young, 2010). The hydroseed contained 320 parts per billion of Aroclor 1248 as well as the pesticides DDT and DDE. Interestingly, the sample collected by the City of Spokane has a homologue pattern very similar to that of Aroclor 1248.

The hydroseed congeners from the City's sample were converted to percent of total PCB by weight and are plotted against Aroclor 1248 in the same units in Figure 23 below. The two congener patterns are quite similar. Note that PCB-11 is present in the hydroseed, but not the Aroclor. This indicates a secondary source of PCBs from pigment that is relatively minor compared to the Aroclor.

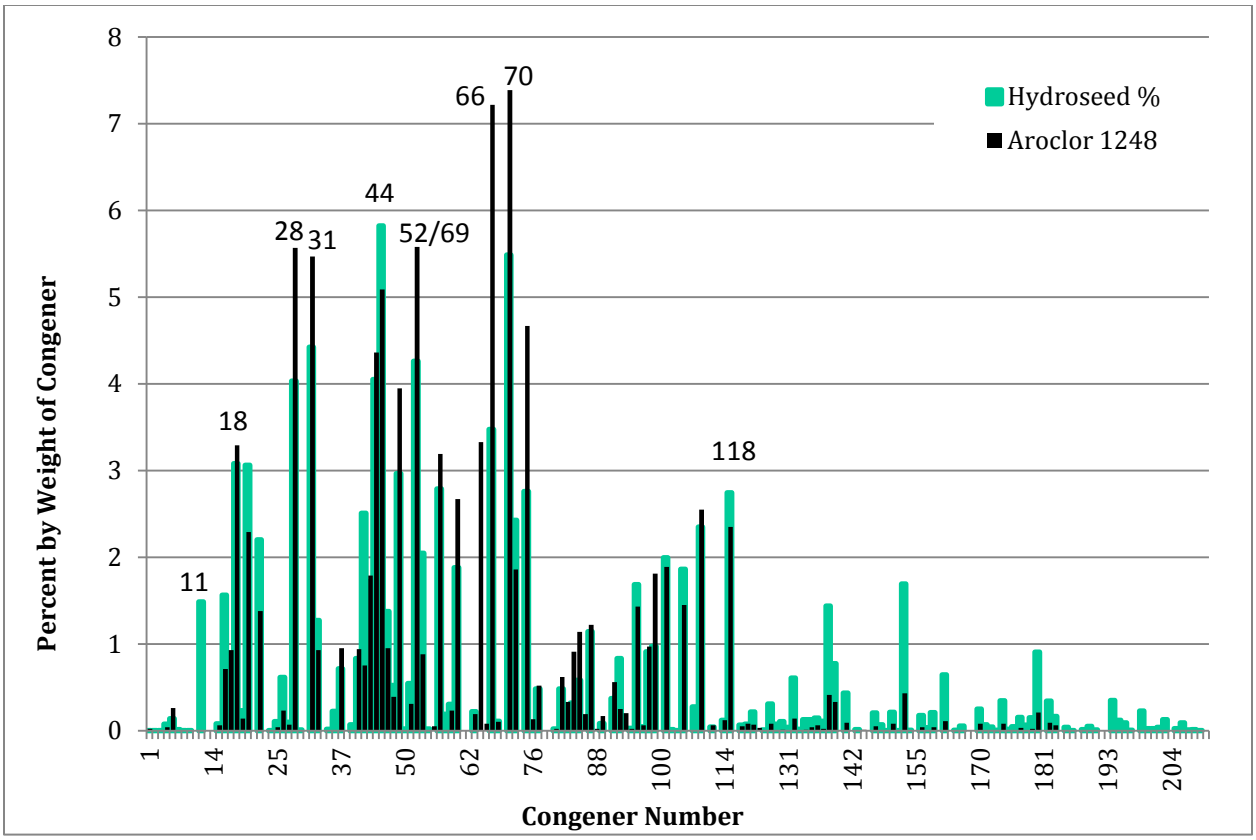


Figure 23. Hydroseed and Aroclor 1248 Congener Distributions

Pipe Material

There are hundreds of miles of PVC pipe used in the City's sanitary and storm sewer systems. Dischargers in the Spokane region have been collecting sanitary and stormwater samples for ultra low-detection PCB analysis, and many of these samples have traveled through miles of PVC pipe prior to collection. In an effort to screen the potential for PCB contribution from pipe material, PVC pipe, cast in place pipe (CIPP) liner and shortliner pipe repair materials were sampled.

The type of PVC sampled was ASTM 3034 collected from a new, unused eight-inch diameter pipe. CIPP is constructed from a felt tube saturated with resin and coated with polyurethane, and is cured inside an existing pipe. The section of CIPP liner sent in for analysis was originally collected from a construction project in northeast Spokane in April, 2013. It was kept in an office environment and not exposed to the elements after that time. Shortliner pipe repair is constructed in the same way, and made of a polyester-fiberglass liner impregnated with thermosetting epoxy resin. A test section of shortliner was cured in a new pipe on the ground surface at the City's Sewer Maintenance Department in October, 2014 for use in this sampling study.

Pieces of pipe were sent to the laboratory for analysis to help determine the PCB content in the material itself. The potential for PCBs to leach from the pipe material to stormwater and sanitary

sewage is outside the scope of this project, but future analysis is warranted based on the results shown in Table 9.

Table 9. Pipe and Pipe Repair Material Total PCBs

Material	Total PCB (ug/kg)
PVC (ASTM 3034) Pipe	1.999
CIPP Liner	1.110
Shortliner	17.780

