Polychlorinated biphenyls in pigments: inadvertent production and environmental significance

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Polychlorobiphenyls are toxic, bioaccumulative, and persistent chemicals whose intentional manufacture has been banned throughout the developed world. Polychlorobiphenyls may be generated inadvertently during the production of certain pigments, including diarylides. This inadvertent production is allowed under various regulatory schemes, such as the Toxic Substances Control Act in the United States and the Stockholm Convention on Persistent Organic Pollutants. Generally, these regulations require polychlorobiphenyl levels in batches of pigment to be less than certain regulatory limits, usually 50 ppm. A growing body of evidence suggests that the use of pigments is dispersing polychlorobiphenyls throughout the environment. Polychlorobiphenyl congeners associated with pigments have been found throughout the United States in sediments and in surface waters at levels exceeding the prevailing water quality standards. A recent Japanese government study reported measured polychlorobiphenyl concentrations well above 50 ppm in several commercial batches of azo pigments. A strong case may thus be argued that pigment manufacturers should modify existing production processes to reduce, ideally prevent, the formation of polychlorobiphenyls, or develop new pigments that do not have the potential to form polychlorobiphenyls. This paper, the result of a collaboration involving environmental scientists (LR and JG) and a pigment chemist (RC), reviews the evidence for environmental contamination from inadvertent polychlorobiphenyl production in specific pigments, together with a rationalisation of the conclusions based on the reaction mechanisms involved in their manufacture. Broad measures are proposed that might address these issues, both from environmental and from chemical perspectives.

Editor-in-Chief's recommendation: *This Feature article is a thought-provoking paper that will help frame the continuing debate about the impact of the coloration industry on concentrations of a set of persistent contaminants, polychlorinated biphenyls (PCBs), present in the ecosystem. The authors, who are globally renowned experts within the fields of environmental science and colourant chemistry, shed light on complex issues that centre on the unintentional generation of PCBs during pigment manufacture or breakdown. Not only do they review evidence for a link between concentrations of PCBs in the environment and pigment industry activity, but for the first time in an overview on this subject they devote substantial attention to rationalising chemical mechanisms for the formation of specific PCBs during the synthesis of particular commercial pigments. While the paper advocates more diligent and widespread enforcement of existing PCB-related regulations, it recognises that alternative legislative frameworks that are more appropriate to pigments may be required. In addition, the authors propose ways of eliminating those colourants that are connected with PCBs. However, they also take a pragmatic approach in calling for manufacturers to adopt methods of pigment production that minimise PCB generation in those instances where product replacement faces technical and economic difficulties. This Feature article will therefore be of great interest to those who create and handle pigments as well as materials that contain them.*

Polychlorinated Biphenyls: the Background

PCB is the commonly used abbreviation for a group of organochlorine compounds referred to as polychlorinated biphenyls or polychlorobiphenyls [1]. These materials, represented by the general structure shown in Figure 1 and the formula $C_{12}H_{10-x}Cl_x$, are based structurally on a biphenyl ring system to which 1–10 chlorine atoms may be attached. The various configurations of chlorine atoms give rise to 209 possible PCB congeners, numbered 1–209 on the basis of the number and positions of chlorine atoms according to the IUPAC convention. Congeners having equal numbers of chlorine atoms belong to the same homologous group and share similar physicochemical properties.

Polychlorinated biphenyls are anthropogenic chemicals with no known natural sources. PCBs were formerly used extensively as insulating materials in electrical equipment, hydraulic oils, and heat transfer systems, with smaller quantities used for other industrial purposes. Their high stability, while formerly a technical advantage, means that they are highly persistent in the environment, and they are thus classified as persistent organic pollutants (POPs) [2]. In the US, about 99% of all intentional PCB production was carried out by Monsanto, the products sold under the trade name Aroclor [2]. In Europe, PCBs were produced under trade names such as Phenoclor (France), Fenclor (Italy), Askarel (United Kingdom), and Clophen (Germany) [3]. Breivik et al. [3] estimate that 1 325 810 t of PCBs was produced intentionally via these 'legacy' sources, with 80% of this occurring in just four countries (the United States, West Germany, the USSR, and France). These commercial formulations were invariably mixtures sharing broadly similar congener patterns. While 209 congeners are possible, a much smaller number were recognised as significant in commercial products. The Aroclors were numbered, with
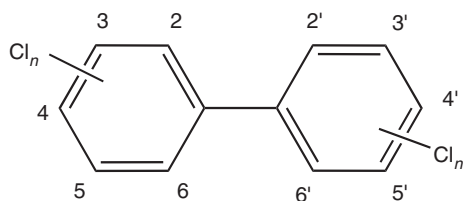
**Figure 1** The general structure of a polychlorinated biphenyl

the first two digits denoting the number of carbons (12) and the second two denoting the percentage of chlorine by weight in the finished product [4]. For example, Aroclor 1242 contained 42% chlorine by weight. The one notable exception to this convention was Aroclor 1016, a product of distillation of Aroclor 1242, with which it shared a similar congener fingerprint [4]. Aroclor 1242 accounted for about 51% of US production. With Aroclors 1016, 1248, 1254, and 1260, these five products accounted for about 98% of US production [2].

In addition, PCBs may be generated inadvertently in a range of chemical processes. In 1983, the US Environmental Protection Agency (EPA) published a list of 70 chemical processes with the potential to generate PCBs [5]. This list included not only processes such as the production of chlorinated benzenes and other chlorinated aromatics, where there are obvious potential sources of PCBs, but also processes not aimed at chlorinated chemicals, for example glycerol, where the source is less obvious. While the EPA found that these processes have the potential to generate PCBs, they did not establish that they actually do so [5]. The manufacturing processes leading to certain pigments are recognised as a source of inadvertent PCB generation [5]. Guo *et al.* [6] estimated that about 8 t of PCBs is generated via the production of organic pigments each year. This estimate was based on an estimate of worldwide production of organic pigments of about 250 000 t in 2006, with about 25%, or 62 500 t, being diarylide yellows [7]. This production estimate was then multiplied by 125 ppm, which is the highest concentration of PCB 11 allowed in pigments under the Toxic Substances Control Act (TSCA). This number is dwarfed by the amount of legacy PCBs produced, which has been estimated to be 1.3 million t globally. Based on the mixture of Aroclors produced in the United States [8] and their congener composition [9], about 0.011% of all US PCB product consisted of PCB 11. If this same proportion applies globally, then a total of about 147 t of PCB 11 was produced via legacy PCBs. This is equivalent to the amount of PCB 11 produced via pigments in about 20 years. Based on the evidence provided in this review, it may be argued that, as legacy production has stopped, pigments are potentially the largest source of PCBs in production today. In addition, given that pigments are used worldwide while legacy PCB production and use were concentrated in a few countries, pigments could be the main source of PCBs in many countries.

This article is the result of a collaboration involving environmental scientists who have been leading recent research into PCB sources in the environment (LR and JG), together with a chemist with extensive experience of the pigment industry (RC), aiming to present a balanced current perspective on the issues. The paper reviews the evidence

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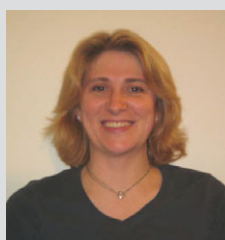
Dr Lisa Rodenburg is a hybrid chemist/engineer who has worked in the environmental field for nearly 20 years. Her interests are in the sources and fate of persistent organic pollutants, especially PCBs. She focuses on the cycling of pollutants at watershed, regional, and global scales. She has published over 40 papers in high-ranking international journals.

Dr Jia Guo obtained her PhD in Environmental Science under the supervision of Dr Lisa Rodenburg. Her dissertation focused on the fate and transport of PCBs, especially inadvertently produced PCBs.

for environmental contamination from inadvertent PCB formation in the case of certain pigments, and presents a mechanistic rationalisation based on the chemistry of the processes involved in the pigment manufacture. The authors also propose broad measures that might be introduced to address a range of issues both from environmental and from chemical perspectives.

Polychlorinated biphenyls are considered to be PBTs: chemicals that are *persistent* (they do not readily break down in the environment), *bioaccumulative* (they accumulate in living tissues), and *toxic* (they cause adverse health effects). The toxicity of PCBs is a complex subject [10,11], in part because legacy PCB products often contained highly toxic materials such as polychlorinated dibenzo-*p*-dioxins and -furans. Also, data generated from high-dosage animal testing do not necessarily extrapolate to human responses resulting from exposure to low concentrations. Some of these confounding factors have been addressed by toxicity studies using high-purity PCB congeners [12], and by epidemiological studies. For example, a study of residents of Anniston, Alabama, where PCBs were produced, demonstrated a strong link between higher PCB serum levels and elevated blood pressure [13]. There remains some division in expert opinion, varying from those who feel that PCBs exhibit no serious health concerns at ppb exposure

levels to those who feel there is no safe concentration. It is known that some congeners are more toxic than others. PCB congeners that have at least four chlorine atoms and either zero or one chlorine in the *ortho* (2/2′/6/6′) position (see the numbering system in Figure 1) are of particular concern. They are classified as 'dioxin-like', meaning that they induce the aryl hydrocarbon hydroxylase as well as other enzymes, such as those associated with cytochrome P450 [14]. Toxic equivalency factors (TEFs) have been established for these 12 congeners [15]. PCBs (all congeners) are classified as probable human carcinogens [16]. They are neurotoxins and endocrine disruptors. They can cause chloracne and affect sexual, skeletal, and mental development. Congeners with one or two chlorine atoms are known to be hydroxylated by various biological and abiotic processes, and there is growing evidence that the hydroxylated metabolites are toxic [17]. A growing body of evidence suggests that the toxicity of PCBs originates in part from the formation of hydroxylated PCBs, which have been found to exert certain toxic effects that are not exhibited by the parent PCBs. In addition, hydroxylated PCBs sometimes induce toxic effects at lower concentrations than the parent PCBs [17]. A discussion of the toxicological issues associated with the specific congener PCB 11, as far as they are understood, is given later in this review.

