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Review

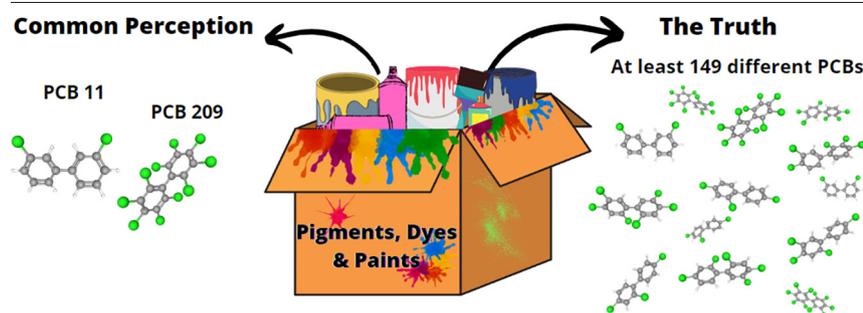
A review of the mechanisms of by-product PCB formation in pigments, dyes and paints

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HIGHLIGHTS

- 149 different PCBs identified in pigments, dyes and paints.
- Total PCB concentrations recorded as high as 919 mg kg⁻¹.
- PCB profiles in pigments, dyes and paints can be variable and highly complex.
- Congener profiles from 140 different samples compiled in one place.

GRAPHICAL ABSTRACT



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ABSTRACT

There has been an increased awareness of paints and pigments as a source of by-product PCBs in the environment. The majority of existing work has focused only on reporting the presence of the main PCBs in different products with a specific focus on the most PCB congeners, PCB11 and PCB209. This gives the impression that only a handful of PCBs are found in paints. However, this is not the case. PCB profiles in paints and pigments can be just as complex as commercial technical mixtures. This review identified the presence of 149 different PCBs in paint samples. For reference, only 141 different PCBs have been reported in all of the 5 main commercial Aroclor formulations (A1016, A1242, A1248, A1254 (early & late) and A1260). The total PCB concentrations in some paint samples can be substantial, with concentrations as high as 919 mg kg⁻¹ reported in azo pigments. When trying to identify sources of PCBs in the environment, pigments, dyes and paints are often overlooked. In this manuscript, we have compiled congener profiles from 140 different samples from the available scientific literature and presented this in the supplementary information as valuable resource for others to use in source identification applications. We have also proposed detailed mechanisms for the formation of PCBs in pigments, dyes and paints. In many cases, the PCB congeners predicted by these mechanisms provide an excellent match for what has been observed in the scientific literature. We have also identified several additional classes of pigments that are expected to contain PCBs but have yet to be verified by experimental data.

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1. Introduction

Polychlorinated biphenyls (PCBs) are anthropogenic organic chemicals with a biphenyl structure substituted with one to ten chlorines. Due to the multiple positions of substitution, there are 209 different PCBs, commonly referred to as congeners and numbered based on the amount and position of the chlorines (Ballschmitter and Zell, 1980; Guitart et al., 1993). PCBs were produced as commercial mixtures that have historically been used for a variety of applications including in transformers, capacitors, paints, and carbonless copy paper (Markowitz, 2018). However, due to their toxicity and persistence in the environment, the use of commercial mixtures of PCBs has been phased out and they are no longer intentionally manufactured (Markowitz, 2018; Erickson, 2001). PCBs are classified as persistent organic pollutants (POPs) along with several other compounds and thus their use and manufacture is restricted worldwide (Erickson, 2001). PCBs were commercially produced under the trade name Aroclor in the United States, and various other names (e.g. Clophen, Phenoclor, Kanechlor and Sovol) in other parts of the world (Markowitz, 2018). These commercial mixtures contained specific PCB congener patterns allowing easy identification from each other or other PCB sources. Many regulations exist controlling the levels of PCBs in water, soil, and various products due to their toxicity to humans and other organisms (Markowitz, 2018; IPCS, 2003; IPCS, 1993). Although PCBs are no longer produced for commercial purposes, they may be formed as by-products in other chemical processes. Regulations controlling emissions of these by-product PCBs vary across the world with some specific countries (e.g. U.S.A.) allowing ‘some inadvertent generation of PCBs to occur in excluded manufacturing processes’ (U.S. EPA, 2021). Interestingly the U.S. regulations for release of wastewater containing by-product PCBs are far less stringent than for release of wastewater containing Aroclor commercial mixtures. For by-product PCBs, the regulations are based on any one PCB congener with 100 µg/L (100 ppb) for wastewater or 2 µg/g (2000 ppb) per resolvable gas chromatographic peak for any product or waste. The clean water act in the US has total PCB concentration (sum total PCBs or total Aroclors) water quality criteria based on chronic exposure through drinking water and fish ingestion of 79 pg/L (0.000079 ppb) (U.S. EPA, 2019). This large discrepancy in criteria concentrations may provide insight into how by-product PCB concentrations are increasing in importance in comparison to commercial PCB mixtures.

As the use and environmental levels of PCB technical mixtures declined worldwide, the relevance of by-product PCBs to environmental contamination has increased. These by-product PCBs have been called many different names in the scientific literature: incidental PCBs (i-PCBs), inadvertent PCBs (i-PCBs), and unintentional PCBs (u-PCBs). The production of these PCBs is not a desired outcome of the chemical synthesis that generated them. They are accidentally produced leading to the various names listed above. They are all by-products (impurities) of chemical reactions.

Therefore, they will be referred to by the common term by-product PCBs throughout this paper. By-product PCBs have been detected in a wide range of environmental samples (Basu et al., 2009; Hu and Hornbuckle, 2010; Hu et al., 2011; Guo et al., 2014; Vorkamp, 2016; Bartlett et al., 2019; Megson et al., 2019; Megson et al., 2021; Anezaki et al., 2016). By-product PCBs may be produced from a variety of industrial sources including waste incineration (Ikonomou et al., 2002; Li et al., 2017; Pandelova et al., 2006), the operation of engines (Cheruiyot et al., 2017), and various other industrial processes including waste water treatment (Munoz, 2007). Significant recent attention has been paid to by-product PCB production from pigments, paints, and dyes. This includes products which are present in commercial mixtures of paints as they contain a variety of different chemical constituents (Bieleman, 2008; Freitag and Stoye, 2008). Recent studies have found high levels of PCBs in pigments, indicating that this may be a noteworthy environmental concern (Anezaki et al., 2015; Anezaki and Nakano, 2014; Hu and Hornbuckle, 2010; Jahnke and Hornbuckle, 2019; Shang et al., 2014). A review on how these PCBs can enter the environment has been provided by Anh et al. (2021).

Pigments are materials which are used as colorants in paints and other products and are generally insoluble in the medium in which they are applied (Herbst and Hunger, 2004).. A variety of different pigments have been associated with by-product PCBs including; azo pigments, phthalocyanine pigments, diketopyrrolo pyrrole (DPP) pigments, dioxazine pigments, and titanium dioxide (Vorkamp, 2016).

Dyes are colorants which in contrast to pigments are generally soluble in the medium in which they are applied (Hunger, 2007). Dyes usually have similar chromophores to those found in pigments, with additional functional groups to make these compounds more suitable for use as dyes. These functional groups are usually charged, with groups such as sulfonic acids commonly used to make the dyes water soluble. Common chromophores in dyes include azo, phthalocyanine, and dioxazine (Hunger, 2007). We were unable to identify any studies in the scientific literature where dyes were tested for by-product PCB formation. However, due to their structural similarities to pigments they are suspected to contain by-product PCBs and so will be investigated in this manuscript.

