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Global Distribution and Local Impacts of Inadvertently Generated Polychlorinated Biphenyls in Pigments

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Supporting Information

ABSTRACT: The non-Aroclor congener 3,3′-dichlorobiphenyl (PCB 11) has been recently detected in air, water, sediment, and biota. It has been known since at least the 1970s that this congener is produced inadvertently during the production of certain organic pigments. PCB 11 was previously measured at parts-per-billion (ppb) levels in various printed materials obtained in the US. In this work, PCB 11 was detected in samples of common consumer goods including magazines, advertisements, maps, postcards, brochures, napkins, and garments from 26 countries in five continents at concentrations ranging from 0.27 to 86 ppb. Leaching tests confirmed that PCB 11 could be released from these materials into water. We also examined whether the known sources of PCB 11 were large enough to account for the levels of PCB 11 measured in the air, water, soil and sediment of the Delaware River Basin. A mass flow analysis suggests that the outflows and sequestration of PCB 11 in the basin total between 30 and 280 kg y^{-1}. If PCB 11 concentrations in pigments were at the maximum average (125 ppm) allowed under the Toxic Substances Control Act (TSCA), the estimated input of PCB 11 to the Delaware River Basin would be on the order of 42 kg y^{-1}. Despite the large uncertainty in these numbers, the results suggest that pigments may plausibly account for the levels of PCB 11 measured in the environment.

■ INTRODUCTION

Efforts in the United States to control polychlorinated biphenyl (PCB) contamination have generally focused on legacy PCB sources, such as Aroclors that were banned from production in the 1970s. PCBs are regulated as the sum of all 209 congeners, however, regardless of source. Recently, PCBs from non-Aroclor sources have received much attention. Among these non-Aroclor congeners is 3,3′-dichlorobiphenyl (PCB 11) that has been reported in various environmental media[1−6] thanks to US EPA's method development in congener-specific analysis of the entire PCB list.[7] PCB 11 was detected at levels often exceeding the federal water quality standard for the sum of PCBs (64 pg L^{-1}) in surface waters across the US.[8−13]

PCB 11 has mostly been associated with diarylide yellows, a group of dichlorobenzidine-based azo pigments that comprises the majority of classical organic yellow pigments,[8] but PCB 11 as well as other PCB congeners are found in a variety of pigments. The levels of PCB 11 that have been found in pigments vary widely. The Ecological and Toxicological Association of the Dyestuffs Manufacturing Industry (ETAD) stated in 2011 that "...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···".[14] Some published reports indicated that levels of PCBs in pigments, inks, and paints were in the ppb range or lower,[8,14−19] but a few recent investigations reported detection up to 2,000 ppm of PCBs in some yellow pigments.[20−22] US and international law requires manufacturers of any product that may contain inadvertent PCBs to test their products. The maximum concentration of PCBs allowed in these products under the Toxic Substances Control Act (TSCA) in the US is an average of 25 ppm, not to exceed 50 ppm at any time.[23] However, the concentrations of mono- and dichlorobiphenyls are discounted in the calculation of the sum of PCBs. The present Code of Federal Regulations (40 CFR 761.3 from 2013) states the following: "For any purposes under this part, 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".[23] In other words, pigments could contain an average of 125 ppm and a maximum of 250 ppm PCB 11 without exceeding the US federal limit. In the European Union, Council Directive 89/677/EEC set a limit of 50 ppm for the sum of PCBs in pigments with no discounting factors for mono- and dichlorobiphenyls.[24] These regulations cover not only the manufacture but also the processing and commercial distribution of PCB-containing products. Import is synonymous with manufacture under these regulations. Manufacturers are not required to disclose test results;, however, and in

