Pigments and inadvertent polychlorinated biphenyls (iPCBs): Advancing no and low iPCB pigments for newsprint, and paper and paperboard packaging

Prepared For:
The Spokane River Regional Toxics Task Force

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Northwest Green Chemistry
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Authored by:
Amelia Nestler, Ph.D.
Lauren Heine, Ph.D.
Anna Montgomery, Ed.D.

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Abbreviations

CASRN	Chemical Abstract Service Registry Number
C.I.	Color Index
CMYK	Cyan, Magenta, Yellow, and Key (Black)
CPMA	Color Pigment Manufacturers Association
CWA	Clean Water Act
ETAD	Ecological and Toxicological Association of Dyes and Organic Pigments Manufacturers
FAO	Food and Agriculture Organization of the United Nations
iPCBs	inadvertent PCBs
JECFA	Joint FAO/WHO Expert Committee on Food Additives
m	meter
mg	milligram
NGC	Northwest Green Chemistry
NIOSH	National Institute of Occupational Safety and Health
NPDES	National Pollutant Discharge Elimination System
OSHA	Occupational Safety and Health Administration
PCBs	polychlorinated biphenyls
PELs	Permissible Exposure Limits
ppm	parts per million
ppq	parts per quadrillion (1 ppq = 0.000000001 ppm)
P.B.	Pigment Blue
P.G.	Pigment Green
P.Y.	Pigment Yellow
SRRTTF	Spokane River Regional Toxics Task Force
TSCA	Toxic Substances Control Act
µg	microgram
WHO	World Health Organization

Executive Summary

In an effort to decrease polychlorinated biphenyl (PCB) and other toxic chemical contamination in Washington waters, the Spokane River Regional Toxics Task Force (SRRTTF) is working on multifaceted approaches to reduce loading that include both regulatory and voluntary initiatives. PCBs can be divided into two broad groups based on their origins: legacy and inadvertent. Legacy PCBs were intentionally manufactured for use in products from 1921-1977, and have been banned in the U.S. since 1979 (EPA, 1979). However, they are still found in legacy products such as electrical equipment and old caulking in buildings and may continue to be a source when leaked from contaminated sites (EPA, 2019). Inadvertent PCBs (iPCBs) are currently produced as byproducts from manufacturing other products.

This project addresses inadvertently generated PCBs (iPCBs) that are released into waterways, with a focus on iPCBs from pigments used in newsprint, and in paper and paperboard packaging materials. We address current business and government procurement policies and regulations relevant to iPCBs, and identify potential alternative pigments that are reasonable substitutes for pigments that are high in iPCBs. It builds on prior work prepared by Northwest Green Chemistry for SRRTTF (Heine, 2018). Whether or not iPCBs in pigments used on individual packages and newsprint present a risk to users of those materials is not the focus of this paper. Rather, the issue is that iPCBs in pigments are ubiquitous and provide a steady flow of additional PCBs into products and the environment on a global scale.

Pigments used on paper and packaging materials contaminate recycling streams that hinder both recycling businesses and our collective ability to achieve a safe and healthy 'circular economy'. A circular economy is defined by Geissdoerfer, Savaget, Bocken, and Hultink "as a regenerative system in which resource input and waste, emission, and energy leakage are minimised by slowing, closing, and narrowing material and energy loops. This can be achieved through long-lasting design, maintenance, repair, reuse, remanufacturing, refurbishing, and recycling" (2017, p. 762). Additionally, calls for a circular economy are growing. An economy that 1) eliminates waste and pollution by design, 2) keeps products and materials in use, and 3) regenerates natural systems.

Another consequence of the continued discharge of iPCBs into waterways is that it decreases the effectiveness of expensive, ongoing remediation efforts designed to protect human and environmental health. This is occurring at a time when the government in China, the primary destination for paper and plastic wastes for many years, is no longer accepting these wastes for recycling. There is a growing call to action to address plastic and other wastes that pollute the ocean and other water bodies.

To advance movement toward a circular economy, prevent iPCB exposure to humans and the environment, and ensure recycling infrastructure can support domestic demand, a number of leading companies and local government agencies have created procurement policies or enacted regulation. Procurement and regulation are two potential pathways to increase adoption of alternative pigments and process controls and encourage innovation. This advances the circular economy by decreasing and eventually eliminating contaminants from the circular material stream. In this report, we review current regulations and procurement policies that address iPCBs from pigments and identifying promising practices and innovation opportunities.

We also identify alternatives to pigments known to contain iPCBs after summarizing pigment and iPCB chemistry considerations. Our initial focus is on yellows and blues/greens as they constitute the bulk of iPCB generation from pigments. Future work should include consideration of other pigment colors. We identify opportunities for process controls or synthesis modifications that limit or eliminate iPCB formation, as well as alternative pigments whose syntheses are unlikely to generate iPCBs. It is outside the scope of the project to address the hazards or life cycle impacts of these alternatives. However, this is important alternatives assessment work that is recommended to ensure that the recommended alternatives are not regrettable substitutions.

The purpose of this research and report is to educate SRRTTF members and other interested parties on the chemistry, supply chain considerations, regulations, and business procurement policies related to iPCBs. It is intended to provide actionable intelligence for next steps to reduce iPCBs effluent into the Spokane river. By identifying sources, preliminary alternatives, drivers for change including regulation and voluntary corporate procurement policies, and interested parties SRRTTF can take the next strategic step. A workshop to address gaps in current technology or information, to convene interested parties, and to create, harmonize, adopt, or implement iPCB procurement is recommended.

Using, in part, the information gathered and questions raised in this report, and in line with the goals of the SRRTTF, we recommend pulling together stakeholders from the newsprint and paper and paperboard packaging supply chain, including users, recyclers and other disposers, and impacted communities to develop unified procurement and substitution approaches and to identify the most critical ongoing research needs. The SRRTTF is in initial planning stages for such a workshop, with a focus on discussing solutions and identifying action steps. Our vision includes forming workgroups to advance solutions and take action to reduce and eventually eliminate iPCBs in pigments. Recommendations for potential workgroup topics and suggested participants and expert speakers are included in this report.

Introduction

Polychlorinated biphenyls (PCBs) are a class of man-made organic chemicals consisting only of carbon, hydrogen and chlorine atoms. The number of chlorine atoms and their location in a PCB molecule determine many of its physical and chemical properties. Varying the number and locations of chlorine atoms on the biphenyl backbone results in 209 variations known as PCB congeners. Figure 1 shows a selection of example PCB congeners.

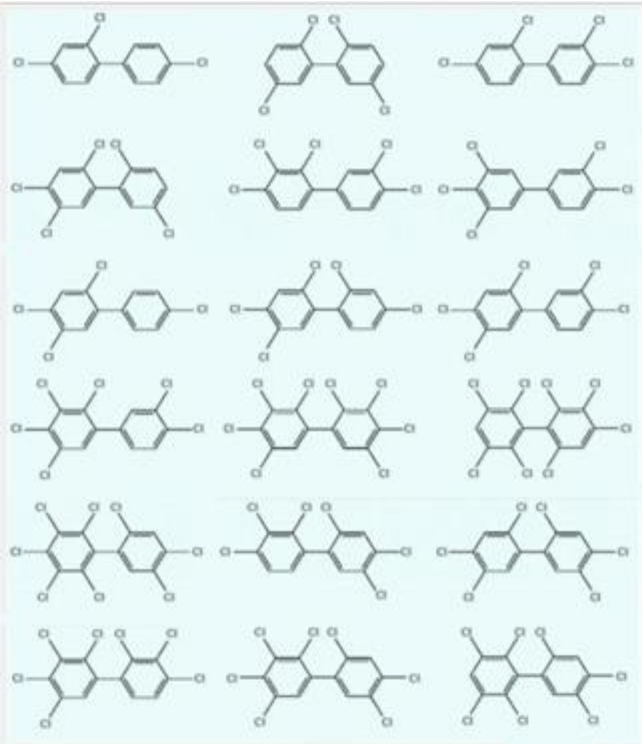


Figure 1. A selection of PCB congeners (Plísková, Vondrácek and Canton).

PCBs can be divided into two broad groups based on their origins: legacy and inadvertent PCBs. Legacy PCBs refer to those that were intentionally manufactured for use in products. Inadvertent PCBs (iPCBs) refer to those that are produced as by-products or contaminants from manufacturing other products. The focus of this whitepaper are the iPCBs since they are an unintended byproduct in pigments, inks, and packaging that results in environmental exposure and eventual human exposure after they are disposed of.

PCBs as a chemical class are toxic, persistent, and bioaccumulative, hazards which are well addressed in prior work. As early as the 1930s and 1940s, researchers had identified PCBs as a dermal irritant (Schwartz, 1936) and carcinogen (Des Ligneris, 1940). By the 1970s a body of literature outlining the toxic, persistent, and bioaccumulative effects of PCB warranted ban of their manufacture and limited most uses in the US (EPA, 1979). Their persistence means that legacy PCBs remain and continue to contribute to contamination alongside new releases of iPCBs. Their bioaccumulation means that PCBs biomagnify up the food chain, building up in species like salmon and posing a risk to populations consuming those species. Those for whom salmon and other fish traditionally comprise a large portion of their diets, including members of the Spokane Tribe, are particularly vulnerable to PCB contamination from fish caught from the Spokane River. Puget Sound orcas also consume salmon as a primary portion of their diet, and face health risks associated with their lifetime exposure to PCBs (Hickie, 2007). The survival of Washington's Southern Resident orcas is threatened by numerous forces. The Southern Resident Orca Task Force has identified reducing "the exposure of Southern Resident orcas and their prey to contaminants" as one of four necessary goals to support orca recovery (Southern Resident Orca Task Force, 2018, pg. 6). Details of how to achieve this reduction includes accelerating the implementation of the PCB procurement policy and sharing of information about PCB-free products. Release of PCBs into the environment negatively impacts human and environmental health.

The Spokane River Regional Toxics Task Force (SRRTTF) is working on multifaceted approaches to reduce loading that include both regulatory and voluntary initiatives. This report addresses iPCBs that are released into waterways, with a focus on iPCBs from pigments used in printed materials that can be recycled, particularly in newsprint and in paper and paperboard packaging materials. Our initial scope was limited to yellow pigments, and later expanded to include blue and green pigments. While these pigments are just one of many sources of iPCBs (Ecology, 2015), they are used in newsprint and paper and paperboard packaging and are contaminating recycling streams and interfering with efforts to promote both recycling and to meet water quality standards for the Spokane River. This paper examines the currently used yellow, blue, and green pigments for printing inks, including why they are the dominant pigments used today, and explores options for alternative pigments.

Reducing contamination from PCBs, both legacy and inadvertent, is a global challenge that affects water bodies worldwide. This paper further examines regulations that address iPCBs and procurement policies designed to comply with, or exceed, regulatory PCB limits. Regulations, some in place for decades, generally limit PCBs in substances like pigments to 25 - 50 ppm. In the U.S., discounting factors permit additional mono- and bi-chlorinated phenyls, such as PCB11. The amount of PCB11 in a sample is discounted by 5, permitting up to 250 ppm PCB11 in a sample if it is the only congener present.

Governments and businesses have begun the process of implementing procurement policies to address iPCBs from pigments. Policies vary significantly, ranging from no-PCB (no detect) to low PCB (<0.1 ppm), and may or may not provide any preference for incremental improvements via relatively lower PCB levels. Some policies require testing, while others rely on supplier claims. Washington State's policy is the most developed, with detailed training materials and a successful pilot case study in road paints. HP, Inc. and Apple have both begun the process of implementing their low-iPCB procurement policies that will limit iPCB levels in pigments used in their products to <0.1 ppm.

This paper begins by discussing the chemistry of pigments and the performance characteristics that are necessary to consider for their use in printing inks for newsprint and paper and paperboard packaging. Yellow pigments are discussed first including identifying the primary yellow pigments used and how iPCBs are generated in their manufacture. Alternatives to those yellow pigments are then discussed along with identification of key tradeoffs. The same topics are then addressed for blue pigments. Relevant parties, particularly pigment manufacturers and printing ink users, were interviewed to better understand the industry landscape (Appendix II).

From there, we transition into a discussion of how to encourage the use of alternatives. Government regulation, government procurement policies, and voluntary business procurement policies are reviewed. We look at some governmental regulatory approaches, including the Toxic Substances Control Act (TSCA), Clean Water Act (CWA), and tribal perspectives in the U.S., as well as, the Stockholm Convention internationally. We also look at government procurement policies, particularly the well-developed policy from Washington State. Policies from the City of Spokane are also examined. Voluntary business procurement policies, such as those established by both HP, Inc., and Apple are also discussed. As in the discussion of technical parameters, relevant parties were interviewed to improve incorporation of diverse perspectives (Appendix II).

The paper is not intended to be a thorough overview of international, state, and local regulations and procurement policies, nor a complete accounting of all voluntary business procurement policies. However, it offers examples in order to understand the connection between regulation and procurement and demonstrate that large corporate voluntary procurement policies have lower limits than regulations require. This bodes well for the adoption of lower iPCB limit procurement policies by additional stakeholders.

The chemistry side: Pigments, iPCBs, and performance

Note: The following sections of the report rely heavily on personal communications from pigment specialists in industry, including Romesh Kumar (Sr. Technical Sales Manager - North America, Clariant Plastics & Coatings USA) and another specialist who chose to remain anonymous. Other references are as noted. *Industrial Organic Pigments*, 3rd Edition, by Willy Herbst and Klaus Hunger in 2004 was also invaluable for pigment chemistries and use.

The uses of colored pigments can be broadly split into three categories: the coatings and paints industry, the printing inks industry, and the plastics and fibers industry (Herbst, 2004). The printing inks industry leads in the consumption of pigments, consuming about 50% of the pigment market (Hunger, 2012). Diarylide pigments, which range from yellow to orange, are commonly used for printing inks. Due to the substrates used to synthesize them, PCBs are generated during their synthesis and contaminate the resulting pigment and inks made using the pigments (Rodenburg, 2015). In 2001 alone, the estimated trade sales volume worldwide of diarylide yellow pigments for printing inks alone was 60,000 metric tons (Herbst, 2004).

Performance: Pigments in newsprint, and in paper and paperboard packaging

Printing ink is composed of solid pigment in resin dispersed in a solvent (water or organic) with other performance additives (Figure 2). Pigments used in newsprint, and in paper and paperboard packaging, have stringent performance requirements to ensure the proper quality of the final product and the efficiency (and low cost) of the process. These include considerations such as transparency, color strength, color consistency, adherence, gloss, viscosity, dispersibility, drying time, soak through, soap/water resistance, durability/UV resistance, thermal stability, and cost (Table 1). Many of these properties interrelate; for example, poor color strength can result in needing to use too much pigment, which then negatively impacts viscosity. Despite the hundreds of organic pigments available, only a limited subset is suitable for printing inks.