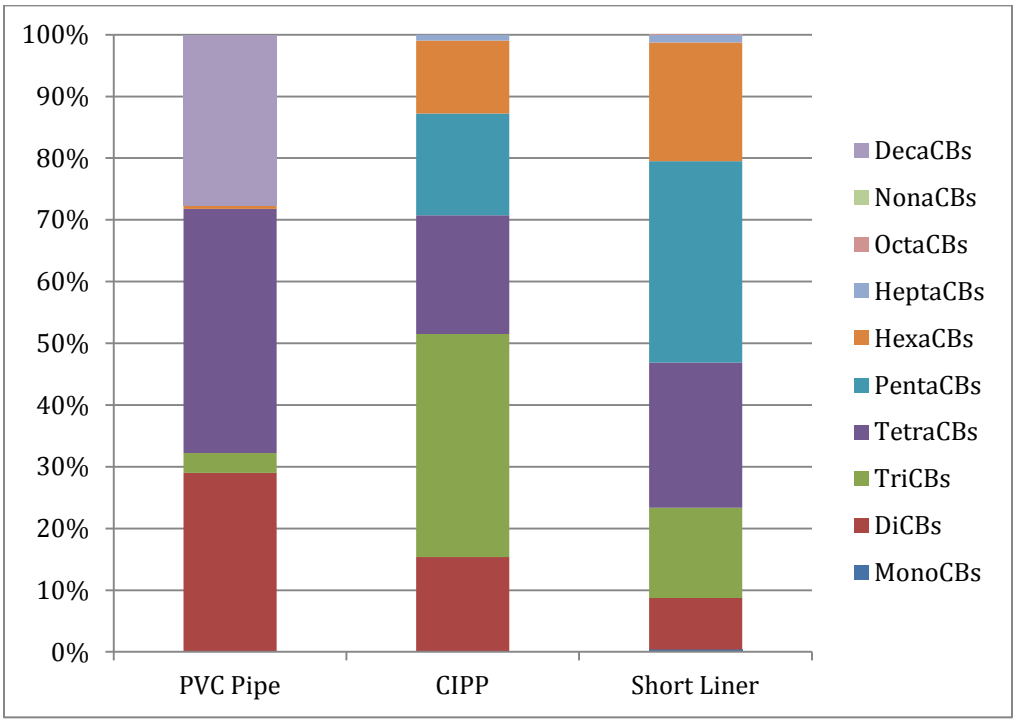


Figure 24. Pipe Material Homologue Patterns

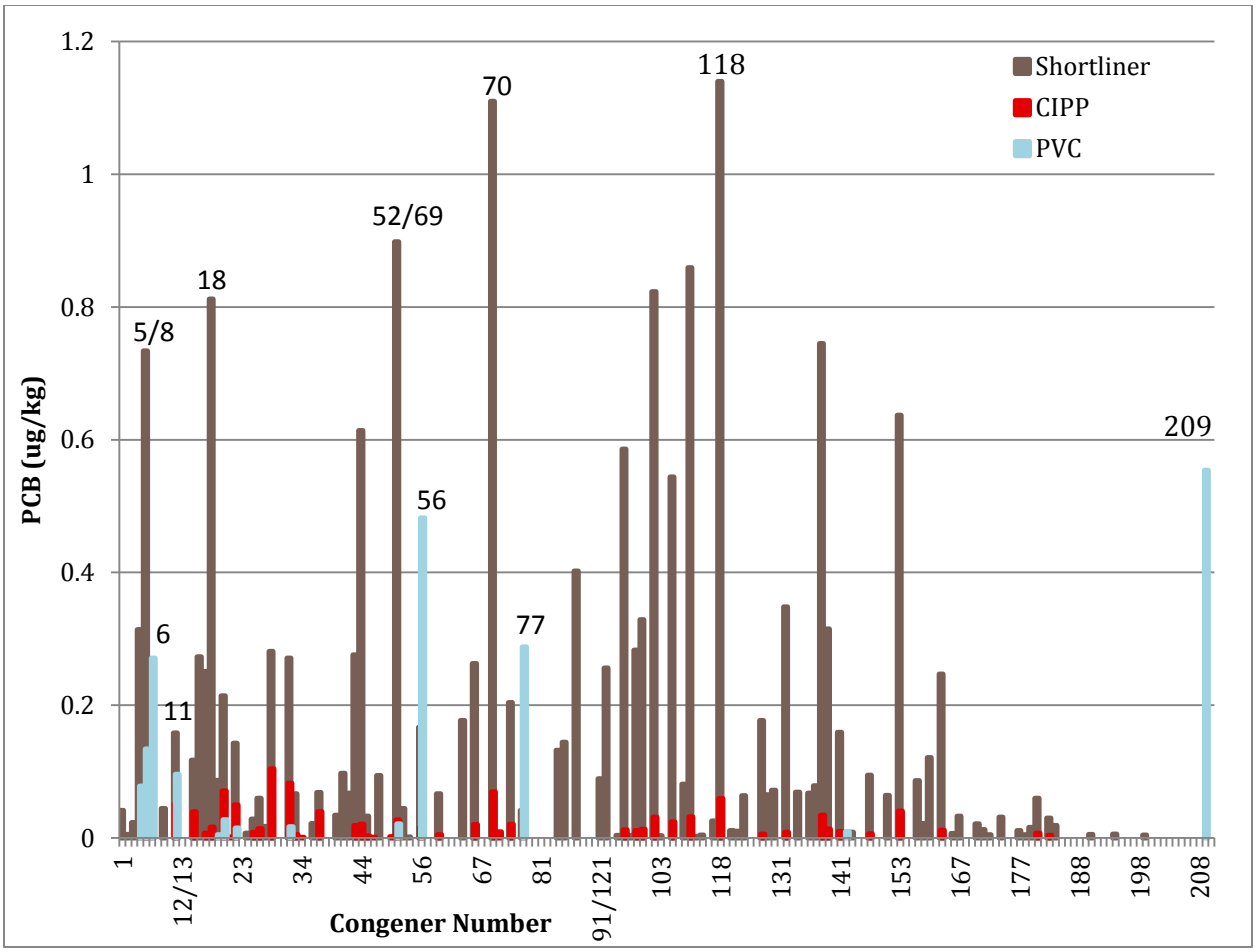


Figure 25. Pipe Material PCB Congeners

Figure 25 shows congener patterns for the sampled pipe materials. Congener distributions (percent of total PCB) for the pipe materials were then compared to congener patterns for Aroclors. The PVC and CIPP samples did not appear to correlate with Aroclor patterns. The Shortliner sample appears to correlate somewhat with a combination of two or more Aroclors. Specifically, a combination of both Aroclors 1242 and 1248 matches the shortliner sample the most closely (Figure 26).

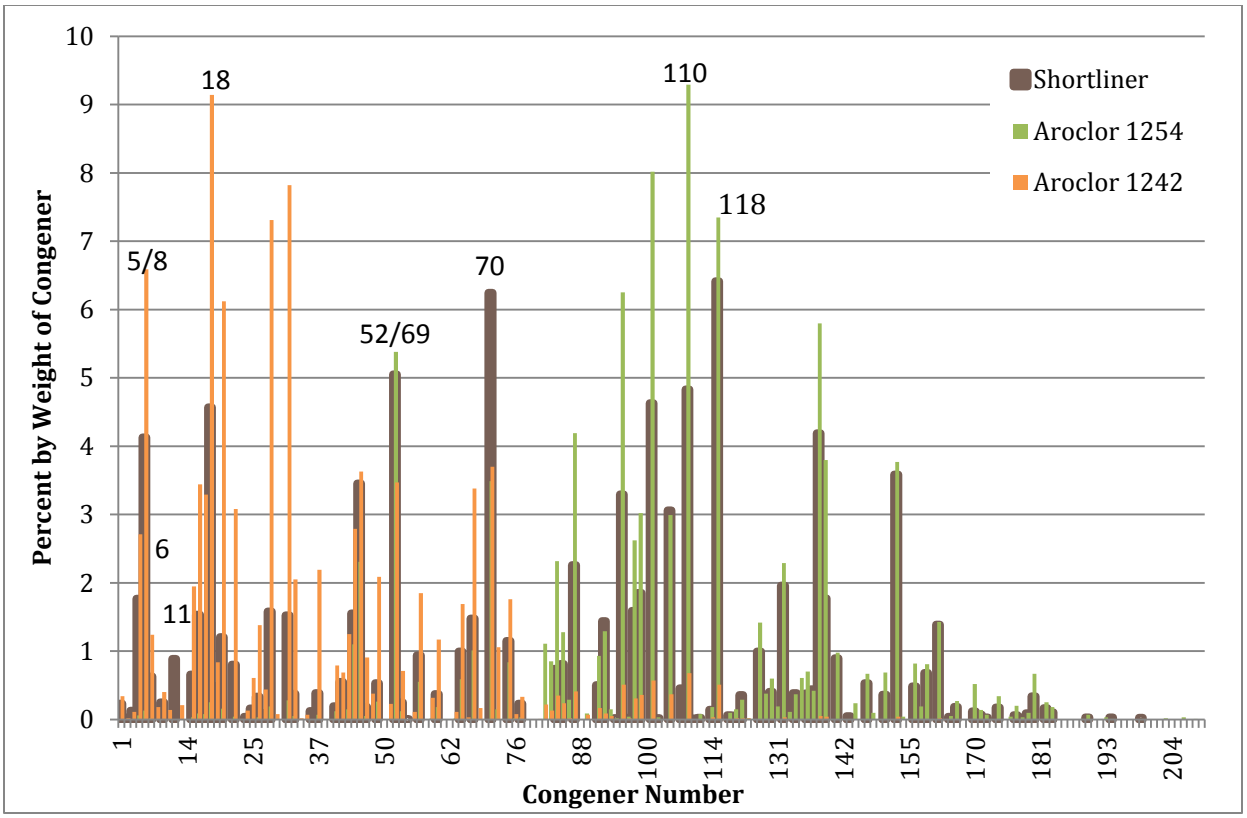


Figure 26. Shortliner Congener Distribution Compared to Aroclors 1242 and 1254

Firefighting Foam

Discharges from emergency firefighting activities are an exempt activity under the Phase II Eastern Washington Municipal Stormwater Permit. However, these discharges can easily enter a storm sewer system without proper containment and contribute contaminants to the environment. Alcoseal 3-3 Class B firefighting foam was sampled. Ingredients listed on the MSDS sheet include hydrolyzed protein, fluorosurfactants, 1,2 benzoisothiazelin, and hexylene glycol. The total PCB concentration was **0.029 ug/kg**. The associated congener and homologue patterns are shown in Figure 27.

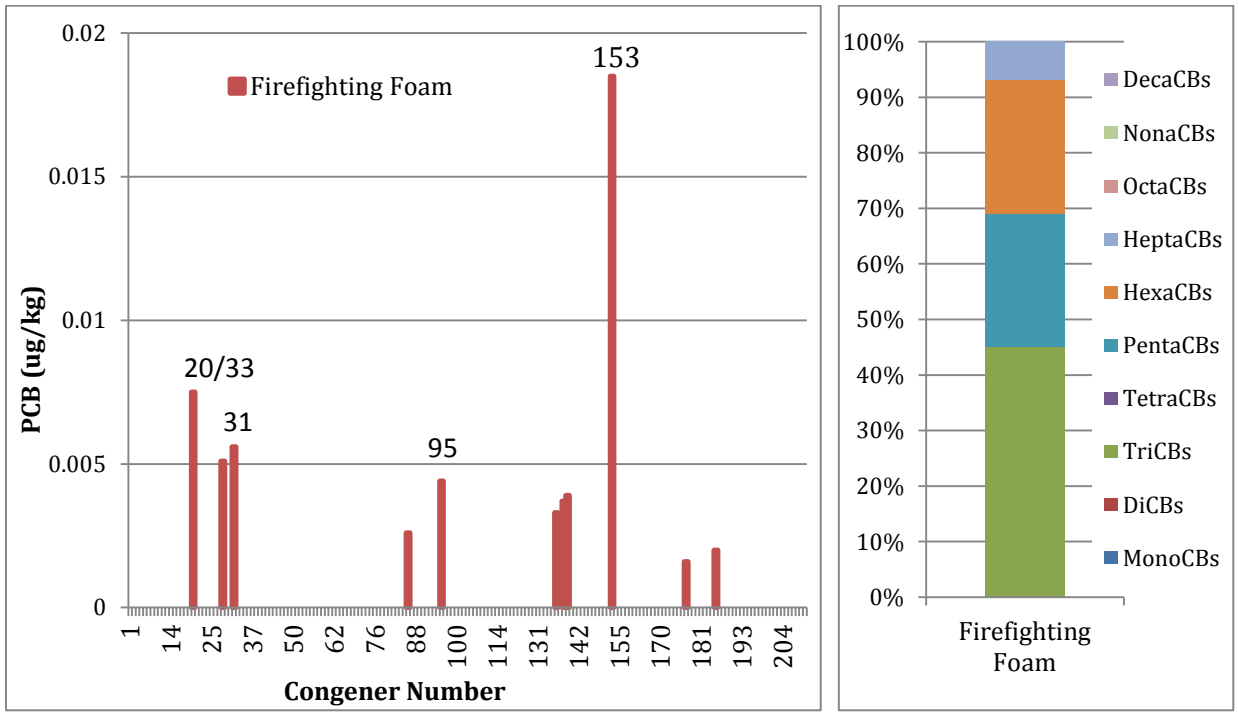


Figure 27. Firefighting Foam PCB Congeners and Homologue Pattern

Cleaners and Degreasers

Inadvertent PCB generation is possible with the manufacture of soaps, detergents, surfactants, and degreasers (Munoz, 2007). A detergent made by Hotsy was sampled as well as Simple Green degreaser.