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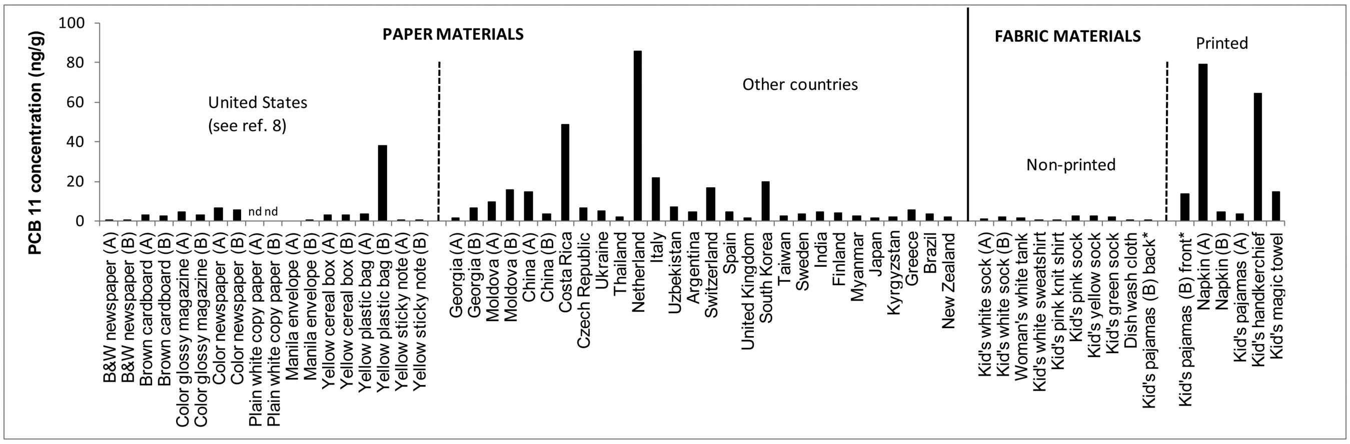

Figure 1. Concentrations of PCB 11 measured in printed materials (from the US previously reported[8]) and fabric materials. Only one sample of each material was analyzed. (A) and (B) represent the same type of materials but are not duplicates. Average concentrations reported where two extraction methods were used (see Table S1 of the Supporting Information). Clothing samples denoted with an asterisk (*) are the front and back pieces of the same garment. Note: nd = not detected, limit of detection = 0.10 ng g^{-1}.

many cases it is not clear whether testing is actually performed. In 2012, the Japanese ministries investigated byproduct PCBs in 588 organic pigments and found nearly 39% of tested items, mostly pigment reds and yellows, contained PCBs at concentrations from 0.5 to 2000 ppm.[20]

In response to the presence of PCBs in pigments used in printing inks in consumer goods, the State of Washington, USA, recently passed Bill 6086,[25] which states the following: "No [state] agency may knowingly purchase products or products in packaging containing polychlorinated biphenyls above the practical quantification limit except when it is not cost-effective or technically feasible to do so". The practical quantification limit using a method such as 1668 would be on the order of 1 ppb, or 50,000 times lower than the 50 ppm allowed under the TSCA.

World-wide production of color organic pigments was estimated to be about 250,000 t (t) in 2006, with about 25%, or 62,500 t, being diarylide yellows.[26] In the past decade, much of this production has shifted from the US and Europe to China and India. Thus, enforcement of TSCA and the European regulations now relies primarily on the testing of imported pigments. However, products that incorporate pigment, from raw inks to finished goods such as textile-printed clothing, are not tested. Assuming the average concentration of PCB 11 in diarylide yellow pigments is the maximum of 125 ppm, the maximum amount of PCB 11 produced by this route was about 7,800 kg y^{-1} worldwide as of 2006. The amount produced could be much smaller than this if the actual concentrations of PCBs in pigments are lower, but it could also be higher if pigments are not being tested for PCB levels and are routinely exceeding the levels set forth by TSCA, the Stockholm Convention, and the European Union's directives.

What fraction of the PCBs generated during pigment production is released to the environment? Is the amount of PCB 11 released to the environment from pigment use large enough to account for the levels of PCB 11 measured in environmental compartments? To answer these questions, we have constructed a mass flow analysis for the Delaware River. Like many urban waterways in the US, the Delaware River has been found to contain PCB 11 contamination even though no diarylide yellow pigment manufacturers were reported in this area (i.e., no facilities in the Toxics Release Inventory (TRI) report releases of 3,3′-dichlorobenzidine or related compounds used in pigment synthesis).[27] Therefore, the objectives of this study are (1) to establish that pigment applications dominated by printing inks is a source of PCB 11 worldwide; (2) to demonstrate that PCB 11 leaches out of printed materials into the water column; and (3) to assess the magnitude of emissions required to reach PCB 11 levels measured in the watershed and airshed of the Delaware River Basin and determine whether the known sources are adequate to produce the measured concentrations.