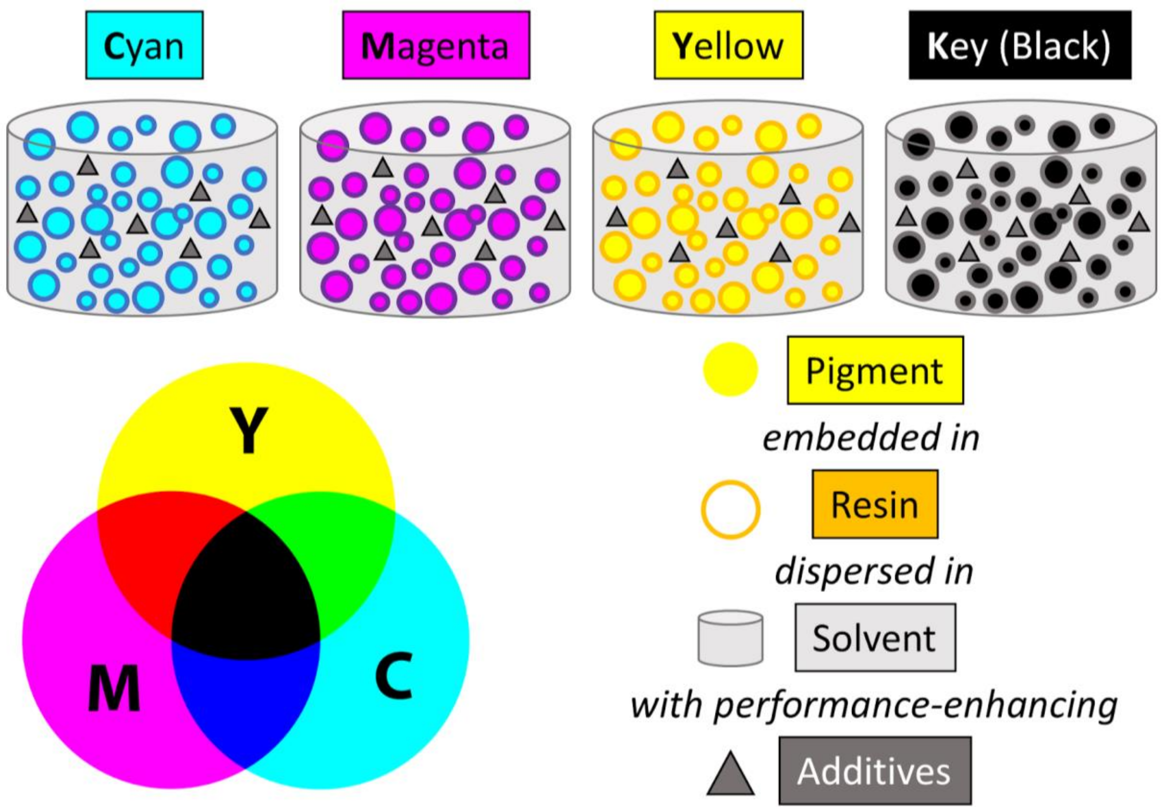


Figure 2. Printing ink components using the example of the Cyan, Magenta, Yellow, and Key (Black) (CMYK) system.

Table 1. Pigment performance properties.

Property	Description
Transparency / Opacity	When colored pigments are laid down sequentially, as in most printing processes, transparency is desired for mixing colors. For example, if orange is desired, the printer might lay down red, then yellow. If the yellow is too opaque, it overly dominants the final color. Some opacity is desired for printing on colored surfaces, such as brown packaging.
Color strength, color power	Intensity of color provided per unit of pigment. Higher color strength means less pigment is required, which can improve viscosity and drying time and decrease costs.
Color consistency / matching	Colors provided by pigments must be consistent between batches and even between systems. For example, the color used for John Deere tractors must be maintained between the actual tractor, the branding on packaging/advertisements, and tractor toys.
Adherence	Ability of the pigment to stick to the substrate. While critical for metal substrates, it is typically not a challenge with paper substrates.
Gloss	Shininess. Desirable for appearance, marketing.
Viscosity / rheology	Low viscosity is necessary for the ink to flow at a reasonable and steady state during printing.
Dispersibility	Pigments must remain evenly dispersed throughout the ink, not clumping or aggregating, to ensure even color and smooth flow.
Drying time	Rapid drying time permits faster printing speeds without smearing.
Soak through	When pigments soak through the substrate and are visible on the other side or in subsequent layers.
Soap or solvent resistance	In some applications, pigment must remain adhered to the substrate despite soap, water, or other solvent presence.
UV resistance	In some applications, pigment must resist photobleaching. However, for most newsprint and paper and paperboard packaging applications, this is a lower priority.
Thermal stability	In some applications, pigment must be stable at high heat.
Cost	Cost per unit pigment. Pigments are typically sold by weight, providing easy cost comparisons. However, the amount of pigment required to achieve the same color may be different when changing chemistries.
Additional sources: M. Kinter and J. Jones, personal communication, May 9, 2010; Herbst, 2004; Hunger, 2012; K. Brewer and C. Wray, personal communication, May 8 2019; C. Flanders, personal communication, April 29, 2019.	

These performance properties are defined by the pigment chemistry, the resin the pigment is embedded in, the solvent system used (water or organic), any other additives used, and the particle size. The pigment chemistry can limit the solvent options, compatibility with resins/additives, and potential particle sizes. Different companies may prepare the pigment using different process techniques, resins, etc., so a given pigment chemistry from company A may not be suitable for printing ink, while the same pigment chemistry from company B would be. The same company may offer multiple preparations of the same pigment, each suitable for different end uses.

Currently used yellow pigments for printing ink

Diarylide yellows are very commonly used for printing inks, including printing inks for newsprint, and paper and paperboard packaging. They have roughly two times the color strength of other yellows and oranges, and are compatible with a broad range of solvents and applications. Unfortunately, diarylide yellows are all suspected to be contaminated with iPCBs as a result of the reagents used to manufacture them and the necessary conditions for their synthesis.

Pigment Yellow (P.Y.) 14 is by far the most commonly used; it is a green-shade yellow. P.Y. 83, a red shade yellow, is also quite common. Both are shown in Figure 3. P.Y.s 12, 13, and 17 are also regularly used in printing inks today. All of these are diarylide yellows.

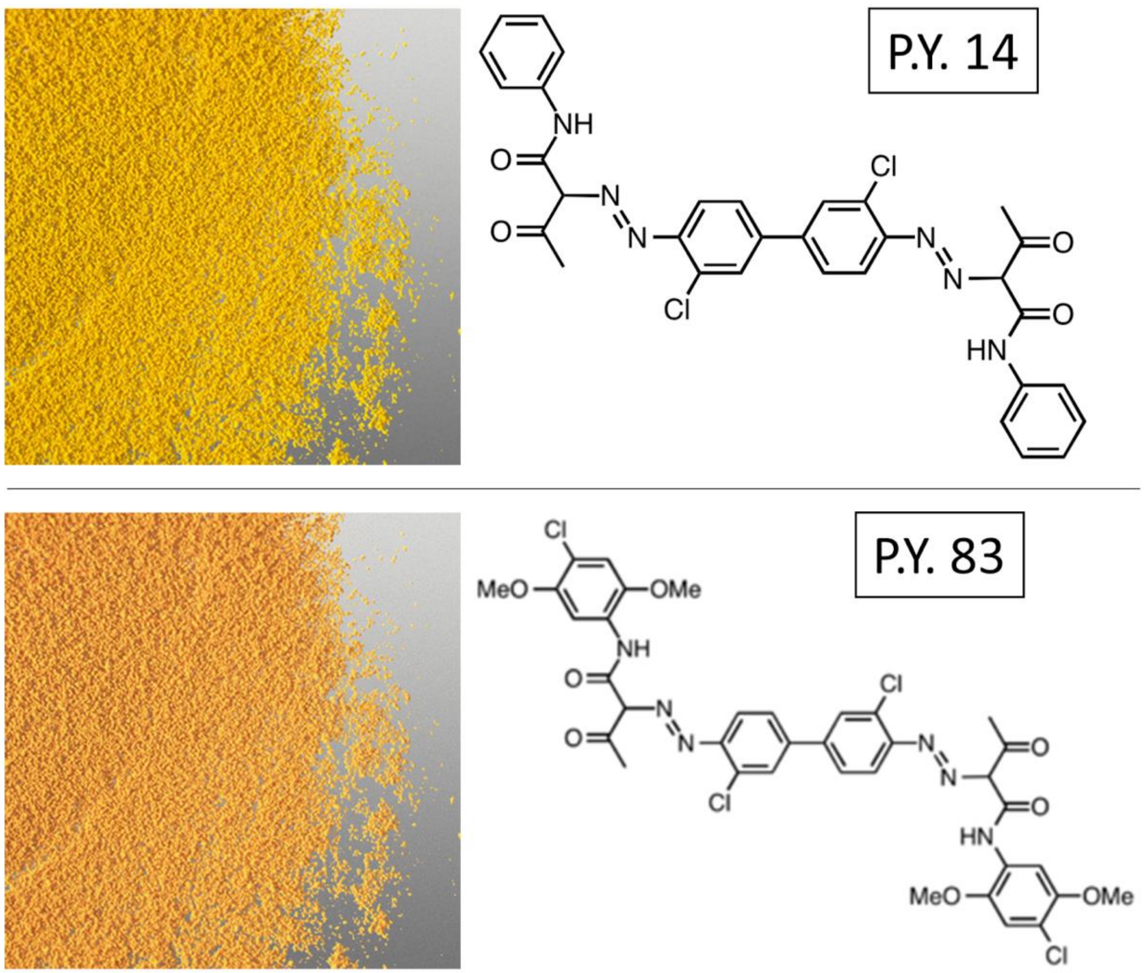


Figure 3. Appearance (left) and structure (right) of P.Y. 14 (top) and P.Y. 83 (bottom).

P.Y. 14, a green-tint yellow, is by far the dominant yellow used in printing inks. P.Y. 83, a red-tint yellow, is second. Image source (appearance): http://www.clariant.com. Image source (structures): Wikipedia.

Yellow pigments for printing: Structure, synthesis, and iPCBs

While other chemistries can result in yellow, the relevant chemistries for printing include the monoazo and disazo pigments (Herbst, 2004). Both are based on the azo group (–N=N–). Monoazo pigments contain one azo group, while disazo pigments contain two. Pigments exist with additional azo groups (tris, tetra, poly, etc.) but are not used commercially at this time. Azo pigments are synthesized in a two-step process: 1) diazotization, and 2) coupling.

Diazotization is a chemical reaction in which a diazo group is formed, which is two linked nitrogen atoms at the terminal position; the resulting compound is referred to as a diazonium compound. Many of these compounds are explosive in a solid state, so this synthesis reaction is typically rapidly followed by coupling without further purification of the diazonium compound (Hunger, 2012). The coupling component has a hydrogen that is favorable for displacement; it is at this site that the diazonium compound and the coupling compound form a bond. Reactions are typically performed on ice due to the instability of diazonium compounds (Hunger, 2012).

After synthesis, many azo pigments require finishing and/or after-treatments (Herbst, 2004; Hunger, 2012). These treatments optimize particle size, shape, and distribution, influencing the final performance properties of the pigment. Reagents for these syntheses are cheap and readily available, and the synthesis methods are relatively uncomplicated. These factors combined with the excellent performance properties of diarylide yellows has resulted in their dominance in the printing ink market (Herbst, 2004; Hunger, 2012).

The synthesis of P.Y. 14, the most commonly used yellow pigment in printing ink, is shown in Figure 4. iPCBs are formed during the synthesis of the diarylide yellows due to the diazo group used for their synthesis: 3,3'-dichlorobenzidine (Figure 4, DCB, Panel A) or similar tetrachlorobenzidine compounds. Compare the structure of 3,3'-dichlorobenzidine to the structure of PCB11, which is also known as 3,3'-dichlorophenol (Figure 4, PCB11, Panel C). The sole difference is the presence of amine groups. PCB11 is not the only PCB formed as a byproduct during diarylide synthesis, but it is a good marker for inadvertent generation in pigments because it is not typically found in legacy sources (Rodenburg, 2015). PCB52 is also found in diarylides, typically those synthesized with tetrachlorobenzidine, but PCB52 common in legacy sources as well. This means that PCB52 found in the environment cannot be as clearly assigned to pigment sources as PCB11. Techniques, such as Positive Matrix Factorization, have been applied to tease apart the more diverse sources of PCB congeners such as PCB52 (Capozzi, 2019).

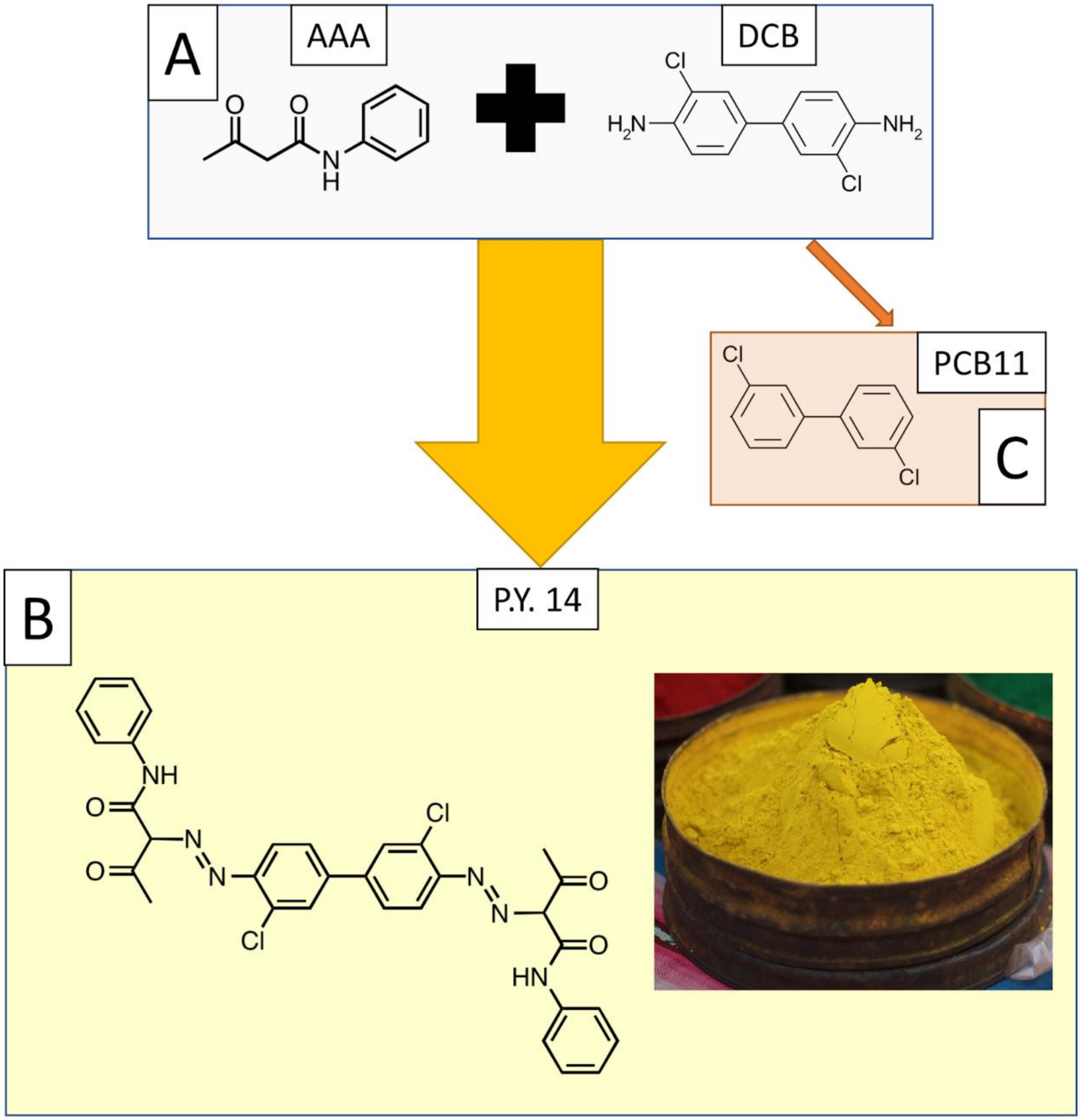


Figure 4. Synthesis of P.Y. 14 and formation of iPCBs as byproducts.

