Evidence for Unique and Ubiquitous Environmental Sources of 3,3′-Dichlorobiphenyl (PCB 11)

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The non-Aroclor congener 3,3′-dichlorobiphenyl (PCB 11) has been recently detected in air, water, biota, sediment, and suspended sediment. Although it has been known since at least the 1970s that this congener is produced inadvertently during the production of diarylide yellow pigments, this work presents the first evidence that the use of these pigments in consumer goods results in the dispersion of PCB 11 throughout the environment at levels that are problematic in terms of achieving water quality standards for the sum of polychlorinated biphenyls (PCBs). In this work, PCB 11 is measured at ppb levels in consumer goods that are likely to be discarded in ways that allow them to enter wastewater treatment plants and combined sewer overflows, including newspapers, magazines, cardboard boxes used for food packaging, and plastic bags. Also, using data sets acquired for the purpose of calculating total maximum daily loads (TMDLs) for PCBs, PCB 11 loads to the New York/New Jersey Harbor and Delaware River are calculated. Despite the fact that there are no known manufacturers of diarylide yellow pigments in the Delaware River watershed, the loads of PCB 11 to the Delaware River exceed the TMDL for the sum of PCBs by nearly a factor of 2. The ratio of PCB 11 to a characteristic dechlorination end product, PCB 4 (2,2′-dichlorobiphenyl), in these data sets indicates that dechlorination is not a significant source of PCB 11 in these systems. In the upper Hudson River, where extensive dechlorination of heavy PCB congeners occurs, the ratio is just 0.012. In contrast, downstream in the NY/NJ Harbor as well as in the Delaware River the ratio is much higher and more variable. Pigment use therefore appears to be the main source of PCB 11 in these systems, and this congener is likely to present a significant obstacle to achieving PCB water quality standards throughout the United States.

Introduction

Polychlorinated biphenyls (PCBs) are a class of persistent organic pollutants (POPs) that have been targeted for elimination by the United Nations Environment Programme as one of the "dirty dozen" POPs (*1*). In the United States, the production and use in commerce of PCBs was banned by a series of legislative acts, including the 1973 act that prohibited the use of PCBs in open applications. These open applications included the use of PCBs as a transfer agent in carbonless copy paper. An important and often overlooked loophole in the various laws regulating PCB use was that the inadvertent production of PCBs was allowed to continue as long as monitoring requirements were met. Despite this exclusion, PCBs in the United States and in many other countries are regulated as the sum of all 209 congeners (∑PCBs). In the United States, the Clean Water Act requires that waterways in which ∑PCBs exceed the applicable water quality standard must be subjected to a process in which a total maximum daily load (TMDL) is calculated, promulgated, and implemented. Thus, although inadvertent production of PCBs is not banned in the United States, it will increasingly be subject to regulation via the Clean Water Act and the TMDL process.

The dichloro congener 3,3′dichlorobiphenyl (PCB 11) is produced inadvertently during the production of diarylide yellow pigments, which are the most common yellow pigments used in printing as well as a wide variety of other applications (*2*). The original 1979 Code of Federal Regulations (*3*) specifically states that "after July 1, 1979, processing and distribution in commerce of diarylide or phthalocyanin pigments that contain 50 ppm or greater PCBs is permitted only for persons who are granted an exemption." Worldwide production of color organic pigments was estimated to be about 250 million metric tons in 2006, with about 25% of the market being diarylide yellow pigments (*4*). About 65% of the total production of color organic pigments is used in printing (*4*). PCB 11 concentrations in printing inks with yellow pigments have been measured to be on the order of 15 ppb (*5*). Given that an average of 40% composition in printing inks are pigments (*6*), PCB 11 concentrations in diarylide yellow pigments are roughly 38 ppb. Therefore, worldwide production of PCB 11 via the manufacture of diarylide yellow pigments is estimated to be 1.5 t in 2006.

The recent development of a reference method for PCB analysis in environmental samples based on high resolution mass spectrometry (Environmental Protection Agency, EPA, method 1668A) has enabled researchers to measure PCB 11 routinely. In 2002, Litten (*7*) reported concentrations of PCB 11 as high as 225 ng L^{-1} in the effluents from two wastewater treatment plants in the New York/New Jersey Harbor area. These two plants received waste from pigment manufacturers. The load of PCB 11 to the harbor from these two plants was estimated to be about 100 kg y^{-1} at the time these samples were collected (*8*). That same year, King et al. (*9*) reported PCB 11 as a dominant PCB congener in water, suspended particulate material, and mussel tissues in Halifax Harbour. They noted the connection between PCB 11 and pigment production, and hypothesized that intermittent discharges from one or more unidentified industrial sources were the most likely source of PCB 11. Since that time, PCB 11 has been reported in the water column and in air at many locations (*10*−*12*). In recent work (*13*), we reported that PCB 11 is ubiquitous in the tidal Delaware River, and that it can be used as a tracer for wastewater and combined sewer overflows (CSOs), even in watersheds where there are no known manufacturers of diarylide yellow pigments.

