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Discussion

Is current generation of polychlorinated biphenyls exceeding peak production of the 1970s?

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HIGHLIGHTS

- Peak production of Aroclor PCBs in U.S. was 85 Million lb. in 1970s.
- Production of by-product PCBs in U.S. may have been ~100 Million lbs. in 2019.
- Many existing monitoring programs don't measure by-product PCBs so miss this risk.
- Should by-product PCBs be considered a pollutant of emerging concern?

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ABSTRACT

Polychlorinated biphenyls (PCBs) are man-made chemicals that were once widely produced as commercial mixtures for various industrial applications. PCBs were later recognized as environmental pollutants and health hazards, leading to their global phase-out and strict regulations on their production, use, and disposal. Most investigations on PCBs focus on measuring the specific PCBs present in commercial mixtures or marker compounds representing those mixtures. However, there are new sources of PCBs that are gaining more attention. These 'by-product PCBs' are inadvertently produced in certain chemical and product formulations. Our estimates show that U.S. legislation currently permits the generation of more by-product PCBs (~100 million lb. (~45,000 Tonnes) per year) than during peak commercial production of the 1970s (85 million lb. (~39,000 Tonnes) per year). These PCBs are currently going un-detected in most investigations. Therefore, they may be a posing a growing, unmonitored environmental and human health risk. Most people assume PCBs to be legacy pollutants from historically formulated commercial mixtures. However, our research suggests that due to the emergence of by-product PCBs they may need to be reconsidered as an emerging pollutant of concern.

1. Introduction; what is different about by-product PCBs and are they an issue of concern?

By-product PCBs are PCBs that are inadvertently generated during a variety of different chemical processes. They have been referred to as inadvertent PCBs, incidental PCBs (i-PCBs), and non-Aroclor PCBs. The PCBs historically produced in commercial mixtures (Fig. 1) can differ from the specific PCBs produced during these processes (Fig. 2). Due to cost constraints, many studies in North America use Aroclor PCB measurements for monitoring programs which pre-emptively assumes all PCBs are only from Aroclor commercial mixtures. PCB monitoring in studies other parts of the world predominantly select a subset of the 209 PCBs for routine monitoring (e.g. 7 indicator PCBs 28, 52, 101, 118, 138, 153 and 180 Fig. 1). Whilst these are excellent indicator PCBs for identifying the presence of commercial mixtures, they are largely absent from sources of by-product PCBs such as paints (Hannah et al., 2022). This means that by-product PCBs continue to remain largely undetected in the vast majority of PCB monitoring programs. It is only studies that monitor a wider range of PCBs, usually all 209 congeners, that are starting to identify by-product PCBs in environmental samples. Herkert et al. (2018) reported that PCBs attributed to polyester resins and silicone sealants (PCB 11, 47, 51, and 68) were dominant congeners in some residential properties. Megson et al. (2022) estimated that between approximately 4–50 % of PCBs in marine mammal samples may