The bioaccumulation potential of PCBs also varies across congeners. Generally, congeners with more chlorine atoms have lower vapour pressures, lower aqueous solubility, and higher octanol–water partition coefficients, so that they tend to partition towards organic matter in sediment and towards lipids in organisms, including humans [18]. They are therefore more bioaccumulative and are less likely to be transported over long distances, as they will remain strongly sorbed to sediment. Congeners with fewer chlorine atoms have higher vapour pressures, greater aqueous solubility, and lower octanol–water partition coefficients. They are more mobile (e.g. more easily wash away with water or volatilise into air) and less likely to bioaccumulate.

Regulatory Framework for Polychlorinated Biphenyls

Polychlorinated biphenyls are one of the 'dirty dozen' addressed under the first Stockholm Convention on Persistent Organic Pollutants, adopted in 2001 [19]. Under this programme, 'parties to the Convention are obliged to eliminate equipment and oils containing PCBs from use by 2025 and bring these under environmentally sound waste management by 2028' [20]. A total of 152 nations have signed the Stockholm Convention, including the members of the European Union, Russia, China, India, and Japan. The United States has not ratified the Stockholm Convention, and is not likely to, although the existing environmental US laws are designed to accomplish many of the same objectives. Along with many other programmes aiming to reduce PCB contamination, the Stockholm Convention has focused on the elimination of legacy sources from electrical and other equipment, although PCBs are listed under both categories A (intentional production) and C (unintentional production) of the Stockholm Convention. 'Specific chemical production processes

releasing unintentionally formed persistent organic pollutants' are mentioned as potential sources of PCBs.

In the United States, the intentional production of PCBs was banned in the TSCA of 1976, which also explicitly acknowledged the issue of inadvertent PCB formation. The TSCA contained a loophole allowing for inadvertent production, which specifically mentioned the pigment industry. The original 1979 Code of Federal Regulations states that 'after July 1, 1979, processing and distribution in commerce of diarylide or phthalocyanine pigments that contain 50 ppm or greater PCBs is permitted only for persons who are granted an exemption'. The concentration of PCBs allowed in these products under the TSCA is an average of 25 ppm, not to exceed 50 ppm at any time [5]. However, TSCA also introduced discounting factors for PCB congeners with one or two chlorine atoms. The present Code of Federal Regulations states: 'inadvertently generated *non-Aroclor* PCBs are defined as the total PCBs calculated following division of the quantity of monochlorinated biphenyls by 50 and dichlorinated biphenyls by 5′ [21]. Under TSCA, production is synonymous with import, such that imported batches of pigment must meet the same standards. Finished products containing pigments are also covered under the regulations. While importers must certify that their products comply with the regulation, it is not clear how much actual testing of materials for PCBs is carried out. The European Union ratified the Stockholm Convention in 2005. The EU regulations that implement the Stockholm Convention, regulation (EC) No. 850/2004, set a limit of 50 ppm for the sum of PCBs in pigments, with no discounting factors. These regulations cover not only the manufacture but also the processing and commercial distribution of PCB-containing products.

In the United States, the TSCA is on an unfortunate collision course with other environmental regulations, most notably the Clean Water Act (CWA). Under the CWA, the US EPA sets water quality standards (WQSs) for many pollutants to protect human health and the environment. For the sum of all PCB congeners, the federal WQS is 64 pg l^{-1} (parts per quadrillion or ppq) [22], contrasting with the TSCA 50 ppm limit in pigments, roughly nine orders of magnitude higher. Under the CWA, economic factors may not be considered in the development of WQSs. States are permitted to set their own WQS. The most restrictive is New York State, where the standard for PCBs is an essentially unattainable (and almost unmeasurable) 1 pg l^{-1}. There is concern that the difference between the TSCA limit and the WQS may be a recipe for failure. Many facilities that discharge to surface waters, such as wastewater treatment plants (WWTPs) and recycled paper mills, may be taking in waste including products containing pigments with residual PCB levels of several ppm, which comply with TSCA. While many WWTPs are quite efficient at removing PCBs from their waste stream, there is concern that even the most efficient plants may not be able to attain the level of removal that would be required to comply with the CWA, nor is there any existing and cost-effective technology that would allow them to do so. This raises the question as to whether the 50 ppm PCB limit in pigments required under the TSCA is sufficiently restrictive to achieve the required WQS in the United States.

Industrial Pigments that May Contain Polychlorinated Biphenyls

Pigments are ubiquitous materials, used mostly in the coloration of paints, printing inks, and plastics, but also to an extent in a wider range of substrates, including paper, textiles, rubber, glass, ceramics, cosmetics, crayons, and building materials such as cement and concrete [23–26]. It has been known for some time that certain commercial organic pigments may contain trace quantities of PCBs [27]. The issues involved have assumed increasing significance as evidence of the environmental consequences has grown, and also as analytical techniques capable of quantifying trace amounts of PCBs have developed in sophistication and sensitivity. Pigment manufacturers, presumably conscious of the situation with specific products, have been responsible for addressing the issues to ensure compliance with regulations that specify maximum permissible levels. However, individual organisations have generally appeared
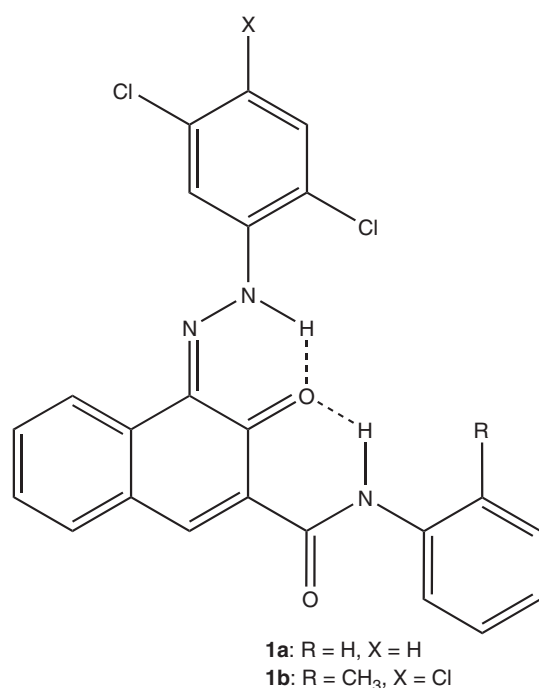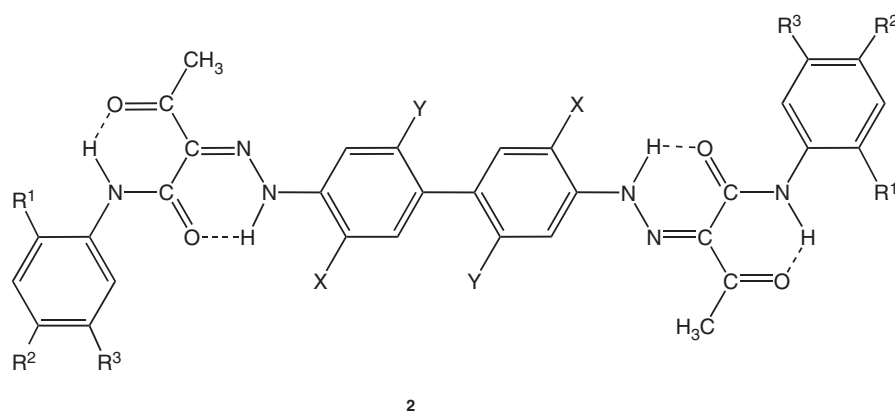
reluctant to engage in open discussion on the issues, and there is a scarcity of reported analytical data. A particularly important feature in the context of assessing the current situation is the fact that organic pigment manufacture, formerly dominated by multinational companies located in the developed world (the United States, Europe, and Japan), has in recent decades transferred almost entirely to the developing world, notably China and India, with their products being exported worldwide.

Azo pigments are the dominant chemical class of yellow, orange, and red organic pigments [23]. Although usually defined as structures containing one or more azo groups (–N=N–), they invariably exist in the ketohydrazone form, as illustrated in this review. Azo pigments provide high intensity and brightness of colour and are capable of providing reasonable to very good technical properties. A prime reason for their commercial importance is their cost effectiveness, which is due to the nature of the manufacturing processes. They are usually produced in virtually quantitative yields, using commodity starting materials in processes carried out in water, at or below ambient temperatures.

A small group of azo pigments for which it appears that there has been an historical issue with inadvertent PCB formation contain monoazo pigments derived from a dichloro- or trichloroaniline as the diazo component. These are moderately significant commercial products, exemplified by CI Pigment Red 2 (**1a**) and CI Pigment Red 112 (**1b**) (Figure 2), based on naphtharylamide coupling components. CI Pigment Red 2 is a relatively low-cost, mid-red pigment used primarily in printing inks. CI Pigment Red 112 is a higher-performing product used in printing inks, paints, and plastics. While there is little discussion in the open literature on the issues, there is evidence from a few patents describing methods to minimise PCB formation that industry has seen the need to act [28,29]. In addition, as discussed later in this review, PCB formation appears mechanistically reasonable in the case of these products.