The Hotsy Super XL detergent contained **0.003 ug/kg** total PCBs. A laboratory duplicate was analyzed, containing 0.068 ug/kg total PCBs. This product contains trisodium phosphates, alkaline builders, and surfactants. Congener distributions from the primary sample are shown in the figure below, containing only PCB-36.

The Simple Green degreaser contained **0.068 ug/kg** total PCBs, with nearly half of this total from PCB-11. The ingredients consist of primarily water with 2-butoxyethanol, ethoxylated alcohol,

tetrapotassium pyrophosphate, sodium citrate, and a proprietary mix of fragrance and polymeric colorant.

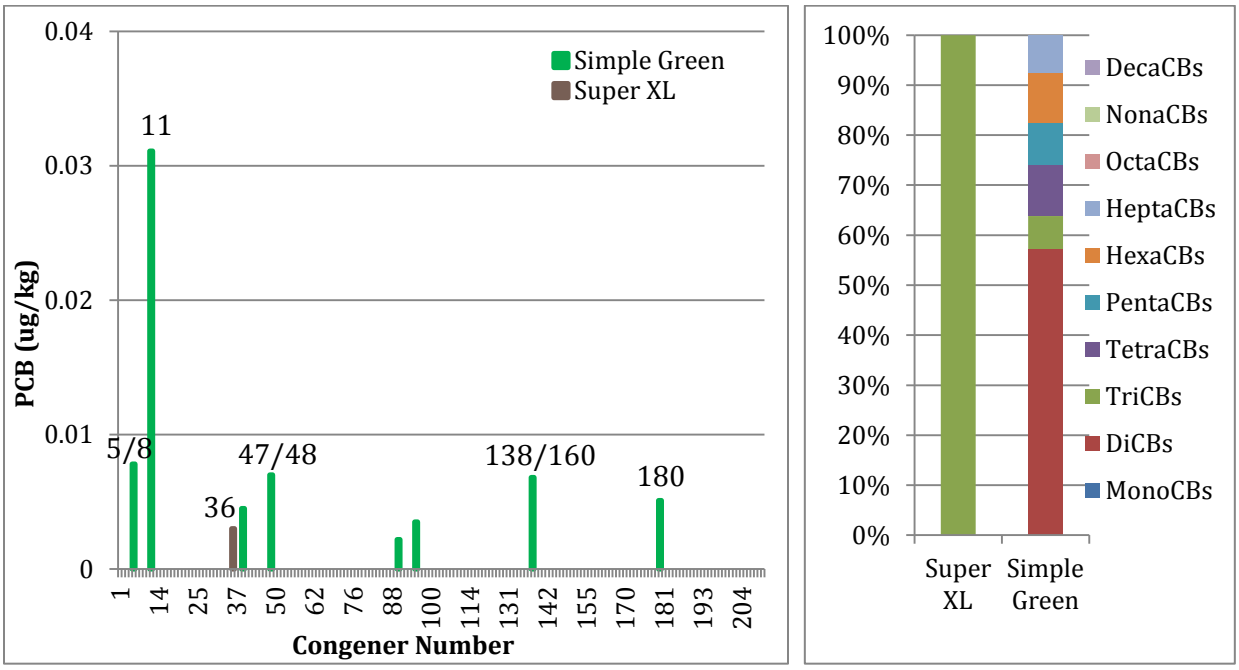


Figure 28. Simple Green and Super XL PCB Congeners and Homologue Pattern

Personal Care Products

Sampling in the storm and sanitary sewer systems over the past several years has indicated that total PCB concentrations in the sanitary sewer collection system are slightly greater than average concentrations in stormwater. So, in addition to products that can contribute PCBs to stormwater, five personal care products that may contribute PCBs to the sanitary sewer collection system were sampled. The products sampled were liquid and contained pigments. Table 10 shows the product brands sampled, total PCBs, pigments listed in the ingredients, and the so-noted 'ingredients of interest.' Many of these products have a long list of ingredients. Those ingredients that are chlorinated, contain benzene rings, or are suspected to be associated with inadvertent PCB production based on the literature search are included in Table 10 as ingredients of interest.

Table 10. Personal Care Products

Brand	Total PCB (ug/kg)	Ingredients of Interest	Pigments
Dial Antibacterial hand soap (pomegranate and tangerine)	0.037	Triclosan, tetrasodium EDTA, sodium chloride, polyquaternium-7	Yellow 6, Red 33, Red 40

Brand	Total PCB (ug/kg)	Ingredients of Interest	Pigments
Tide Original laundry detergent	0.174	Ethanolamine, Benzene sulfonic acid (sodium salt and monoethanolamine salt), disodium diaminostilbene disulfonate, dimethicone (type of silicone)	Liquitint® Blue HP (Polymeric colorant)
Dawn Ultra antibacterial dish soap	0.083	Chloroxylenol, sodium chloride	Yellow 5, Blue 1
Suave Naturals shampoo	0.058	Tetrasodium EDTA, ammonium chloride, methylchloroisothiazolinone	Blue 1, Red 33
Aquafresh Extreme Clean Whitening toothpaste	0.032	Glycerin, titanium dioxide, sodium saccharin	Red 30