■ MATERIALS AND METHODS

Measurement of PCB 11 in Consumer Goods. Methods of measurement of PCB 11 and other congeners in printed materials such as newspapers and plastic bags were described previously.[8] Further details are provided in the Supporting Information. Because pigments are supplied globally with primary use in printing inks, PCB 11 was measured in samples of printed materials and other consumer goods that were collected from 26 countries in North America, South America, Europe, Asia, and Oceania. Paper from magazines, advertisements, maps, postcards, brochures, and a variety of textile and clothing for kids and adults were analyzed. The printed materials were stored for 1 day up to several weeks until being processed. The clothing was purchased a few days before analysis and was not washed before extraction.

Leaching Test of PCB 11 in Printed Materials. A simple 48-h column leach test was performed using milli-Q water as the leachant to evaluate the leaching potential of PCB 11 from printed materials with pigment use. Test materials included color newspapers, commercial flyers, and food and beverage packaging boxes collected in the US. Details are provided in the Supporting Information.

Mass Flow Analysis of PCB 11 in the Delaware River Basin. Import of PCB 11 into the Delaware River Basin was estimated in order to determine whether it is adequate to account for the measured and estimated stocks and flows of PCB 11 within and exiting the basin. Underpinning our analysis of mass flows is the assumption that the watershed is either at steady state with respect to PCB 11 flows or that PCB 11 flows and concentrations are increasing over time. This assumption is explored in more detail below. This analysis is based primarily on PCB concentrations measured by the Delaware River Basin Commission (DRBC) in surface water (2002−2003), sewage treatment plant influents and effluents (2005−2009), and surficial sediment (2008−2010) as part of the effort to develop a Total Maximum Daily Load (TMDL) for PCBs in the tidal Delaware River.[28,29] These data sets were all therefore collected under a Quality Assurance Project Plan (QAPP) approved by the US EPA and using EPA method 1668A.[7] Atmospheric PCBs were measured by active[30] and passive[6,31] sampling (2005−2011) as part of the Delaware Atmospheric Deposition Network (DADN). Eight soil samples were collected on the campus of Rutgers University in 2012 for PCB analysis. Major and minor removal processes of PCB 11 in the basin were selected for mass outflow estimates to be compared with total input from pigments. The results were further validated by a comprehensive Level III fugacity model.

■ RESULTS AND DISCUSSION

PCB 11 in Printed Materials. PCB 11 concentrations in printed materials sampled in the US were previously reported from nondetect to 38 ng g^{-1} (Figure 1).[8] PCB 11 levels in these products are many orders of magnitude lower than the levels of ΣPCBs found in carbonless copy paper in 1972, when PCB concentrations were reported as high as 64.7 mg g^{-1}.[32] Recycled paper may contain PCBs from recovery of carbonless copy paper, although the concentration has decreased due to volume reduction. Recycled PCB-containing paper has historically been used for food packaging with a tolerance limit of 10 ppm unless an impermeable barrier is present between the packaging material and food product (21 CFR 109.30 from 2004).[33]

In the present study, PCB 11 was detected from 1.5 to 86 ng g^{-1} in printed materials that were collected from another 25 countries on five continents (Figure 1). These findings suggest that printed materials may be a source of PCB contamination worldwide. PCB 11 was below the limit of detection (LOD = 0.10 ng g^{-1}) in samples of white copy paper and one of the manila envelopes.[8] This suggests that the presence of PCB 11 in the printed materials is due to the ink, not passive absorption from the atmosphere. Hence PCB 11 is primarily associated with color, especially yellow, printing. PCB 11 was by far the dominant PCB congener detected in the paper samples. Some other PCB congeners in the tri- through hexa-chlorinated homologues were also detected. Several studies in the US, Japan, and China reported PCB 11 detection in azo-type paint pigments that cover a range of vivid colors such as reds, oranges, and yellows.[18,21,22] Therefore, we conclude that PCB 11 is ubiquitously present as a byproduct in commercial pigment applications, particularly in printed materials.