A second group of azo pigments that have been implicated in inadvertent PCB generation are the diarylide yellow and orange pigments [23,30]. These products are disazo pigments derived from 3,3′-dichlorobenzidine (DCB), or to a lesser extent 3,3′,5,5′-tetrachlorobenzidine, as the bis-diazo component. The yellow pigments (**2**) are based on acetoacetarylide coupling components (Figure 3 and Table 1) and

1a: R = H, X = H
1b: R = CH₃, X = Cl

Figure 2 Azonaphtharylamide pigments (**1**) derived from dichloro- or trichloroanilines as diazo components

2

Figure 3 The general structure of a diarylide yellow pigment (**2**)

Table 1 Substituent pattern in commercial diarylide yellow pigments

Compound	CI Pigment Yellow	R^1	R^2	R^3	X	Y
2a	Y12	H	H	H	Cl	H
2b	Y13	CH$_3$	CH$_3$	H	Cl	H
2c	Y14	CH$_3$	H	H	Cl	H
2d	Y17	OCH$_3$	H	H	Cl	H
2e	Y55	H	CH$_3$	H	Cl	H
2f	Y63	Cl	H	H	Cl	H
2g	Y77	CH$_3$	H	Cl	Cl	H
2h	Y81	CH$_3$	CH$_3$	H	Cl	Cl
2i	Y83	OCH$_3$	Cl	OCH$_3$	Cl	H
2j	Y113	CH$_3$	Cl	H	Cl	Cl
2k	Y124	OCH$_3$	OCH$_3$	H	Cl	H
2l	Y152	H	OC$_2$H$_5$	H	Cl	H
2m	Y170	H	OCH$_3$	H	Cl	H
2n	Y171	CH$_3$	Cl	H	Cl	H

Table 2 Substituent pattern in commercial diarylide orange pigments

Compound	CI Pigment Orange	R
3a	O13	H
3b	O34	CH$_3$

Figure 5 The structure of copper phthalocyanine (**4**)

the orange pigments (**3**) on pyrazolones (Figure 4 and Table 2). These pigments are of high commercial significance, having for nearly a century provided the dominant yellow products for the inks used in high-volume, low-cost printing of magazines, newspapers, and other printed paper products, and they are also important in printed textiles. A few products are used more widely, for example in paint applications, the most notable being CI Pigment Yellow 83 (**2i**) (Table 1). The presence of PCBs in this group of pigments has been recognised since at least the 1970s when the TSCA was written, although the issue appears to have been raising serious concern only since the methods for measurement of PCBs have advanced.
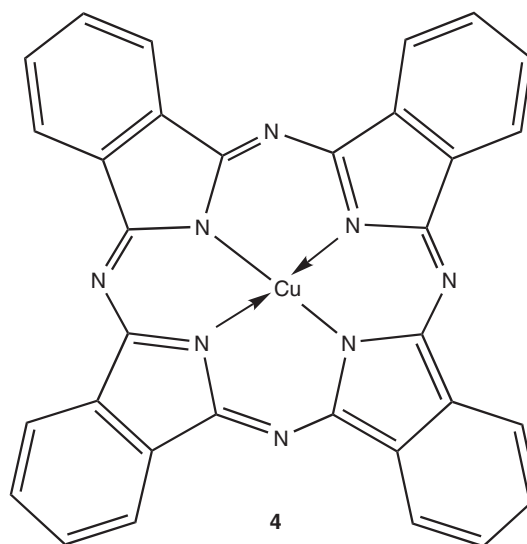
The single most important organic pigment is copper phthalocyanine (CuPc, CI Pigment Blue 15, **4**) (Figure 5) [23]. The most important green organic pigment is CI Pigment Green 7, a CuPc derivative in which the 16 ring H-atoms are replaced virtually completely by chlorine. CuPc pigments provide brilliant, intense colours and exceptionally high stability at modest cost, and are universally used in the range of pigment applications. There is some evidence that PCBs may be formed in the manufacture of these pigments, although the situation is less conclusively established than is the case with the specifically identified azo pigments.

## The Presence of Non-Aroclor Polychlorinated Biphenyls in Pigments

The issues associated with PCBs in pigments assumed a relatively low profile for decades, for two main reasons. Firstly, the 'legacy' PCBs, referring to intentional commercial production, were by far the dominant sources worldwide, while other sources were assumed to be negligible in comparison. In the decades since PCBs were banned, legacy sources have greatly diminished, such that inadvertent sources have become proportionately more important. Secondly, the analytical techniques used to measure PCBs in environmental samples have evolved remarkably since the 1970s. The major leap forward took place in 1999 when the US EPA published method 1668 for the measurement of PCBs in environmental matrices using high-resolution gas chromatography and high-resolution mass spectrometry (HRGC/HRMS) [31]. This method allowed the quantification of all 209 PCB congeners, whereas older methods only quantified a subset of congeners associated with commercial PCB formulations. Congeners not typically associated with the legacy sources, commonly referred to as non-Aroclor PCBs, began to be reported by various US agencies that were required to use the new method. As a result of investigations that have followed, researchers have become
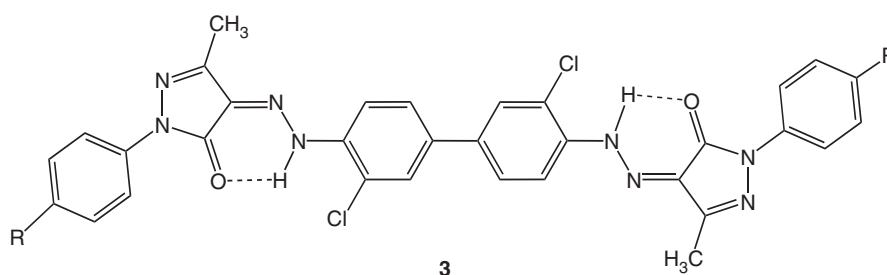
Figure 4 The general structure of a diarylide orange pigment (**3**)

increasingly concerned that pigments might be an important source of these congeners in the environment. However, the issue of inadvertent PCB production has received less attention in the EU, probably because the prevailing methods used to measure PCBs address a much shorter list of congeners, which does not include those that are increasingly associated with pigments. For example, the widely used 'Dutch method' (method NEN 5734) measures only seven congeners (PCBs 28, 52, 101, 118, 138, 153, and 180) representative of commercial formulations [32].

Measuring PCBs in pigments is challenging primarily owing to difficulties in extraction and sample preparation. There are no internationally recognised standard methods for the analysis of PCBs in pigments. It is possible that extraction of pigment and associated pigment products (such as inks) may only access PCBs on the surface of the particles.

A specific PCB that is considered in some detail in this review, including the evidence that its inadvertent production is associated with diarylide pigments, is PCB 11 (3,3′-dichlorobiphenyl, **5**) (Figure 6). This congener is found in only very small quantities in the Aroclors. Among the five main Aroclors, PCB 11 is present at its highest level (a maximum of 0.02%) in the congener pattern of Aroclor 1016 [9]. As a dichlorobiphenyl, taking into account the discounting factor of 5, PCB 11 is allowed in pigments at an average level of 125 ppm and a maximum of 250 ppm under current US federal regulations. A structurally related PCB, for which an association with pigments has been suggested, is the tetrachloro derivative, PCB 52 (2,2′,5,5′-tetrachlorobiphenyl, **6**) (Figure 6). In contrast to PCB11, PCB 52 is a main constituent of many Aroclors [9].

Other PCBs have been detected in pigments. A wide congener range, including several that are dioxin-like, was found in commercial pigments from the United States and Japan [33,34]. PCBs 11 and 52 were most frequently detected in azo pigments and the highly chlorinated PCBs, including PCBs 206 and 208 and the fully chlorinated PCB 209, were associated with phthalocyanine green pigments [33,34]. These three congeners are also considered as non-Aroclor PCBs owing to their low levels in the commercial products. Among the five main products, PCB 209 is present at its highest level (a maximum of 0.08%) in the congener fingerprint of Aroclor 1260 [9].

Concentrations of Polychlorinated Biphenyls in Pigments

Over the years, pigment manufacturers have not widely reported the levels of PCBs observed in their products, nor
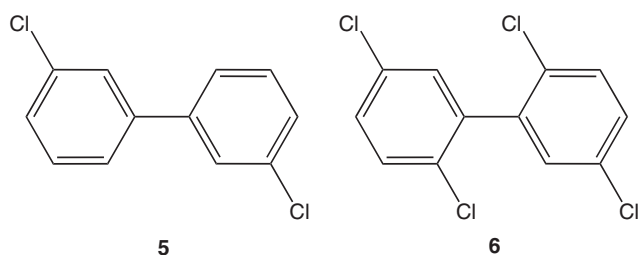
the methods that they have used to determine the levels. In the limited range of data that have been reported, the levels of inadvertent PCBs found in certain pigments vary significantly. In the absence of a substantial body of data, it remains a matter of speculation as to whether this arises from differences in manufacturing processes, features of the analytical methodology used, or by a combination of factors. According to the US EPA, the Dry Color Manufacturing Association (DCMA) reported a PCB 11 level in a diarylide yellow pigment at approximately 70 ppm in 1981, when the maximum concentration was regulated at an average of 50 ppm, with exemptions up to 500 ppm [35,36]. The Ecological and Toxicological Association of Dyes and Organic Pigments Manufacturers (ETAD) acknowledged the presence of byproduct PCBs in pigments in a 2011 statement: 'there are minute traces of inadvertently generated PCBs in some pigments (usually less than 5 ppm), and values up to 20 ppm have occasionally been measured …' [27]. In a 2010 study, a series of 'commercial paint pigments' obtained in the United States were found to contain PCBs in the range 2–200 ppb [33]. It is not clear what materials were actually tested in this study, but if they were paints or stainers, lower concentrations of PCBs than in pigment powders would be expected. The total concentration of PCBs was reported to be as high as 740 ppm in commercial pigments sold in Japan [34]. Members of the Japanese Dyestuff and Industrial Chemicals Association (JDICA) voluntarily conducted analytical investigations and found evidence of PCB formation as a byproduct of the manufacture of certain organic pigments, reporting their results to the Japanese Ministry of Economy, Trade, and Industry (METI) in 2012. In a first METI report, based on investigations by six major companies, PCBs were detected in 57 out of 98 pigments, quoting levels exceeding the internationally accepted maximum of 50 ppm for samples of five pigments, CI Pigment Yellow 13 (**2b**), CI Pigment Yellow 83 (**2i**), CI Pigment Yellow 165, CI Pigment Red 2 (**1a**), and CI Pigment Red 112 (**1b**) [37]. In a subsequent METI report in 2013, which included some reanalysis in cases where there may have been some doubt over the analytical method used, PCB levels in excess of 50 ppm (up to 2000 ppm) were reported, not only for these five pigments but also for samples of CI Pigment Yellow 12 (**2a**), CI Pigment Yellow 17 (**2d**), CI Pigment Yellow 55 (**2e**), CI Pigment Yellow 81 (**2h**), and CI Pigment Orange 34 (**3b**) [38]. These Japanese studies provide definitive evidence that certain pigments have been manufactured and distributed with a level of PCBs well in excess of that permitted, although it is not clear how representative these particular samples are of the global production of these pigments. While the congener patterns were not reported, a clear problem with diarylide pigments is demonstrated. No phthalocyanine pigments were implicated in the Japanese study, although PCBs were detected in CuPc pigments in a US study, with PCB 209 as the predominant congener in CuPc green [33]. The pigment manufacturer BASF has stated that their Heliogen pigments contain levels of less than 2 ppm PCB in CuPc blue and in the range 2–25 ppm in CuPc green [39]. However, this cannot be considered as a guarantee that all batches of the pigments from the wide range of manufacturers comply with the regulations.