Paint refers to pigmented coatings which are applied to a surface, with the more general term coating also referring to non-pigmented materials such as varnishes (Freitag and Stoye, 2008). As paints and coatings are used for a wide variety of purposes on different surfaces, there are many different possible chemical components of paint. The components of paint are often classified as belonging to one of four major groups: binders, plasticizers, pigments and additives. Binders, sometimes called resins, are macromolecular compounds which affix the paint to the surface, and are therefore usually the most important and largest component of paints (Freitag and Stoye, 2008). Plasticizers are usually organic liquids which are present to help form films, however, most modern binders also act as

plasticizers and so are not often used (Freitag and Stoye, 2008). Pigments or extenders are responsible for the color of paints, they are normally solids dispersed in the paint medium. Paint additives comprise of a wide variety of chemicals added in small portions to alter the properties of the paint product (Bieleman, 2008).

Although the formation of by-product PCBs in pigments has been recently reviewed (Rodenburg et al., 2015; Anh et al., 2021; Vorkamp, 2016; Grossman, 2013), this manuscript provides a more detailed understanding of the mechanisms of PCB formation in pigments, dyes, and paints. It also comprehensively lists all PCBs recorded in samples rather than focusing on the major PCBs present (Supplementary information). This was performed by searching both the scientific literature and wider “grey” literature. This manuscript aims to explain why we see the specific PCBs we do in different products and also aims to identify if there are other potential sources of by-product PCBs in pigments, dyes and paint products that have not been identified to date.

2. Methodology

A systematic review of the available literature was performed using the following search terms on SciFinderⁿ and Google Scholar; “‘PCB’ AND ‘paint’ OR ‘dye’ OR ‘pigment’”. This resulted in a total of 508 manuscripts for review on SciFinderⁿ and several thousands on Google Scholar. Due to the large number of non-relevant papers returned by Google Scholar the review focused on papers returned in the SciFinderⁿ search. This information from the scientific literature was supplemented with web-based search engines to help identify specific mechanisms for formation. A series of excellent reviews on PCBs in paint have been produced recently (Rodenburg et al., 2015; Anh et al., 2021; Vorkamp, 2016; Grossman, 2013). The differentiating factors of this manuscript are on establishing potential mechanisms for formation and documenting every PCB identified in pigments dyes and paint. Therefore, the review needed to deviate from the traditional systematic review framework and incorporate information from a wider range of sources.

3. Mechanisms of PCB formation in pigments

Pigments have been shown to be an important source of by-product PCBs in the environment (Rodenburg et al., 2015; Anh et al., 2021; Vorkamp, 2016; Grossman, 2013). This has resulted in research aimed at identifying which specific PCBs are present in different pigments and at what concentrations. However, in many cases formation mechanisms and explanations as to why these PCBs are present have not been fully described. The existing literature also focuses on the main PCBs present in each pigment. While this is useful to help identify different sources, it has led many to believe only a handful of PCBs (e.g. PCB 11 and 209) are present in pigments. This is misleading as approximately 150 different PCBs have been reported in pigments (listed in SI Table 1). The available literature was reviewed, and by-product PCBs have been detected in azo pigments, phthalocyanine pigments, DPP pigments, and titanium dioxide. In addition, our review identified a new set of 7 different pigments that are potential sources of by-product PCBs.

3.1. Azo pigments

Diazonium salts are versatile organic reagents which can undergo a number of chemical reactions in addition to the azo coupling relevant to pigment production (Forstinger et al., 2015). The relevant competing reaction during coupling that results in unintentional side products is dediazotization. In this class of reaction, a radical or cation is formed with the resulting loss of nitrogen gas (Forstinger et al., 2015). The first step of dediazotization reactions is the breaking of the Ar—N bond, giving off N₂. This can occur through either a heterolytic or homolytic pathway (SI1), however it is the homolytic pathway that is most likely to result in formation of by-product PCBs (Galli, 1988). This proceeds via a single electron transfer mechanism, requiring a reducing agent and resulting in the

production of an aryl radical (Galli, 1988). Typically, copper(I) is shown as the reducing agent in this process due to its use in the Sandmeyer reaction, a reaction in which the diazonium group is replaced by chlorine (SI1). It is expected that these processes occur during the production of the pigments, and the resulting PCBs remain in the final pigment product as an impurity. To illustrate how these mechanisms can lead to by-product PCBs during pigment production, examples for two pigments (Red 112 and Yellow 12) are presented in Fig. 1. Pigment red 112 (PR112) is a monoazo Naphthol-AS pigment, while pigment yellow 12 (PY12) is a disazo pigment. These are chosen to illustrate the difference in PCB formation between the two major classes of azo pigments.

For monoazo PR112, the resulting aryl radical formed from dediazotization is the 2,4,5-trichlorophenyl radical. This radical can then undergo either of the three reactions outlined in Fig. 1, leading to several possible PCBs. The simplest reaction, shown in pathway A, is the recombination of two aryl radicals. However, this is unlikely to occur as the relative concentration of radicals in solution at any time should be quite low and so the chances of two reacting together are small. Abstraction of a hydrogen atom by this radical, shown by pathway B, would lead to 1,3,4-trichlorobenzene. Reaction with the chloride anion, shown by pathway C, would give 1,2,4,5-tetrachlorobenzene. Both compounds can then react further with aryl radicals leading to PCBs. The trichlorobenzene resulting from pathway B can then react with the 2,4,5-trichlorophenyl radical to give three different PCBs as shown by the colored arrows. The blue arrow leads to PCB 153, the same product as formed by pathway A, while an attack at the position shown by the green arrow results in PCB 146, and the red arrow PCB 149. In terms of relative abundance, it is expected that PCB 153 should be the most prevalent, followed by PCB 146, and PCB 149. However, all three congeners are expected to be major products present in similar quantities. The only PCB congener which can be formed from reaction of the aryl radical with the tetrachlorobenzene formed by pathway C is PCB 187, and this is expected to be found in much lower abundance than PCB congeners resulting from trichlorobenzene. This is because the chloride reaction in pathway C is unfavorable and expected to occur less than hydrogen abstraction.

For disazo PY12, the PCB formation pathway changes due to the presence of a biphenyl in the dye structure itself (Fig. 1a) which leads to predominantly PCB 11. While the arylation of aromatic compounds mechanism could in principle occur, it does not lead to PCBs (instead to tri and tetraphenyls). The two important mechanisms are abstraction of a hydrogen atom and reaction with the chloride anion. With two different potential aryl radicals, there are three different possibilities which can result in PCBs (Fig. 1c). Initially there are two possible pathways for reaction, pathway A which is the abstraction of a hydrogen atom and pathway B, reaction with a chloride anion. As this started with a diradical, both of these reactions can happen again as shown by pathways A1 and B1 for H abstraction and pathways A2 and B2 for reaction with chloride anion. The three products formed are thus PCB 11 from pathway A1, PCB 35 from pathways A2 and B1, and PCB 77 from pathway B2. In terms of relative abundance, it is expected that PCB 11 is the most prevalent followed by PCB 35, and finally PCB 77 as the hydrogen abstraction pathway is much more likely to occur.

While the mechanisms in Fig. 1 are the primary routes of PCB formation for azo pigments, there are some pigments which have been found containing PCBs despite containing nitro substituents (Shang et al., 2014). PCBs are expected to be formed in a similar manner with mechanisms proposed in SI1.