Panel A: P.Y. 14 is synthesized from acetoacetanilide (AAA) and 3'3-dichlorobenzidine (DCB). Panel B: When combined using the proper conditions, AAA and DCB react to form P.Y. 14. The vast majority of AAA and DCB is consumed forming P.Y. 14. Panel C: A small minority of DCB undergoes a different reaction and forms PCB-11 and other PCBs, resulting in ppm contamination of the pigment with iPCBs. The precise mechanism for the transformation of the substrate to PCBs has not been proven, though realistic mechanisms have been identified (Rodenburg, 2015). Image source (structures): Wikipedia. Image source (appearance): Fatima Valer from Pixabay.

Decreasing iPCB byproduct synthesis in yellow pigments

As the component responsible for iPCB byproducts during diarylide pigment synthesis is a central component of the pigment, alternate synthesis schemes resulting in the same final pigment are not a practical solution. However, it is possible that iPCB generation could be minimized using process controls, such as minimizing the time between the diazotization and coupling steps or controlling reaction temperatures or pH levels (Rodenburg, 2015). Manufacturers may already have implemented some or all of these potential controls; the exact process is considered a trade secret. Depending on which mechanism is responsible for the conversion, consideration of what reducing agents are present or the addition of free radical scavengers could also minimize iPCB production.

Process controls can reduce iPCB generation during pigment synthesis, but are unlikely to eliminate it. It remains to be seen how low iPCB generation can be dropped using process controls, and if that is low enough to avoid the current downstream discharges from recycling. The exact process used to synthesize pigments are typically considered a trade secret, as these control the quality of the resulting pigment (e.g. purity, average particle size, particle size range, tendency to aggregate, etc.) and its usefulness for different applications.

Alternative no or low iPCB yellow pigments for printing ink

Some monoazo pigments have been proposed as alternatives to the diarylides currently dominating the printing ink industry, including P.Y.s 1, 3, 74, and 65. Monoazo pigments tend to have less color strength than diarylide yellows, and are suitable in a fewer number of solvents. All are suitable for waterborne printing inks, which are common for newsprint, and paper and paperboard packaging. One advantage of many monoazo pigments is that they are more UV resistant than most diarylides. P.Y. 155, a non-diarylide disazo pigment, has also been suggested as an alternative. The structure of these pigments and the diarylides they might replace as shown in Figure 5.

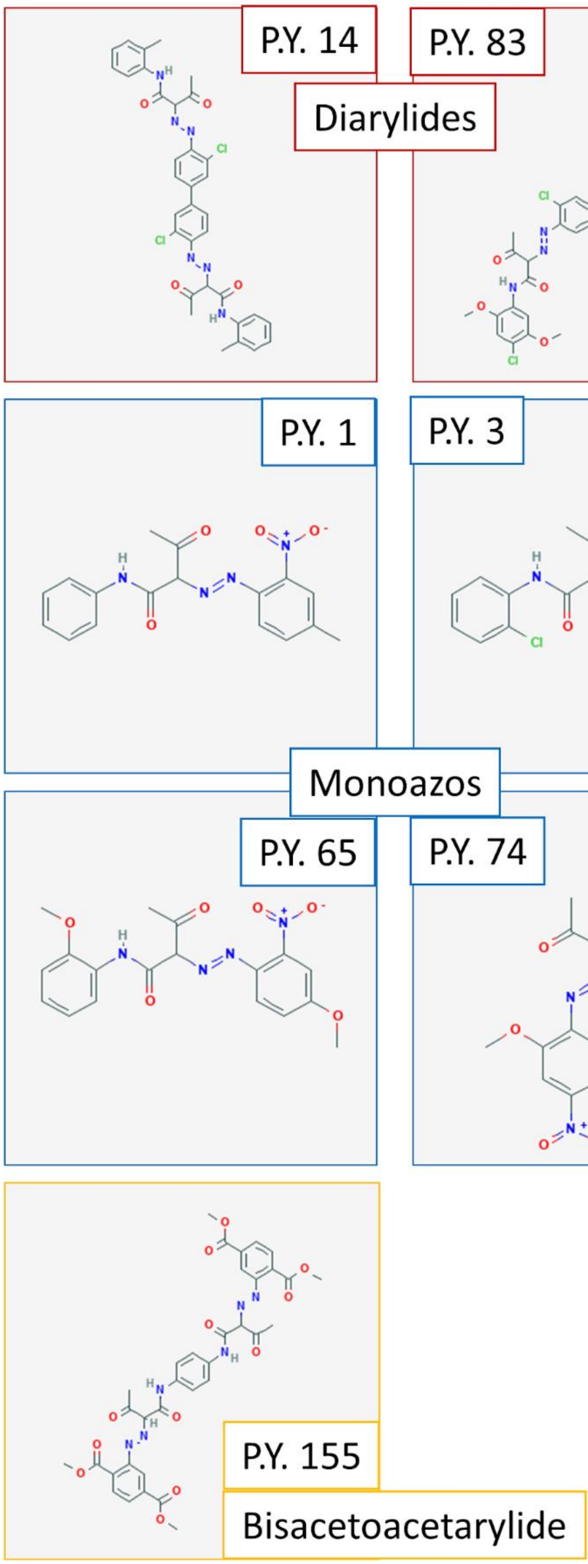


Figure 5. Diarylides for printing ink and their potential alternative monoazos and bisacetoacetarylide.

Image source (structures): Pubchem. Oxygens are shown in red, nitrogens in blue, and chlorines in green; all others are shown in grey/black. Diarylides are outlined in red. Monoazos are outlined in blue. The bisacetoacetarylide is outlined in yellow.

P.Y. 74 (monoazo) has similar color properties to P.Y. 14, the dominant yellow pigment used for printing inks today. It has greater color strength than other monoazo pigments: An ink containing 4.2% P.Y. 74 can match an ink containing 4.5% P.Y. 12 (diarylide) (Herbst, 2004). As with other monoazos, P.Y. 74 has increased UV resistance compared to diarylide yellows. Today, P.Y. 74 is used in printing inks and in paints (Herbst, 2004). Experts have recommended P.Y. 74 as the most likely suitable replacement for P.Y. 14. The barrier to adoption is the increased cost, which is shared in common with the other alternatives. However, that increase may be minor compared to other product costs, especially as production of P.Y. 74 ramps up.

Interestingly, P.Y. 1 (monoazo) was historically used as the dominant yellow for printing inks before the introduction of diarylide yellows. The diarylides were preferred due to their color strength: An ink containing 8-11% P.Y. 1 could be replaced by an ink containing only 4-6% P.Y. 14 (diarylide) (Herbst, 2004). The downside to switching to diarylides was a decrease in UV resistance. However, for most printing ink applications, the decreased UV resistance was still sufficient. Newsprint and paper and paperboard packaging must be protected from rain and are rarely stored exposed to sunlight for any length of time before reaching consumers. These goods have limited lifespans in consumers' hands, and are rarely expected to survive extended exposure to sunlight or the elements in general. P.Y. 1 is still used for printing inks today in applications where increased UV resistance is necessary, such as billboards. P.Y. 3 is used for similar limited printing ink applications today. Both could substitute for P.Y. 14 for waterborne inks, but not solvent-based inks. Notably, even though P.Y. 1 was historically the dominant yellow, printing technology has significantly advanced since changing to the diarylide yellows.

P.Y. 155 has also been suggested as a potential alternative to P.Y. 14. This pigment is a bisacetoacetarylide pigment. This class tends to have good solvent resistance, including resistance to soap and butter, and good color strength, though not as strong as the diarylides (Herbst, 2004). P.Y. 155 has good UV resistance and is currently used in industrial finishes for commercial vehicles, tractors, and farm implements.

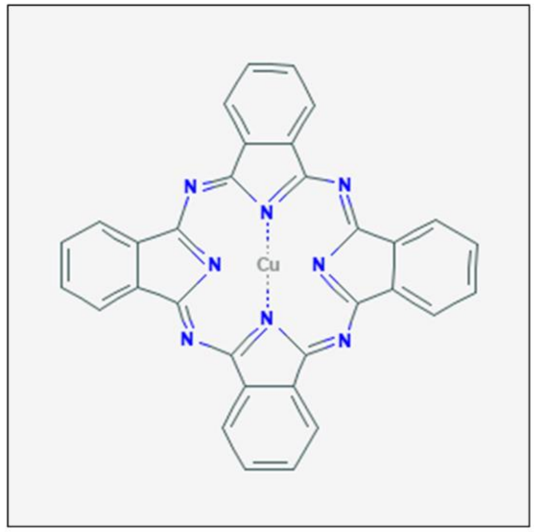
P.Y. 65 (monoazo) has been suggested as an alternative for P.Y. 83. However, its technical properties are inferior, particularly with regards to color strength. The necessity of using significantly more pigment negatively impacts other ink properties, such as viscosity. However, further development of P.Y. 65 might yield a suitable preparation for printing inks. P.Y. 65 is also more expensive than the diarylide yellows.

A current disadvantage to all of these options is lack of availability. Diarylide yellows dominate the market and industry has risen to meet these demands over decades. Insufficient raw materials are available to switch all printing ink from diarylides to a single alternative or even a combination of these alternatives. Further information is needed to better understand what transitions need to occur to make a broad scale switch.

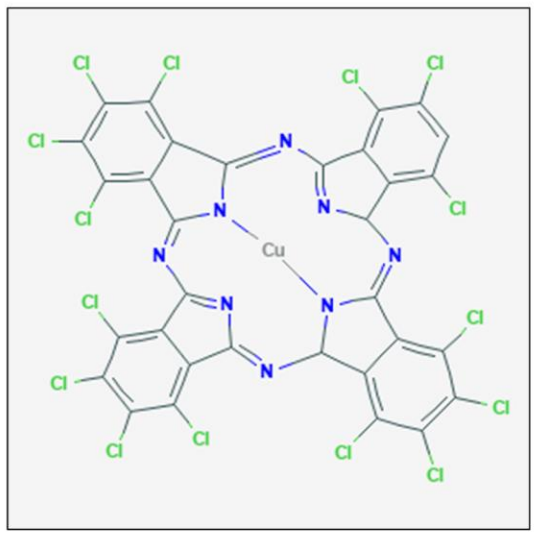
A separate advantage to these options is the decreased exposure of workers to 3,3'-dichlorobenzidine, a probable human carcinogen (EPA, n.d.). We recommend evaluating the hazard and exposure potential of the chemicals used to synthesize the alternatives, necessary to avoid regrettable substitutions.

Currently used blues and greens for printing ink

Pigment Blue (P.B.) 15 (Figure 6, top) derivatives are the dominant blues used in printing ink for newsprint and paper and paperboard packaging, particularly P.B. 15:3. Other P.B. 15 derivatives, such as 15:1 and 15:2, find applications in specialty printing inks. Pigment Green (P.G.) 7 (Figure 6, bottom) is also used, though it is more expensive than using mixtures of P.B. 15 derivatives and suitable yellow pigments (Herbst, 2004).



Pigment Blue 15



Pigment Green 7

Figure 6. Appearance (left) and structure (right) of P.B. 15 (top) and P.G. 7 (bottom).

Image source (appearance): Wikipedia. Image source (structures): PubChem. Nitrogens are shown in blue, and chlorines in green; all others are shown in grey/black.

Blues and greens: Structure, synthesis, and iPCBs

The majority of commercially relevant blue and green pigments fall into the phthalocyanine class (Herbst, 2004). This class is based on modified porphine rings, which are the same complex ring structures found in the heme in hemoglobin and chlorophyll. For printing ink pigments, copper is commonly the metal complexed with the porphine ring, which may be halogenated or otherwise modified.

Copper phthalocyanine pigments are commonly synthesized by treating phthalic anhydride with urea, copper(I) chloride, and a catalytic amount of ammonium molybdate at high temperatures

(Rodenburg 2015) (Figure 7). Chlorinated phthalic anhydrides are added to generate the chlorinated versions (Herbst, 2015). This process may be performed in the presence of organic solvents, such as dichlorobenzene or trichlorobenzene. Chlorine is present in the form of copper(I) chloride. When these solvents are used at high heat in the presence of chlorine, higher molecular weight PCBs are generated, such as the fully chlorinated congener PCB209 (Rodenburg 2015, Herbst 2004). This issue is exacerbated with copper phthalocyanine pigments that are more chlorinated, such as Pigment Green 7 (Figure 6). Synthesis of more highly chlorinated copper phthalocyanine pigments can include adding excess chlorine to the reaction (Rodenburg, 2015).

P.B. 15 (Figure 6) is a common copper phthalocyanine blue pigment. Modifications result in derivatives, such as 15:1 or 15:2. These modifications result in different crystal shapes, stabilization, and sometimes the presence of >0 - 1 chlorine atoms on the porphine ring (Herbst, 2004). P.B. 15 mixed with appropriate yellows is often used for green in printing ink due to lower costs.

Avoiding iPCB formation in the synthesis of blue and green pigments

No alternative pigments suitable for printing ink are known. However, it is unnecessary to use dichlorobenzene or trichlorobenzene solvents during the synthesis of copper phthalocyanine pigments (Versars, 1978; Herbst, 2004; Rodenburg, 2015). High-boiling hydrocarbons, such as kerosene or naphthalene, and alcohols and glycols can replace these chlorinated solvents and avoid the generation of iPCBs during the synthesis process (Versars, 1978; Herbst, 2004; Rodenburg, 2015). Regarding the hydrocarbons, one downside is the possibility of fire and explosion which must be considered in the design of the production unit (Herbst, 2004). Further research is necessary to fully understand the hazards and impacts of the alternatives in order to avoid a regrettable substitution. Another alternative is to simply not use solvents at all, which is known as the “dry-bake” process. This process results in less pure pigment and is rougher on the production units (Herbst, 2004).