PCB 11 in Fabric Materials. PCBs were also measured in a variety of dyed and pigment-printed clothing including knit shirts, pajamas, handkerchiefs, and socks for both kids and adults. Although the clothing samples were obtained in the US, most were manufactured outside the US in countries such as China and Honduras. PCB 11 concentrations in color fabrics varied between 0.27 and 79 ng g^{-1} (Figure 1 and Table S1). Some other PCB congeners such as PCB 52 (2,2′,5,5′-tetrachlorobipheny) that may also form from azo pigments[18,21] were also detected. PCB 11 was not detected in 2 of 3 laboratory blanks of quartz fiber filters (LOD = 0.10 ng g^{-1}). However, the concentration of PCB 11 in white clothing was around 1−2 ng g^{-1}, with most other PCB congeners below detection limit. This indicates that the fabric material is not acquiring PCB 11 through passive uptake from the air, because this process would allow a wide variety of congeners to accumulate in the fabric. Instead, PCB 11 may be entering the cloth via cross-contamination, probably during the production or dyeing of the cloth or the sewing and processing of the garment. Concentrations of PCB 11 in many of the other dyed materials were similar to those in the white clothing, indicating that these materials, too, may acquire PCB 11 as a cross-contaminant. All of the items with levels of PCB 11 well above 2 ng g^{-1} contained a printed design that did not penetrate through the fabric, a process known as textile printing of which 80% in the US uses pigments.[34] This design could have contained diarylide yellow or other pigments containing PCB 11. In one case, the front and back pieces from the same pajama top were extracted separately. PCB 11 concentration in the front piece printed in yellow was about 20 times more than that in the back piece dyed in red. Thus, PCB 11 in clothing primarily results from pigment, not dye, use. This is expected since dichlorobendine-based azo dyes are no longer manufactured because of their potential to release toxic amines.[35] Nevertheless, the presence of PCB 11 in clothing suggests that a primary route of entry of PCB 11 into wastewater is the washing of clothing. Future studies should assess the extent to which PCB 11 leaches out of clothing under conditions that simulate clothes washing (i.e., elevated water temperatures, presence of detergent and/or bleach).

Leaching of PCB 11 from Printed Materials. PCB 11 leached out of the test materials in all 22 experiments over the 48-h test using Milli-Q water as leachant. The fraction of PCB 11 that leached from printed materials ranged from 6% in a color newspaper and a product packaging box to 81% in a beverage packaging box (Figure S1). The varying fractions from the same type of material are likely due to pigments of different properties such as color and composition. Leaching of PCBs from these materials is likely to be more extensive under real-world conditions, because natural waters contain surfactant-like substances (such as humic acids)[36] and because materials could be exposed to leachant for longer than 48 h.

Taken together, the presence of PCB 11 in printed and fabric materials poses potential human exposure through dermal absorption. The environmental release of PCB 11 from these materials contributes additional routes of exposure via inhalation and digestion. In a few recent investigations, researchers detected PCB 11 and its hydroxylated metabolites in human sera collected from both urban community and rural areas with no historical PCB sources.[37,38] Nevertheless, the risk associated with PCB 11 among the general population was not assessed due to lack of data on toxicity and exposure.

Mass Flows of PCB 11 in the Delaware River Basin. In this mass flow analysis, we have assumed that the system is at or near steady state with respect to PCB 11 concentrations. This is not the case for Aroclor PCB congeners. For them, the sediments act as an internal load to the system, because they accumulated a PCB burden when concentrations were higher before the PCB ban of the 1970s and are releasing some of this reservoir now that concentrations have declined. The DRBC estimated that the sediments of the Delaware River contributed about 40% of the PCB burden in the water column.[27] We find it unlikely that this is the case for PCB 11, however, for several reasons. First, the production and use of color organic pigments has been relatively steady over time,[26,39] as opposed to the drastic reduction in Aroclor emissions following implementation of the TSCA. Second, Hu et al.[40] measured the sedimentary PCB 11 profile in the Great Lakes and found that it matched the history of pigment production in the US. Assuming this is also true in the Delaware River, there is no gradient that would drive PCB 11 out of the sediments and into the water column. Third, we attempted to measure PCBs in a sediment core collected in Woodbury Creek near Philadelphia.[41] Most PCB congeners that are associated with Aroclors were detectable and displayed maximum concentrations at about 1975, with a decrease of a factor of 5 since then. In contrast, PCB 11 was not detectable in any of the core slices (LOD = 100 pg g^{-1}). This suggests that historical PCB 11 concentrations in the sediments of the Delaware River are relatively low and have stayed low for at least 50 years. Our measurements are in agreement with those of the DRBC, who measured an average concentration of PCB 11 in surficial sediments of the Delaware of 110 pg g^{-1}, and a median concentration of 30 pg g^{-1}.[28] Fourth, PCB 11 is much less hydrophobic and has a higher vapor pressure than most of the Aroclor congeners, such that it is primarily removed from the system via volatilization, and the sediments cannot retain a large enough reservoir to account for all of this volatilization. The top 10 cm of sediment in the Delaware River (with an area of about 2000 km^2) contains a median PCB 11 concentration of about 30 pg g^{-1}, which means this reservoir holds only about 3 kg of PCB 11 (assuming a solids concentration of 500 g L^{-1} in surficial sediments). For these reasons, our assumption that PCB 11 is at or close to steady state in the Delaware River Basin is justified, and the sediments are not an important source of PCB 11.