Due to the wide array of azo pigments available and their ubiquitous use, they are among the most widely tested for PCBs. Our review identified 62 different samples that have been analysed, with a total of 83 different PCBs detected. Some samples did not contain detectable levels of PCBs, but when PCBs were detected total PCB concentrations ranged from 0.004 mg kg⁻¹ to 920 mg kg⁻¹ (SI Table 1). Results for total PCB concentrations and specific congeners are variable, however there was an excellent correspondence between the main predicted and observed PCBs for the majority of pigments, with the exception of PY5 and PY16 (Table 1). Monoazo naphthol AS pigments are predicted to contain a high proportion

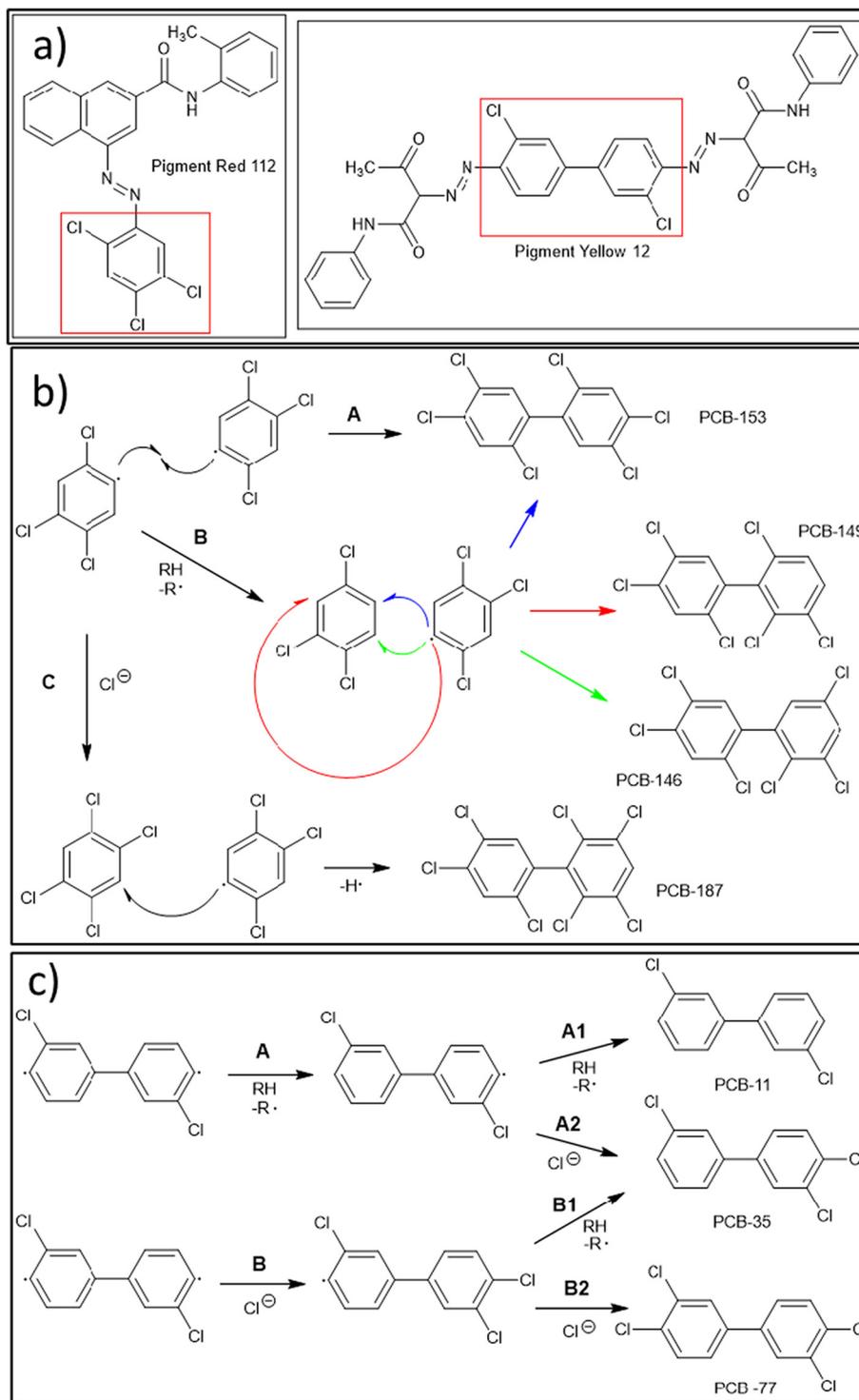


Fig. 1. a) Chemical structures of monoazo PR112 and disazo PY12. Highlighted in red are the monoazo and disazo core of the pigments. b) Potential PCB formation pathways from aryl radical derived from PR112 (Galli, 1988). c) Potential PCB formation pathways from aryl radical derived from PY12 (Galli, 1988). Colored arrows represent the position a reaction occurs at and the corresponding product that is produced. (Further information provided in the SI).

of PCB 52 (PR9), or PCBs 146, 149, and 153 (PR112), or no PCBs at all (PR22, PR188/PO69, PR170, PY74 and PY154). Disazo pigments and nitro containing monoazo pigments are expected to be dominated by PCB 11. There were several PCBs that were not predicted by our mechanisms but were detected in the samples (e.g. PCB 28 and 52 in PY12 and PY5). These may have been created by radical rearrangement; however, it is also feasible that the source of these by-product PCBs (and others present but not predicted by our proposed mechanisms) is not the pigments

themselves but another component of the tested paints. Several pigments contained PCBs that were not predicted by mechanisms, these included trace levels of PCB 11 in PY154 as well as all congeners found in PY1, PY65, PY97, and PY191, which are predicted to contain no PCBs based on our mechanisms. For each of these pigments an additional functional group (methyl or methoxy) was present on the phenyl ring associated with PCB production based on our mechanisms. We were unable to find a mechanism which could adequately explain the loss of these functional

Table 1

Reported relative concentrations of PCB congener profiles for azo pigments compared against PCB profiles predicted by mechanisms. Samples from the same pigment type were averaged and a selection of the most abundant PCBs are reported, the full dataset is presented in the SI.

PCB	Monoazo Naphthol AS pigments				Disazo Pigments										Nitro Monoazo Pigments					Sulphonate Monoazo Pigments		
	PR9	PR112	PY97	PY154	PY12	PY13	PY14	PY16	PY17	PY55	PY81	PY83	PY152	PO13	PO16	PY1	PY3	PY5	PY65	PO36	PY191	
1																						
2																						
3																						
4																						
6																						
7																						
11				100%	64%	94%	90%	60%	90%	97%	23%	98%	98%	85%	76%	84%	82%	45%	56%	7.8%	35%	
16																						
28					14%			13%	2.8%							9.9%		25%	16%		40%	
33																						
35					1.1%	1.7%	2.4%		1.4%	2%		1.4%	0.8%	9.5%	15%		10%			11%		
47																						
51																						
52	87%		64%		19%						75%							13%				
68																						
77					1.4%	2.3%	5.3%	14%	3.1%	1%		0.4%	0.8%	5.0%	8.8%	5.4%	5.6%	17%	22%	81%	23%	
90			33%																			
91																						
92	0.1%		2.4%																			
95	0.2%																					
98																						
101	2.3%										0.1%											
126																			3.4%		1.0%	
146		37%																				
149		20%																				
153		13%									0.1%											
187		6.8%																				
209								11%	2.8%													
					Predicted from mechanisms			Major	Minor	Not predicted												

groups in the conditions used for pigment synthesis and therefore suspect that PCBs detected in these samples were due to another component of those paints.