Herbst 2004 suggests that this switch to other solvents has already, for the most part, occurred. However, details of pigment synthesis are typically considered trade secrets, and some evidence exists showing that phthalocyanine pigments currently in use are still contaminated with iPCBs (METI, 2012). It is possible that not all manufacturers have switched, that additional mechanisms are present that generate iPCBs during synthesis, or that the reagents are already contaminated with PCBs before the synthesis. In the 70s, only a handful (around 6 or 7) manufacturers and importers of phthalocyanine blues and greens operated in the U.S. (Versars, 1978). Of these, one was already using kerosene and had essentially no PCBs, while the others used trichlorobenzene and had levels around 100-300 ppm PCBs, though one analysis reported levels as high as 1000-2000 ppm PCBs.

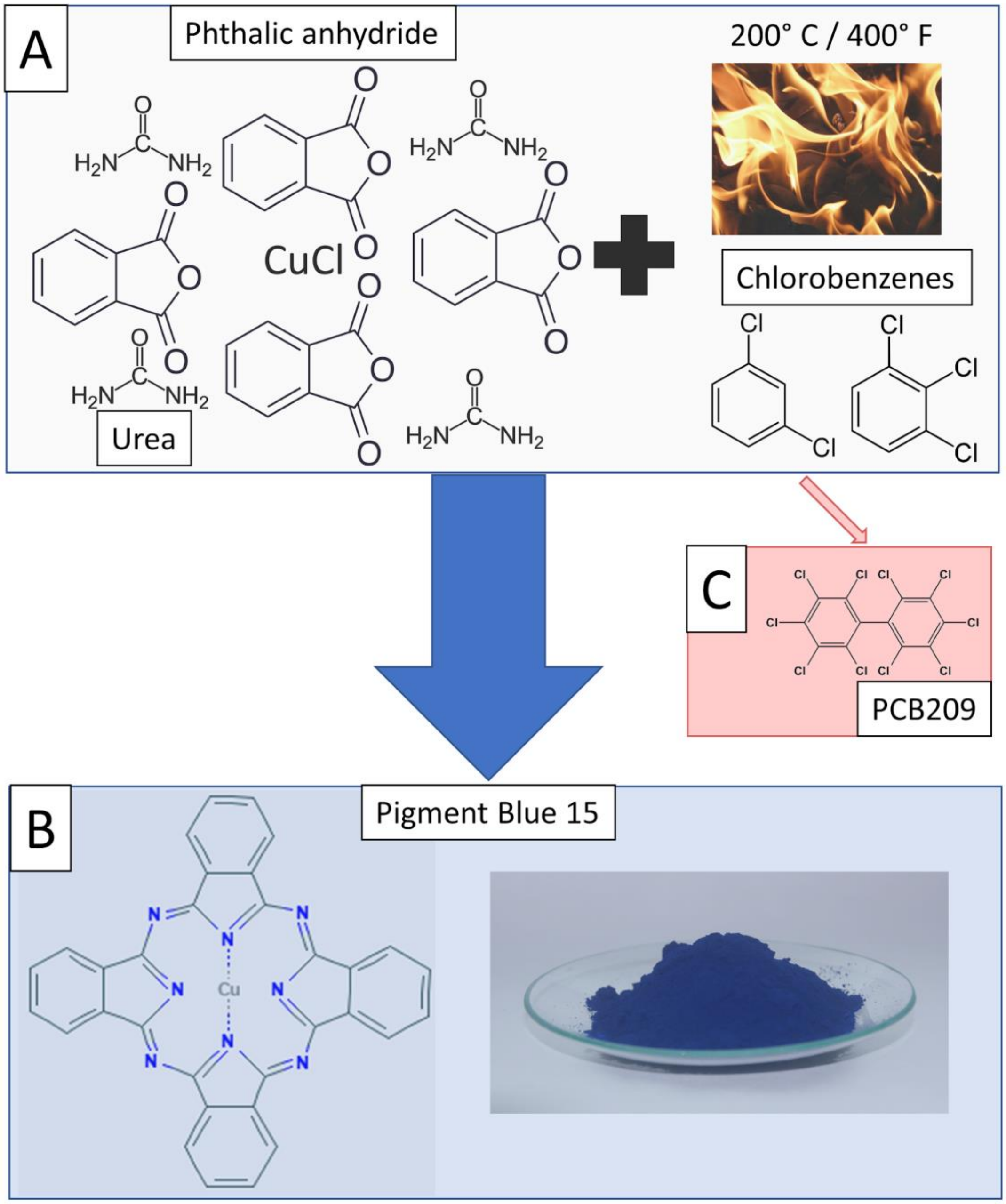


Figure 7. Synthesis of P.B. 15 and formation of iPCBs as a byproduct.

Panel A: P.B. 15 is synthesized from phthalic anhydride, urea, and copper(I) chloride (CuCl) in the presence of high heat (200° C / 400° F). This is typically done in the presence of solvents like chlorobenzenes (dichlorobenzene, left; trichlorobenzene, right) to improve efficiency. Panel B: The dominant product is P.B. 15. Panel C: In the presence of high heat, chlorobenzenes can undergo reactions to form PCBs. When chlorine is also present, as it is here from copper(I) chloride, even higher molecular weight PCBs can be formed (Rodenburg, 2015). PCB209 is shown here. Image source (structures): Wikipedia (Panels A, C) and PubChem (Panel B). For the structure of P.B. 15 in Panel B, nitrogens are shown in blue and all other elements are shown in grey/black. Image source (appearance, Panel C): skeeze from Pixabay.

Driving Demand for Alternatives

With improved technology to test PCB concentrations, identified alternatives known or being developed, and known threats to human and environmental health, there is renewed interest in revisiting the 1970s PCB limits set by the EPA. In the Pacific Northwest these concerns revolve around higher fish consumption rates among tribal and other populations where fish is a staple of their diet, resulting in disproportionate rates of exposure. Higher exposure rates lead to increased incidence of cardiovascular disease and diabetes. In addition, protecting wildlife is a priority, including Orcas, whose populations have been impacted by the bioaccumulation of legacy and inadvertent PCBs. The recent report by Governor Inslee's Southern Resident Orca Task Force has identified PCBs as a major contaminant and risk factor to the health of Orca whales (Southern Resident Orca Task Force, 2018). Some local, tribal, and state governments have adopted lower regulatory limits than the federal government mandates in response. In addition, large corporations at the forefront of sustainability, have acknowledged their influence on demand by creating procurement policies designed to accelerate the adoption of safer alternatives by lowering allowable PCB limits. Before covering the details of these regulations and procurement policies, it is helpful to better understand the supply chain for pigments, inks, and packaging, as well as how PCBs enter the environment.

Procurement Policies and Regulations: Government and business approaches to reducing iPCBs

Action influencing the supply chain is necessary to encourage the switch to no or ultra-low iPCB pigments. Here we explore the printing ink supply chain and life cycle, identifying what we know and where there are important gaps in understanding. We also explore regulatory approaches and voluntary procurement policies that address iPCBs and pigments.

Supply chain

Successful procurement policies engage all actors involved in the supply chain. The pigment supply chain and life cycle for printing inks involves numerous actors as pigments transition from powders to dispersions to inks before being printed, branded, used, and discarded (Figure 8) (Appendix I). Appendix III identifies specific individuals or organizations that represent each stage of this supply chain. One company may span multiple roles. For example, a pigment manufacturer may also make dispersions and even inks. And a brand may manufacturer its own ink and/or do its own printing.

The pigment manufacturer synthesizes the pigment and determines what resins or additives are present in the pigment as a powder. This actor plays a critical role in determining pigment properties which influence final ink properties, such as the pigment particle size. The dispersion manufacturer suspends the pigment powder in solvent, which could be water or an organic solvent. At this stage, high levels of pigment are used, with 30-40% pigment in solvent being

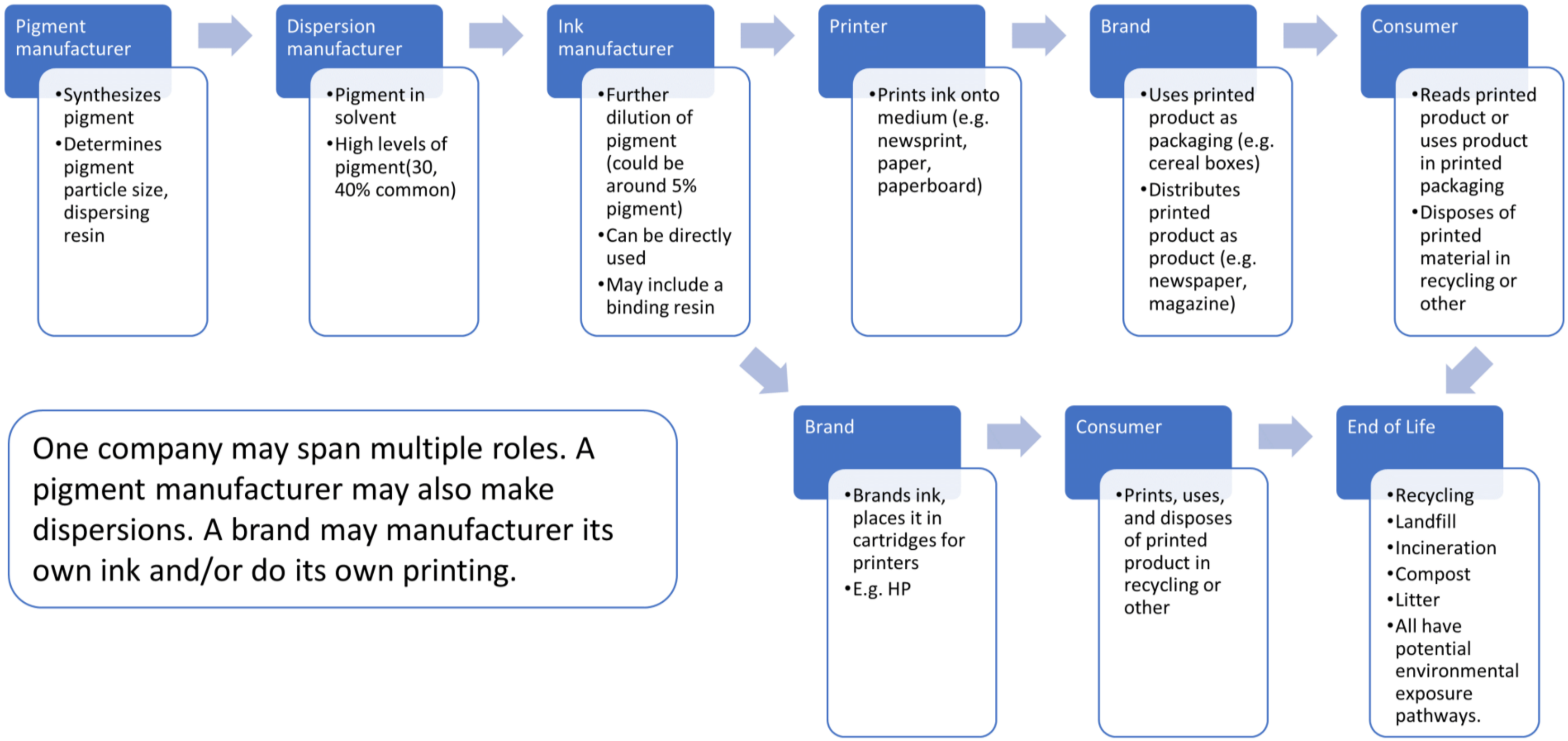


Figure 8. The pigment supply chain and life cycle for printing ink.

common. The ink manufacturer further dilutes the dispersion, adding solvent and potentially binding resins or other additives, with final pigment levels tending to be closer to 5% in the ink.

Printing ink may be used in two ways. One path involves a printing company that prints the ink onto a medium, such as newsprint or packaging. This is then picked up by the brand. For packaging, the brand uses the printed material to contain and display the product. The consumer would then use the product and dispose of the packaging. Similarly, for newsprint, the consumer would read the printed product and then dispose of it.

A second path involves a company branding the ink and placing it in cartridges for printers. This is then sold to the consumer, who prints the ink on the product, uses the product, and then disposes of the spent cartridges. Regardless of the path used, the ink is printed onto a material that is subsequently used and then discarded.

Disposed printed products may be recycled, landfilled, incinerated, composted, or littered. All of these pathways involve potential environmental exposure. When recycled, iPCBs from the pigments can end up in the wastewater from the recycling plant and enter the Spokane River. PCBs are present in landfill leachate (Öman, 2008). However, US EPA has shown that in certain approved landfills (permitted, licensed, or registered by a state as a municipal or non-municipal non-hazardous waste landfill) the PCBs are unlikely to migrate into groundwater or soil (US EPA, n.d.), though this EPA analysis may be more permissive of PCB leaching than would be acceptable when considering the highly stringent standards currently in place in Washington. Modern incinerators destroy a significant portion of PCBs inputted, though not all, while also generating small quantities of PCBs (Dyke, 2005). Compost would not destroy PCBs and therefore provides a direct pathway to soil contamination when used as soil amendment. Litter provides a direct pathway to whatever medium it is littered in and subsequently transported through. Regardless of disposal method, environmental exposure and subsequent transport and exposure to Spokane River is possible and may be significant given the stringent water quality standards necessary to ensure human and environmental health.

As end of life controls are currently inadequate to completely manage PCB contamination from pigments, upstream management is necessary to fully control emissions to Spokane River. Selection of no or ultra-low iPCB pigments limits is one approach. Two avenues to impact change are to set regulatory limits and/or create government and business procurement policies. Governments can create and enforce regulation to advance the transition from higher iPCB pigments to lower iPCB pigments. In the US this happens at the federal, state, and local level. Purchasers, such as governments and businesses, and brands can influence the market via procurement policies. Purchasers may only purchase pigment-containing products, not pigments themselves, still have the ability influence the market by including requirements or preferences that require or encourage their suppliers to select no or low iPCB pigments. Such policies can drive industry to produce pigments that typically contain iPCBs with even lower levels; or to substitute pigments containing iPCBs with pigments that do not.

Regulations

Internationally and in the U.S., PCBs in products are addressed in two parts: Intentional PCBs and unintentional (inadvertent) PCBs (iPCBs). Intentional use of PCBs for applications such as use in transformers and other products has been banned. The use, sale, manufacture, import, and/or export of products containing iPCBs is generally limited to a maximum total concentration of iPCBs to 50 ppm, sometimes with an average limit of 25 ppm, though lower limits have been proposed. This is a total sum of all congeners except in the U.S., where monochlorinated biphenyls and bichlorinated biphenyls are discounted. Regulations reviewed in this paper are summarized in Table 2. Some additional regulations and advisories on PCBs are covered in Appendix IV.

These regulations that address iPCBs in products can align poorly with regulations on PCBs in discharges to the environment. Permissible contamination levels in pigments under the Toxic Substances Control Act (TSCA) exceed permissible discharge levels in the Spokane River under the Clean Water Act (CWA) by nine orders of magnitude (Table 2). Newsprint from around the world has been tested for PCB11, and levels ranging from 1.6 ppb - 16 ppb PCB11 were found, levels five to six orders of magnitude higher than permissible discharge levels to the Spokane River (Guo, 2014). A variety of printed materials were sampled in WA Department of Ecology study (Ecology, 2016). Printed materials (newsprint, magazines, comic books) had 1.1 ppb - 53.5 ppb PCBs, again five to six orders of magnitude higher than permissible discharge levels to the Spokane River. Additional recyclable packaging sometimes contained even higher levels. For example, box containers tested in this study contained 2.7 ppb to 226 ppb PCBs.