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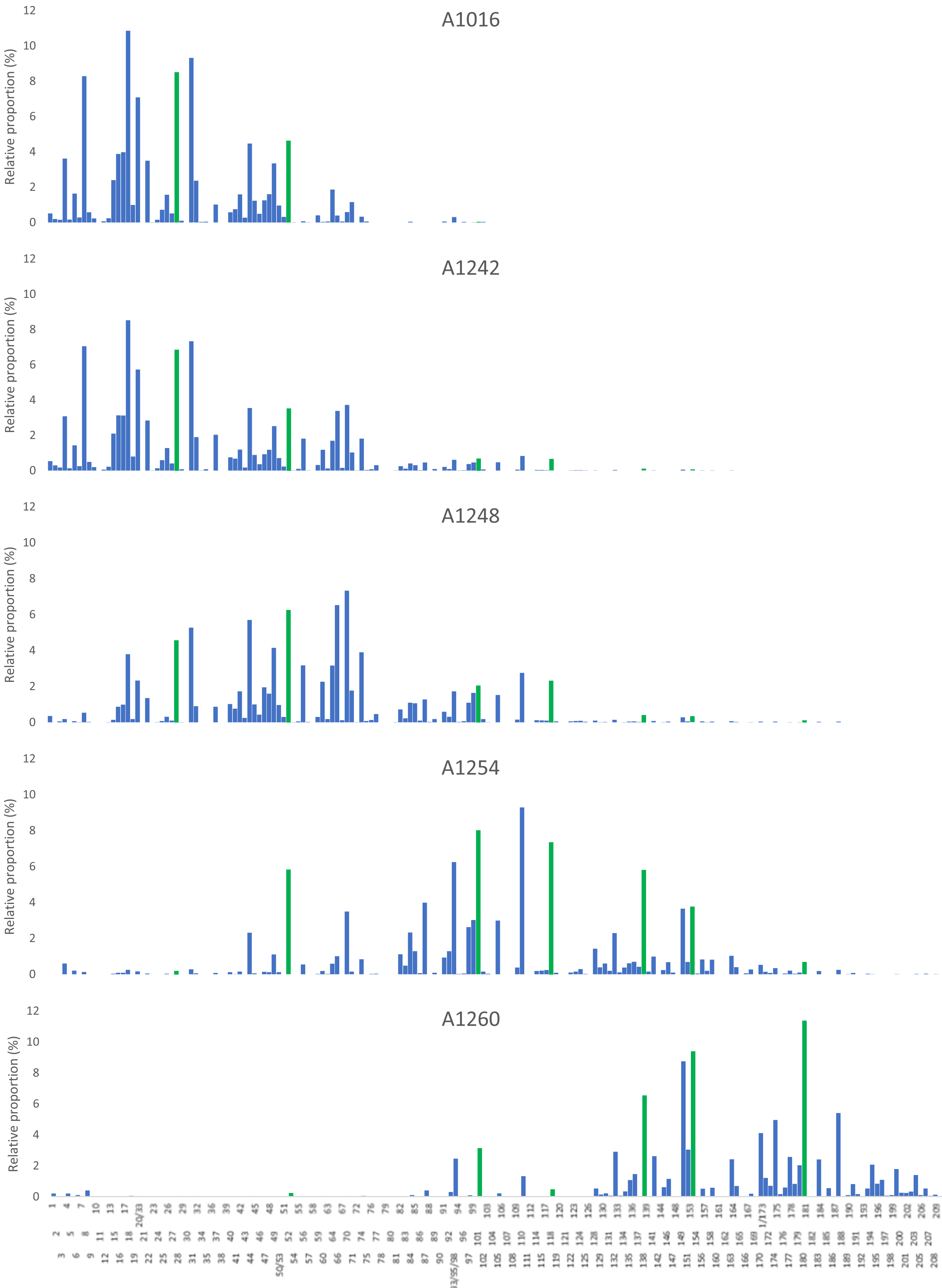

Fig. 1. PCB profile in 5 most used Aroclors (data obtained from (Frame et al., 1996). PCBs in green represent the 7 indicator PCBs commonly included in routine PCB monitoring studies.