Mass Inflow into the Basin. As noted above, the worldwide PCB 11 production from diarylide yellow pigments was estimated to be as much as 7,800 kg y^{-1} in 2006 based on the maximum allowable concentration of PCB 11 in pigments of 125 ppm under the TSCA. Because some researchers have measured concentrations of PCBs in pigments as high as 2000 ppm, it is possible that worldwide production of PCB 11 is even higher. In addition, PCB 11 is found in other types of pigments. Since the pigment market has been either flat or growing slowly over the last few decades,[26] this estimate probably remains valid for the period of examination. The US market consumed 20% of color organic pigments produced worldwide in 2010.[42] Assuming that regional pigment use is proportional to population (the Delaware River Basin comprises 2.7% of US population[43]), PCB 11 imported into the basin via use of pigments is estimated to be 42 kg y^{-1} (or 115,000 mg d^{-1}) in 2006 if pigments contain 125 ppm of PCB 11. In comparison, the TMDL for ΣPCBs in Zones 2 through 6 of the Delaware River totals only 2,256 mg d^{-1}.[28,29]

Mass Outflow/Storage. Processes discussed in detail here are storage in landfills and outflow via volatilization from the land or water surface to the atmosphere. Sequestration in soil is likely to be large but cannot be estimated directly; it is addressed in the fugacity model (see below). Three other processes were also quantified, but they remove or sequester less than 1 kg y^{-1} of PCB 11, and so are discussed in the Supporting Information: outflow via the Delaware River to the Atlantic Ocean (0.068 kg y^{-1}), storage in the surficial sediment of the Delaware River (0.077 kg y^{-1}), and storage in the sludge from municipal wastewater treatment (0.28 kg y^{-1}). Other processes can be assumed to be negligible (see Supporting Information).

Storage in Landfills. PCB 11 may be sequestered in landfills along with paper and other pigment-containing products that are not recycled. In a survey of azo-colorants in Denmark, the final disposal of azo pigments associated with printing inks was distributed among landfill (24%), soil (7%), and incineration (69%).[44] Assuming these ratios are the same for PCB 11 in the Delaware River Basin, maximum sequestration of PCB 11 in landfill is estimated around 10 kg y^{-1} based on the maximum inflow of 42 kg y^{-1}. However, municipal solid waste (MSW) handling is quite different in the US,[45] where from 2000 to 2011 about 54% of all municipal solid waste was landfilled, about 12% incinerated, and about 26% recovered for recycling (but about 65% of this material was not actually recycled). It is not clear whether these percentages apply to printed materials. Paper and paperboard comprise about 28% of MSW, but pigments may also be present in food waste (via food packaging), textiles, and plastics. For paper and paperboard, about 54% is recovered for recycling, but the recycling process involves deinking which may release PCBs in the ink to the environment or may sequester them in the deinking waste. Only about 17% of textiles are recycled and just 1.7% of plastics. Based on these statistics, we estimate that 50% of all of the PCB 11 present in consumer products is landfilled. If the input of PCB 11 into the watershed is 42 kg y^{-1}, then this would imply that 21 kg y^{-1} is landfilled. Note that this estimate is dependent on the amount estimated to be imported into the estuary. If the estimated import were to change, then the absolute amount sequestered in landfills would also change, although the fraction (50%) stays the same.