Table 2. Regulations addressing iPCBs in pigments.

Regulation	**TSCA**	**Stockholm Convention**	**U.S. Tribal positions**	**CWA**
Applies to	Pigments	All products	Pigments	Water quality
PCB limit	25 ppm average / 50 ppm max; discounting factors allow more mono- and bi-chlorinated phenyls	As implemented by parties; some have no clear limit while others implemented similar to TSCA; US is not a party	Some tribes propose 0 ppm limit in TSCA	1.37 ppq (Spokane Tribe), 7 ppq (Washington State), 170 ppq (federal)
Address iPCBs in pigments?	Yes	Intended to; main convention documents do not explicitly call out iPCBs in pigments	Yes	Yes, applies to PCBs from any source that enter the designated water body

These regulations take into account the bioaccumulative and persistent properties of PCBs, as well as their ubiquitous presence in the environment. These properties drive the extremely low limits on PCBs, as low levels of exposure build up in biological tissue and may result in significant exposure over time.

Toxic Substances Control Act of 1976 (TSCA)

TSCA is a federal law in the United States of America 15 U.S.C. §2601 passed in 1976. TSCA was reformed in 2016 with the Lautenberg Chemical Safety Act for the 21st Century and this did not alter its position on PCBs (EPA, 2016). TSCA bans intentional production and import of intentionally added PCBs and limits iPCBs in pigments to an average of 25 ppm, not to exceed 50 ppm in any given instance. This level was set because it was not expected to impact industry with the exception of producers and users of diarylide yellows and phthalocyanine blues and greens (Versars, 1978). However, discounting factors allow for larger quantities of PCBs with one or two chlorine atoms. Monochlorinated biphenyls are divided by 50, and bichlorinated biphenyls, like PCB11, are discounted by 5. This means that the US allows an average of 125 ppm PCB11 with a max of 250 ppm PCB11 in any given sample if it is the only congener present. PCB11 is the dominant PCB congener in diarylide yellows, allowing higher levels of total PCB contamination for these pigments.

TSCA limits consider economic and technical feasibility as well as human and environmental health (EPA, 1982). Previous considerations of using alternative solvents for phthalocyanines and switching away from diarylides concluded that it was technically feasible in both cases, though substantially more costly for pigment manufacturers in the case of diarylides than phthalocyanines (Versars, 1978). This feasibility should be reconsidered, including impact on downstream industry (e.g. waste management, including recycling) and societal costs and benefits given advancements in chemical manufacturing and printing technology in the past forty plus years.

Clean Water Act of 1972 (CWA)

Federal law in the United States of America 33 U.S.C. §1251 passed in 1972. CWA permits the United States Environmental Protection Agency (EPA) to set water quality standards that are protective of human and environmental health. States and tribes may set more stringent standards. These standards determine permissible discharge levels into water bodies like the Spokane River under National Pollutant Discharge Elimination System (NPDES) permits. These discharges may contain iPCBs from pigments. For example, a paper recycling plant that processes paper printed with pigments that contain iPCBs would likely have PCBs in their discharges.

Standards are calculated using a formula set by the federal government; different pollutants use different formulas. The formulas were updated in 2015, and not all states or tribes use the updated formulas (D. Barton, personal communication, June 7th, 2019). Washington State and Idaho are using the updated formulas, while the Spokane Tribe of Indians and Oregon do not. These formulas rely on two external variables: the fish consumption rate and cancer risk rate. The formulas also consider untreated drinking water consumption. States and tribes may set their own fish consumption rates and cancer risk rates, and submit these for approval to EPA.

The fish consumption rate is the amount of fish in grams consumed per person per day and is designed to be protective of sensitive populations. The EPA considers a default 17.5 grams per person per day (EPA, 2000). Washington State uses a value of 175 grams per person per day, considering the higher fish consumption rates of many populations along the rivers and ocean. Oregon uses the same rate, but Idaho's fish consumption rate is only 65 grams per person per day. The Spokane Tribe of Indians' fish consumption rate is based on heritage consumption, and is set at 865 grams per person per day.

The cancer risk rate is the acceptable rate of cancer from lifetime exposure to this pollutant. EPA recommendations consider 1 in a million (10^{-6}) appropriate for the general population, though 1 in 100,000 (10^{-5}) is acceptable for the general population as long as the risk to more highly exposed subgroups (sportfishers or subsistence fishers) does not exceed 1 in 10,000 (10^{-4}) (EPA, 2000). Both Oregon and the Spokane Tribe of Indians use 10^{-6}, while Idaho uses 10^{-5}, while Washington's cancer risk rate has been in flux. In 2016, Washington submitted water quality standards based on 10^{-6}, with exceptions for some chemicals (including PCBs) that used 10^{-5}. This addressed concerns that more stringent water quality standards based on 10^{-6} for these chemicals were not practical (D. Barton, personal communication, June 7th, 2019). These exceptions were rejected. Washington began implementing water quality standards based on 10^{-6}. An industry group petitioned EPA to reconsider the rule in February 2017, and EPA reversed their decision in May 2019. Implementation of this change requires the EPA to undergo a rulemaking process to withdraw the federally-promulgated human health criteria (Ecology, 2019). On June 6th, 2019, Washington Attorney General Bob Ferguson filed a lawsuit challenging that reversal (Washington State Office of the Attorney General, 2019).

The federal water quality standard set under CWA is 170 ppq (parts per quadrillion) (0.00000017 ppm) (40 CFR § 131.45). The Washington standard, based on 10^{-6} cancer risk rate, was set under WAC 173-201A-430 to 7 ppq (0.000000007 ppm) for human health water quality criteria. The Spokane Tribe of Indians' water quality standards is even lower, at 1.37 ppq (0.00000000137 ppm) (Spokane Tribe of Indians, 2010). Discharges of pollutants to these waters is controlled by National Pollutant Discharge Elimination System (NPDES) permits. Discharges of PCBs upstream from the Spokane Tribe of Indians' reservation must still consider how that discharge impacts PCB levels when the water enters the reservation. Ecology is currently considering variances for five point source dischargers to the Spokane River (Ecology, 2019). A variance, if approved, would maintain an ultimate goal of achieving the water quality standard or the highest attainable condition for the Spokane River. However, achieving this goal would occur over a longer period of time in a stepwise process (Ecology, 2019).

Tribal Positions

Tribes can be more at risk of exposure to PCBs from inadvertent sources than the public at large. Tribal members often consume traditional diets high in fish and other aquatic organisms that accumulate PCBs. Exposure to PCBs has been linked to higher incidence of diabetes in tribal populations (Aminov, Haase, & Carpenter, 2016; Codru et al. & Akwesasne Task Force on the Environment, 2007). Elevated PCB exposure has also been correlated with cardiovascular disease (Goncharov et al. & Akwesasne Task Force on the Environment, 2008).

The National Tribal Toxics Council does not consider the 50 ppm iPCB allowance for pigments to be sufficient to be protective of human or environmental health (NTTC, 2013). In a comment letter to the EPA, the Confederated Tribes of the Umatilla Indian Reservation (CTUIR) requested that the level of iPCBs allowed be reduced to 0 ppm, specifically calling out dyes, pigments and inks (CTUIR, 2010). In this letter, CTUIR asserts pre-existing rights secured by treaty "of taking fish", including the necessity that the fish are safe to consume. While the SRRTTF is focused on the Spokane River, this issue impacts tribes in other parts of the nation as well.

Tribes also do not consider the EPA's guidance for deriving water quality standards, found in *Methodology for Deriving Ambient Water Quality Criteria for the Protection of Human Health* (EPA, 2000), to be sufficient to protect tribal health and tribal treaty rights (D. Barton, personal communication, June 6th, 2019). This methodology states: "*With AWQC derived for carcinogens based on a linear low-dose extrapolation, the Agency will publish recommended criteria values at a 10^{-6} risk level. States and authorized Tribes can always choose a more stringent risk level, such as 10^{-7}. EPA also believes that criteria based on a 10-5 risk level are acceptable for the general population as long as States and authorized Tribes ensure that the risk to more highly exposed subgroups (sportfishers or subsistence fishers) does not exceed the 10^{-4} level."* (EPA, 2000, pg. 1-12). As fish consumption is protected by treaty rights, tribes consider it a violation of their treaty to allow higher risk of adverse health effects for tribal populations who exert those rights and have higher fish consumption rates.

Stockholm Convention

The Stockholm Convention (Stockholm Convention, 2001)) is an international treaty adopted in 2001 and entered into force in 2004. The United States is not a party to the Stockholm Convention. PCBs are listed twice in the Stockholm Convention, both in Annex A, Elimination, Part I, and Annex C, Unintentional Production, Part I. The listing in Annex C is relevant to iPBCs in pigments. It requires Article 5 compliance, which dictates that each Party develop an action plan to reduce or eliminate releases from unintentional production. Article 5 includes the suggestion to promote the development and use of substitute materials, when appropriate.

The Stockholm Convention itself does not specify a particular limit on iPCBs in pigments. However, some individual parties, such as Canada, implementing the Convention have set a 50 ppm max limit and 25 ppm average limit on iPCBs (Canada, 2010). No discounting factors for PCBs with one or two chlorine atoms are considered in the Canadian rule. Canada is currently behind schedule on PCBs, including clean-up of legacy PCBs (P. Miller, personal communication, May 24, 2019).

Procurement policies

Both governments and businesses have developed and implemented procurement policies designed to address iPCBs in pigments (Table 3). Table 3 covers the limits set, testing required, products covered, implementation guidance, and current state of compliance. Governments include Washington State and the City of Spokane. Washington State has the most developed procurement policy that addresses iPCBs. ETAD, an association of pigment manufacturers, encourages best practices to limit iPCB levels. Some businesses have implemented procurement policies to limit the amount of PCBs. Overall, these policies are in their early stages. These businesses set standards and expect their suppliers to meet them. To date, suppliers have not indicated the levels set will be problematic, and the businesses are in the process of verification. Dell also has a procurement policy that could address iPCBs, but further research is needed to understand how it is applied.

Table 3. Government and business procurement policies addressing iPCBs in pigments.

Policy	**Washington State**	**City of Spokane**	**ETAD**	**HP**	**Apple**
PCB Limit	0 ppm	0 ppm	Meet regulations; encourages best practices	<0.1 ppm	<0.1ppm
Product level	Product purchased	Product purchased	Pigments	All products, verification at pigment level in progress	All products
Testing	Required	Optional	N/A	Upon request	Upon request
Products covered	All products likely to contain iPCBs, large purchases only; legislation includes all products	Ordinance does not specify which products; the intent is all products	Pigments	All products	All products
Guidance	Detailed guidance and training for procurement specialists, clear language in request for bids	Very little guidance developed, but request for bids included test method details	Identifies conditions likely to result in iPCB formation	Procurement specifications are detailed overall, but pigments/ iPCBs in progress	Procurement specifications are detailed overall, but pigments/ iPCBs in progress
Current status	Preference only; at least one bid successful (road paint) and one did not receive any testing results (food packaging)	Unenforced currently; first request for bids (deicer) received no bids	Level of compliance by members is unknown	Verification in progress; suppliers have not indicated that compliance will be an issue	Suppliers have not indicated that compliance will be an issue

Washington State

In 2014, Washington State passed the Preferable Purchasing Law requiring development and implementation of a procurement policy on PCBs in products and packaging (RCW 39.26.280). The Washington State Department of Enterprise Services (WA DES) developed the procurement policy in collaboration with the Washington State Department of Ecology. This policy is the most developed procurement policy to date.

Washington's policy applies large contracts; direct buy (smaller purchases) are not covered. The language for preference is included in solicitations for products and/or packaging that are likely to contain PCBs. These fall into three categories based on potential impact to the environment:

- Low risk. These products and/or packaging are unlikely to need testing.
- Moderate risk. These products and/or packaging may need testing. Consider the quantity being purchased and the relative cost of testing versus the cost of the product. Consider whether there is an alternative that is at a lower risk point.
- High risk. It is highly recommended to require testing. However, consider the amount of the product and whether or not there is an alternative at a lower risk point.

In addition, all three levels suggest that they request plain packaging if colored packaging is currently used. The moderate and high-risk level further suggest that procurement specialists should always inform the manufacturer if PCBs are a reason their product wasn't purchased.

There is no requirement to test, but testing improves the bid's score. The score includes considerations for societal benefit (e.g. local business preference), cost, and environmental benefit (e.g. no PCBs). For products for which PCB testing is required, a 5% added preference is scored for products with a certification of no PCBs (according to US EPA Analytical Method 1668c). Products containing relatively lower PCBs can receive a more general preference. This policy went into effect January 1, 2019.

WA DES developed accessible training and educational material to educate those involved in procurement:

- Documini explaining the motivation behind the legislation
- PCBs Risk Calculator for helping procurement professional assess products
- PCBs & Procurement Desk Aid providing step by step instructions for procurement professionals
- PCBs & Procurement eLearning
- WA State PCBs & Procurement Website

These tools are intended to educate procurement specialists on the highly technical nature of this policy.

WA DES used Washington State's Department of Transportation (WSDOT)'s master contract for paint materials to pilot the new procurement policy. The solicitation contained language explaining the new PCB preference, and prohibited certain pigments known to contain iPCBs. In response to the procurement solicitation, four vendors submitted bids. One vendor submitted test results from a third-party lab following EPA Method 1668c, and received the preference.

Three vendors met the specifications by not using the prohibited pigments but did not submit test results. A total of three of the four vendors were approved for purchases: The vendor that included test results, and two of the three vendors that did not. The fourth vendor was not approved. The preference provided to the vendor that submitted test results gave them a weighted score that resulted in their selection over this fourth vendor.

Notably, all of these paints contain titanium dioxide. The issue of iPCBs in titanium dioxide had not been brought up prior to this pilot and is currently being explored by SRRTTF in collaboration with titanium dioxide manufacturers (Heine, 2019). Currently, it is a requirement of the paints due to its ability to improve reflectivity of the paints, which allows people to see the lines better at night. The tested paint, with no detection of PCBs, also includes titanium dioxide, demonstrating that it is possible to have paints with titanium dioxide and no detection of PCBs.

A common challenge mentioned throughout discussions on WA's procurement policy was the language in the law around zero PCBs. This requirement led to the development of a policy that requires no detection of PCBs to the practical quantification limit. Using EPA 1668c, this limit varies depending on the medium, so it is not possible to provide a blanket limit for all products. In some cases, incremental improvements are possible now but achieving no PCBs is not. Similar to the perfect being the enemy of the good, there is concern that specifications requiring zero PCBs can disincentivize lower PCB products.