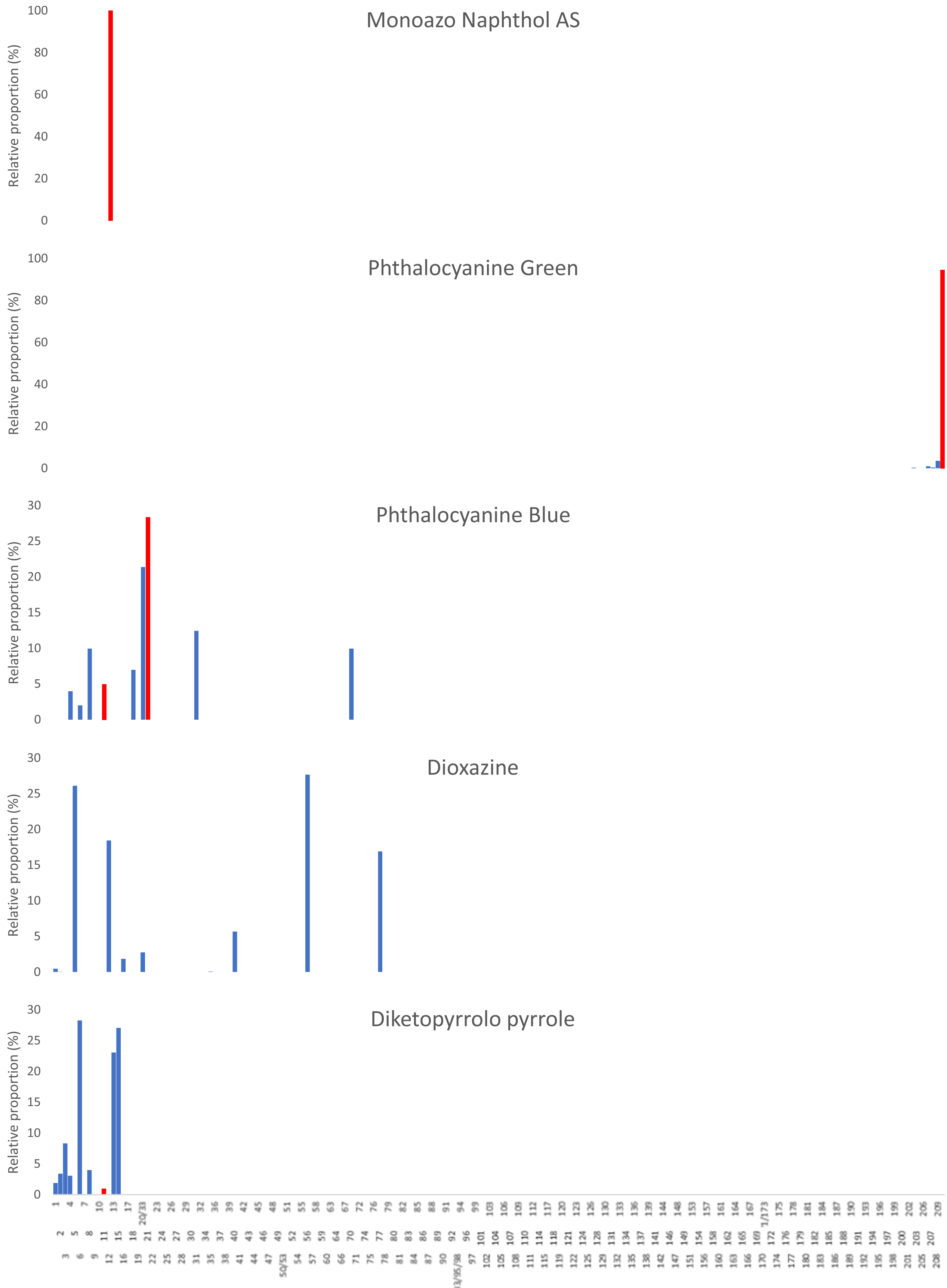

Fig. 2. PCB profile in paints comprising Azo, Phthalocyanine, Dioxazine and Diketopyrrolo pyrrole pigments (data obtained from Hannah et al., 2022, Anezaki and Nakano, 2014, Anezaki and Nakano, 2015, Hu and Hornbuckle, 2010). PCBs in green represent 7 indicator PCBs commonly included in routine PCB monitoring studies (note they are all absent). PCBs in red were not recorded in the 5 most commonly used Aroclors.

be by-product PCBs. Even in areas such as Portland Harbor (a superfund site known to be impacted with commercial mixtures of PCBs), by-product PCBs were estimated to contribute 6.6 % of the total PCB load (Megson et al., 2023). In China, soil and sediment samples display PCB profiles showing a dominance of by-product PCBs compared to PCBs from commercial mixtures (Mao et al., 2021; Yu et al., 2023). These studies show that by-product PCBs can be important sources of PCBs in the environment. Should they therefore receive more attention?

2. Current legislative approach

On a global level, PCBs are currently listed in the Stockholm Convention under Annex A (elimination) and Annex C (Unintentional production). Under Annex A, parties must take measures to eliminate the production and use of PCBs. For commercial PCB mixtures, this has largely been achieved as most countries had ceased production of commercial mixtures by the early 1980s (IARC, 2016). Under Annex C, parties must take measures to reduce the unintentional releases of chemicals listed, with the goal of continuing minimization and, where feasible, ultimate elimination. PCBs were first listed on the Stockholm convention as part of the 'dirty dozen' in 2004 and there continues to be activities focused on minimizing PCB releases to meet 2025 and 2028 goals (Stockholm Convention, 2019). However, to date a lot of the effort for Annex C has been related to minimizing unintentional release of legacy PCBs from commercial mixtures. Little attention has been paid to minimizing or eliminating by-product PCB production and subsequent release into the environment. This needs urgently addressing as all PCBs are considered toxic, not just legacy PCBs from commercial mixtures (IARC, 2016).