Figure 6 The structures of PCB 11 (**5**) and PCB 52 (**6**)

Polychlorinated Biphenyls from Pigments in Consumer Products

Polychlorinated biphenyls have been measured in a variety of consumer goods, including commercial paints, printed paper, textile-printed clothing, and plastics. Dichlorobiphenyl was measured at a level of 15.5 ppb in printing inks containing yellow pigments in a 1992 study [40]. The congener most often found in the studies is PCB 11, reaching concentrations as high as 86 ppb in consumer materials, and appears to be correlated with the presence of yellow pigments [6,41]. Concentrations are generally highest in yellow items and lower in items printed in other colours. Most Aroclor PCB congeners are undetectable in consumer goods, with the exception of PCB 52, which may also be associated with pigments [6,41]. In all cases, the congener pattern of PCBs found in commercial pigments and in consumer products is not similar to that in any of the Aroclors. The yellow printed materials that contain measurable levels of PCB 11 typically do not contain any other congeners, indicating that the PCBs are not taken up passively, for example by absorption from the air which contains a wide range of PCB congeners. Unpigmented materials, such as white paper, do not contain measurable amounts of PCB 11 or other congeners associated with pigments [6,41]. Samples of white clothing were found to contain low levels of PCB 11 (1–2 ppb), similar to the levels found in material coloured with (presumably non-diarylide) dyes, including socks that have been dyed yellow. Both cotton and polyester garments were tested. It may be that many of these garments pick up the PCB as a cross-contaminant during the processing of the garment. In contrast, clothing printed with a yellow design can contain up to 79 ppb of PCB 11 [6].

Evidence that Polychlorinated Biphenyls Can Be Mobilised from Pigment-containing Products

It has been suggested that the release of PCBs from pigments into the environment is improbable, on the basis that they are strongly bound to the pigment particles and that the pigments are generally contained in a polymeric matrix in their application [27]. However, several lines of evidence demonstrate the mobility of certain PCBs, particularly the less chlorinated PCB 11. It was speculated that PCB 11 may volatilise into ambient air because of its high vapour pressure, resulting in its detection and significant abundance in urban air [42] . There is some evidence that the atmospheric level of PCB 11 may be dependent on human activity. The contribution of PCB 11 to total airborne PCBs is reported to be considerably higher in residential areas than in industrial and semi-rural areas of South Korea [43]. Elevated concentrations of PCB 11 in an indoor environment indicate possible emission, for example from materials within the room [43]. A strong statistical correlation was found between airborne PCB 11 levels and population density in the Great Lakes Region [44], whereas the relationship was much weaker in the Philadelphia metropolitan area [45]. In addition to direct emission, it is conceivable that PCBs may also enter the atmosphere through volatilisation from the water column that receives PCBs from WWTP effluent, stormwater run-offs, landfill leachate, etc. [6].

Tests have confirmed that PCB 11 leaches out of pigment-printed paper, even under mild conditions. In a 48 h test using ultrapure water as a leachant, between 6 and 81% of PCB 11 was mobilised from printed paper and cardboard samples, although it is not clear whether the PCB 11 was released into the dissolved phase or whether it was present in the particle phase, i.e. as abraded paper or pigment [6]. The water quality standard for PCBs applies to the whole water concentration, i.e. the sum of the dissolved and particle phase concentrations. Because surfactant-like substances, such as humic acid, increase leaching ability [46], there may be higher potential for leaching from printed materials into the environment in situations where surfactants are present in surface water, landfill and industrial site leachate, and sewage. It is also possible that PCB 11 in printed clothing will leach out during garment laundering, which utilises surfactant, mechanical agitation, and often elevated temperatures.

Levels of Pigment-associated Polychlorinated Biphenyls in the Environment

Different PCB congeners behave differently in the environment. Highly chlorinated congeners such as PCB 209 sorb to soil and sediment and therefore remain close to their origin. In contrast, PCBs with fewer chlorine atoms, such as PCB 11, are more mobile because they dissolve more readily in water and volatilise into air. PCBs can be transported over long distances via the atmosphere and redeposited to land or water. This may explain why, for example, they are found in uninhabited regions such as the Arctic and Antarctica [47–51]. Because of its environmental mobility, PCB 11 is found ubiquitously, with highest concentrations in the water column. One of the first reports of the environmental presence of PCB 11 and its potential association with pigments came from Litten *et al.* [52]. Unexpectedly high levels of PCB 11 were detected in treated effluent from US wastewater treatment plants receiving production waste from pigment manufacture. That same year, King *et al.* [53] reported high concentrations of PCB 11 in water, suspended particulate material, biota, and sediments from Halifax Harbor, Nova Scotia, Canada.

A number of subsequent studies have demonstrated the presence of PCB 11 in the urban and rural atmosphere of several US cities, the US Great Lakes Region, South Korea, and Japan [34,42–44,54]. In most cases, its spatial distribution is rather different from the Aroclor PCBs, which usually follow an 'urban fractionation effect', thus suggesting a distinctive source for PCB 11. Surprisingly, in the polar regions, PCB 11 was detected in the air at levels comparable with those measured in urban atmospheres [47,49,50]. PCB 11 comprised up to 20% of total PCBs found in samples of soil, sediment, lichen, and moss from Antarctica [50], and as high as 4.5% in ice and snow from the Arctic [49]. These findings suggest the potential for long-range atmospheric transport (LRAT) for this congener.

Municipal solid waste incinerators (MSWIs) are another potential environmental source of non-Aroclor PCBs, including PCBs 11 and 209, which may be released either

by direct emission from PCB-containing combustion materials or through formation from carbon and chlorine precursors. Traces of PCB 11 were measured in the stack gas from MSWIs in South Korea, although the contribution to total PCBs was minimal [55]. Typical Swedish municipal waste was found to generate flue gases and ashes containing PCB 11 as high as 7% of total PCBs during combustion between 200 and 450 °C in a laboratory-scale waste incinerator [56]. The flue gases were dominated by mono- and dichlorinated PCBs. PCB 11 was among the most abundant PCBs, a feature associated with favoured formation of *meta* and *para* substituted congeners in such situations. Kim *et al.* [57] investigated PCB emissions from Japanese waste incinerators with regard to the types of incinerator, combustion temperatures (from 740 to 920 °C), and the nature of waste materials. While PCB 11 was detected in all flue gas samples, significantly higher concentrations, as well as certain dioxin-like PCBs, were measured in two of the eight samples, in these cases considered to be due to lower combustion temperatures or to waste plastic in the combustion materials. Ogura *et al.* [58] estimated that incineration is roughly equal in importance to legacy sources as a source of dioxin-like PCBs in Japan, but they did not specifically consider PCB 11. Incineration is far more common in Japan than in the United States. Japan incinerates 78% of its garbage [59], versus just 12% in the United States [60]. Japan is home to 1500 incinerators which combust 38 million t of garbage annually, while 29 million t is incinerated in the much larger area of the United States. Thus, while incineration may be a significant source of PCBs, including PCB 11, in some countries, it is unlikely to be important in the United States, where high levels of PCB 11 have been measured.

Another potential source of PCB 11 is abiotic photochemical dechlorination during atmospheric transport. Yao *et al.* [61] found that PCB 11 is produced during the photolysis of higher-molecular-weight PCBs in alkaline 2-propanol. Atmospheric deposition is an important source of PCBs to some water bodies, such as Lake Michigan. However, if PCB 11 were formed from photolysis of other PCBs, then the temporal trends in PCB 11 concentrations should follow those of the other congeners. They do not (see 'Temporal patterns of PCB 11' below).

In US surface waters where PCBs have been measured using EPA method 1668, PCB 11 has always been detected. These water bodies include (listed from east to west): New York/New Jersey Harbor [41], Delaware River [41], Houston Ship Channel, Texas [62], several rivers in New Mexico [63], Portland Harbor (terminus of the Willamette River, Oregon) [64], and San Francisco Bay [65]. Figure 7 illustrates the PCB 11 levels in some US water bodies. Concentrations of PCB 11 alone often exceed the federal WQS for the sum of PCBs (64 pg l^{-1}). Although not the case for the Delaware River, PCB 11 still exceeds the local applicable WQS standard, at about 9 pg l^{-1}. New York State has set its WQS at 1 pg l^{-1}, a level that is exceeded by PCB 11 alone in all samples collected in the NY/NJ Harbor. PCB 11 has also frequently been found in environmental matrices other than air and water. It was reported in soil from urban regions, farmlands, and e-waste dismantling areas in China [66,67]. The bioaccumulation potential of PCB 11 was confirmed by detection in striped bass from Long Island Sound, United
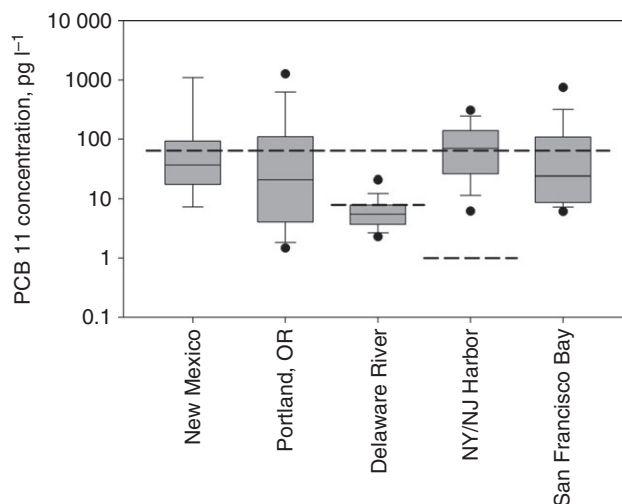
Figure 7 PCB 11 concentrations in water bodies across the United States. The Federal WQS for the sum of all PCB congeners is 64 pg l^{-1}, while the various local WQSs are sometimes lower (dashed lines). In this box and whisker plot, the top dot, top error bar, upper box edge, middle line, lower box edge, lower error bar, and bottom dot represent the 95th, 90th, 75th, 50th (median), 25th, 10th, and 5th percentile concentrations respectively

States [68], and in grey seals from Sable Island [69] and mussels and lobsters from Halifax Harbor [53] (both Nova Scotia, Canada). The presence of PCB 11 in human milk and serum samples indicate human exposure to environmental sources [70,71].