Another challenge is that there is no requirement for testing. All testing is voluntary. A manufacturer would have to determine that the benefit of preference in procurement is worth the expense of increased testing. Increasing the preference amount or identifying and publicizing other drivers may increase voluntary testing.

- Year implemented: 2019
- Driver for policy: Contamination of Spokane River, issues achieving water quality limits (main sponsor, Senator Billings, the legislator for Spokane)
- Products covered: All products except direct buys; language included in solicitations that are likely to contain PCBs
- Enforcement: Test results from accredited lab required for preference
- Challenges: “no PCBs” language difficult to define & does not reward low PCB products, testing is voluntary

City of Spokane

In 2014, the City of Spokane implemented a preference for products and products in packaging that do not contain PCBs (City of Spokane Municipal Code Section 07.06.172). This followed the passage of the law in Washington State, but went into effect in 2014 while the Washington State policy did not go into effect until 2019.

The Spokane policy indicates that when cost-effective and technically feasible, purchasers must select products or products in packaging that do not contain PCBs above the practical quantification limit. US EPA Method 1668 is specified for the practical quantification limit, but there is no requirement for testing every product. Cost effective means that compliance would not increase the price more than 25%.

Language has been included in one request for bids (RFB) in 2015 (City of Spokane, 2015). This RFB required testing following EPA Method 1668c or equivalent. No bids were submitted in response to this RFB. This negative experience led to dropping the PCB language in future RFBs (D. Greenlund, personal communication, April 25, 2019). While the City of Spokane language requires products to be free of PCBs, the Washington State language only requires a preference for PCB-free or lower PCB products.

- Year implemented: 2014
- Driver for policy: Contamination of Spokane River; struggles to meet water quality limits
- Products covered: Ordinance does not specify which products; intent is all. Was applied in initial RFB for deicer.
- Enforcement: Currently none
- Challenges: Lack of response to RFB including PCB language; presumed to be due to the presence of PCB language

Pigment manufacturers: ETAD Industry Association

The Ecological and Toxicological Association of Dyes and Organic Pigments Manufacturers (ETAD) position on iPCBs in pigments states that, while some pigments contain iPCBs, these trace levels are not hazardous and ETAD members use best available techniques to ensure that the generation of iPCBs is kept to a minimum (ETAD, 2011). This document did not identify what those techniques are. From communications with pigment specialists, however, pigment manufacturers view the precise process used to synthesize pigments as a trade secret.

According to ETAD, typical levels are usually less than 5 ppm, with occasional contamination up to 20 ppm. These levels are well within the regulatory limits. Further, the iPCBs are present both on the surface and in the interior of pigment crystals, and the interior iPCBs are unlikely to result in any exposure to humans or the environment. They also identify three signs that a pigment is likely to contain iPCBs:

1. The pigment contains chlorine as part of its molecular structure.
2. The raw materials for synthesizing the pigment contain chlorine.
3. Chlorine-containing aromatic solvents are used in their synthesis.

HP Inc.

HP Inc.'s procurement policy does not allow any intentionally added PCBs and restricts the level of inadvertent PCBs to <0.1ppm (HP Inc., 2018). HP Inc. established this limit based on benchmarking with other companies and a desire to have a lower control limit in place than the regulatory limit of 50 ppm current established under US TSCA (K. Brewer and C. Wray, personal communication, May 8 2019). This applies to all materials, including pigments and pigment-containing products. While all suppliers agree to these limits according to their contract, HP Inc. focuses compliance assurance on areas of highest risk. Currently, HP Inc. is requesting certification from pigment suppliers directly to provide additional assurance to printing customers. An additional driver was the need to support HP Inc. sales teams who have to respond to the Washington State procurement legislation passed in 2014 (RCW 39.26.280, discussed below).

- Year policy set: 2018
- Driver for policy: Quality assurance for print customers, Washington State procurement policy.
- Product level: Pigment itself, whole products as purchased
- Products applied to: Pigments at a higher risk to contain iPCBs, all products and packaging
- How enforced: All suppliers agree to General Specification for the Environment (GSE) and none have indicated that compliance with the iPCB limit is an issue. Some suppliers will be asked to certify that they meet the limit based on risk to the materials supplied; currently requesting certification from pigment and ink suppliers.
- Challenges: Managing the supply chain. While they are asking for additional testing or controls (which costs money), they want to maintain a good relationship with their supply chain.

Apple

Apple's procurement policy restricts PCBs to non-detect, which they define as <0.1 ppm (Apple, 2016). This applies to all materials. Apple does not require routine testing for PCBs in pigments or pigment containing products currently, but they do reserve the right to require analytical testing of any substance (Apple, 2018).

- Year policy set: 2018
- Product level: Homogeneous material; could be the pigment, but typically would be a material the pigment is incorporated into
- Products applied to: All products
- How enforced: Apple requires suppliers to follow the standards set in the Regulated Substances Specification (Apple, 2019)

Dell

Dell's Restricted Material's Guide limits PCBs to not detectable, but does not reference pigments (Dell, 2018). Further investigation should be completed to understand the intention of the limit and how it is currently being implemented.

Promising practices and innovation opportunities: Procurement and regulations

The current regulations are insufficient to reduce iPCB levels to those that are fully protective of tribal and vulnerable populations and the environment and that meet water quality limits in

Washington. Our review of current iPCB regulations and procurement policies reveals potential promising practices, as well as innovation opportunities.

Regulations

Regulations need to set specific limits and to be enforced to be effective. Many parties to the Stockholm Convention do not consider iPCBs and pigments in their local implementation. While the Stockholm Convention explicitly addresses inadvertent (unintentional) PCBs in Annex C, the issue of pigments and iPCBs is not addressed as a potential source (UNEP, 2008). Rather, "very few data on inadvertent generation of PCB exist" (UNEP, 2008, pg. 19). Even countries who do include iPCBs and pigments set the limits at 25-50 ppm, allowing continued inadvertent production of iPCBs. However, the Stockholm Convention does provide an opportunity to further disseminate information about pigments as a source of iPCBs and about strategies to reduce or eliminate the generation of iPCBs during pigment synthesis.

Regulations require verification and enforcement, or some actors may ignore them, inadvertently or intentionally. Japan determined that a number of pigments imported into the country had excessive (>50 ppm) levels of iPCBs, including both diarylide yellows and phthalocyanine greens. Reds, oranges, and browns were also implicated (METI, 2012). The extent to which diarylide yellows and phthalocyanine blues and greens in use in the U.S. or used in or on products in the U.S. exceed current regulations is unknown.

PCB limits

Both business and government procurement specialists and scientists involved in procurement limits on PCBs consider the "no PCB" limit implemented by Washington State to be problematic (K. Brewer and C. Wray, personal communication, May 8 2019). From a scientific perspective, no test can verify that a product is absolutely free of PCBs. It can only confirm that there are no PCBs at or above the limit of detection. With EPA Method 1668c, the limit of detection changes for every medium tested; it is different for PCBs in plastic compared to PCBs in water, for example. Further, PCB contamination is widespread, and even pigments that are not expected to generate PCBs during their synthesis may be contaminated at low levels. A practicable limit, such as the <0.1 ppm used by HP and Apple, may be more realistic considering current testing limitations than 0 ppm / non-detect.

Verification

Some form of verification is necessary to ensure that products meet the procurement standards. While testing is the best approach for ensuring compliance, smaller purchasers in particular should consider alternatives to testing, such as specifying pigments likely to contain no or ultra-low iPCBs. Procurement specialists should also consider the frequency of testing and the product level of testing.

Washington State's approach is to require testing using an EPA method. This test may be cost-prohibitive to some manufacturers. While a big purchaser like Washington State can require this kind of testing, a smaller purchaser like a city or county may not have sufficient financial pull to convince businesses to invest in this testing. These smaller purchasers may find success piggy-backing off of larger efforts. By copying Washington State's policy, a city or county can point to the greater financial opportunity of Washington State preference as a reason to comply. Similarly, a city or county could rely on a database of tested products, like the one Washington State is pulling together. For example, the City of San Francisco environmentally preferable procurement intends to consider the road paints tested for Washington State (C. Geiger, personal communication, May 24, 2019). If tested paints meet their performance standards, it is likely that the Washington State effort will spread to San Francisco and beyond.

Other considerations for testing:

1. How frequently should products be tested?
   Ideally, products should be tested on a regular basis to ensure no unexpected contamination and to verify that no changes have been made. They should also be tested any time the formulation changes. Practically, testing frequency will depend on the financial pull of the procurer.
2. What level of product should be tested?
   Testing at the pigment level functionally improves the limit of detection. Every further step, from dispersion to ink to product, decreases the concentration and the likelihood of detection of iPCBs that were present in the pigment. However, the targeted pigments may not be the sole source of PCB contamination in the final product.

An alternative to testing is to specify which pigments are permissible. Washington State also found success here with the road paint pilot. By disallowing diarylide yellows in yellow road paint, they eliminated a likely source of iPCB contamination. Even though only one company went through with the test to confirm, it is likely that all of the paints contain relatively lower iPCB contamination than road paints containing diarylide yellows.

Certifications

Some voluntary sustainability and material health certifications, such as Cradle to Cradle, Made Safe, and Sustainable Green Printing Certification, include restrictions on contaminants. Future certifications or revisions to these certifications could include restrictions on PCBs in products and/or packaging that would address the issue of iPCBs in pigments. Certifications can be preferred for procurement over setting limits for specific contaminants and requiring testing. Certifications enable procurement specialists to tackle complex technical issues, such as the issue of iPCBs in pigments, without requiring intensive training. Certifications can also be communicated to individuals involved in small purchasing more readily.

Supply chain engagement

Engaging the supply chain, preferably down to the level of the pigment manufacturer, is important for getting at the heart of iPCB formation in pigments. Pigment manufacturers control the processes used to synthesize the pigments that are manufactured into printing inks and used on newsprint and paper and paperboard packaging. Each step through the supply chain is further removed from the decisions about how to control iPCB generation during synthesis and about which pigment chemistries are used. A brand typically specifies use of a certain color palette, without regard to which pigment chemistries are used. And with each step, the iPCBs in the pigment are diluted and become more difficult to reliably and repeatedly detect.

However, engaging the supply chain can be challenging. Purchasers want to maintain positive relationships with suppliers. Suppliers may be recalcitrant to changing their processes or may be invested in specific pigment chemistries. Suppliers are typically expected to pay for testing without any anticipated increase in payment by the purchaser.

Availability

Currently, alternative yellow pigments may not be sufficiently available to switch away from diarylide yellows. Further research is needed to understand:

- the magnitude of substitution that is currently possible,
- the necessary actions to generate a greater supply of the alternatives, and
- the magnitude of substitution that would be possible given those actions.

Given these limitations, it may be necessary to consider which current uses of diarylide yellows are most likely to cause the worst exposure issues, and to prioritize those uses for alternatives. This prioritization is likely necessary even if it is possible to ramp up the supply of alternatives, as increasing supply will take time. Uses with fewer exposure issues can be replaced later as the supply increases.

Unified procurement policy

When every jurisdiction and business has a different procurement policy, it can be challenging for businesses to meet all of the varying requirements, and businesses may lack the incentive to do so for smaller purchasers. Harmonizing procurement policies to a single standard improves the ability of businesses to comply and increases the incentive to comply. A limitation of this approach is that concessions may be necessary to get diverse parties to agree to a unified policy, weakening the resulting policy.

Discussion

Efforts to realize the vision of the circular economy recognize the critical need to eliminate the use of hazardous substances in products. For example, one of the six characteristics of plastic packaging for a circular economy in the New Plastics Economy Vision of a Circular Economy for Plastic is that “All plastic packaging is free of hazardous chemicals … The use of hazardous chemicals in packaging and its manufacturing and recycling processes should be eliminated (if not done yet)” (New Plastics Economy, 2019). Eliminating iPCBs from pigments is necessary to fully realize the vision of circular newsprint, paper and paper packaging streams. This whitepaper identifies opportunities to reduce iPCBs in pigments through process controls, and to eliminate iPCBs in pigments by changing synthesis methods or by selecting alternative pigments. Additional research is necessary to implement this shift in pigment syntheses and use.

With thousands of tons of pigments used every year and a lengthy supply chain, this shift in pigment syntheses and use cannot happen universally, nor overnight. Insufficient raw materials are currently produced for some of these changes. Future research should include consideration of:

- the magnitude of substitution that is currently possible,
- the necessary actions to generate a greater supply of the alternatives, and
- the magnitude of substitution that would be possible given those actions

It will be necessary to prioritize the shift based on uses most likely to result in exposure (environmental and human). If pigment quantities remain insufficient despite efforts to increase the supply of raw materials, it may be necessary to consider other strategies including prioritizing industry sectors that may be able to do without certain colorants, or determining which industries can use iPCB-containing pigments with the least exposure potential.

This paper addresses yellow pigments and blue/green pigments commonly used in printing ink for newsprint and paper and paperboard packaging. Other colors of pigments are used for these purposes, such as reds, whites, and blacks. Further research is necessary to understand the extent of iPCB contamination in other pigment colors used for these applications. SRRTTF is currently undertaking some of this research by looking at iPCB contamination in titanium dioxide, used as a white pigment.

The hazards of PCBs are well-established, particularly for higher molecular weight PCBs such as those found in the phthalocyanine blues/greens. To reduce or eliminate iPCBs, we propose alternative synthesis processes, such as changing solvents during the synthesis of phthalocyanine blues/greens, and alternative pigments, such as certain monoazo yellows instead of diarylide yellows. The reagents and solvents may be hazardous themselves, or generate other unintended and undesirable byproducts. For example, some alternative solvents for the synthesis of phthalocyanine blues/greens are explosive. In theory, explosive reagents can be controlled and managed, avoiding any actual harm. In practice, industrial explosions do occur. It will be necessary to consider the hazards and exposure potentials of the currently used solvents and the alternatives, including physical properties such as explosivity in order to avoid regrettable substitutions.

The pigment industry and downstream users have risen to the challenge of phasing out hazardous cadmium, lead, and chromium pigments, improving human and environmental health with their innovation and diligence. What can we learn from these experiences? A scan back through history, some quite recent, may identify additional promising practices for encouraging this shift away from iPCB-containing pigments.

In order to address the suggestions, questions and challenges described above, a workshop pulling together the supply chain, users, recyclers and other disposers, and impacted communities is recommended and is being planned. This workshop will focus on solutions:

- What are the current technical challenges in switching pigments or synthesis methods? What research and development steps are needed to address these?
- Can process controls reduce iPCB levels sufficiently?
- What regulations or voluntary procurement policies can encourage adoption of no or low iPCB pigments? Is a unified procurement policy feasible?
- What further research is critical to understand potential unintended consequences of the proposed changes?