3.2. By-product PCBs from dioxazine pigments

By-product PCBs have been recorded in dioxazine pigments with the majority of focus on the most widely used commercial products, pigment violet 23 and 37 (PV23 and PV37) (Anezaki et al., 2015; Anezaki and Nakano, 2014). While it is generally accepted that the source of these by-product PCBs is due to the dichlorobenzene solvent regularly used to synthesize these pigments, the specific mechanism is not discussed in detail. The synthesis of dioxazine pigments involves the reaction of chloranil with a substituted aniline in dichlorobenzene. Chloranil has been previously identified as a source by-product PCBs and so could be a potential source of PCB contamination in dioxazine pigments (Liu et al., 2012). However, congeners found in chloranil do not match those which were found in PV23 and PV37. Therefore, we present potential mechanisms of by-product PCB formation from 1,2-dichlorobenzene to explain the by-product PCBs observed experimentally. The decomposition of chlorobenzenes to give POPs under thermal conditions has been well studied, providing insight into the likely path of PCB formation from 1,2-dichlorobenzene (Mulholland et al., 1992; Larson and Chuang, 1994; Rouzet et al., 2001; Liu et al., 2001). In the synthesis of dioxazine pigments, the reaction temperatures are generally up to 200 °C, and so some of the same reactions may occur as when these chlorobenzenes are heated at 400 °C or more in the case of pyrolysis (Herbst and Hunger, 2004). The mechanism proposed for PCB formation in the production of dioxazine pigments is based on radical reactions of 1,2-dichlorobenzene which is also the case for phthalocyanine pigments (Fig. 2, SI2). There are three possible radicals which can be formed from 1,2-dichlorobenzene, one from the loss of a chlorine and two from the loss of hydrogen (Mulholland et al., 1992). There are two potential pathways by which these radicals can be formed, either a homolytic bond cleavage with the resulting loss of a hydrogen or chlorine radical, or

the abstraction of a hydrogen or chlorine atom by another radical in solution (Mulholland et al., 1992). In both cases, the same three aryl radicals will be formed, so these pathways do not change the mechanisms of PCB formation. It is expected that the loss of a hydrogen atom is favored over the chlorine, and so dichlorobenzene radicals should form much more frequently than chlorobenzene radicals (Mulholland et al., 1992). As there are three different radicals formed, it is expected that PCB formation mechanisms will be very complex with many different species in solution. Due to this, it can be challenging to determine which by-product PCBs are formed during the production of dioxazine pigments and will vary depending on what is used during the production processes. However, in general it is expected that di and tetrachlorinated PCBs should make up the majority of PCBs formed (Fig. 2).

Only a few studies have reported on the presence of PCB congeners in dioxazine pigments (Anezaki et al., 2015; Anezaki and Nakano, 2014). In total, 9 samples have been analysed from 2 pigments (PV23 and PV37). These were shown to contain a total of 19 different PCBs with total PCB concentrations ranging from 38 mg kg⁻¹ to 0.18 mg kg⁻¹ (SI Table 1). The two pigment types analysed show a very clear and characteristic congener pattern across all pigments tested (Table 2). The congener pattern reported in the literature matches those predicted by the proposed mechanisms. PCBs 40, 56, and 77 are predicted as the major congeners formed, with PCB 56 present at the highest proportion, and this was represented in the experimental data. If benzene is present in the reaction mixture, then the production of high proportions of PCB 5 and 12 is also expected.

3.3. By-product PCBs from phthalocyanine pigments

The formation of by-product PCBs during the production of phthalocyanine pigments has been known for a long time, with PCBs attributed to chlorobenzene solvents used in their production as early as 1976 (Uyeta et al., 1976; Buchta et al., 1985). While it is well understood that by-product PCBs are present in these pigments and that chlorobenzene solvents are responsible for their formation, the exact mechanism is not

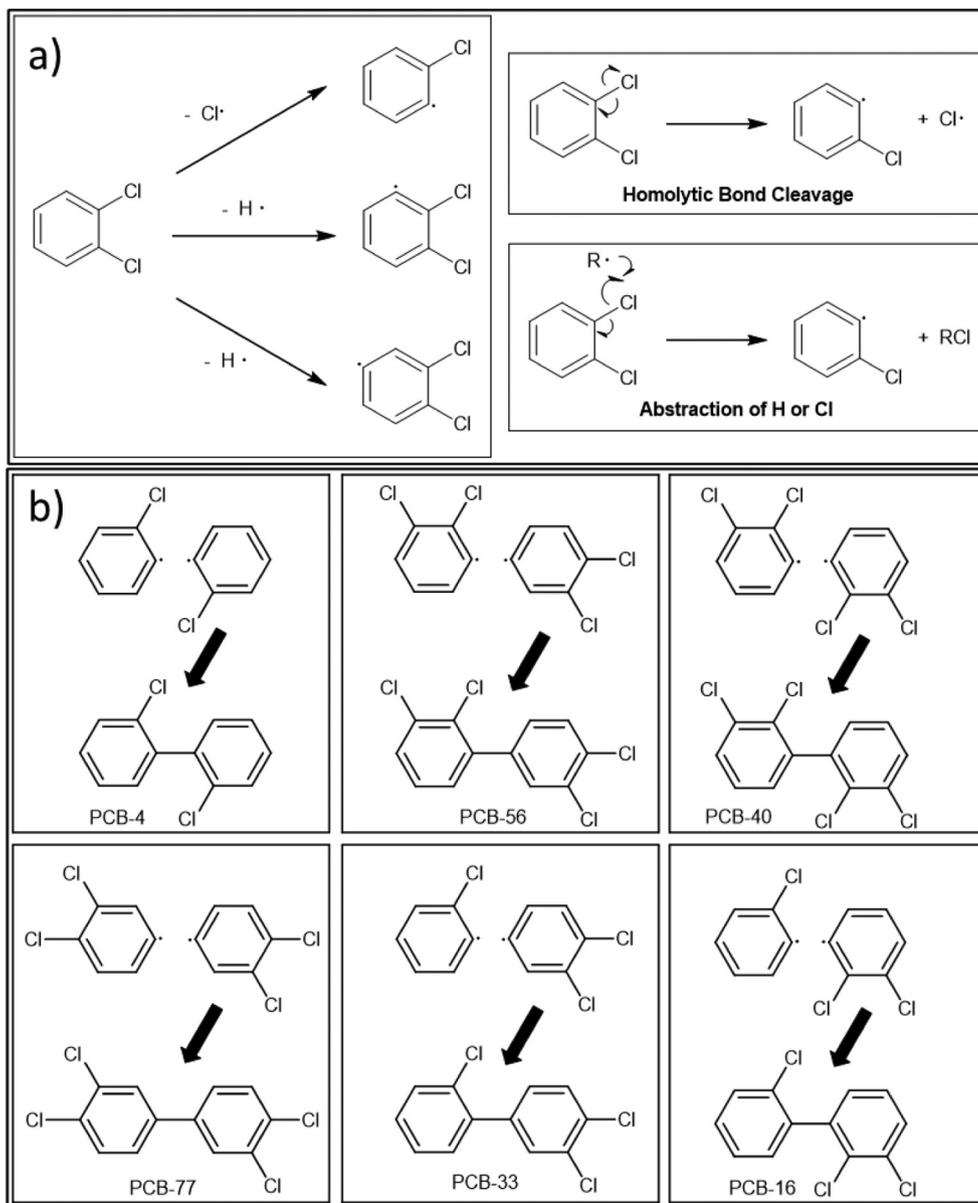


Fig. 2. a) Three possible radicals formed from 1,2-dichlorobenzene (left). Two pathways of radical formation, homolytic bond cleavage (top right) or abstraction of hydrogen or chlorine (bottom right) (Mulholland et al., 1992). b) Radical-radical recombination reactions to form six different PCBs during the production of dioxazine pigments. (Further information is provided in the SI).

well understood. One possibility is that by-product PCBs are formed by radical reactions of chlorobenzene. This mechanism has been previously proposed to explain by-product PCBs in phthalocyanine pigments (Anezaki and Nakano, 2014; Hu and Hornbuckle, 2010; Jahnke and

Hornbuckle, 2019). While this mechanism is feasible (and is the same one used to explain by-product PCBs in dioxazine pigments) an alternative mechanism is also presented in SI3 due to the conditions of phthalocyanine synthesis. As there are differences in the by-product PCBs formed during phthalocyanine synthesis, focus will be placed first on the phthalocyanine blue pigments, and then on the phthalocyanine green pigments that are created from additional chlorination of phthalocyanine blue.