The Link Between Pigments and Environmental Polychlorinated Biphenyls

In order to address the question as to whether it is plausible that pigments present a source large enough to account for the levels of some PCB congeners, such as PCB 11, found in the environment, Guo *et al.* [6] conducted a mass flow analysis of PCB 11 in the Delaware River Basin, where one of the best, most comprehensive datasets on environmental PCBs was available. Their analysis demonstrated that, if PCBs are present in pigments at the maximum levels allowed under the TSCA, they are a large enough source to account for the PCB 11 found in the air, water, and sediment of the basin, although virtually all of the PCBs would have to be released from the pigments into the environment. Alternatively, if the pigments contain higher levels of PCBs than are allowed by law, measured PCB 11 levels in the environment could be accounted for on the basis of incomplete release.

Congener fingerprints for the five main Aroclors are shown in Figure 8. The Aroclors (and other commercial PCB formulations) contain only traces of PCBs 11 and 209. In order to address whether these congeners arise from inadvertent generation, and from pigments in particular, congener fingerprinting, based on the concept that each source or process produces a distinctive mix of congeners in relatively constant ratios, may be used. If the congener fingerprint in the environment contains congeners that are typically observed in certain pigments, this provides evidence that the pigment is the source of the environmental contamination. Using this approach, PCB sources have
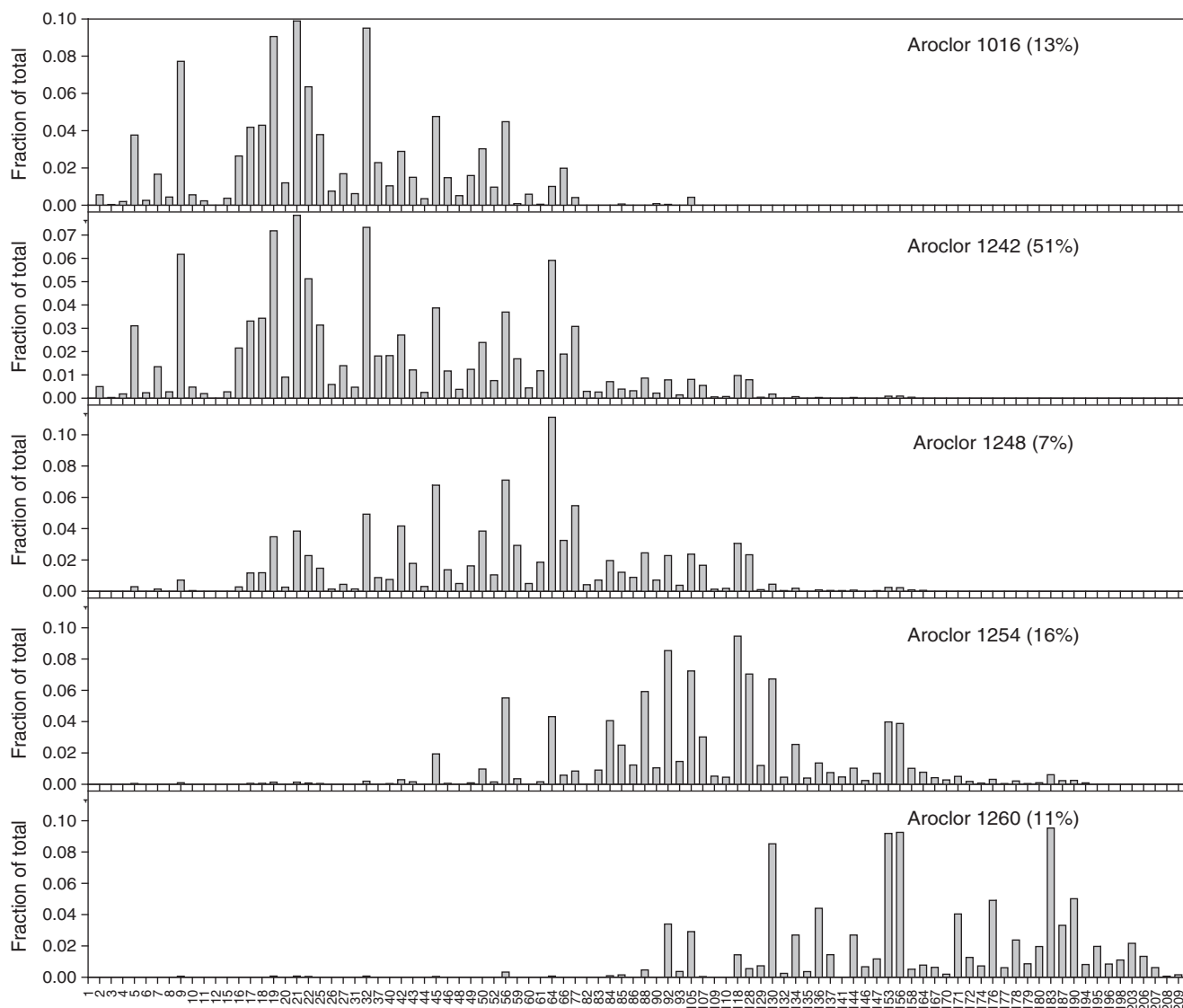
Figure 8 Congener fingerprints of the five main Aroclors. The congener number is shown on the *x*-axis, and the percentage contribution to the total is shown on the *y*-axis. Note the near total absence of PCBs 11, 206, 208, and 209 [30]

been investigated in many systems, including the water, sediment, and discharges in the Delaware River [72–74]. As visual examination of the PCB fingerprints is not sufficiently discriminating, statistical models can be used to extract source fingerprints from complicated congener patterns. The source profiles generated by this source apportionment approach suggest, in general, that most of the PCBs 11, 206, 208, and 209 in the environment arise from sources not associated with the legacy Aroclors. Figure 9 shows some congener profiles from a dataset of 89 PCB congeners measured in 645 samples of effluent from Delaware River facilities that are permitted under the CWA to discharge into the river [73]. Factors 1 and 6 (top and bottom panels) represent the main sources of PCBs 11 and 209 respectively. Factor 1 was identified as wastewater and stormwater run-off. PCB 11 and other pigment-associated PCBs may conceivably enter wastewater by leaching from disposal of printed paper products and during laundering of clothing, etc. As wastewater and stormwater aggregate pollution from across the urban landscape, sources of PCB 11 other than pigments are also possible. Note that the factor containing high levels of PCB 11 does not contain

PCBs associated with incinerators, such as PCBs 77, 105, 118, and 156 [56].

An alternative potential route to PCBs with low chlorine levels is from biological metabolism of more highly chlorinated PCBs. Anaerobic bacteria can metabolise chlorinated compounds in one of very few natural processes that degrade PCBs in the environment. In the process, chlorine is replaced by hydrogen. In general, *meta*- and *para*-chlorine atoms are replaced, but not *ortho*-chlorine atoms [75]. Thus, a main product of PCB dechlorination is PCB 4 (2,2′-dichlorobiphenyl), which contains two chlorine atoms in *ortho* positions. Early studies proposed the formation of PCB 11 from degradation of highly chlorinated PCBs, either through photoreaction or through microbial dechlorination [76–79]. However, most of the potential precursors (e.g. PCBs 77, 126, and 169) are not abundant enough in any of the commercial PCB mixtures to account for the extensive environmental contamination with PCB 11 [9,41,42]. From the analysis results shown in Figure 9, two of the source profiles were associated with the microbial dechlorination of PCBs [73]. Factor 2 is dominated by PCB 4, indicating that it arises from bacterial dechlorination. It is notable that PCB
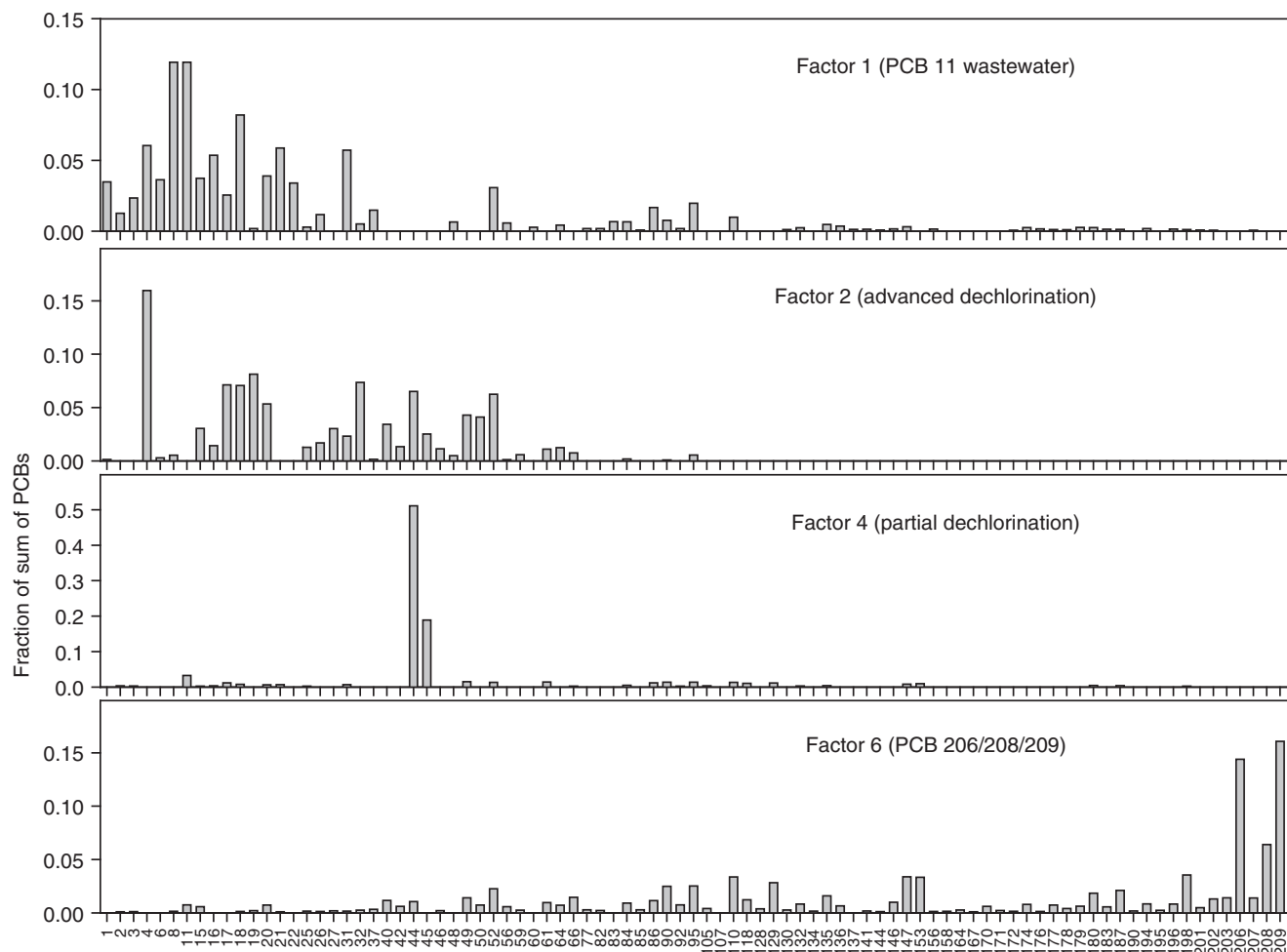
Figure 9 PCB source profiles (congener patterns) identified in discharges to the Delaware River [70]. Seven profiles were found. The three not shown resembled Aroclors 1248, 1254, and 1260 (see Figure 8). PCB congener numbers are on the *x*-axis, and the fraction of the total is on the *y*-axis