Volatilization to the Atmosphere. The average concentration of atmospheric PCB 11 in the Delaware River Basin was about 6 pg m^{-3} with a small relative standard deviation (RSD) of 29% via passive air sampling conducted during March to June 2008.[31] A 2005 passive sampling campaign measured PCB 11 from 4 to 44 pg m^{-3} in the same airshed.[6] PCB 11 concentrations were mostly well above 6 pg m^{-3} from long-term monitoring of atmospheric PCBs by high-volume air sampling in this area. Specifically, airborne PCB 11 averaged 14 pg m^{-3} at Camden, New Jersey, 22 pg m^{-3} at New Brunswick, New Jersey, and 20 pg m^{-3} at Lums Pond, Delaware.[46]

A simple box model was constructed to calculate the emission required to maintain the average PCB 11 concentration in the airshed of the basin. Since the basin area is about 13,500 square miles, or 35,000 km^2, the airshed is assumed as a box with a square bottom in the same width (W) and length (L) of 187,000 m. The multimedia urban model (MUM), developed by Diamond et al.,[47] divides the air compartment into lower air from 0 to 50 m that is in contact with impervious surfaces and upper air from 50 to 500 m that is above most building heights. Therefore, two model scenarios were considered with atmospheric mixing height (H) of 50 and 500 m, respectively. Because the variation in PCB 11 concentrations measured in the air at the earth's surface is low, it is reasonable to assume that the box is well mixed.

The steady-state mass (M, g) of PCB 11 in the air box is calculated by eq 1

$$M = C_a \cdot W \cdot L \cdot H \tag{1}$$

where C_a is the average PCB 11 concentration in the atmosphere (g m^{-3}); W, L, and H is the width, length, and height (m) of the air box, respectively. Major removal processes of PCB 11 from the atmosphere include advection by wind and reaction with hydroxyl (OH) radicals. Atmospheric deposition is negligible for low molecular weight PCBs such as PCB 11.[30]

Table 1. Emission Rates and Concentrations of PCB 11 in the Delaware River Basin Calculated by the Level III Fugacity Model under Various Environmental Scenarios (A–D)[a]

	emission rate to bulk compartment (kg y^{-1})						concentrations of PCB 11 in bulk compartment							
							air (pg m^{-3})		water (pg L^{-1})		soil (pg g^{-1})		sediment (pg g^{-1})	
model scenario	air	water	soil	sediment	total emission (kg y^{-1})	air depth (m)	cald	repd	cald	repd	cald	repd	cald	repd
A	3.1	2.9	2.0	0	8.0	50	6.0	6	15.2	15.6	3.1	30	45	30
B	45	2.0	31	0	78	500	6.0		15.0		36		44	
C	2.9	2.0	21	0	26	50	20	20	15.8		27		47	
D	254	2.5	2.0	0	259	500	20		15.6		5.3		46	

[a]Reported median concentrations of PCB 11 in each bulk compartment are included for comparison.

The advective loss is calculated as a flushing rate (k_w, s^{-1}) by eq 2

$$k_w = u/W \tag{2}$$

where u is the wind speed (m s^{-1}). The average wind speed in the watershed was around 4 m s^{-1}.[48] The removal rate by reaction with OH radicals (k_{OH}, s^{-1}) is calculated by eq 3

$$k_{OH} = k \cdot C_{OH} \tag{3}$$

where k is the OH reaction rate constant (2.2×10^{-12} cm^3 s^{-1}) obtained from that of a similar dichlorobiphenyl, i.e. PCB 4, and C_{OH} is the global average concentration of OH radicals (9.7×10^5 molecules cm^{-3}).[49]

Finally, the emission rate (I, mg d^{-1}) is calculated as the product of steady-state mass of PCB 11 in the air box and the sum of all rate constants using eq 4.

$$I = M \cdot (k_w + k_{OH}) \cdot 1000 \cdot 86400 \tag{4}$$

With an atmospheric mixing height of 50 m, an emission of 21,000 mg d^{-1} or 7.8 kg y^{-1} is required to meet the most conservative estimate of average atmospheric PCB 11 concentration of 6 pg m^{-3} in the basin. This is within the maximum estimated inflow of 42 kg y^{-1}. With an atmospheric mixing height of 500 m, an emission of 210,000 mg d^{-1} or 78 kg y^{-1} is required to produce an average concentration of 6 pg m^{-3}, which exceeds the maximum estimate of 42 kg y^{-1}. To achieve an average concentration of 20 pg m^{-3}, which is observed from active air sampling at Lums Pond, Delaware, an input of 26 kg y^{-1} is needed if the mixing height is 50 m, and 260 kg y^{-1} if the mixing height is 500 m. Because a typical height of 1–2 km vertical mixing is observed during daytime driven by convection from heated land surface and a stable boundary layer of 50–200 m is formed during the night,[50] both model scenarios have their own merit in describing the actual environmental conditions. However, the uncertainty in the mixing height renders the uncertainty in the estimated emissions very high.