In order to address these challenges, individuals and organizations representing iPCBs and pigments across their life cycle should be involved, including the printing ink supply chain, brands, purchasers, and representatives of waste management and the environment (Appendix I). Some specific individuals and organizations have been identified in Appendix III as a starting list to use to identify potential expert speakers and participants. Due to the ubiquitous use of printed packaging and printed products, numerous companies could be engaged to represent brands and for purchasers. National brands have a large impact and the purchasing power to have greater influence than local brands. However, local brands may connect with the motivation and see opportunities to market as “Spokane River Safe” as more persuasive than national brands. With regards to government purchasers, waste management, and environmental representatives, we recommend focusing on those relevant and local to the Spokane River, though those outside of the region may have valuable perspectives to add and could address the national perspective. Inclusion of diverse perspectives throughout the life cycle of iPCBs and pigments contributes to the resilience, acceptance, and creativity of solutions discussed.

This workshop could culminate in the formation of workgroups to continue the discussions, and research and to propose and advance actionable solutions to reduce and eventually eliminate iPCBs in pigments associated with paper recycling processes. Together, these efforts will improve human and environmental health and help usher in a functional and colorful circular economy.

References

Apple. (2016). Apple Regulated Substances Specification 069-0135-J. Retrieved from https://www.apple.com/environment/pdf/Apple_Regulated_Substances_Specification_March2016.pdf

Apple. (2018). Apple Regulated Substances Specification 069-135-K. Retrieved from https://www.apple.com/environment/pdf/Apple_Regulated_Substances_Specification_Sept2018.pdf

Apple. (2019). Apple Environmental Responsibility Report, 2019 Progress Report, covering fiscal year 2018. Retrieved from https://www.apple.com/environment/pdf/Apple_Environmental_Responsibility_Report_2019.pdf

Aminov, Z., Haase, R., & Carpenter, D. O. (2016). Diabetes in Native Americans: Elevated risk as a result of exposure to polychlorinated biphenyls (PCBs). *Reviews on Environmental Health*, *31*(1), 115-119.

Canada. (2010). Response to letter, *Invitation to submit additional information related to quantities of a chemical occurring as unintentional trace contaminants in products and articles*. Retrieved from http://chm.pops.int/Default.aspx?tabid=1695

Capozzi, S. L., Jing, R., Rodenburg, L. A., & Kjellerup, B. V. (2019). Positive Matrix Factorization analysis shows dechlorination of polychlorinated biphenyls during domestic wastewater collection and treatment. Chemosphere, 216, 289-296.

City of Spokane. (2014). Spokane Municipal Code Section 07.06.172. Preference for Products and Products in Packaging That Does Not Contain Polychlorinated Biphenyls.

City of Spokane. (2014). Ordinance C35099. 0320 PCB Product & Products in Packaging Procurement Policy.

City of Spokane. (2014). Environmentally Preferable Purchases Admin 5600-14-07, LGL 2010-0027. Revision Effective Date: November 18, 2014. Retrieved from http://www.responsiblepurchasing.org/resources/policies/city/spokane_2014.pdf

City of Spokane. (2015). Request for Bids #4165-15, Description: Corrosion inhibited liquid magnesium chloride.

Codru, N., Schymura, M. J., Negoita, S., Rej, R., Carpenter, D. O., & Akwesasne Task Force on the Environment. (2007). Diabetes in relation to serum levels of polychlorinated biphenyls and chlorinated pesticides in adult Native Americans. *Environmental health perspectives*, *115*(10), 1442-1447.

Confederated Tribes of the Umatilla Indian Reservation (CTUIR) Department of Natural Resources Administration (DNR). (2010). Re: CTUIR DNR Comments on Docket ID No. EPA-HQ-OPPT-2009-0757, Polychlorinated Biphenyls (PCBs); Reassessment of Use Authorizations (Federal Register/Vol. 75, No. 66/Wednesday, April 7, 2010/Proposed Rules) [Letter written to Office of Pollution Prevention and Toxics (OPPT), U.S. Environmental Protection Agency (EPA)]. Retrieved from http://www.zendergroup.org/nttc/UmatillaCommentToANPRMonPCBs.pdf

Dell. (2018). Materials Restricted for Use. Retrieved from https://i.dell.com/sites/doccontent/corporate/corp-comm/en/Documents/restricted_materials_guid_us.pdf

Des Ligneris, M. J. (1940). Precancer and carcinogenesis. *The American Journal of Cancer*, *40*(1), 1-46.
Dyke, P. H. (2005). PCB and PAH Releases from Incineration and Power Generation Processes. Almondsbury, Bristol, U.K. Retrieved from https://assets.publishing.service.gov.uk/government/uploads/system/uploads/attachment_data/file/290401/sp4-052-tr-e-e.pdf
Ecological and Toxicological Association of Dyes and Organic Pigments Manufacturers (ETAD). (January, 2011). ETAD position on the presence of traces of PCBs in some organic pigments. Retreived from https://etad.com/en/component/attachments/?task=download&id=78:2011_etad-position-on-the-presence-of-pcbs-in-pigments
Ecology. (November 2015). Polychlorinated Biphenyls in Consumer Products. Retrieved 6/6/2019 from https://fortress.wa.gov/ecy/publications/SummaryPages/1604014.html
Environmental Protection Agency (EPA). (2000). Methodology for Deriving Ambient Water Quality Criteria for the Protection of Human Health. Retrieved 6/7/2019 from https://www.epa.gov/sites/production/files/2018-10/documents/methodology-wqc-protection-hh-2000.pdf
Environmental Protection Agency (EPA). (1979). PCB regulation. Retrieved from https://archive.epa.gov/epa/aboutepa/epa-bans-pcb-manufacture-phases-out-uses.html.
Environmental Protection Agency (EPA). (1982). Economic Analysis for the final rule to exclude closed and controlled processes from the PCB ban. Office of Pesticides and Toxic Substances, U.S. Environmental Protection Agency, Washington, D.C.
Environmental Protection Agency (EPA). (2016). Summary of the Toxic Substances Control Act. Retrieved from https://www.epa.gov/laws-regulations/summary-toxic-substances-control-act.
Environmental Protection Agency (EPA). (2019) About PCBs. Retrieved from https://www.epa.gov/pcbs/learn-about-polychlorinated-biphenyls-pcbs.
Food and Agriculture Organization of the United Nations (FAO). (April 2, 2008). Dioxins in the food chain. Prevention and control of contamination. Retrieved from http://www.fao.org/uploads/media/FAO_Fact_Sheet_020408.pdf
Geissdoerfer, M., Savaget, P., Bocken, N. M., & Hultink, E. J. (2017). The Circular Economy–A new sustainability paradigm?. *Journal of cleaner production*, *143*, 757-768.
Goncharov, A., Haase, R. F., Santiago-Rivera, A., Morse, G., McCaffrey, R. J., Rej, R., ... & Akwesasne Task Force on the Environment. (2008). High serum PCBs are associated with elevation of serum lipids and cardiovascular disease in a Native American population. *Environmental Research*, *106*(2), 226-239.
Guo J, Capozzi, S.L, Kraeutler, T.M., and Rodenburg, L.A. (2014) Global Distribution and Local Impacts of Inadvertently Generated Polychlorinated Biphenyls in Pigments. Environmental Science and Technology, 48, 8573-8580.
Heine, L.H. and Trebilcock, C. (October 16, 2018). Inadvertent PCBs in Pigments: Market Innovation for a Circular Economy. Published by Northwest Green Chemistry for the SRRTTF.
Heine, L.H. and Pavlick, R. (February 27, 2019). The Potential for Generating Inadvertent PCBs through TiO_2 Manufacturing Using the Chloride Process. Published by Northwest Green

Chemistry for the SRRTTF. Retrieved from http://srrttf.org/wp-content/uploads/2019/02/5b-SRRTTF-TiO2-2019_02_18.pdf

Herbst, W. and Hunger, K. (2004) Industrial Organic Pigments, 3rd edition. Hofheim, Germany. Verlag GmbH & Co. KGaA Weinheim.

HP Inc. (2018). HP Standard 011 General Specification for the Environment HX-00011-00. Retrieved from http://h20195.www2.hp.com/v2/getpdf.aspx/c04932490.pdf

Hickie, B.E., Ross, P.S., Macdonald R.W., and Ford, J.K.B. (2007). Killer Whales (Orcinus orca) Face Protracted Health Risks Associated with Lifetime Exposure to PCBs. Environmental Science & Technology 2007 41 (18), 6613-6619. DOI: 10.1021/es0702519

Japan Ministry of Economy, Trade, and Industry (METI). (2012). Administrative Guidance for Manufacture/Import etc., of Organic Pigments Containing By-product PCBs. Retrieved 5/30/2019 from https://www.meti.go.jp/policy/chemical_management/english/cscl/files/publications/review/guidance_for_pigments_120213.pdf

National Tribal Toxics Council (NTTC). (2013). PCBs in Everyday Items. Retrieved from http://tribaltoxics.org/?page_id=300655

New Plastics Economy. (2019). New Plastics Economy Global Commitment Spring 2019 Report. Retrieved from https://www.ellenmacarthurfoundation.org/assets/downloads/GC-Report-Summary.pdf

National Institute of Occupational Safety and Health (NIOSH). (Page last reviewed November 29, 2018). NIOSH pocket guide to chemical hazards. Entries on chlorodiphenyl (54%) and chlorodiphenyl (42%) are accessed here: https://www.cdc.gov/niosh/npg/npgd0126.html and here: https://www.cdc.gov/niosh/npg/npgd0125.html

Öman, C. B., & Junestedt, C. (2008). Chemical characterization of landfill leachates – 400 parameters and compounds. Waste Management, 28(10), 1876–1891. https://doi.org/10.1016/J.WASMAN.2007.06.018

Plísková , M, et al. "Impact of polychlorinated biphenyls contamination on estrogenic activity in human male serum." Environmental Health Perspectives (2005). <https://openi.nlm.nih.gov/detailedresult.php?img=PMC1281266_ehp0113-001277f1&req=4>

Rodenburg, Lisa, Jia Guo and Robert Christie. (2015) "Polychlorinated biphenyls in pigments:" *Coloration Technology*. Retrieved from https://ecology.wa.gov/DOE/files/5e/5eba04f9-d41f-4e9f-ad9c-a98a01a431ca.pdf

Schwartz, L. (1936). Dermatitis from synthetic resins and waxes. *American Journal of Public Health and the Nations Health*, *26*(6), 586-592.

Southern Resident Orca Task Force. (November 16, 2018). Southern Resident Orca Task Force Report and Recommendations. Retrieved 6/6/2019 from https://www.governor.wa.gov/sites/default/files/OrcaTaskForce_reportandrecommendations_11.16.18.pdf

Spokane Tribe of Indians. (February 25, 2010) Water Quality Criteria for Toxic Pollutants in the Spokane Tribe of Indians Surface Water Quality Standards, February 25, 2010, Resolution 2010-173. Retrieved 5/30/2019 from

http://www.spokanetribe.com/upload/FCKeditor/Final%20Revised%20Water%20Quality%20Standards.pdf
Stockholm Convention. (May 22, 2001). Stockholm Convention of persistent organic pollutions. Retrieved from http://www.pops.int/TheConvention/Overview/TextoftheConvention/tabid/2232/Default.aspx
United Nations Environment Programme (UNEP). (2008). Guidelines on Best Available Techniques and Provisional Guidance on Best Environmental Practices relevant to Article 5 and Annex C of the Stockholm Convention of Persistent Organic Pollutants, Specific chemical production processes releasing chemicals listed in Annex C.
Versar, Inc. (May 16, 1978). Microeconomic Impacts of the Proposed ‘PCB Ban Regulations’, Final Task Report. Submitted to US EPA.
Washington Legislature. (2014). RCW 39.26.280. Preference—Products and products in packaging that does not contain polychlorinated biphenyls—Limitations—Products and products in packaging containing polychlorinated biphenyls.
Washington State Department of Ecology (Ecology). (2015). PCB Chemical Action Plan. Action Plan. Olympia, WA: Washington State Department of Ecology. Online. 2018. https://fortress.wa.gov/ecy/publications/documents/1507002.pdf
Washington State Department of Ecology (Ecology) (2019). Updates to the surface water quality standards. Retrieved from https://ecology.wa.gov/water-shorelines/water-quality/water-quality-standards/updates-to-the-standards
Washington State Department of Ecology (Ecology) (June 12, 2019). WSR 19-13-030, Preproposal Statement of Inquiry, CR-101 (October 2017) (Implements RCW 34.05.310). Retrieved from https://ecology.wa.gov/DOE/files/35/35e31cb8-7c0a-4ad3-b63c-69b3b7f62a70.pdf
Washington State Department of Enterprise Services. (2018). PCBs Preference in Procurement - Desk Aid. Retrieved from https://des.wa.gov/sites/default/files/public/documents/About/Procurement_reform/training/CourseResourcesJobAids/PCB/PCBsPreferenceDeskAid.pdf?=f7b99
Washington State Department of Enterprise Services. (2018). Enterprise Services Policy No. POL-DES-280-00. Purchasing Preference for Products and Product Packaging That Do Not Contain Polychlorinated Biphenyls (PCBs). Retrieved from https://des.wa.gov/sites/default/files/public/documents/About/Procurement_reform/Policies/DES-280-000PCB.pdf?=8e816
Washington State Department of Enterprise Services. (2018). PCBs risk calculator. Accessed on 3/5/2019 at https://des.wa.gov/sites/default/files/public/documents/About/Procurement_reform/training/NonStateEmp/PCB/RiskCalculator/story_html5.html
Washington State Department of Enterprise Services (2018). Documini: PCBs documentary. Viewed 5/14/2019 at https://youtu.be/EZOQdBr1dyc
Washington State Department of Enterprise Services (2018). PCBs & Procurement training. Accessed on 5/14/2019 at https://des.wa.gov/services/contracting-purchasing/policies-training/contracts-procurement-training-development/contract-management-training-program/pcbs-procurement-training

Washington State Department of Environmental Services (2019). PCBs & Procurement eLearning. Access on 5/14/2019 at https://des.wa.gov/sites/default/files/public/documents/About/Procurement_reform/training/NonStateEmp/PCB/story_html5.html

Washington State Office of the Attorney General. (June 6, 2019). *AG Ferguson Sues Trump Administration Over Reversal of Water Quality Protections* [Press Release]. Retrieved 6/7/2019 from https://www.atg.wa.gov/news/news-releases/ag-ferguson-sues-trump-administration-over-reversal-water-quality-protections

Appendix I: Landscape Analysis of Players in the Pigment and Printing Ink Supply Chain across the Life Cycle

Some organizations fit within multiple categories. For example, HP is both a brand and a printing ink manufacturer. Many pigment manufacturers may also manufacture dispersions.