11 is completely absent in factor 2, suggesting that it is not generally formed by dechlorination. Factor 4 is associated with a less complete dechlorination, with four chlorine atoms remaining, and PCBs 44 and 45 are formed primarily. There is a small amount of PCB 11 in factor 4, suggesting that dechlorination may produce some PCB 11, but this only accounts for a small fraction (less than 10%) of the PCB 11 mass in the system, while factor 1 accounts for the vast majority.

Another line of evidence indicating that dechlorination is not the dominant PCB 11 source is the fact that PCB 11 is not correlated with PCB 4, even in areas where it is well documented that bacteria actively dechlorinate PCBs. This type of dechlorination was first observed in the sediment of the Hudson River (feeding into the NY/NJ Harbor). The Upper Hudson River is heavily contaminated with PCBs owing to the former manufacture of electrical components at two factories owned by General Electric. As a result, bacteria in the sediment have been under heavy selective pressure to utilise (and thereby detoxify) PCBs via dechlorination. In this region, the ratio of PCB 11 to PCB 4 is in the range 0.004–0.2, with a relative standard deviation (RSD) of 54% [41]. Elsewhere, the ratio is much larger and more variable, ranging from 0.2 to 9 with an arithmetic mean of 1.7 (RSD = 110%) [41].

Temporal Patterns of PCB 11

The main method that environmental scientists use to investigate long-term temporal trends is the measurement of sediment cores. The cores are sliced into many layers, and measurements of isotopes of cesium and lead are used to indicate the age of each slice to within a few years. By this method, scientists can determine whether the temporal trends in pollutant concentrations correspond to the trends in production volumes of suspected sources. In sediment cores from Lake Ontario, Lake Erie, and the Indiana Harbor Ship Canal, all three displayed PCB 11 concentration profiles that correlated reasonably with US production figures for pigments [76]. Concentrations of all PCBs were virtually zero until about 1940. Like virtually all industrial chemicals, including Aroclors, pigment production experienced rapid growth after World War II. PCB 11 concentrations increased until about 1980, and then declined simultaneously with a decline in production around this time. Aroclor production in the United States was at its maximum earlier than this (1975), and had essentially ceased by 1980. PCB 11 concentrations were not correlated with the concentrations either of the sum of PCBs or of other congeners in these sediment cores, a further indication that PCB 11 is not associated with legacy Aroclors. The

temporal pattern of PCB 11 concentrations also did not correlate with the time trends in incineration, which came under much stricter environmental controls after the passage of the Clean Air Act in 1970. Levels of PCB 11 in the sediment cores did not decline after 1970, but instead increased until about 1980.

Similarly, ice cores from high-elevation glaciers can reveal the history of net inputs of persistent organic pollutants arising from atmospheric transport from populated areas. In a recent investigation, 209 PCBs, including PCB 11, were measured in an Arctic ice core representing deposition between 1957 and 2009, as well as in a surface snow sample representing recent deposition during 2009–2010 [48]. In this case, the historic fluxes of total PCBs and PCB 11 showed no distinct deposition trend that was correlated with the commercial production of PCBs. The reason for this may arise, in part, from variations in the pathways and frequencies of trajectories from likely source regions. PCB 11 was detected as a dominant dichlorobiphenyl in all samples, especially the surface snow, with a contribution of 4.5% to total PCBs, and the highest flux was observed among all periods for this congener. Samples of ice cores also showed elevated PCB 11 fluxes during 1957–1966 and 1998–2009, with consistently lower fluxes between these periods, indicative of emissions from past and ongoing sources. This investigation, along with other studies in the polar regions [47,51], suggests that PCB 11 has been emitted in significant quantities into the atmosphere at lower latitudes since at least 1957.

The temporal trends of atmospheric PCB 11 levels have been investigated in the United States and Japan. According to Basu *et al.* [44], the atmospheric PCB 11 concentration in the US Great Lakes Region did not follow the temporal trend of total PCBs, which were decreasing slowly over time. No significant pattern was observed for PCB 11 during the sampling period (2004–2007), except for one out of five sites where the atmospheric concentration showed a significant increase. This suggests that PCB 11 is not primarily formed via photochemical reduction of higher-molecular-weight PCBs, as this pathway would result in PCB 11 trends following those of the higher-molecular-weight precursors. In another study, monthly variations in PCB 11, 52, and 209 during 2005–2011 were reported for two urban/industrial cities in Japan [34]. The ratio of PCB 11 to total dichlorobiphenyls (PCB 11/DiCB) in the atmosphere varied between seasons, with a higher contribution in summer, whereas the ratio of PCB 52 to total tetrachlorobiphenyls (PCB 52/TeCB) remained constant throughout the sampling period. As PCB 52 also originates from legacy PCBs, the atmospheric burden of PCB 52 is believed to largely result from those sources. In contrast, the large variations in PCB 11/DiCB over seasons confirmed that atmospheric PCB 11 was not associated with legacy PCBs. The ratio of PCB 209 to total PCBs also displayed a slight seasonal trend, suggesting non-Aroclor sources, such as pigments or combustion, for PCB 209.

Toxicity of PCB 11

Whereas general understanding of PCB toxicity has evolved considerably in recent years, relatively little is known specifically about the toxicity of PCB 11. Although lacking *ortho*-chlorine atoms, it is not considered 'dioxin-like' because it has fewer than four chlorine atoms for which such a level of toxicity is assumed. However, other toxicity pathways have been identified as important for congeners with fewer chlorine atoms. In various studies, PCB 11 has been reported to produce neurotoxic effects in rat cells, including a decrease in dopamine content, protein kinase C translocation, and formation of reactive oxygen species [80–83]. In an *in vitro* study with human platelets, PCB 11 alone did not induce either platelet aggregation or generation of the bioactive mediator 12-hydroxyeicosatetraenoic acid (12-HETE). However, a synergistic effect on 12-HETE formation was observed when the cells were incubated with a combination of PCBs 11 and 77 [84]. Given the potential risks of exposure to airborne PCBs, an *in vivo* rat study was recently conducted to investigate the distribution and elimination of inhaled PCB 11 and its potential metabolites. PCB 11 was completely absorbed in the lung after inhalation exposure and quickly distributed in all tissues. Rapid elimination of PCB 11 was observed from lung, serum, and liver, with half-lives of around 2 h. The major hydroxylated metabolite 4-OH-PCB 11 was detected in liver only and was readily excreted [85,86]. However, an *in vitro* study with human cells demonstrated that 4-OH-PCB 11 was more potent than PCB 11 in inducing cell growth inhibition and decreasing clonogenic survival through elevated levels of reactive oxygen species [87].

Although it is difficult to relate the effects observed *in vitro* to effects in humans, generally PCB 11 displays toxic effects *in vitro* that are similar to those exhibited by other PCB congeners. Therefore, PCB 11 and other pigment-associated PCBs may cause effects in humans similar to the legacy PCBs, i.e. probable carcinogenicity, neurotoxicity, endocrine disruption, chloracne, and sexual, skeletal, and mental developmental changes [16].

The Mechanisms Involved in Polychlorinated Biphenyl Formation during Pigment Manufacture

ETAD proposed in their 2011 report [27] that 'the pigments most likely to show trace PCB contamination are those that: contain chlorine as part of their molecular structure; use chlorine-containing raw materials; use chlorine-containing aromatic solvents in their synthesis'.

This proposition is in a sense self-evident in that there can be no PCBs formed if there is no chlorine involved.

Recent Japanese reports have identified a number of azo pigments as exceeding the internationally recognised limits for residual PCBs [37,38]. It is of particular interest that these pigments were entirely derived from the two groups discussed previously in this paper: (a) monoazo pigments **1** (Figure 2) derived from a di- or trichloroaniline as the diazo component; (b) diarylide disazo pigments **2** (Figure 3) and **3** (Figure 4) derived from 3,3′-dichlorobenzidine (or 3,3′,5,5′-tetrachlorobenzidine) as the bis-diazo component.

In all cases, it is significant that reasonable mechanisms may be proposed for PCB formation as discussed in this section. It is also of interest, and indeed reassuring, that there is no credible evidence for PCB formation in other groups of industrial azo pigments.

In the first group, three pigments are implicated in the Japanese reports. Of these, CI Pigment Yellow 165, which appears to be derived from a dichloroaniline as the diazo component and a pyrazolone coupling component, is reported to be a minor product in Japan, while it is barely used elsewhere [25]. CI Pigment Red 2 (**1a**) and CI Pigment Red 112 (**1b**) are more important products. There is evidence from the patent literature that companies have for some time recognised the issues arising from these pigments and sought ways to minimise PCB levels [28,29]. According to the European Patent Office database, the approach appeared to have had sufficient value for the assignees to maintain patent coverage for nearly the maximum possible 20 years.