3.3.1. Phthalocyanine blue

Determining exact PCB congeners present in phthalocyanine blue pigments can be challenging because it is possible for different isomers of di and trichlorobenzene, or even non-chlorinated solvents, to be used as a solvent in their synthesis. This has been reflected in the literature, with some samples of phthalocyanine blue finding no PCBs at all (likely due to the use of non-chlorinated solvents) while others have been found to contain a variety of mono to hexachlorinated PCBs (Hu and Hornbuckle, 2010; Jahnke and Hornbuckle, 2019; Anezaki and

Table 2

Reported relative concentrations of PCB congener profiles for dioxazine pigments compared against PCB profiles predicted by mechanisms.

PCB	Dioxazine Pigments	
	PV23	PV37
5	22%	45%
12	22%	31%
40	4.9%	2.7%
56	25%	12%
77	15%	5.5%
Predicted from mechanisms		Major Conditional

Table 3

Reported relative concentrations of PCB congener profiles for Phthalocyanine blue and green pigments compared against PCB profiles predicted by mechanisms. As so many different PCBs are predicted only PCBs present at greater than an average of 5 % in samples have been included.

PCB	Phthalocyanine Blue					Phthalocyanine Green		
	PB15	PB15:1	PB15:3	PB15:2	unknown	PG7	PG36	Unknown
1	No PCBs detected	No PCBs detected	No PCBs detected		9.9%			
4				5.5%		2.4%	6.0%	
5				6.7%	19%	6.7%		
6						20%	19%	
8							8.1%	
11						9.8%	6.9%	5.9%
12				5.8%	10%	8.0%	6.6%	
20/33					7.1%			
21					9.5%			
26				30%				
209				40%	13%	85%	50.4%	50%
				Predicted from mechanisms				Major

Nakano, 2014) (SI Table 1 & Table 3). The mechanism proposed for PCB formation in production of phthalocyanine blue pigments is based on the same radical reactions of 1,2-dichlorobenzene that have been discussed for dioxazine pigments (Fig. 2). Like with dioxazine pigments, it can be challenging to determine which by-product PCBs are formed during the production of phthalocyanine blue pigments and will vary depending on what is used during the production processes. However, in general, it is expected that di and tetrachlorinated PCBs should make up the majority of PCBs formed. Our review identified only 5 phthalocyanine blue samples that have been analysed, a total of 38 different PCBs were detected with concentrations ranging from non-detect to 0.057 mg kg⁻¹ (SI Table 1).

3.3.2. Phthalocyanine green

There are two potential mechanisms that can result in the generation of by-product PCBs in phthalocyanine green pigments, both leading to the same PCB congeners (SI3). The first mechanism involves chlorination of PCBs formed during the creation of phthalocyanine blue and results in the creation of a wide range of different PCBs but will ultimately result in production of PCB 209. The second mechanism involves the Ullmann reaction of hexa and pentachlorinated benzenes. In a reaction between two molecules of hexachlorobenzene, the only PCB congener formed is the decachlorinated PCB 209. For the reaction of hexachlorobenzene with pentachlorobenzene, the nonachlorinated PCB congeners 206, 207, and 208 can all be formed. Reactions between two molecules of pentachlorobenzene are expected to be quite minor since pentachlorobenzene is formed in much lower quantities than hexachlorobenzene. This would result in a small proportion of octachlorinated PCBs to be formed, and this has been confirmed in the literature (Anezaki and Nakano, 2014; Hu and Hornbuckle, 2010; Jahnke and Hornbuckle, 2019). Often phthalocyanine blue pigments are partially chlorinated, so these may also result in some higher chlorinated congeners based on the same mechanisms as green pigments. While phthalocyanine green pigments are formed from near complete chlorination (of 16 possible sites), partially chlorinated blue pigments generally contain only 1–4 chlorines per phthalocyanine molecule. Our review identified 13 paint samples containing Phthalocyanine green pigments that have been analysed. In total, 84 different PCBs were detected with concentrations ranging from 0.01 mg kg⁻¹ to 2.45 mg kg⁻¹ (SI Table 1).

Several studies have looked at the presence of by-product PCBs in phthalocyanine blue and green pigments. Results generally match what is predicted by the mechanisms with by-product PCBs present across the entire mono to decachlorination range. Dominant PCBs present in phthalocyanine blue pigments vary but are generally mono to trichlorinated PCBs or PCB 209. Phthalocyanine green pigments contain high proportions of PCB 209, but with notable contributions from other less chlorinated PCBs in some samples (SI Table 1 & Table 3).

3.4. By-product PCBs from diketopyrrolo pyrrole (DPP) pigments

By-product PCBs have been recorded in DPP pigments with the majority of focus on the most widely used commercial product, pigment red 254 (PR254) (Anezaki et al., 2015; Jahnke and Hornbuckle, 2019). The mechanisms of PCB formation in DPP pigments are not well explained in the literature. A mechanism for formation as shown in SI3 has been previously proposed which involves the loss of the nitrile group forming a benzene radical (Anezaki et al., 2015). While this radical based mechanism could explain the PCB congener patterns observed, there is some question as to whether this mechanism is possible due to the strength of the C—C bond which is broken. Alternative mechanisms involving the preferential formation of radicals from breaking the aryl-H bond may also be important (Sonya-T-Emad-Rad and Metcalfe, 1993). PCB congeners found in DPP have been almost exclusively those with only one chlorine substituent per ring. Dichlorinated PCBs can be expected from radical mechanisms involving chlorinated benzene in PR254 and between chlorinated benzene and benzene radicals in when PR255 is also synthesized (Fig. 3, SI4).

The presence of by-product PCBs in DPP pigments have not been widely reported with our review identifying data originating from 3 studies and 11 samples (Anezaki et al., 2015; Anezaki and Nakano, 2014; Jahnke and Hornbuckle, 2019). These studies provide data for PR254 analysed by itself, and mixtures of PR254 with PR255 or PR108 produced by various manufacturers and in different countries (Anezaki et al., 2015). One sample of PO73 was also analysed. This contained several different congeners, but we were unable to predict any appropriate mechanisms for formation and so we expect these PCBs are present due to another constituent of the paint. In total, 25 different PCBs have been recorded in DPP pigments with concentrations ranging from 0.002 mg kg⁻¹ to 2.35 mg kg⁻¹ (SI Table 1). Overall, PCB congener patterns found in DPP pigments matches predictions from the proposed mechanisms. All dichlorinated PCB congeners predicted to be in these pigments were identified. The dichlorinated congeners also largely followed what was expected in terms of relative abundance, with PCBs 13 and 15 being the major congeners detected, and PCBs 3, 4, 6, and 11 as more minor products. The exception to this is PCB 8 which was expected to be a more predominant component but was found in smaller proportions than expected (SI Table 1 & Table 4).

3.5. By-product PCBs from titanium dioxide

Despite being one of the pigments most widely associated with by-product PCBs, mechanisms of by-product PCB formation during the production of titanium dioxide is poorly understood. Mechanisms of chlorination in the first step of the synthesis of TiO₂ are not known, so it is expected that this may be a complex process (Andrade Gamboa et al., 1999). It has been reported that the carbochlorination process by which TiO₂ is