The focus on legacy PCBs is further evidenced through the disparity in existing chemical regulations in many countries. Currently, there are differences in the way PCBs are regulated depending on whether they were produced as commercial mixtures (e.g., Aroclors) or unintentionally as by-products (e.g., in paints). For example, in the U.S. the concentration of the sum of all PCB congeners or all isomers or homologs or Aroclor in water (based on aquatic life risk) cannot exceed 0.000064 ppb (US EPA, 2002). However, the concentration of one single inadvertently generated PCBs in discharged water from a manufacturing site cannot exceed 100 ppb (US EPA, 1984). This is a 1.5 million fold difference in concentration that is linked to whether the PCB was intentionally produced or not and highlights the need for more stringent regulation of by-product PCBs. We recognize that these guidelines differ in how they are derived and their intent, but the dramatic difference leads to the potential release of individual PCB congeners in wastewater that may overwhelm the environmental guideline that is based on commercial PCBs.

PCBs have been one of the most widely studied chemical classes over the last 4 decades. Research into PCBs in the environment began at a time when by-product PCB production was not properly understood or considered to be an issue. A common argument for not prioritising efforts to quantify unintentionally produced PCBs in the environment is that the total volume of by-product PCB sources would be very small compared to the quantity of PCBs generated during the production of PCB commercial mixtures. Whilst this may have been the case during peak production of PCB commercial mixtures, its argument loses more credibility each year. Releases of PCBs from commercial mixtures to the environment continue to decline (Breivik et al., 2007) (Fig. 3). In contrast, by-product PCB production continues largely unchecked. The total volume of PCBs produced in commercial mixtures has been investigated in detail with global estimates in the range of 1.3 million tonnes (Breivik et al., 2007; IARC, 2016; US EPA, 1976). Action taken due to legislation means that not all of these PCBs will enter the environment. Breivik et al. (2007) estimated that in 2019, global emissions of legacy PCBs from commercial mixtures to the environment were 137.9 Tonnes (approximately 304,000 lb) (Fig. 3).

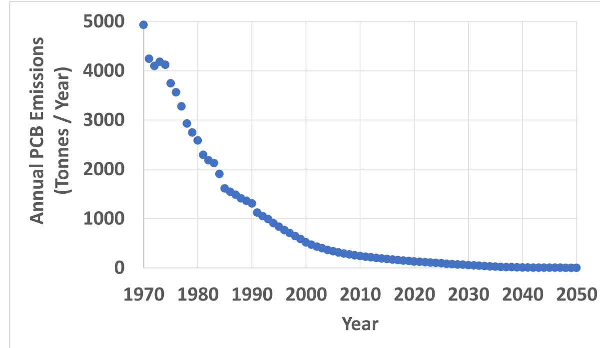

Fig. 3. Modelled annual emissions of Σ22PCBs from commercial mixtures produced using data from Breivik et al. (2007).

3. Identifying the scale of by-product PCB production

Although the total inventory and emission rate of PCBs in commercial mixtures has been well quantified, the same cannot be said for by-product PCBs. Panero et al. (2005) produced an inventory of approximately 70 different chemicals/chemical classes that have the potential to generate PCBs. However, within the scientific literature, the only area to have been investigated in any detail has been paints and pigments (Hannah et al., 2022; Anh et al., 2021; Vorkamp, 2016). There are additional sources within the grey literature (City of Spokane, 2015) that confirm the presence of PCBs in a much wider range of commercially available products, yet these have received little attention.