The second group consists of the highly important diarylide pigments, which are implicated in the release of PCB 11 into the environment on the basis of the body of evidence presented in this review. However, there has been a different source of concern over the years with diarylide pigments, associated with the high toxicity and suspected carcinogenicity of the common starting material 3,3′-dichlorobenzidine (DCB, **7**) (Figure 10). In view of hazards presented in the workplace, the use of DCB in pigment manufacture requires careful, controlled handling, generally with specifically devised procedures and equipment, and ideally involving no human contact. Although reassurances are broadly given that the pigments themselves are essentially non-toxic, evidence has been reported that they may cleave thermally at temperatures above 200 °C to give a monoazo compound, and that prolonged heating above 240 °C causes further decomposition leading to the release of DCB [88]. As a result of these observations, the use of diarylide pigments has declined in applications where high temperatures are likely to be encountered, especially in thermoplastics. For these applications, alternatives that do not give rise to this issue are available within the range of commercial organic and inorganic pigments, although often at higher cost. Over the decades, organic pigments based on 3,3′-dichlorobenzidine have been much more significant commercially than textile dyes based on this intermediate. It should be noted that 3,3′-dichlorobenzidine-based dyes have not been produced in the United States since 1986 [89]. These features, coupled with the fact that Guo *et al.* [6] did not find elevated levels of PCBs in dyed clothing imported into the United States, suggest that textile dyes are probably not a primary source of PCB 11 in the United States.
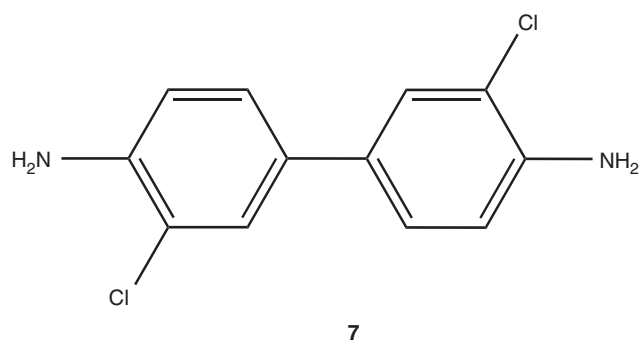
The discussion that follows presents informed speculation on the potential mechanisms by which PCBs may form inadvertently during the manufacture of these two groups of azo pigments, supported by literature precedent. Proposals are also made concerning how the side reactions that lead to PCBs might be minimised to provide products with reduced PCB levels. All classical azo pigments are synthesised by variations of the same standard synthetic route [24]. The synthesis involves a two-stage sequence of reactions, diazotisation and azo coupling (Scheme 1), both carried out in water. The industry has long recognised how vital it is to control carefully the synthesis conditions in order to maximise yields and to minimise side reactions that can lead to impurities, and consequently adversely affect both product quality and environmental acceptability.

Diazotisation involves the treatment of a primary aromatic amine ($ArNH_2$), the diazo component, with nitrous acid to form a diazonium salt ($ArN_2^+Cl^-$). Nitrous acid (HNO_2) is generated by treating sodium nitrite with a strong acid, usually hydrochloric acid, in which situation the active nitrosating agent is nitrosyl chloride. It is important to maintain careful control of the temperature, usually in the range 0–5 °C. The main reason for this is the instability of diazonium salts, which decompose readily with the evolution of nitrogen. Diazonium salts are ideally prepared in solution as required and used immediately to synthesise the azo pigment. Azo coupling involves reaction of the diazonium salt with coupling components at or just below ambient temperature. There is usually an optimum pH range for a specific azo coupling reaction, dependent on the coupling component used. As a general rule, it is desirable to carry out the reaction at the lowest pH at which coupling takes place at a reasonable rate. The rate of addition of the diazonium salt to the coupling component is commonly controlled to ensure that a diazonium salt excess is never allowed to build up in the coupling medium. Disazo pigments, such as the diarylides **2** and **3**, are prepared by bis-diazotisation of a diamine, e.g. DCB (**7**), followed by reaction with two equivalents of the coupling component. Based on an inspection of structures **1** to **3**, and consideration of the mechanistic possibilities, it appears most likely that the source of the PCBs is the diazo component, a di- or trichloroaniline in the case of the monoazo pigments and 3,3′-dichlorobenzidine (DCB) in the case of the diarylide pigments.

In the azo coupling reaction that forms the pigment, the nitrogen atoms of the diazonium salt are retained. However, it is well known that diazonium salts also undergo a range of reactions in which the nitrogen is eliminated, referred to collectively as dediazoniation, a topic that has been the subject of systematic reviews [90,91]. For the most part, these reactions have been studied with a view to optimising their preparative qualities. There has been little investigation into their role in side reactions leading to inadvertent formation of traces of byproducts, or into their prevention or

Figure 10 The structure of 3,3′-dichlorobenzidine (**7**)
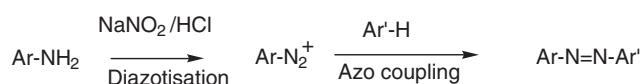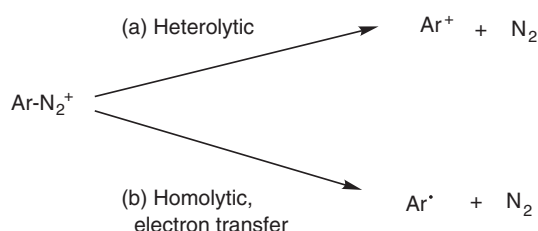

Scheme 1 Synthesis of azo pigments

minimisation. There are two principal mechanisms for such reactions, illustrated generally in Scheme 2, involving (a) heterolytic processes and (b) homolytic processes.

The heterolytic process forms an aryl cation (Ar^+) that commonly undergoes reaction with nucleophiles present in the reacting system, e.g. with water, to form phenols, and with chloride ions to form chloroaromatics. This latter reaction may merit consideration as a potential source of PCB formation. However, it appears that a more likely mechanism for their formation in azo pigment manufacture involves the homolytic process and the intermediacy of aryl free radicals. This conclusion is supported by the fact that PCB formation from free radical reactions is well known [1]. As shown in Scheme 2, the process is initiated by electron transfer from a reducing agent, and the aryl radical is formed following nitrogen elimination.

Scheme 3 shows two well-established general reactions (a) and (b) of the aryl radical [91]. Free radical combination, route (a) in Scheme 3, can lead to biphenyl derivatives, apparently providing a plausible mechanism for inadvertent PCB formation in the case of pigments, such as CI Pigment Red 2 (**1a**), CI Pigment Red 112 (**1b**), and CI Pigment Yellow 165, derived from diazotised di- and trichloroanilines. In the case of CI Pigment Red 2 (**1a**), this mechanism would be expected to lead predominantly to the formation of the tetrachlorobiphenyl PCB 52 (**6**), and from CI Pigment Red 112 (**1b**) to the hexachorobiphenyl PCB 153.

Another frequently encountered reaction of aryl radicals is hydrogen abstraction, route (b) in Scheme 3, from an appropriate hydrogen donor [91]. Preparatively, reagents
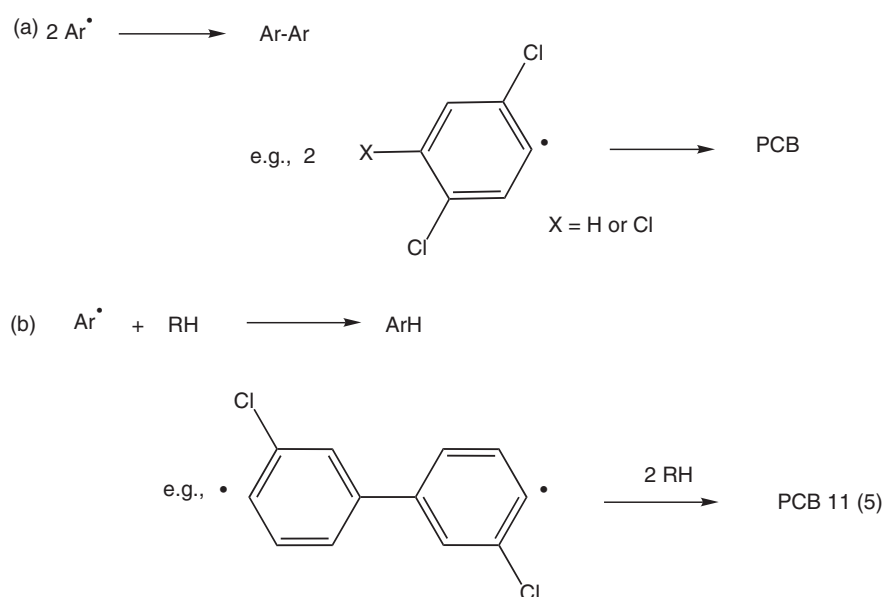
such as hypophosphorous acid and ethanol may be used to carry out this reaction. This reaction presents a plausible mechanism for inadvertent formation of PCB 11 in the manufacture of diarylide pigments, as a result of bis-dediazoniation of the bis-diazonium salt, either as illustrated in route (b) or in separate stages. Heterolytic dediazoniation followed by reaction of the resulting aryl cation with chloride ion would be expected to lead to 3,3′,4-trichlorobiphenyl (PCB 35) or 3,3′,4,4′-trichlorobiphenyl (PCB 77) and does not present an obvious route to PCB 11. In the case of diarylides manufactured from 3,3′,5,5′-tetrachlorobenzidine, such as CI Pigment Yellow 81 (**2 h**), the hydrogen abstraction process would be expected to lead to PCB 52 (**6**).