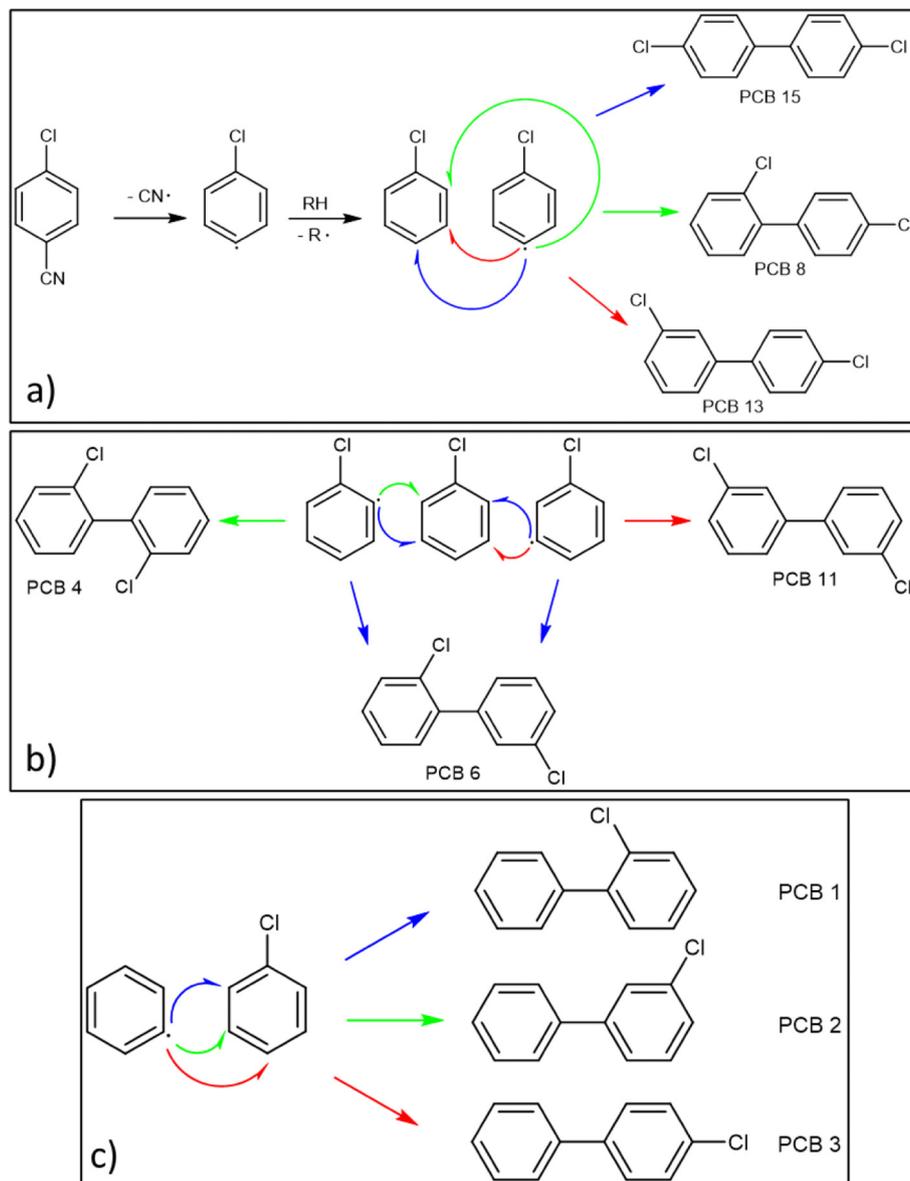


Fig. 3. Overview of proposed mechanisms of PCB formation in DPP pigments a) reactions of chlorobenzene radicals during synthesis of PR254 b) reactions of chlorobenzene with the ortho and meta radicals to create PCBs during synthesis of PR245 c) Reactions of the benzene radical with chlorobenzene to produce PCBs during synthesis of PR254 and PR255 (Galli 1998). Colored arrows represent the position a reaction occurs at and the corresponding product that is produced. (Further information is provided in the SI).

synthesized in the chloride process results in chlorinated persistent organic pollutants (POPs) (Andrade Gamboa et al., 1999; Landsberg et al., 1985; Landsberg et al., 1988). Along with several other POPs, the PCB most

commonly produced during carbochlorination processes is PCB 209 with smaller amounts of some nona, octa, and even hexachlorinated congeners (Landsberg et al., 1985). While the exact mechanism of formation of these PCBs is not known, it can be assumed they are formed in some way by the reaction of carbon with chlorine gas as shown in Fig. 4 (Ctistis et al., 2016). In an interesting observation, it was found that when the carbochlorination conditions were carried out in the absence of a metal, only fully chlorinated POPs such as PCB 209 were formed (Landsberg et al., 1988). This suggests that the metal is required to form lower chlorinated congeners, and that the lower chlorinated PCBs are actually formed by dechlorination of PCB 209. TiO_2 is currently used as a catalyst for photocatalytic dechlorination reactions, so it would seem feasible that this is the pathway through which lower chlorinated congeners are formed (Chiarenzelli et al., 1995; Ghosh et al., 2012; Kozhevnikova et al., 2019). In these dechlorination reactions, mechanisms are generally believed to be radical based, although it can vary depending on reaction conditions (Kozhevnikova et al., 2019). During dechlorination reactions with TiO_2 , lower chlorinated congeners and those with ortho chlorines were favored

Table 4

Reported relative concentrations of PCB congener profiles for diketopyrrolo pyrrole pigments compared against PCB profiles predicted by mechanisms.

PCB	Diketopyrrolo pyrrole pigments			PO73
	PR254	PR254 PR108	PR254 PR255	
3	16%		1.5%	
4	1.0%		0.9%	60%
6	13%		15%	
8	5.5%		6.2%	6.9%
11	0.8%		8.0%	21%
12				7.1%
13	28%	30%	32%	
15	35%	70%	36%	
	Predicted from mechanisms	Major	Minor	Not predicted

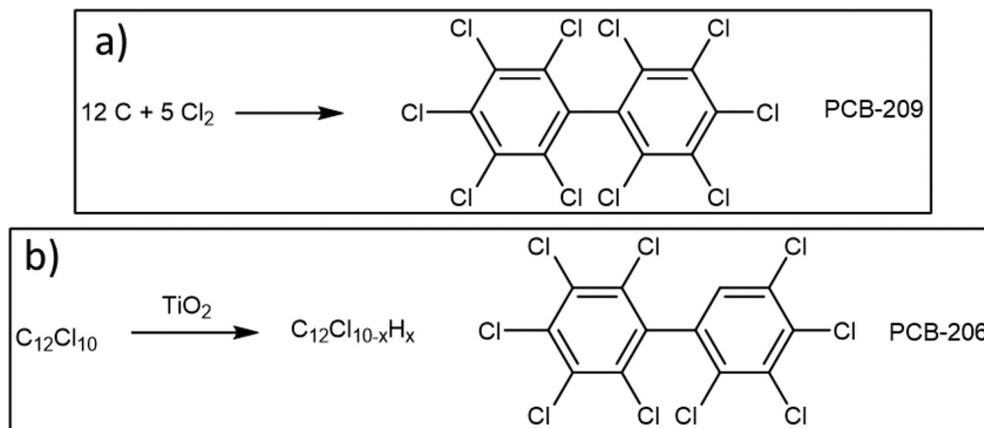


Fig. 4. Overview of by-product PCB formation during titanium dioxide pigment formation, starting with a) reaction of carbon and chlorine gas to give PCB 209 (Ctistis et al., 2016) b) catalysed dechlorination of PCB 209 by titanium dioxide (Kozhevnikova et al., 2019). (Further information is provided in the SI).

for dechlorination (Kozhevnikova et al., 2019). A basic dechlorination process for PCB 209 is shown in Fig. 4. Each chloride lost by dechlorination is replaced by a hydrogen resulting in the formation of a lower chlorinated congener, such as PCB 206.

A comprehensive assessment of all 209 PCBs in titanium dioxide pigments has only been performed by Hu and Hornbuckle (2010). However, there were no PCBs detected in any of the 4 samples they analysed. Ctistis et al. (2016) only detected 9 different PCBs in 1 of 5 samples analysed, but their data was limited to 12 dioxin like PCBs and 6 indicator PCBs. Samples that did not contain any PCBs indicates that the TiO_2 was synthesized by the sulfate process rather than through chlorination. Several investigations in the grey literature have listed PCB 209 as the main congener with notable contributions of PCBs 206 and 208, unfortunately they do not provide full congener specific datasets and it is unclear which specific PCBs were targeted (Stone, 2016; Stone, 2014; Rodenburg, 2012). Information on the congener profiles of titanium dioxide pigments in the scientific literature appears to be more focused on assessing sediments containing waste from titanium dioxide manufacturing areas (Rowe et al., 2007; Du et al., 2008; Hu et al., 2011; Praipipat et al., 2013; Huo et al., 2017; Wang et al., 2014; Rodenburg and Ralston, 2017). These studies show high proportions of PCBs 209, 206 and 208 which gives a characteristic signature dominated by decachlorinated PCB. While it is clear that PCB 209 and the nonachlorinated congeners 206 and 208 are dominant in the production of TiO_2 , many other PCBs are likely to be present. Further studies involving full congener specific analysis of TiO_2 pigments would be useful to confirm which PCBs are present and what mechanisms lead to their formation.