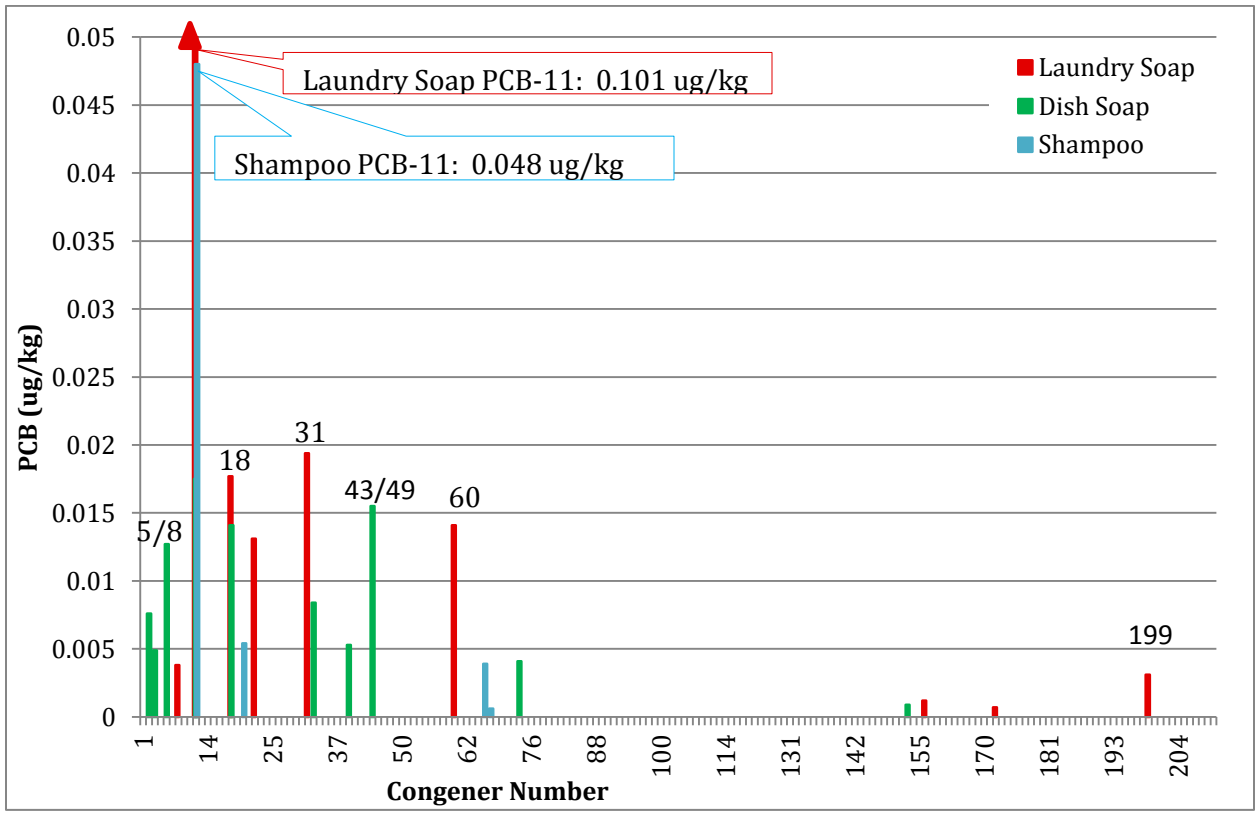


Figure 29. Laundry Soap, Dish Soap, and Shampoo Congeners

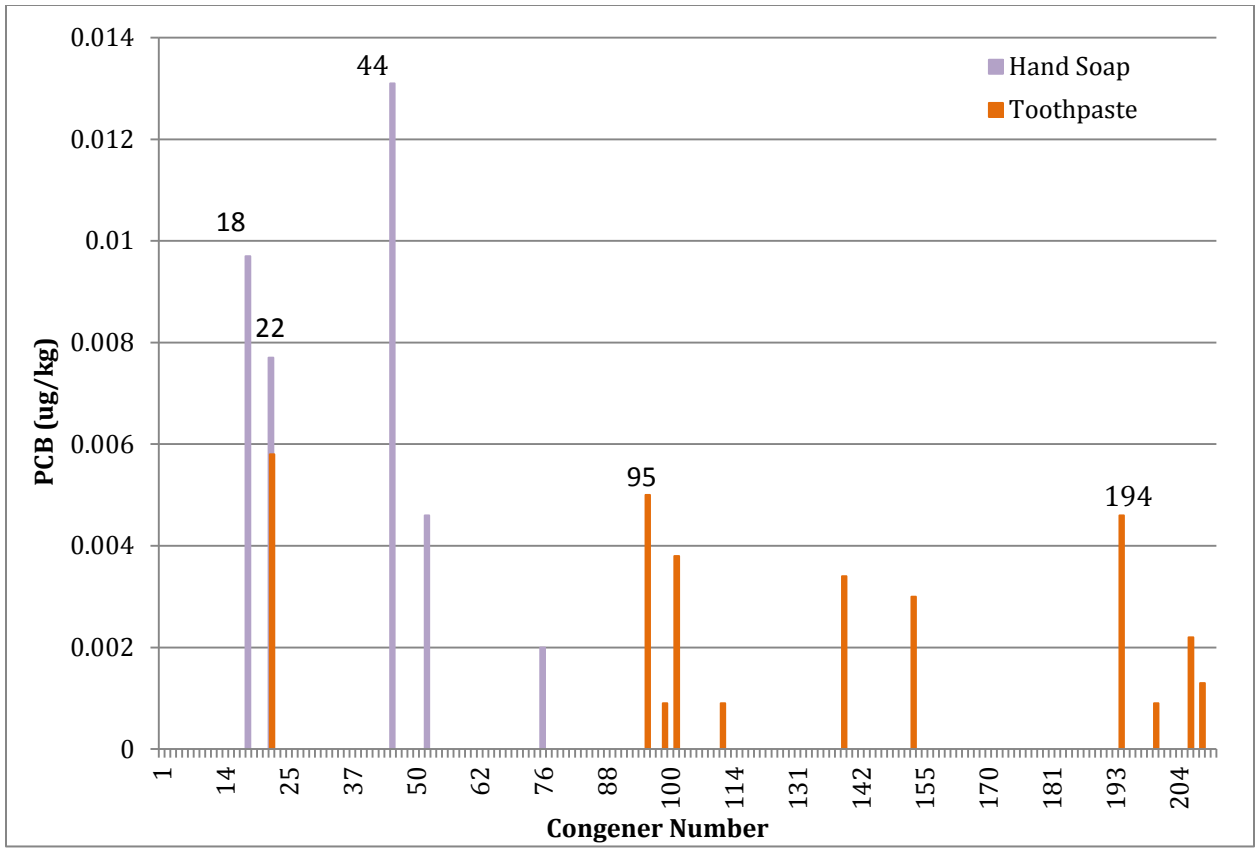


Figure 30. Hand Soap and Toothpaste Congeners

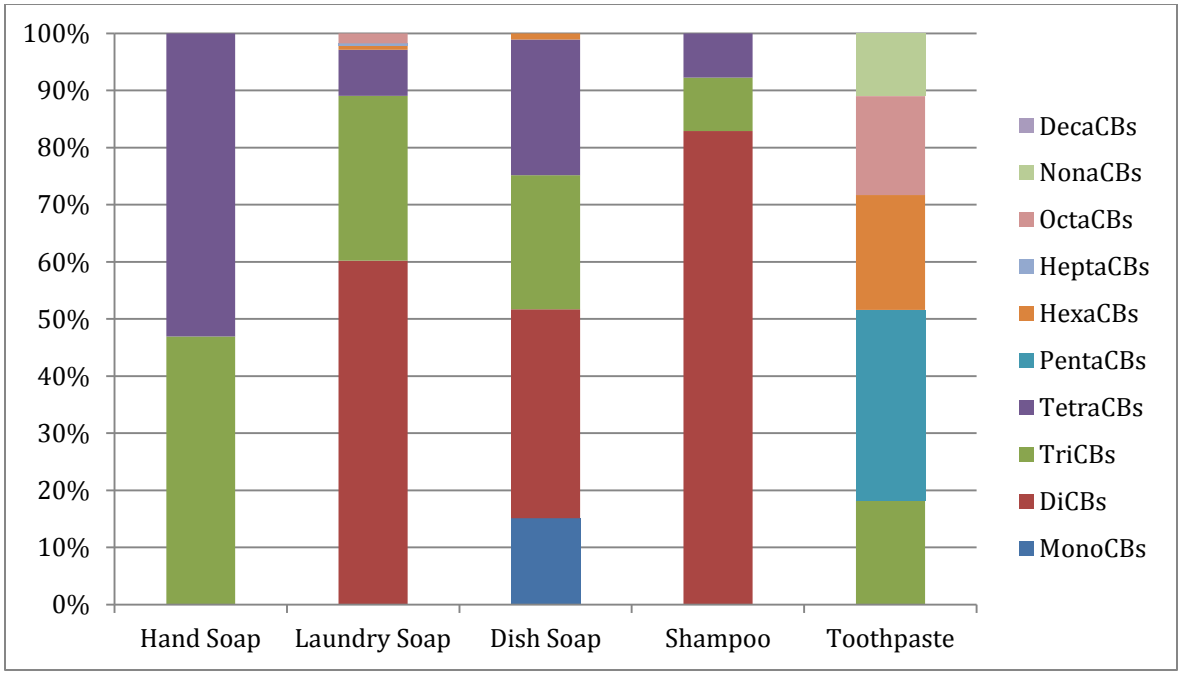


Figure 31. Personal Care Product Homologue Patterns

CONCLUSIONS

PCBs were detected in 39 of the 41 product samples, with a wide range of congener patterns. Figure 32 shows the frequency of detection of each congener in this study. The congeners most frequently detected are the coeluting congeners PCB-52/69 (detected in 30 of the samples) followed by PCB-11 and PCB-28 (detected in 25 of the samples). PCB-52 is one of the most abundant congeners found in the environment, and is found in Aroclor mixtures from 0.1% to 5.6% of the mixture by weight (Frame et. al, 1996). PCB-28 is also commonly found in Aroclor mixtures at up to 8.5% of the total mixture by weight (Frame et. al, 1996). Because PCB-11 was one of the most frequently detected congeners, and it is generally not found in Aroclor mixes, pigments are likely a common source of inadvertently produced PCBs in the products sampled.

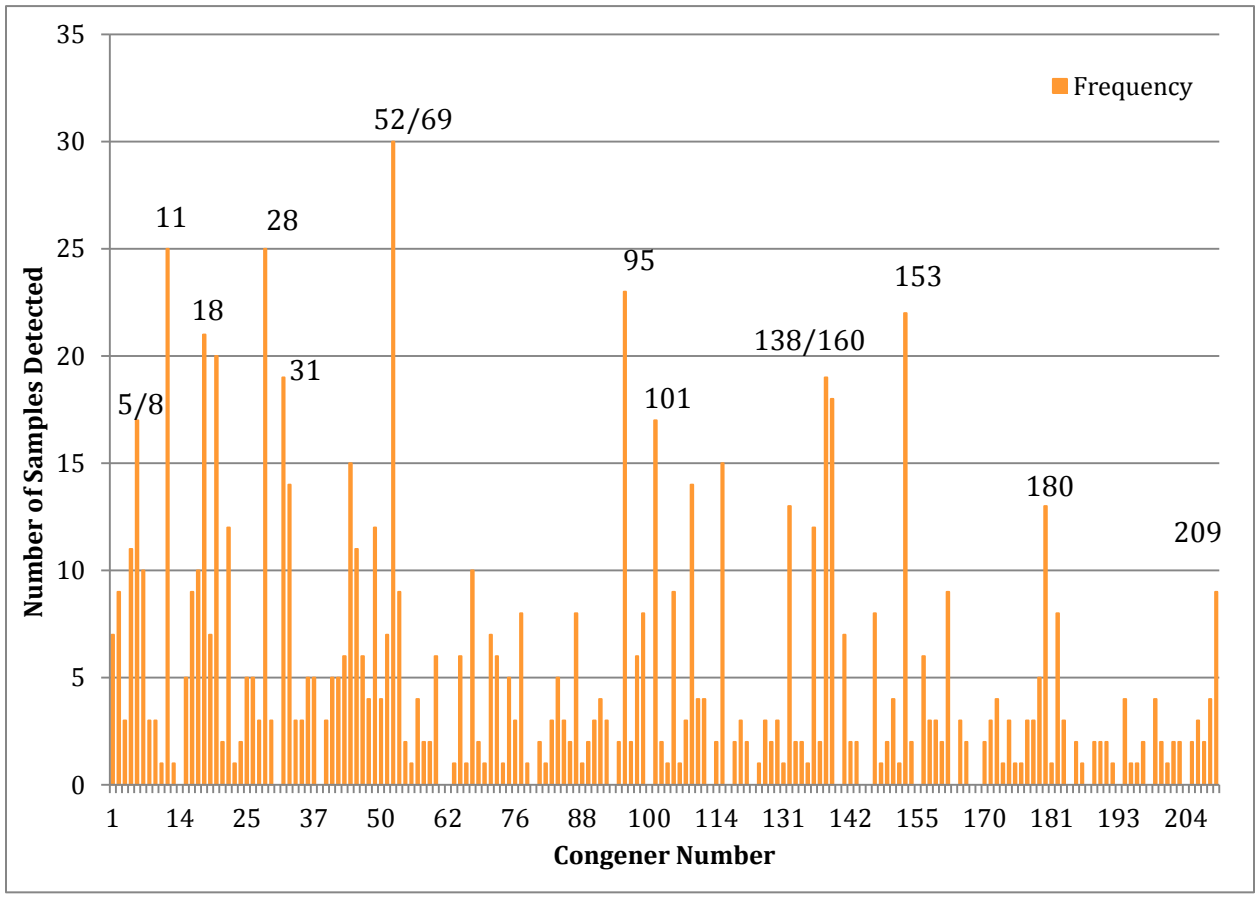


Figure 32. Frequency of Detections per Congener

The results from this report may be used for a number of PCB tracking and reduction activities. Additional research may be needed to determine potential pathways between some of the sampled products and stormwater. For PCB reduction activities, total PCB loading (volume of product used) should be assessed to aid in prioritization. Manufacturers may also be interested in exploring PCB-free alternatives where feasible.