There is little evidence in the open literature to allow an assessment of the methods used by organisations to minimise PCB formation in their products, presumably for reasons of commercial sensitivity, or of the depth of understanding that exists within manufacturing organisations of the mechanisms and conditions leading to PCB formation during pigment manufacture. The level of internal understanding may well vary within different industrial organisations and in the different geographical locations where the pigments are manufactured. In this paper, we have presented sound hypothetical mechanistic proposals that need to be tested by experimental investigation. On the basis of the premise that free radical reactions of the type illustrated in Scheme 3 are involved, some potential approaches to minimisation of PCB formation during azo pigment manufacture are discussed in the following section. It is conceivable, indeed likely, that individual pigment manufacturers will already have considered, and may already use, some of these approaches as examples of the best available techniques (BATs) that manufacturers are required by the various regulations to employ in order to minimise PCB formation [27].

The chemical process factors in azo pigment manufacturing operations that are important to ensure product performance quality, for example in terms of colour and fastness properties, are broadly recognised by industry.

Scheme 2 General mechanisms of dediazoniation

Scheme 3 Potential mechanisms of PCB formation from aryl radicals

Diazotisation is carried out under optimised conditions, and the diazonium salt is used as soon as possible in azo coupling to form the pigment. It is self-evident that minimising the lifetime of the diazonium salt within a process is likely to minimise the possibility of side reactions that might lead to PCB formation. For example, it may be inappropriate to store certain diazonium salt solutions for extended periods before use. A Hoechst patent [28] describes examples of how best practice may be used to minimise PCB levels in monoazo pigments derived from di- and trichloroanilines, such as those implicated in Japanese reports [37,38]. However, in view of growing awareness of the inadvertent PCB issues, experimental investigations, for example using the principles of statistical design, to quantify rigorously the effect of individual process factors on PCB levels would be valuable. Some obvious parameters include starting material purity, concentrations and relative quantities of reactants, reaction temperatures, pH levels, rates of addition, and the industrial mixing technology. The results of such investigations would inform industry in a reassessment of the need for stricter process control measures to minimise not only overall PCB levels but also batch variation.

Aryl radical formation from diazonium salts is initiated by reduction. Initiation by reducing metal ions is well established, and organic reducing agents may also initiate the process [91]. The most commonly encountered anion used preparatively to lead to radical formation is iodide. Chloride and oxygen anions are suggested to be insufficiently reducing to cause electron transfer. It has been tentatively suggested that the nitrite anion used in the diazotisation may have sufficient reducing properties [91]. Manufacturers should consider whether there are potentially reducing species present in their processes, even in the small amounts that could lead to traces of products, e.g. reducing metals and ions, process additives, or impurities in starting materials. Assuming that hydrogen abstraction is involved in the formation of PCB 11, consideration should be given to the hydrogen source. It is not immediately clear from the literature the extent to which water can act as this source, but organic compounds containing active C–H functionality represent a recognised source [91].

It is well known that free radical reactions may be inhibited by a range of species, including radical scavengers. Experimentation with these materials would be of interest both as a means to test the free radical hypothesis and as a potential means to reduce PCB levels. In this context, it is significant that a Hoechst patent [29] claims that PCB levels in azo pigments may be reduced by carrying out the preparation in the presence of alkenes. It is well known that the specific alkenes cited in this patent are capable of reaction with free radicals [91].

Although the structure of copper phthalocyanine blue (CuPc) is complex, its synthesis is straightforward [23]. In the most commonly used process, phthalic anhydride is treated with urea, copper(I) chloride, and a catalytic amount of ammonium molybdate at high temperatures. Mechanistic schemes have been proposed to explain the course of this synthesis, but much of the detail remains to be established unequivocally [92]. The organic starting materials leading to most CuPc blue pigments contain no chlorine, although a small amount of 3-chlorophthalic acid may be incorporated into CuPc stabilised in its α-form. Inorganic chlorine is present in copper(I) chloride. This chlorine has the potential to be incorporated into the organic system in small amounts [92]. An established source of PCB formation in CuPcs involves the use of a dichlorobenzene or trichlorobenzene used as the reaction solvent. A free radical mechanism based on pyrolysis of the chloroaromatic solvents has been proposed, supported by literature precedent [33,93]. There appears to be no justification for the use of such solvents in current manufacturing practice, as there are obvious alternatives in the use of chlorine-free high-boiling solvents or the use of solvent-free 'dry-bake' processes, although this last process can be inefficient.

There appears to be rather more concern with residues of highly chlorinated PCBs, such as PCB 209, in copper phthalocyanine green pigments [33]. Their synthesis involves direct exhaustive chlorination of CuPc blue with excess chlorine at elevated temperatures in a suitable solvent, commonly an $AlCl_3$/NaCl melt. The formation of highly chlorinated PCBs in the manufacture of these pigments, if confirmed, would appear feasible mechanistically in the context of the processes involved. Their formation may possibly involve the degradation of the phthalocyanine ring system in the presence of excess chlorine, but this requires further systematic experimental and analytical investigation.

Conclusions

On the basis of increasingly sophisticated analytical methods, environmental scientists have begun to measure PCB congeners that are not associated with legacy PCB mixtures at levels exceeding the standards applicable across the United States for the protection of human and ecosystem health in water and sediment. Several lines of evidence lead to the conclusion that these sources are associated with specific pigments, especially in the case of PCB 11. Other possible sources, including from microbial or photolytic dechlorination of more highly chlorinated PCB congeners and incineration, can be ruled out. Several studies have demonstrated that PCB 11 is not an important product of PCB dechlorination by bacteria in real environments [41,73]. Incineration and photolytic dechlorination pathways cannot explain why PCB 11 is present in high quantities in wastewater [41,73]. Furthermore, if a photolytic pathway were important, the time trends in PCB 11 concentrations would be similar to those of its precursors (i.e. legacy sources), which they are not [76].

Worldwide, PCBs are generally regulated as the sum of all 209 congeners. These regulations therefore do not account for differences in toxicity among the 209. Such regulations were developed with industrial PCB formulations such as Aroclors (which are complex mixtures of as many as 100 congeners) in mind. More research is needed on the toxicity of PCBs associated with pigments to determine whether this regulatory approach remains appropriate. The regulatory framework that covers most of the world's population limits PCBs in products at levels no higher than 50 ppm. Recent Japanese investigations have confirmed that many batches of azo pigments manufactured in Asia, notably a series of diarylides, contained far higher concentrations than are allowed under the prevailing regulations and international

agreements [37,38]. Thus, an essential first step to address the problem is the strict enforcement of existing regulations. This would require that pigments be tested for PCBs routinely and the results reported to the environmental agency in the country of production or import. While we are advocating a need to focus on the current situation with diarylide pigments, we are by no means advocating complacency with regard to other pigments, for example CuPc blues and greens, which have also been implicated in inadvertent PCB formation. Pigment production has been globalised. In the United States, the Toxics Release Inventory (TRI) can be used to determine where diarylide pigment production occurs, as the starting material, 3,3′-dichlorobenzidine (DCB) **7** is on the TRI list. The list indicates that, in 1988, 14 facilities in the United States reported emissions of DCB. By 2011, that number had dwindled to one. Thus, enforcement of TSCA and similar rules in the EU must now be focused on imported pigments, as production is now substantially located in China and India. Most countries that are large producers of pigments, including China and India, are signatories to the Stockholm Convention. Pigment-producing countries must therefore focus on enforcing their existing environmental laws and, where necessary, adopting new laws in support of the Stockholm Convention. We recommend that the existing ELISA (enzyme-linked immunosorbent assay) methods routinely used for Aroclor PCBs should be validated for measurement of pigment-associated PCBs. The ELISA method is rapid and inexpensive, with detection limits in the ppm range, making it ideal for the purpose of pigment testing. The biggest drawback of the ELISA method is that it measures only the sum of PCBs, not the individual congeners. Thus, the discounting factors allowed under the TSCA for mono- and dichlorobiphenyls would have to be abandoned when using the ELISA method.

Over the years, there has been important research aimed towards replacements for diarylide yellow pigments. Although the research has been aimed largely at providing a means to avoid the use of the highly toxic DCB, many of the new pigment products that have been reported would avoid the inadvertent formation of PCB 11 because they use chlorine-free diamines as bis-diazo components [94,95]. Following the observation that diarylide pigments may degrade at high temperatures with the release of DCB, their use in high-temperature applications, such as mass coloration of thermoplastics, has declined, with alternatives sourced from the existing range of inorganic and organic pigments. However, for printing ink applications, finding substitute products from the existing commercial range is problematic, arguably not possible. High-volume multicolour printing primarily uses pigments of the subtractive primary colours yellow, magenta, and cyan, together with black. The main requirements for the pigment are high intensity and brightness of colour, transparency, and low cost, while durability requirements are often modest. Predominantly, yellow is provided by diarylide pigments, because they fulfil these requirements uniquely. No inorganic pigments are capable of approaching the level of colour strength and transparency required, and there are no alternative yellow organic pigments available that can match the requirements at a comparable cost. Monoazo pigments, for example, are invariably

around half the colour strength of the disazo products. There have been some developments involving fine-particle-size printing ink grades of monoazo pigments that are normally considered primarily for paint applications, a notable example being CI Pigment Yellow 74. In principle, the development of printing ink grades of high-performance yellow organic pigments, such as disazo condensation pigments, benzimidazolones and isoindolines, might offer alternative possibilities, but at much higher cost [23,96].

The development of replacements for diarylide pigments should remain an important target for pigment manufacturers. In view of the limited success so far, it is clear that there are significant challenges. Given that these developments thus have to be considered as unlikely in the short to medium term, it is essential that all manufacturers conduct research to optimise their pigment production processes, aiming to minimise PCB formation, for example using the suggestions described in this review. Appropriate trade groups should consider publishing best practice and request compliance from manufacturers.

Another issue that remains unresolved is whether pigments, particularly diarylides, decompose to release PCBs once they are released to the environment. Although these pigments are considered stable, their behaviour under real-world conditions has never been assessed. Bacteria are said to be the world's greatest chemists, and they are amazingly adept at finding ways to degrade even relatively persistent chemicals. Pigments are exposed to harsh conditions in the environment, including exposure to sunlight for long periods, residing in anaerobic sediments in river, harbours, and sewers, and travelling through WWTPs, where bacteria have evolved under continual exposure to all of the xenobiotic chemicals produced (intentionally and unintentionally) by humans.

There needs to be a particular continuing research focus on PCB 11, not only to address imminently the issue of water quality standards in the United States but also to understand the consequences of its ubiquitous presence for human health and the ecosystem.

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