In an attempt to get an appreciation on the potential scale of by-product PCB production, we searched for production volumes of the 69 different chemicals/chemical classes reported by Panero et al. (2005) that have the potential to generate by-product PCBs. Reliable global production volumes are not easily sought. We therefore used PubChem (National Library of Medicine, 2023) to focus our study on the U.S. for 2019 (the most recent year available). A total mass of PCBs was then calculated assuming that all material conformed to U.S. standards and had a total PCB concentration of 125 ppm (relating to average permissible limit of di-chlorinated PCBs (US EPA, 1984)) (Fig. 4 & Supplementary Information S1). The limit for di-chlorinated PCBs was selected as these PCBs have been most closely associated with by-product PCB production due to the probable mechanisms of formation, but calculations for mono-chlorinated PCBs and tri- deca- chlorinated PCBs are provided in Supplementary Information S1). Assuming these PCBs are present at the limit may lead to an overestimation, but it should be noted that this limit is on a per congener basis, so it may still potentially underestimate of the total PCB load. Multiple congeners can be present at concentrations below these limits. Therefore, this assumption is likely still high, but not a maximum assumption.

Production volumes on PubChem were available for 45 of the 69 different chemicals/chemical reported. Production volumes for 2019 were reported where available, but production volumes from other years were used for some chemicals. Production volumes for chlorinated pesticides and chlorinated pigments/dyes were sourced from (Wieben, 2021) and (IHS Markit, 2018) respectively. Of the remaining 22 chemicals/chemical classes some were no longer manufactured in the U.S. and for others no recent production volumes were reported. For some chemical classes, data was only reported for one or two individual compounds out of a larger group. The total volume of chemicals that may contain by-product PCBs is therefore an underestimate since not all chemical production could be identified. We accept there is a degree of uncertainty involved with these estimates, however they act as a useful back of the envelope calculation to understand if more detailed investigation is required.

When applying the U.S. average limit of 125 ppm for di-chlorinated PCBs we calculated that a total of approximately 95 million lb. (~43,000

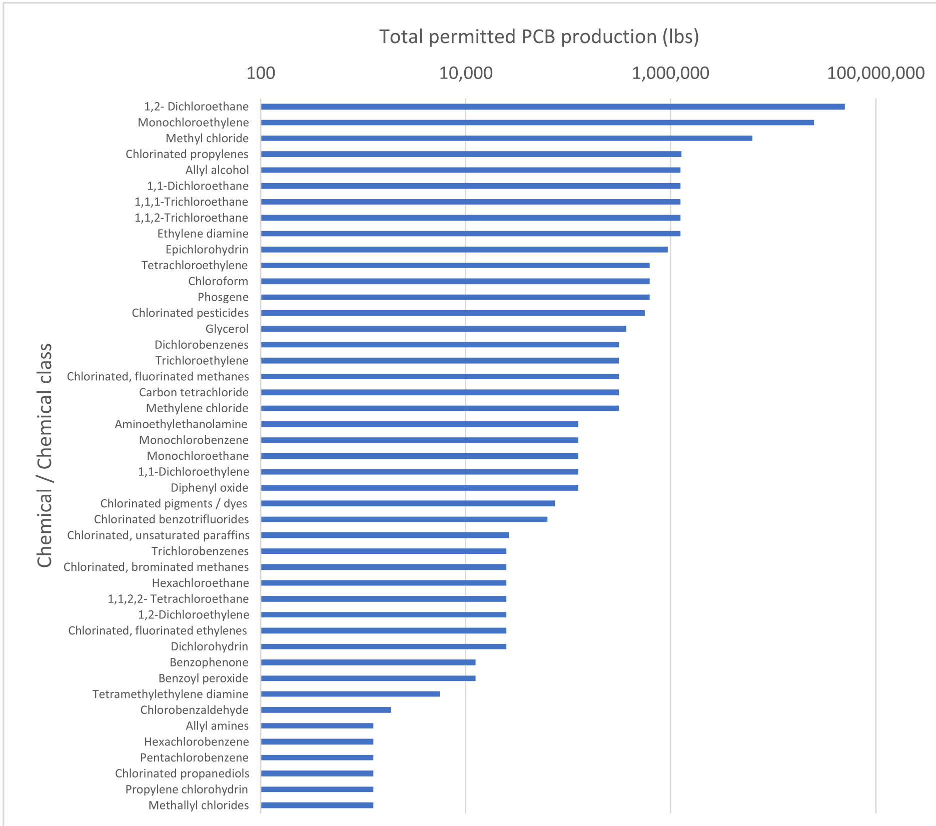

Fig. 4. Total permitted by-product PCB production for 47 different chemicals/chemical classes in the U.S. for 2019 (calculated using limits for di-chlorinated PCBs).