3.6. Other pigments which may contain by-product PCBs

There are several pigments which have not been previously reported to contain by-product PCBs, however due to their production processes these pigments are also expected to be potential sources of by-product PCBs. Additionally, there were several pigments that were analysed but it was either unclear specifically which pigment was used or it was used in combination with another pigment (e.g. Isoindolinone, Quinacridone and Quinophthalone). In some of these instances, there is evidence to support the presence of by-product PCBs in these pigments. However, it is difficult to draw robust conclusions from the samples analysed in the literature. Therefore, these pigments have been highlighted as areas for future studies to investigate by-product PCB formation. Pigments that should be investigated further include: tetrachloroisoindolinone pigments, quinophthalone pigments, quinacridone pigments, thioindigo pigments, pyranthrene pigments, triarylcarbonium pigments, azo pigments with carboxylate or sulfonate groups. Evidence to support the presence of by-product PCBs in these pigments is presented in the Supplementary Information.

3.7. Additional and unclassified pigments

Unfortunately, 19 samples could not be classified from the information provided in the scientific literature (SI Table 1). This group contained a total of 92 different by-product PCBs with concentrations ranging from non-detect to 0.10 mg kg^{-1} . As pigments used in these paints are unknown, this data has been collated separately for completeness. Future studies would benefit from comprehensively classifying the sample details; however we appreciate this may not always be possible as some information could be considered proprietary. In addition to organic pigments, there were also samples of paints containing metal complex (2 samples, Anezaki and Nakano, 2014), iron oxide (4 samples, Hu and Hornbuckle, 2010) and carbon black (1 sample, Hu and Hornbuckle, 2010) based pigments. None of these samples contained PCBs and therefore these pigments are not suspected sources of by-product PCBs.

4. Mechanisms of PCB formation in dyes

Currently, there is relatively little published information on the presence of PCBs in dyes (Zhou et al., 2019). We were unable to find any studies in which PCB congeners were directly measured from dyes themselves. However, as many dyes share common structural patterns with pigments, by-product PCB formation is considered highly likely. Examples of 3 different dyes are presented in Fig. 5, each featuring a different chromophore which is common to by-product PCB formation in pigments. Disperse yellow 241 is an azo dye and is thus expected to be able to result in by-product PCBs by the same pathway as azo pigments (SI1). Direct blue 106 is a dioxazine dye and is expected to give PCBs in the same way as dioxazine pigments (SI2). Direct blue 86 is a phthalocyanine dye expected to have by-product PCBs produced via the same mechanisms as for phthalocyanine pigments (SI3). In general, dyes tend to have more substituents compared to pigments, meaning that in many cases, PCBs may be less likely to form, which may explain why they have not been widely detected. More research is desperately needed to understand which PCBs may be present in dyes.

5. Mechanisms of PCB formation in paint binders, plasticizers, and additives

Due to the vast array of products in paints, there are many different processes and chemicals which are likely to result in by-product PCB formation. Pigments have been the main source of focus for by-product PCBs in paints, however, there are other components of paint (binders, plasticizers, and additives) that can also be sources of by-product PCBs. A review of the literature identified polyvinylchloride (PVC), chlorinated paraffins, and silicones as types of binders, plasticizers or additives that may contain by-

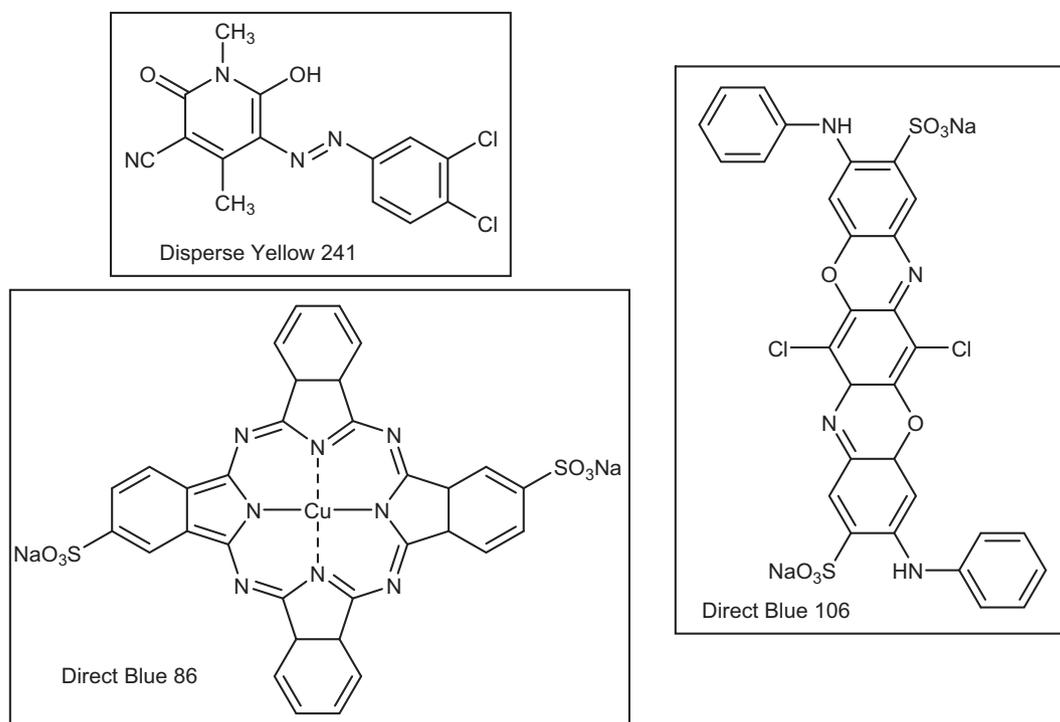


Fig. 5. Three different dyes, disperse yellow 241, direct blue 86, and direct blue 106, each featuring a different chromophore that is comparable to pigments linked with by-product PCB production (Hunger, 2007). (Further information is provided in the SI).

product PCBs. With the exception of silicones, the current information in the scientific literature on these products is very limited.

PVC is a polymer which finds widespread use for many applications, including in paint where it can be used as a binder (Freitag and Stoye, 2008). PVC is derived from polymerisation of the vinyl chloride monomer. It is possible that PCBs are inadvertently created during the production of vinyl chloride from 1,2-dichloroethane (Munoz, 2007). Higher chlorinated congeners (PCBs 207, 208, and 209) have been identified during the production of chlorinated methane (Zhang et al., 2015). Although this cannot be directly applied as evidence for the presence of PCBs in PVC, a similar chlorination process is used for production of the vinyl chloride monomer. Therefore, it is feasible that by-product PCBs may also occur during the production of PVC. The formation of POPs from the combustion of PVC was investigated by Katami et al. (2002) finding dioxin-like PCBs were formed. Unfortunately, no full congener analysis or mechanistic investigations into PCB formation were undertaken (Katami et al., 2002).