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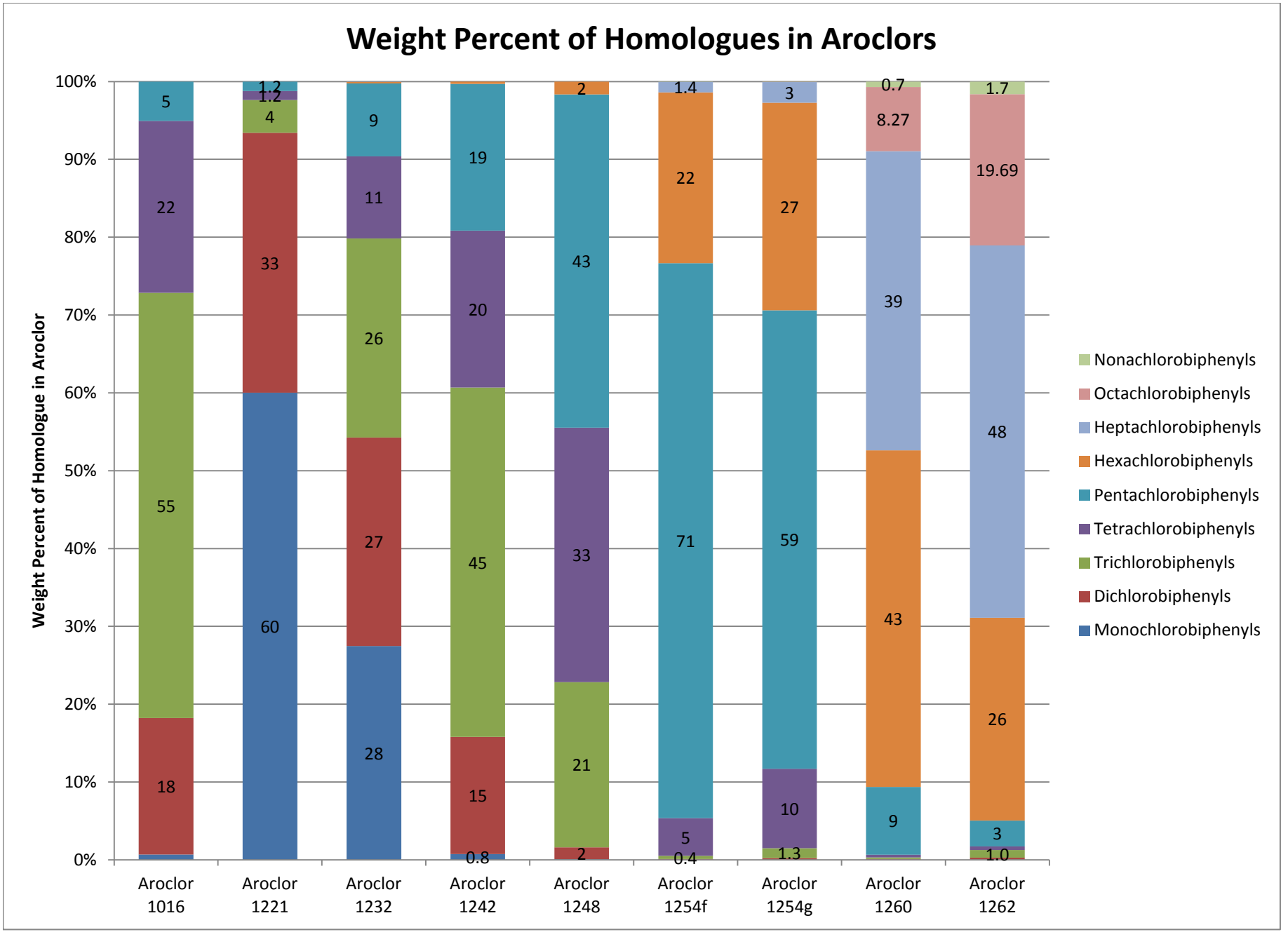
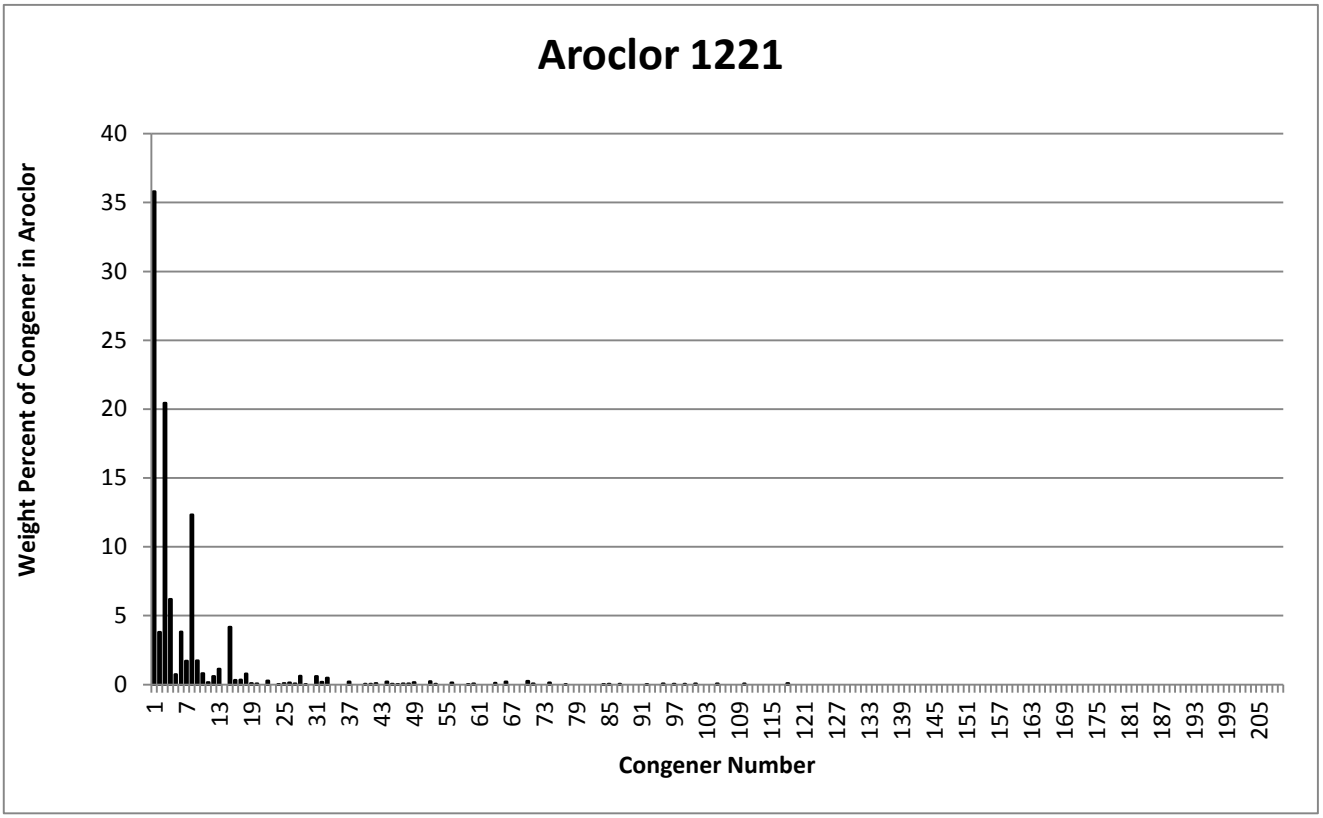
Appendix A