Tonnes) of PCBs could have been legally produced in 2019. For context, the maximum annual production of PCBs from Monsanto in the U.S. was approximately 85 million lb. (39,000 Tonnes) in 1970. Pigments and dyes are the most investigated route for by-product PCB production and are commonly referenced as the probable source of by-product PCBs in the environment. However, PCBs produced by chlorinated pigments and dyes represented <0.1 % of the total potential PCB production (0.75 million lb. (~340 Tonnes) compared to a total of 95 million lb. (~43,000 Tonnes) (Fig. 4 & Supplementary Information S1)).

4. A way forward?

Current legislation is driven towards minimizing exposure from legacy commercial PCB mixtures. However, is it now time for a shift in approach to ensure we minimise PCB exposure from alternate sources? Most human health risk assessments focus on the WHO12 PCBs (Van den Berg et al., 2006), a decision that assumes the main source of PCB exposure is from commercial mixtures. All PCBs are toxic and so now is the time to broaden PCB risk assessments to understand the risks from non-dioxin like PCBs (and their metabolites) from non-legacy sources. By-product PCBs are produced in a different way than intentionally produced PCBs (Hannah et al., 2022). There are a large range of specific chemical mechanisms that result in the generation of different PCB congeners than those produced in commercial mixtures. These PCB congeners go undetected in many environmental assessments which use analytical methods that only determine a handful of indicator compounds (Megson et al., 2019). Many larger monitoring programmes report decreases in overall PCB levels, but they do not include data from by-product PCBs, is it time this should change? We have detailed information on analytical methods capable of measuring all 209 PCBs. We have data systems and analysis methods that allow for the analysis of large variable datasets, such as full congener analysis of all 209 PCB congeners. We have the capabilities to undertake investigations that consider PCBs produced in commercial mixtures and as by-products. What we lack is a detailed understanding of the presence of by-product PCBs in commercial products and the environment.

In this manuscript we assume that all chemicals/chemical classes contained PCBs at a maximum allowable average annual concentration of 125 ppm (for di-chlorinated PCBs). This shows there is the potential for current by-product PCB generation to exceed peak Aroclor production in the 1970s. We do not currently have the necessary data to establish if this is happening. Limited data for PCBs in paint is available (average of 19.4 ppm and maximum of 920 ppm from 142 samples (Hannah et al., 2022)) but more research is needed to establish which PCBs are present in other chemicals/chemical classes to provide a more robust estimate of the potential scale of this problem. The pigment industry is currently under intense scrutiny for by-product PCB production, but this assessment shows it may only be responsible for <0.1 % of the total by-product PCBs produced. Therefore, it may be wiser to prioritise efforts more widely on chemicals/chemical classes with the highest production volumes, as well as chemicals/chemical classes that have open ended uses in commercially available products. It is important to note that many of the chemicals/chemical classes are essential in a wide range of different applications. Implications of any new legislation must be carefully considered to recommendations are protective of the environment but do not have catastrophic financial and practical implications. This will not be an easy task, but is it worth undertaking considering that the current legislative framework permits the annual production of approximately 100 million lb. (~45,000 Tonnes) of by-product PCBs a year?

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CRediT authorship contribution statement

David Megson: Writing – original draft, Formal analysis, Data curation, Conceptualization. **Ifeoluwa Grace Idowu:** Writing – review & editing, Validation, Data curation. **Courtney D. Sandau:** Writing – review & editing.

Declaration of competing interest

D.M. I.G.I & C.D.S. work for Chemistry Matters, a consulting company undertaking environmental forensics investigations including source identification of PCBs. C.D.S reports a relationship with Monsanto Co. that includes: consulting or advisory and paid expert testimony. D.M. I.G.I, as paid consultants to Chemistry Matters Inc., are also therefore associated with these litigation matters.

Data availability

All data are available in the manuscript or the supplementary materials.

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