Chlorinated paraffins have a variety of different uses, and in paints they are often used as additives to act as flame retardants (Bieleman, 2008). There is very little literature on the presence of PCBs in chlorinated paraffins, however they have been mentioned as a potential source of by-product PCBs (Munoz, 2007). Both experimental evidence of PCB formation and the formation of other POPs was provided by (Xin et al., 2019). A more detailed summary of mechanisms leading to PCBs is presented in the supplementary information (SI7). While a detailed description of the congeners expected was not undertaken, in general, it is expected that this pathway would result in mostly mono or dichlorinated PCBs at least in the case of the CP52 (a chlorinated paraffin containing 52 % chlorine) used in this study, while CP70 resulted in mostly di and trichlorinated PCBs (Xin et al., 2018). The source of by-product PCBs in PVC and chlorinated paraffins are linked to the chlorination processes used industrially, which require high heat and pressure. By-product PCBs have been found in the waste products from the production of chlorinated methanes (Markovec and Magee, 1984; Zhang et al., 2015), providing evidence for the incidental production of PCBs from other chlorination processes (see SI7 for additional details).

Silicones can be used as binders for paints, and are frequently used as additives (Freitag and Stoye, 2008). Silicones are known to contain by-product PCBs (Munoz, 2007). There are two main potential sources of by-product PCBs during their production. The first of these is due to the use of 2,4-dichlorobenzoyl peroxide (2,4-DCBP) as a radical initiator during the production of silicone polymers. This initiator is used for several different polymers, so this may be applicable further than just silicones (Herkert et al., 2018). The other potential source of by-product PCBs in silicones is due to the production process of phenyl silicones and the starting materials used in their production.

By-product PCBs in silicone resulting from the decomposition of 2,4-DCBP have been known for some time, with a number of papers published on the by-products from 2,4-DCBP decomposition (Perdih and Jan, 1999; Jan and Perdih, 1991; Herkert et al., 2018; Mao et al., 2020; Mao et al., 2019; Hombrecher et al., 2021). Despite this, only recently have studies begun to understand the significance of by-product PCBs produced from silicones on the environment. The most common by-product PCBs associated with this process are PCBs 47, 51, and 68, each of these being found as significant contaminants at sites located close to silicones or silicone production (Hombrecher et al., 2021; Herkert et al., 2018; Mao et al., 2019; Schettgen et al., 2021). The mechanisms of PCB formation from the decomposition of 2,4-DCBP are well understood and match the experimental findings well (SI6).

The other potential source of by-product PCBs in silicones is from the production of phenyl silicones due to the reaction of chlorobenzene with silicon, a copper or silver catalyst, and chloromethane (SI6). This process can result in the generation of lightly chlorinated PCBs including monochlorinated PCBs (PCB 1, 2 & 3) and dichlorinated PCBs (PCBs 4, 6, 8, 11, 13 & 15) (Anezaki and Nakano, 2015).

While there is compelling evidence that proves the presence of by-product PCBs in silicones, there is less evidence to show that chlorinated paraffins and PVC may be a significant source of by-product PCBs in paint products. Most studies on by-product PCBs focus solely on the pigments as the source of PCBs. However, this literature review identified some paints that contained PCBs that were not expected to be produced from the pigments alone.

6. Conclusions

There has been an increased awareness of paints and pigments as a source of by-product PCBs in the environment. However, there has been some uncertainty as to exactly how these PCBs have been generated as the majority of existing work has focused on reporting the presence of the main PCBs in different products. This gives the impression that only a handful of PCBs are found in paints. This is not the case. PCB profiles in paints and pigments can be just as complex as technical commercial mixtures. This review identified the presence of 149 different PCBs in paint samples. For reference, only 141 different PCBs were reported by (Frame et al., 1996) in the 5 main commercial formulation Aroclors (A1016, A1242, A1248, A1254 (early & late) and A1260). The PCB composition of technical mixtures is highly consistent. Whereas there is much more variability in paint samples, with individual samples containing between 0 and 75 different PCBs. This review also provides a detailed overview of potential mechanisms for PCB formation in paints, pigments, and dyes. The PCBs predicted by these mechanisms provide an excellent match for what has been observed in the scientific literature. However, several samples contained PCBs that could not be explained by PCB formation mechanisms for those pigments. In these instances, it is likely that PCBs have originated from other constituents of those paint samples. Pigments were the most widely investigated source of by-product PCBs, however this review presents evidence to suggest that by-product PCBs may also be produced in dyes as well as in other paint additives. In many cases there is little primary experimental data to show which PCBs are produced during pigment production. Instead, the literature is a combination of proposed reaction mechanisms with experimental data from whole paint samples (which contain more than just the pigments). Future work would benefit from collaborations with industry where samples and experimental data are taken directly from the pigment manufacturing process. This would include targeting analysis towards individual paint constituents (e.g. pigments, binders, plasticizers, or additives), to supplement existing information from whole paint and environmental samples.

When by-product PCBs are detected in the environment it can be challenging to directly associate them to a particular paint or pigment. This review provides a guide to help identify which PCB congeners are indicative of different sources that is backed up both by observed data in the existing literature and theoretical data from proposed chemical formation mechanisms. PCB 11 is closely associated with the production of azo pigments and is regularly identified as a by-product PCB in environmental samples. However, other PCB congeners frequently found in azo pigments include PCBs 28, 35, 52, and 77. These PCBs are also abundant in technical mixtures and so are not often attributed to by-product sources. Dioxazine pigments were found to contain PCBs 5, 12, 40, 56, and 77 with 5, 12, and 56 the dominant congeners. Phthalocyanine green pigments are shown to contain high proportions of PCB 209, along with PCBs 206, 207, and 208. These are created from the chlorination of PCBs present in phthalocyanine blue pigments which have variable PCB compositions in the mono to decachlorinated PCBs range. DPP pigments tend to have only one chlorine atom is on each ring and so are dominated by dichlorinated PCBs such as PCBs 13 and 15. Titanium dioxide is generally associated with PCBs 206, 208, and 209, but more comprehensive analysis of these pigments is needed to see which other PCBs may also be present. Silicone based additives have also been shown to be a potential source of by-product PCBs in paint and contain high proportions of PCBs 47, 51, and 68. Although these PCBs are expected to be the dominant congeners from their respective sources it is important to note the large variability and vast number of PCBs that have been observed in different samples. Full congener specific analysis would be recommended when assessing contributions of by-product PCBs.

Seven additional pigments groups were identified as potential sources of by-product PCBs. These include tetrachloroisoindolinone pigments, quinophthalone pigments, quinacridone pigments, thioindigo pigments, pyranthrone pigments, triarylcarbonium pigments, and azo pigments with a carboxylate or sulfonate group. Several classes of dyes (such as azo,

dioxazine, and phthalocyanine dyes) were also identified as new potential source of by-product PCBs as they have a similar chromophore to pigments known to contain PCBs. Alongside pigments and dyes, PVC and chlorinated paraffins were identified as additives in paint that may also be sources of by-product PCBs. The identification of this multitude of individual PCB congener sources from commercial PCB mixtures provides pause and an increased awareness to environmental practitioners and regulators. PCBs cannot always be assumed to be emanating from commercial mixture sources and are likely coming from multiple mixed sources. These can include by-product PCBs, commercial mixtures and weathered commercial and by-product PCB sources. This makes traditional Aroclor PCB measurements (e.g. those derived from EPA Methods 8082A and 608) fundamentally flawed in their identification of Aroclor PCBs in environmental samples and increases the need for full congener PCB analysis when assessing PCB sources in the environment.

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CRediT authorship contributions statement

Tyler Hannah: Formal analysis, Writing - Original Draft, Writing - Review & Editing, **David Megson:** Conceptualization, Formal analysis, Writing - Original Draft, Writing - Review & Editing, **Courtney Sandau:** Conceptualization, Writing - Review & Editing.

Data availability

Raw data is provided in the Supplementary information

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Co-authors Megson D and Sandau C work for Chemistry Matters undertaking legal cases that involve source apportionment of technical PCB mixtures and inadvertent sources of PCBs.

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