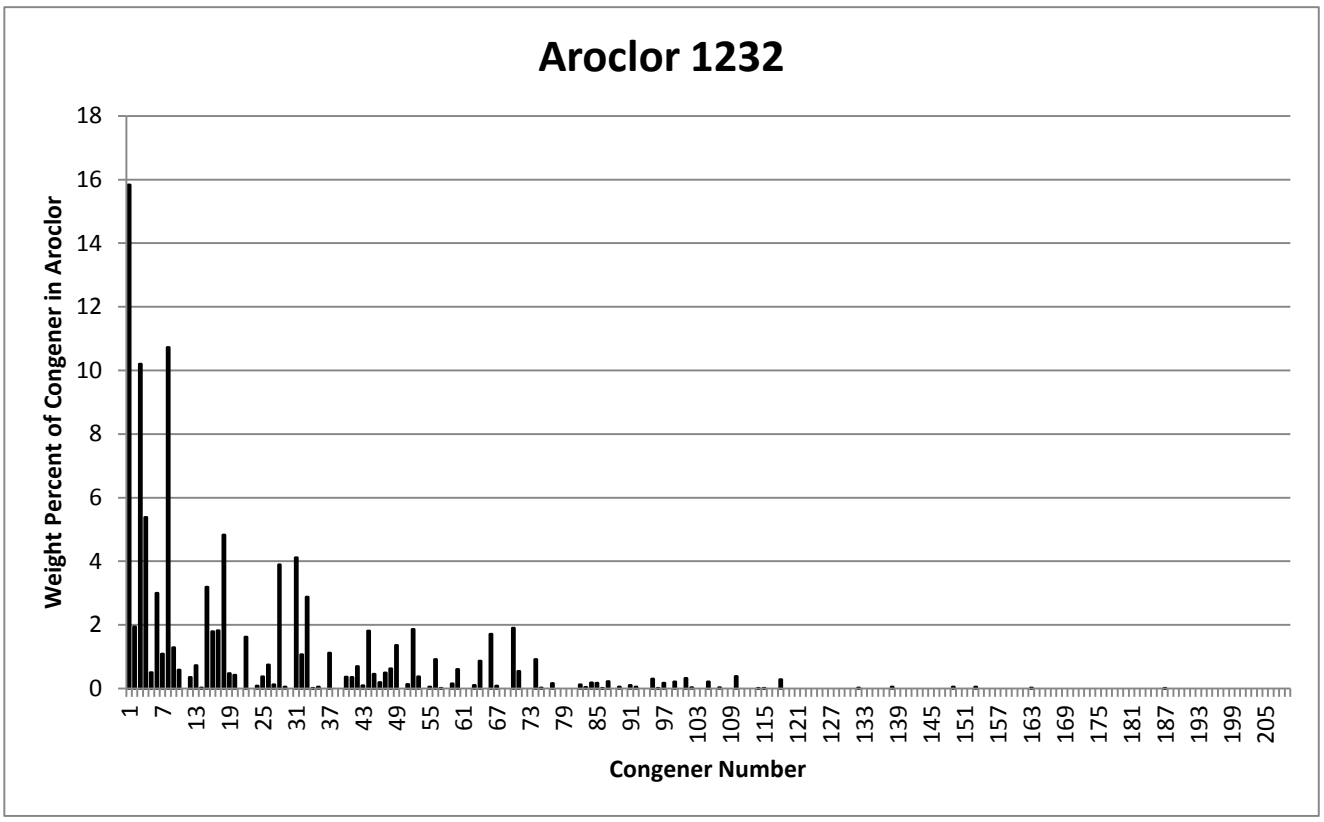
AROCLOR HOMOLOGUES AND CONGENERS



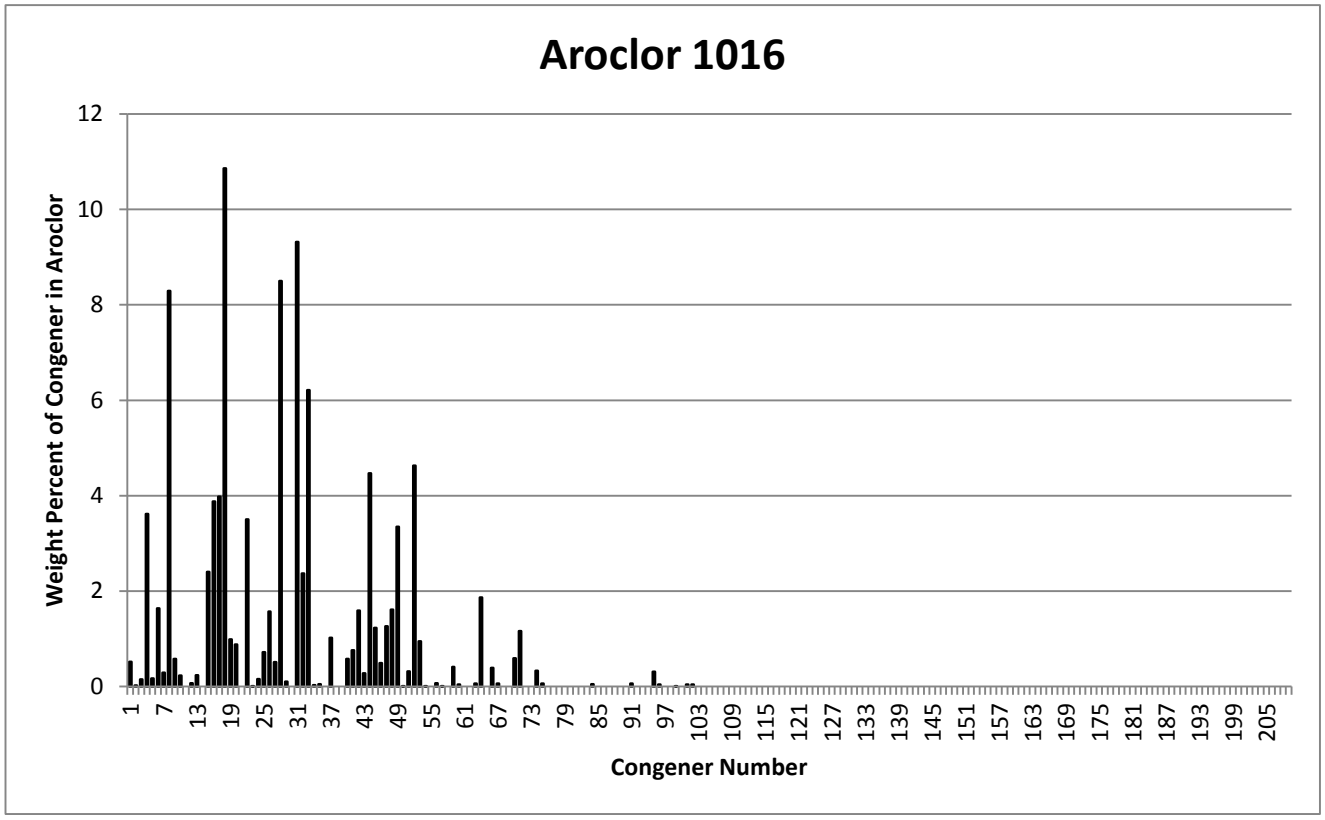
Adapted from ASTDR, 2000.

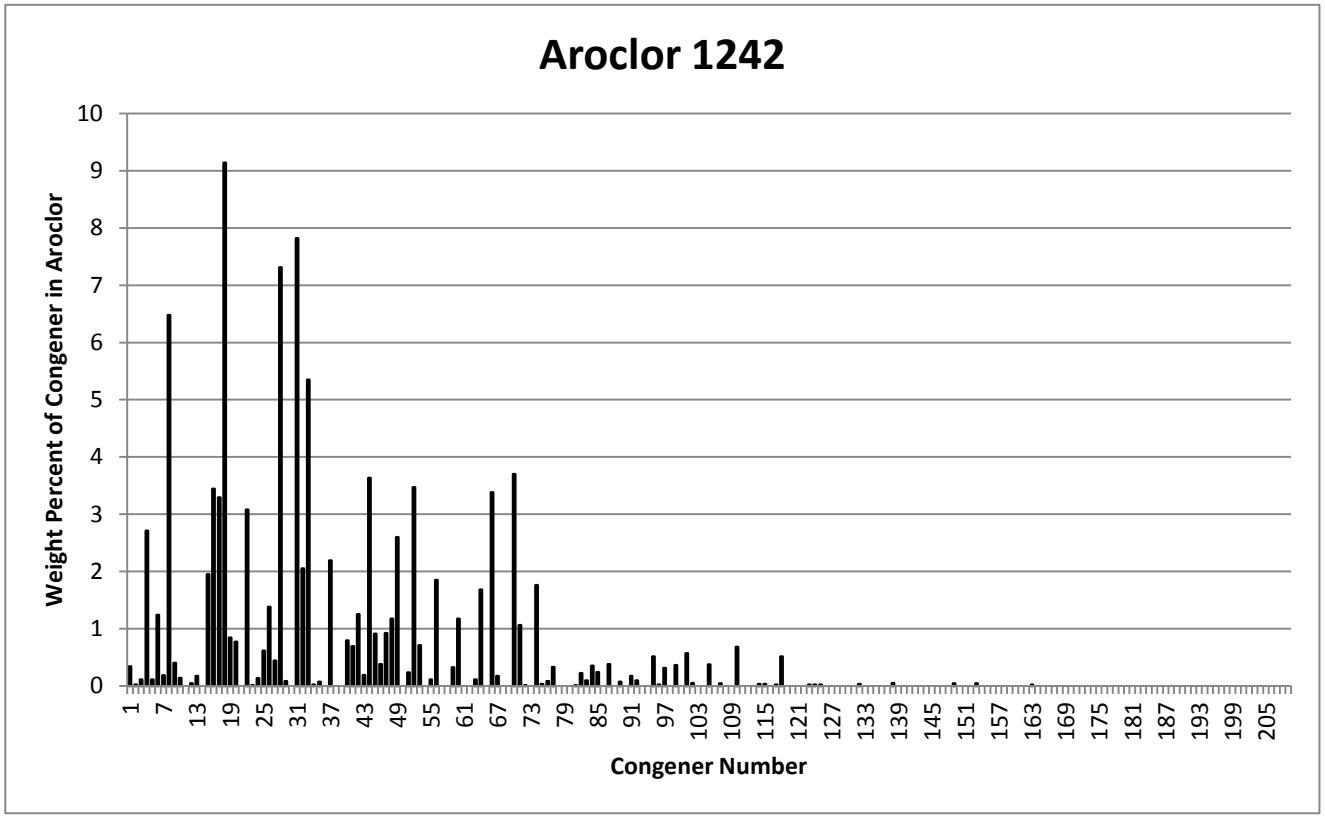
Weight Percent of Congeners in Aroclors





(Adapted from Frame et. al, 1996)