It should be noted that PCB 11 inflow from upwind is assumed to be negligible because the background concentration is considered low surrounding the Delaware River Basin. This assumption is based in part on the measurements of Basu et al.,[51] who observed that PCB 11 concentrations were a function of population and were higher by a factor of about 7 between Chicago and a remote site. These researchers measured geometric mean concentrations of 18 pg m^{-3} in Chicago versus 2.5 pg m^{-3} in Eagle Harbor, Michigan. If the concentration of PCB 11 in the air flowing into the Delaware River Basin is 2.5 pg m^{-3}, the estimated mass flows of PCB 11 volatilizing from the river basin would be reduced by 3 kg y^{-1} at a mixing height of 50 m and by 30 kg y^{-1} at a mixing height of 500 m. In other words, the estimated volatilization of PCB 11 would then decrease to about 5 to 230 kg y^{-1}. Note that these estimates of volatilization are all independent of the amount of PCB 11 imported into the estuary.

Validation by Level III Fugacity Model. A level III fugacity model was applied to validate the mass flow estimates in a multimedia environment. Four bulk compartments including air, water, soil, and sediment containing four subcompartments including air, water, solid, and biota were considered according to the approach described by Mackay and Paterson.[52] The relevant compartmental properties including subcompartment volume fraction, density, organic carbon (OC) fraction, volume, area and depth are provided in Table S2 of the Supporting Information. The model incorporated partitioning between 10 subcompartments, 4 compartmental degradation processes, 13 intercompartmental transfers, and 2 advective flows in air and water. Transport parameters between bulk compartments and rates of advection and degradation within each bulk compartment are summarized in Tables S3 and S4 of the Supporting Information. Equilibrium was assumed between subcompartments within each bulk compartment but not between bulk compartments. The model not only examined the major removals calculated previously but also took into account the other dominant loss processes that were difficult to estimate such as sequestration in soil and soil-air transfer.

The parameters used in the model calculation were either collected from the literature[52] or measured in our laboratory. The atmospheric concentration of PCB 11 was relatively consistent with an average between 6 and 20 pg m^{-3}. Median concentrations of PCB 11 in the Delaware River were 15.6 pg L^{-1} in the water column and 30 pg g^{-1} in the sediment. PCB 11 was detected in one out of eight soil samples in the Delaware River Basin at a concentration of 80 pg g^{-1} (LOD = 30 pg g^{-1}; data not shown). Chemical-specific properties (Table S5 of the Supporting Information) were used to calculate fugacity capacities (Z values) for each subcompartment and summed up for each bulk compartment. Transfer coefficients (D values) were calculated for intercompartmental transfers as well as intracompartmental advection and reaction. Finally, the emission rates were estimated to generate steady-state model output including all fugacities and concentrations. Table 1 lists four model scenarios (A–D) with varying emission rates into each bulk compartment to achieve the range of observed concentrations. No direct emission into sediment was assumed. Diagrams of PCB 11 mass flows in and between four bulk compartments for each model scenario are shown in Figure S2 of the Supporting Information. It should be noted that the emission rates were the most poorly quantified variables in the model; however, they offered invaluable capability of predicting