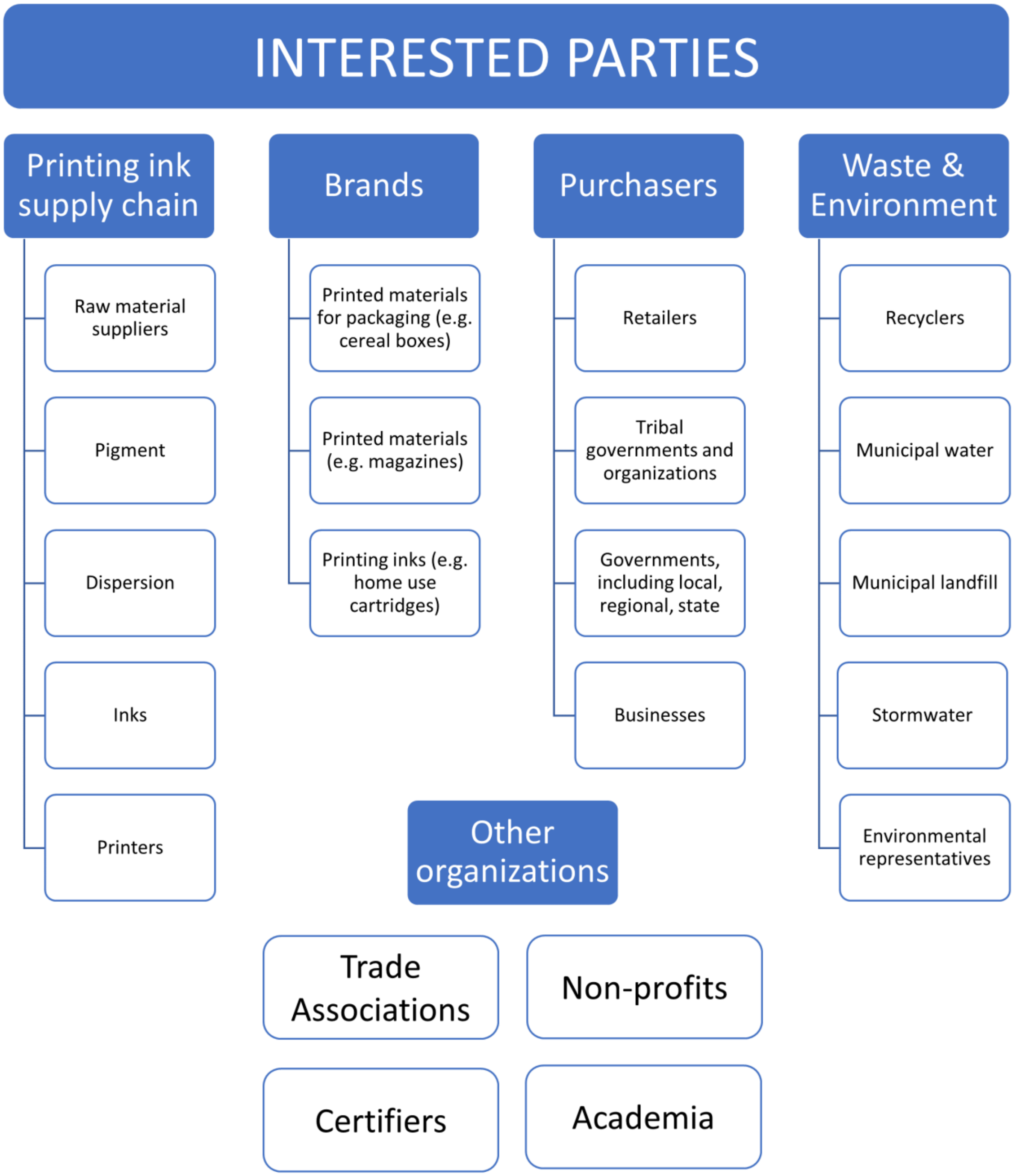


Figure 9. Players in the iPCB, pigment, and printing ink life cycle.

Appendix II: Individuals Interviewed

For this work, we conducted interviews to understand the current landscape of the printing ink supply chain and lifecycle (Table 4), including pigment/dispersion manufacturers, brands using printed materials for packaging, brands selling printing inks, local and state governments, non-governmental advocacy organizations, and businesses.

Table 4. Individuals interviewed for this report.

Category	Organization	Name
Pigment manufacturer	Clariant	Romesh Kumar
	Anonymous	Anonymous
Printers, Brand / packaging, trade association	Sustainable Green Printing Partnership / Specialty Graphic Imaging Association	Marcia Kinter and Gary Jones
Brand / inks, packaging	Apple	Chris Flanders
	HP Inc.	Kathy Brewer and Curtis Wray
Tribal governments and organizations	Columbia River Inter-Tribal Fish Commission	Dianne Barton, https://www.critfc.org/
Government	Washington State Department of Ecology	Tina Simcich
	Washington State Department of Enterprise Services	Christine Warnock, Farrell Presnell, and Sundae Delgado
	Washington State Department of Transportation	Elsa Pond and Doug McClanahan
	City of Spokane	Doug Greenlund
	City of San Francisco	Chris Geiger
Environment, non-profit	Alaska Community Action on Toxics	Pam Miller

Appendix III: Individuals and Organizations Recommended to Consider as Potential Participants in Collaborative Work

We identified individuals and organizations who could be valuable contributors and participants in future work (Table 5).

Table 5. Interested parties identified relating to the pigment and printing ink supply chain and life cycle.

Category	Organization	Name / website
Printing Ink Supply Chain		
Pigment manufacturer, trade association	Color Pigment Manufacturers Association, CPMA	David Wawer, https://www.pigments.org/
	Ecological and Toxicological Association of Dyes and Organic Pigments Manufacturers, ETAD	https://etad.com/
Pigment manufacturer	Clariant	Romesh Kumar, https://www.clariant.com/en/Business-Units/Pigments
	BASF	Steve Camenisch, https://www.basf.com/us/en/legal/contact.html
	Lanxess	http://lanxess.us/lanxess-in-the-usa/contact/
	DIC	http://www.dic-global.com/en/products/pigments/
	Heubach	https://www.heubachcolor.com/about-heubach/contact/
	Sun Chemical	Robert Mott, https://www.sunchemical.com/contact-us/
	Aakash	http://aakashchemicals.com/contact-us/
	Alex Color	http://www.alexcolor.com/contact.php
	Ferror	https://www.ferro.com/contact
	Trustchemusa	http://www.trustchemusa.com/contact
	Dominion Color	https://www.dominioncolour.com/distributors/canada
	Apollo Colors, Inc.	http://apollocolors.com/site/
	Flint Group	http://www.flintgrp.com/
	Shepherd Color Company	https://www.shepherdcolor.com/
Printing Ink Supply Chain		

Category	Organization	Name / website
Pigment manufacturer	Bruchsaler Farben	https://www.bruchsaler-farben.de/en/home/
	Lansco Colors	http://www.pigments.com/
	Tomatec	https://www.tomatec.com/
Printing ink manufacturer, trade association	National Association of Printing Ink Manufacturers, NAPIM	George Fuchs, https://www.napim.org/
Printing ink manufacturer	Actega North America, Inc	http://www.actega.com/wit.html
	Alden & Ott Printing Inks LP	http://www.aldenottink.com/
	Braden Sutphin Ink Co.	http://www.bsink.com/
	Central Ink Corp.	http://www.cicink.com/
	Chromatic Technologies, Inc.	http://www.ctiinks.com/
	Colorcon, No-Tox Products	http://www.colorcon.com/notox
	Graphix Essentials	http://www.graphixessentials.com/gex/contactUs.jsp
	Grand Rapids Printing Ink	http://www.grpi.net/
	Flint Group	http://www.flintgrp.com/
	Gans Ink and Supply Co., Inc.	http://www.gansink.com/
	Gotham Ink & Color	http://gothaminks.com/
	Grand Rapids Printing Ink	http://www.grpi.net/
	Hi-Tech Color, Inc.	http://www.htcolor.com/Welcome.html
	hubergroup North America	http://hubergroup.net/
	Hongtu Industry	http://www.cqink.com/
	Ink Systems, Inc.	http://www.inksystemsinc.com/
	INX International Ink Co.	http://www.inxinternational.com/
	Joules Angstrom U.V. Printing Inks Corp.	http://www.joulesangstrom.com/
	R.A.Kerley Ink Engineers, Inc.	http://www.kerleyink.com/
	LioChem	http://www.liochem.com/
Printing Ink Supply Chain		

Category	Organization	Name / website
Printing ink manufacturer	Magnum Inks & Coating	http://www.magnuminks.com/
	Mallard Ink Co., Inc.	http://mallardink.net
	Megami Ink Mfg. Co., Ltd - U.S. Branch	http://www.megamiink.com/
	Optihue® Inks	http://www.ipaper.com/
	Press Color, Ink.	http://www.presscolorinks.com/
	Siegwerk USA Co.	http://www.siegwerk.com/
	Spinks Ink Company	https://spinksinks.com/
	Sun Chemical Corporation North American Inks	http://www.sunchemical.com/
	Superior Printing Ink Co., Inc.	http://www.superiorink.com/
	Toyo Ink America, LLC.	http://www.tia.toyoink.com/
	US Ink	http://www.usink.com/
	Wikoff Color Corporation	http://www.wikoff.com/
Printers, trade association	Specialty Graphic Imaging Association	Marcia Kinter and Gary Jones, https://www.sgia.org/
	Brands	
Brand / packaging, trade association, certifier	Sustainable Green Printing Partnership	Marcia Kinter and Gary Jones, http://sgppartnership.org/
Inks / packaging	Apple	Chris Flanders, https://www.apple.com/
	HP Inc.	Jim Kildea, Kathy Brewer, and Curtis Wray, https://www8.hp.com/us/en/home.html
	Canon	https://www.usa.canon.com/internet/portal/us/home
	Epson	https://epson.com/usa
	Brother	https://www.brother-usa.com/
	Lexmark	https://www.lexmark.com/en_us.html
	Dell	https://www.dell.com/
	Xerox	https://www.xerox.com/
	Samsung	https://www.samsung.com/us/
	Konica-Minolta	https://www.konicaminolta.com/us-en/index.html
	OKI Data	https://www.oki.com/us/printing/
Printed materials, trade association	News Media Alliance of America	Paul Boyle, https://www.newsmediaalliance.org/

Brands

Category	Organization	Name / website
Printed Materials, trade association	Allied Daily Newspapers of Washington	Rowland Thompson, Melissa Gombosky
Printed materials	Spokesman Review	Rick Sant, http://www.spokesman.com/
	Purchasers	
Retailers	Local Spokane retailers	
Tribal governments and organizations	Columbia River Inter-Tribal Fish Commission	Dianne Barton, https://www.critfc.org/
Tribal government	Spokane Tribe of Indians	Brian Crossley and Ted Knight, https://www.spokanetribe.com/
Government / State	Washington State Department of Ecology*	Karl Rains, Adriane Borgias, and Ken Zarker, https://ecology.wa.gov/
	Washington State Department of Enterprise Services	Christine Warnock, Farrell Presnell, and Sundae Delgado, https://des.wa.gov/
	Washington State Department of Transportation*	Tammie Williams, Elsa Pond, and Doug McClanahan, https://www.wsdot.wa.gov/
Government / Local	City of Spokane*	Doug Greenlund, https://my.spokanecity.org/
	City of San Francisco	Chris Geiger, https://sf.gov/
	City of Post Falls, Idaho*	Craig Borrenpohl and John Beacham, https://www.postfallsidaho.org/
	Waste and Environment	
Recyclers	Inland Empire Paper*	Doug Krapas, http://iepco.com/
Municipal water	Liberty Lake Sewer and Water District*	Tom Agnew and BiJay Adams, http://libertylake.org/
	Hayden Area Regional Sewer Board*	Ken Windram, http://www.harsb.org/
Stormwater	County of Spokane: Utilities, Stormwater*	Rob Lindsay, Mike Hermanson, and Ben Brattebo, https://www.spokanecounty.org/918/Stormwater-Utility
	City of Spokane: Wastewater / Stormwater*	Cadie Olsen, Jeff Donovan, Elizabeth Schoedel, and Mike Coster, https://my.spokanecity.org/publicworks/stormwater/

Category	Organization	Name / website
	Waste and Environment	
Environmental / non-profit	The Lands Council*	Mike Petersen and Amanda Parrish, https://landscouncil.org/
	Lake Spokane Association*	Galen Buterbaugh and Greg Weeks, http://www.lakespokaneassociation.org/
	Spokane Riverkeeper*	Jerry White, Jr. and Lydia Newell, https://www.spokaneriverkeeper.org/
	Kootenai Environmental Alliance*	Dennis Brueggemann and Mike Zagar, http://kealliance.org/
	Alaska Community Action on Toxics	Pam Miller, https://www.akaction.org/
	Northwest Green Chemistry	Lauren Heine, Amelia Nestler, and Anna Montgomery, https://www.northwestgreenchemistry.org/
	Other	
Academia	Researcher studying iPCBs	Lisa Rodenburg, https://eoas.rutgers.edu/about/faculty-directory/lisa-rodenburg/
	Researcher studying persistent organic pollutants, including iPCBs	Keri Hornbuckle, https://hornbuckle.lab.uiowa.edu/
Certifiers	Cradle to Cradle Products Innovation Institute	Matteo Kausch, https://www.c2ccertified.org/
	Green Electronics Council	https://greenelectronicscouncil.org/
	International Electrotechnical Commission	https://www.iec.ch/
	Made Safe	https://www.madesafe.org/
Member of the Spokane River Regional Toxics Task Force		

Appendix IV. Additional Standards and Regulations addressing PCBs

Other water standards: The ambient water criterion for PCBs in navigable waters is 0.001 µg/L (40 CFR § 129.105) (0.000001 ppm, 1 ppq). For drinking water, the maximum contaminant level goal for PCBs is 0 (40 CFR § 141.50). The enforceable maximum contaminant level for PCBs in public water systems is 0.0005 mg/L (40 CFR § 141.61) (0.0005 ppm, 500 ppq).

Other environmental release: Under the National Contingency Plan, all spills involving 1 pound or more PCBs by weight must be reported to the National Response Center. EPA reporting and clean-up requirements are detailed under 40 CFR § 761.125.

Food standards: The Food and Drug Administration (FDA) recognizes that PCBs have become a ubiquitous contaminant in the environment, resulting in certain foods and animal feeds unavoidably containing PCBs (21 CFR § 109.30). Tolerances range from 0.2 ppm (infant and junior foods) to 3 ppm (poultry, fat basis), with an additional tolerance for paper food-packaging material at 10 ppm. The tolerance for fish and shellfish is 2 ppm. Internationally, the Joint Food and Agriculture Organization of the United Nations (FAO)/World Health Organization (WHO) Expert Committee on Food Additives set the provisional tolerable monthly intake of PCBs and dioxins to 70 pg/kg body weight in 2001 (FAO, 2008). They use a monthly intake as opposed to the more commonly reference daily intake due to the long half-lives of PCBs and dioxins.

Workplace: The Occupational Safety and Health Administration (OSHA) regulates workplace exposure to two Arochlor® PCB mixtures: Arochlor® 1242 with 42% chlorine (CASRN 53469-21-9) and Arochlor® 1254 with 54% chlorine (CASRN 11097-69-1) (29 CFR § 1910.1000, Table Z-1). The Permissible Exposure Limits (PELs) are 1 and 0.5 mg/m^3 respectively and are 8-hour time weighted averages. The National Institute of Occupational Safety and Health advisory limits for both mixtures are0.001 mg/m^3 and are 10-hour time weighted averages (NIOSH, 2018).