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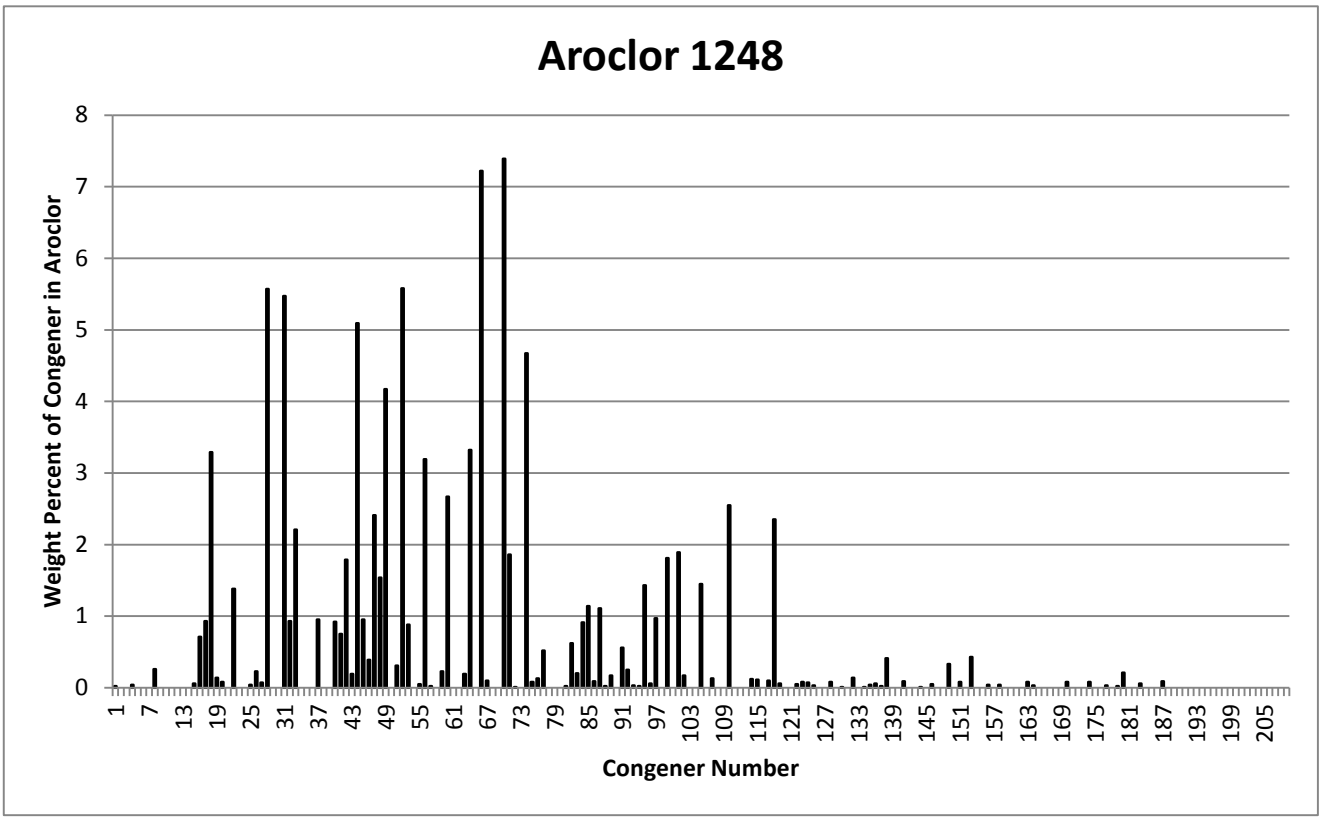

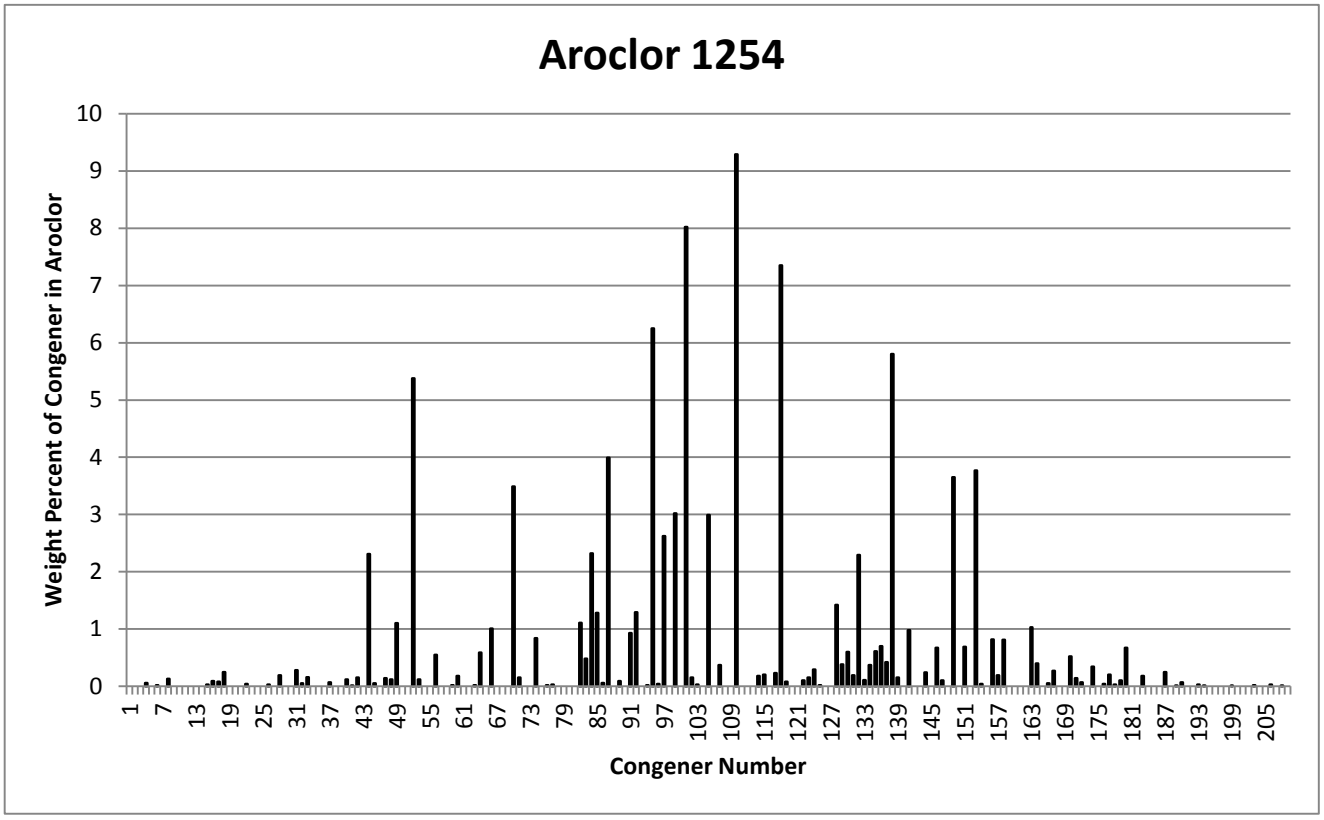

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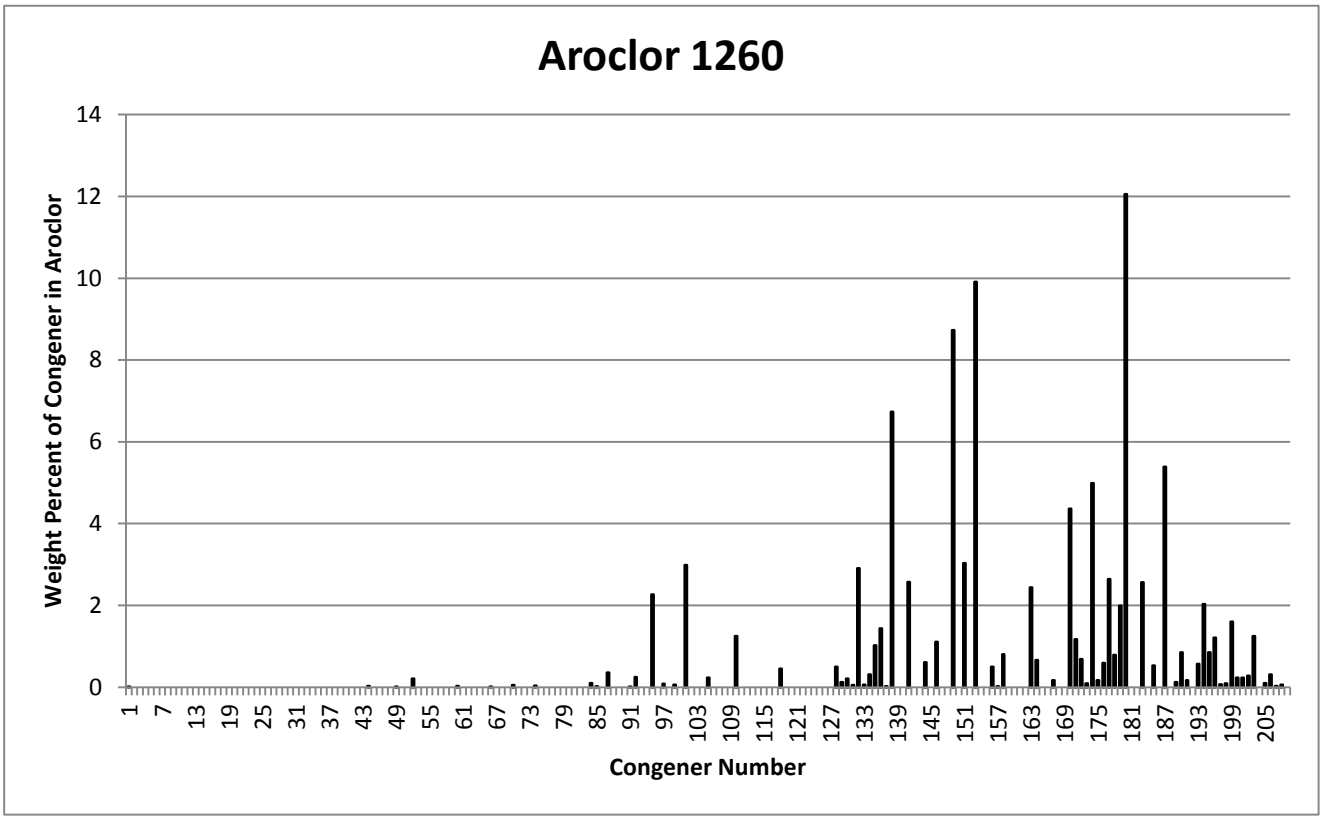