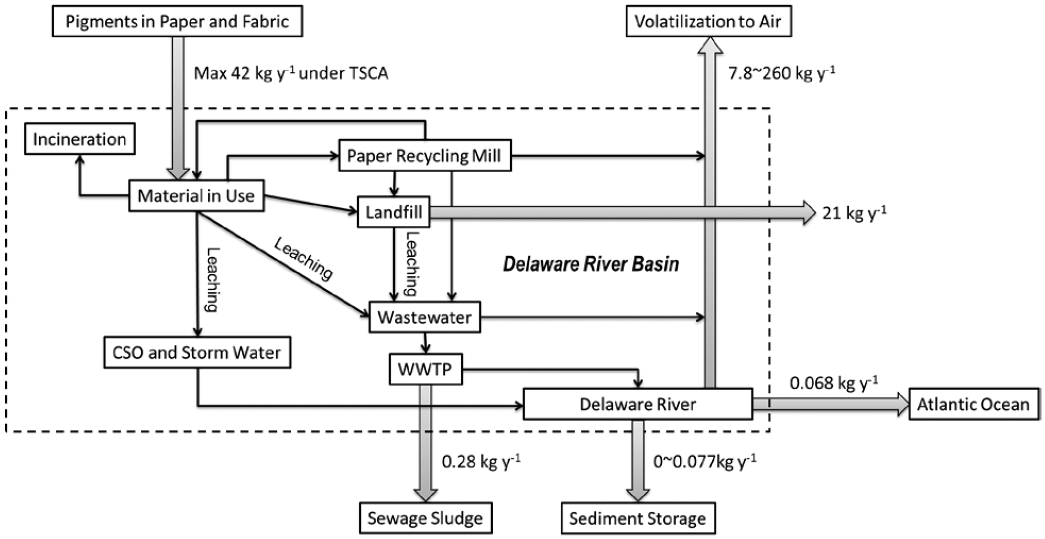

Figure 2. Mass flows of PCB 11 in the Delaware River Basin. External input from pigments is estimated using maximum average PCB 11 concentration (125 ppm) allowed under the TSCA. Estimated losses through volatilization, landfilling, advection, sedimentation, and sewage sludge removal are also given. Note: CSO stands for combined sewer overflows and WWTP stands for wastewater treatment plant.

the likely behavior of chemicals and estimating order of magnitude concentrations. By using the level III fugacity model, the estimated input of PCB 11 into the Delaware River Basin totaled from 8.0 to 259 kg yr^{-1}, which agrees well with previous calculations.

■ SUMMARY OF MASS FLOW ESTIMATES

Estimated mass flows of PCB 11 from production to distribution in the environment are summarized in Figure 2. Our study provides evidence that sources of PCB 11 are primarily associated with diarylide yellow and other pigments that are mostly applied in printing inks. The mass flow analysis of PCB 11 in the Delaware River Basin suggests that total inflows may be as high as 42 kg y^{-1} if pigments contain the maximum of 125 ppm of PCB 11 allowed under the TSCA. Total outflows range from about 30 to 280 kg y^{-1} by calculation of dominant loss processes and are supported by a level III fugacity model.

There are several implications to this mass flow analysis. First, it suggests that a substantial fraction of the PCB 11 contained within the products imported into the Delaware River Basin is released to the environment and can be measured in air, water, soil, and sediment. This is in stark contrast to the assertions of the ETAD, which has stated "...PCBs are present both on the surface and in the solid pigment matrix. This incorporated PCB is unlikely to lead either to human or environmental exposure. Additionally pigments are used to colour paints, inks and plastics and are themselves incorporated into a further matrix making release improbable—until both polymeric matrix and the pigments degrade."[14]

Second, the mass flow analysis suggests that pigments are a large enough source that they can plausibly account for the PCB 11 measured in the air, water, soil, and sediment of the Delaware River Basin. Other possible sources can be ruled out. Dichlorobenzidene-based dyes (as opposed to pigments) could theoretically be a source of PCB 11; however, 3,3′-dichlorobenzidine is no longer used to manufacture soluble dyes since 1986 in the US.[35] This compound is now mostly manufactured outside the US and imported for on-site processing or for use in pigment production.[35] Our investigation of PCB 11 levels in clothing suggests that they may come from pigments, rather than dyes. We know of no processes other than pigment use that could be responsible for the dispersion of PCB 11 in the environment. All of the source apportionment studies conducted for the New York/New Jersey Harbor and the Delaware River suggest that PCB 11 is not associated with Aroclors or microbial dechlorination but is instead correlated with stormwater and wastewater.[27,53] Furthermore, PCB 11 concentrations in the air and sediment of the Delaware River are evenly distributed throughout the watershed,[6,28,54] suggesting the sources are diffuse, as opposed to being associated with a small number of manufacturing facilities. Thus, whatever the source of PCB 11, it is related to some kind of human activity that is dispersed across the Delaware River Basin.

Finally, this investigation has demonstrated that the PCB 11 contained in consumer goods can leach into the environment, where humans and other biota can be exposed. We have demonstrated that this release is not only possible but appears to be extensive, such that most of the PCB 11 incorporated into consumer goods does escape the polymer matrix. Further research is needed to determine whether PCB 11 from pigments poses a risk to humans and biota.

■ ASSOCIATED CONTENT

Supporting Information

Additional information including 5 tables and 2 figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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