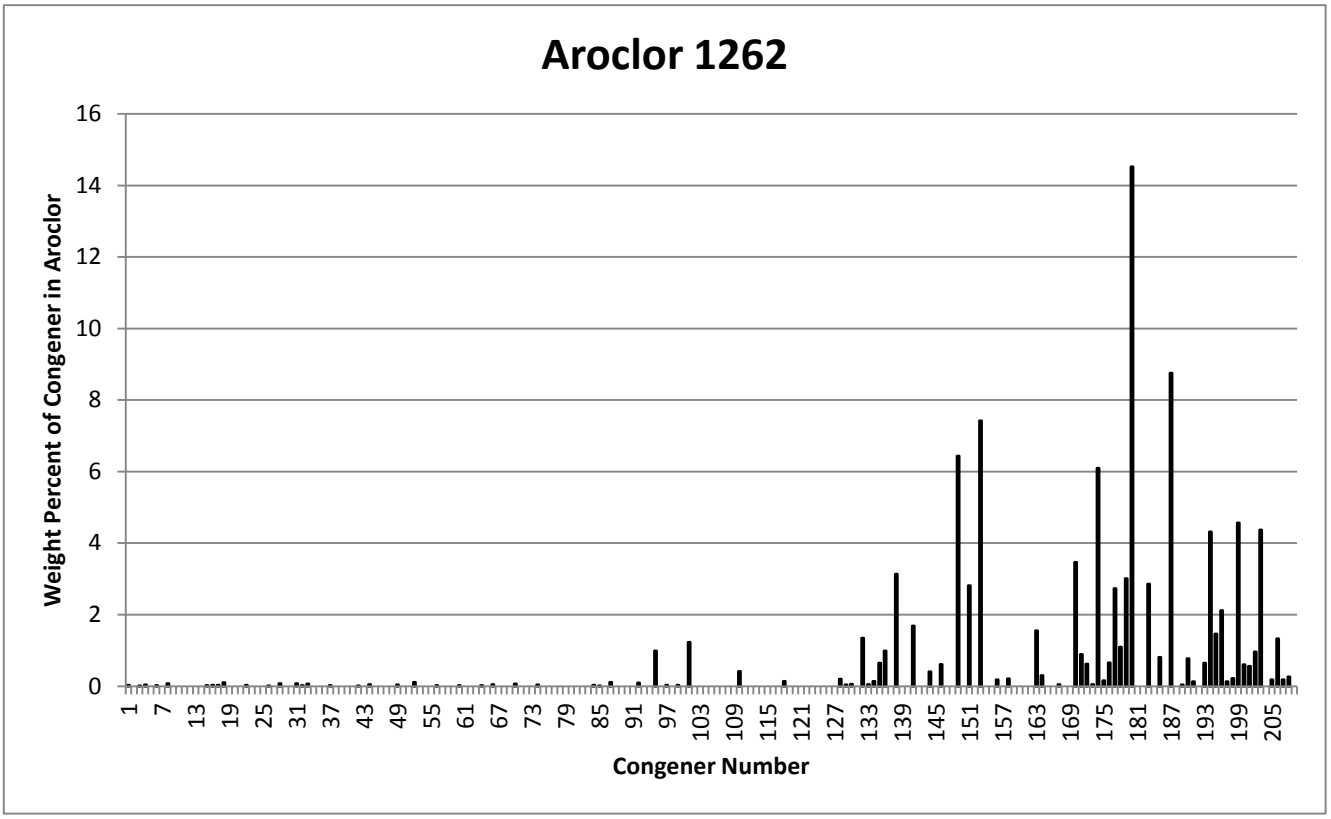

(Adapted from Frame et. al, 1996)

Appendix B

SUMMARY OF RESULTS

Table B-1

Summary of PCB Product Sampling Results

Product Type	Media	Product ID	Total PCB (ug/kg or ppb)	Field Replicate (ppb)	Lab Duplicate (ppb)	Brand
Yellow road paint	Liquid	001	0.732	2.686		Ennis standard #2 - Product # 983712
Yellow road paint	Liquid	002	64.880			Sherwin Williams Promar TM 5713
White road paint	Liquid	003	0.414	0.396		Ennis standard #2 - Product # 983711
White road paint	Liquid	004	0.281		0.220	Sherwin Williams Promar TM 5712
Hydrant Paint	Liquid/Spray	005	0.003		0.010	Rustoleum Pro HP Enamel - Aluminum
Utility Locate Paint	Liquid/Spray	006	21.527			Rustoleum Industrial Choice, Solvent-based - green
Class B Firefighting Foam	Liquid	007	0.029			Alcoseal 3-3 (AR-FFFP)
Deicer	Liquid	008	1.332	1.952		MgCl Freezegard
Deicer	Liquid	009	0.038			Enhanced salt brine with SB Boost
Vehicle wash soap	Liquid	010	0.003		0.068	SuperXL, Hotsy
Vehicle wash soap	Liquid	011	0.068			Simple Green
Pesticide/Herbicide	Liquid	012	<0.0001		<0.0001	2-4D: Nufarm Weedar 64
Pesticide/Herbicide	Liquid	013	6.890			Portfolio 4F, Wilbur-Ellis
Pesticide/Herbicide	Liquid	014	0.012			Roundup Pro Max, Monsanto
Pesticide/Herbicide	Liquid	015	0.316			Crosshair, Wilbur-Ellis
Motor oil	Liquid	016	0.856		0.826	SAE 15W-40 Firebird Heavy Duty EC (bulk), Connell Oil
Motor oil	Liquid	017	0.969			Valvoline Full Synthetic 5W-30
Used motor oil	Liquid	018	0.502	2.375		SAE 15W-40 Firebird Heavy Duty EC, Connell Oil
Diesel	Liquid	019	<0.019			#2 Diesel, dyed
Gasoline	Liquid	020	0.935		0.811	Regular unleaded
Dirt road dust suppressant	Liquid	021	0.091			Asphalt emulsions- EADA
Dirt road dust suppressant	Liquid	022	0.086			Lignosulfonate- Ligno Road Binder (natural polymer in wood)
Dirt road dust suppressant	Liquid	023	3.574			Dustguard Liquid MgCl (different concentration than deicer)
Lubricant	Liquid	024	0.623			MP Gear Lube SAE 85W-140, Phillips 66 Company
Asphalt tack	Liquid	025	0.085			SSR1 asphalt tack
Crack sealer	Solid	026	7.975			Special Asphalt SA Premier (3405- midrange crack sealer)
Asphalt release agent	Liquid	027	0.558		0.443	Soy What, TechniChem Corp.
Hydroseed	Solid	028	2,509.088			Natures Own Hydroseeding Mulch, Hamilton Mfg Inc
PVC pipe	Solid	029	1.999			ASTM 3034 8", Diamond PVC
CIPP liner	Solid	030	1.110			Cast in place pipe liner, installed by SAK
Shortliner	Solid	031	17.780			Infrastructure Repair Systems Inc
Yellow road paint, dried	Solid	032	0.565			Ennis standard #2 - Product # 983712
White road paint, dried	Solid	033	0.379		0.335	Ennis standard #2 - Product # 983711

Product Type	Media	Product ID	Total PCB (ug/kg or ppb)	Field Replicate (ppb)	Lab Duplicate (ppb)	Brand
Thermoplastic tape road striping	Solid	034	10.776			Ennis-Flint Pre-Mark
Antifreeze	Liquid	035	0.018			Kool Green Extended Life (recycled)
Thermoplastic tape road striping	Solid	036	3.325			Ennis-Flint Pre-Mark

Personal Care Products

Product Type	Media	Product ID	Total PCB (ug/kg or ppb)	Field Replicate (ppb)	Lab Duplicate (ppb)	Brand
Hand soap	Liquid	101	0.037			Dial Antibacterial, pomegranate and tangerine
Laundry soap	Liquid	102	0.174			Tide original liquid
Dish soap	Liquid	103	0.083			Dawn Ultra antibacterial
Shampoo	Liquid	104	0.058			Suave naturals
Toothpaste	Liquid	105	0.032			Aquafresh Extreme Clean Whitening

Notes:

Total PCB values have been blank corrected: congeners < 3 times the associated blank value not included in total.

ug/kg = micrograms per kilogram

ppb = parts per billion