Here, we provide evidence that the widespread use of diarylide yellow pigments is a significant source of PCB 11 to urban waterways, and that this source is likely to be large enough that it must be addressed in order to implement TMDLs for PCBs nationwide. The goals of this work are (1)

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TABLE 1. Concentrations of PCB 11 in Consumer Goods Collected in 2008[a]

material	PCB 11 concentration (ng g^{-1} = ppb)
black and white printed newspaper (A)	0.85
black and white printed newspaper (B)	0.45
brown (unprinted) cardboard (A)	3.0
brown (unprinted) cardboard (B)	2.8
color glossy magazine (A)	4.5
color glossy magazine (B)	3.3
color newspaper (A)	6.6
color newspaper (B)	5.7
plain white copy paper (A)	ND
plain white copy paper (B)	ND
manila envelope (A)	ND
manila envelope (B)	0.11
yellow cereal box (A)	3.0
yellow cereal box (B)	2.9
yellow plastic bag (A)	3.4
yellow plastic bag (B)	38
yellow sticky note (A)	0.82
yellow sticky note (B)	0.11
lab blank (GFF) (A)	ND
lab blank (GFF) (B)	ND

[a] ND = not detected.

to provide evidence that PCB 11 can enter urban waterways via the use of diarylide yellow in consumer goods including printed paper and cardboard packaging, (2) to provide evidence that the dominant source of PCB 11 in urban watersheds is not dechlorination of heavier PCB congeners, and (3) to provide a preliminary assessment of the magnitude of these nonpoint PCB 11 sources in two urban watersheds. These goals are addressed by measuring PCB 11 in a variety of consumer goods and by using existing data sets from the NY/NJ Harbor−Hudson River and the Delaware River to assess the loading profile of PCB 11 in these two systems (maps are provided in the Supporting Information). These two water bodies are excellent test beds for examining the sources of PCB 11 because in both systems large, high-quality data sets on PCB concentrations are available. Sediments in the upper Hudson River are highly contaminated with PCBs (*14*), and this is the site of arguably the most extensive documented in situ dechlorination of PCBs in the world (*15*−*20*). This is therefore the ideal location to determine the extent of PCB 11 production via the dechlorination of heavier congeners. The drawback of investigating PCB 11 sources in the NY/NJ Harbor is that there are known manufacturers of diarylide yellow in the watershed. For this reason, the Delaware River represents an excellent test bed for investigating PCB 11 loads that are not associated directly with pigment manufacture as there are no facilities in the Delaware River watershed that produce diarylide yellow pigments. In addition, the Delaware River is already subject to a TMDL for ∑PCBs of about 380 mg d^{-1} (*21*), allowing a useful comparison with PCB 11 loads.

Methodology

Measurement of PCB 11 in Consumer Goods. PCB 11 was measured in samples of printed material and other consumer goods collected in 2008 (Table 1). Paper from color magazines and newspapers, cardboard from food packaging for breakfast cereal, and yellow plastic grocery bags made of high density polyethylene were analyzed. These samples were processed as described previously (*10*). In brief, each sample (∼5 g) was spiked with PCBs 14, 23, 65, and 166 as surrogates. Each sample was Soxhlet extracted in dichloromethane for 24 h. The maximum temperature achieved during extraction was the boiling point of dichloromethane, 40 °C. Because diarylide yellow is reported to be able to withstand temperatures of up to 180−200 °C (*2*), breakdown of diarylide yellow to form PCB 11 during the extraction process is unlikely. Extracts were then reduced in volume by rotary evaporation and separated into two fractions on a column of 3% water-deactivated alumina. The fraction containing PCBs was concentrated under a gentle stream of nitrogen gas to about 0.5 mL and injected with internal standard PCBs 30 and 204 prior to analysis. Glass fiber filters (GFFs) were analyzed as blanks. GFFs were baked at 450 °C for 4 h prior to extraction.

Analysis of PCBs was performed by a gas chromatograph with a tandem quadrupole mass spectrometer detection system (Waters Quattro Micro GC) by a method described previously (*10*). PCB 11 was identified by use of authentic PCB 11 standards (Ultra Scientific). Frame solutions (Accustandard) containing all 209 PCB congeners were analyzed to confirm that no other dichloro PCB congeners coeluted with PCB 11 in the chromatographic system. Recoveries of the PCB 23 surrogate (which was used to surrogate-correct the measured PCB 11 concentrations) averaged 97.7% and ranged from 70% to 127%.

Construction of PCB Loads to the NY/NJ Harbor and Delaware River. Loads of PCB 11 and PCB 4 (2,2′-dichlorobiphenyl) to the NY/NJ Harbor and Delaware River were calculated (Tables 2 and 3). An analysis of the uncertainty in these loads is presented in the Supporting Information.

PCB loads to the NY/NJ Harbor were constructed considering the following inputs: stormwater, wastewater treatment plant effluents, tributaries, and combined sewer overflows (CSOs). Loads were calculated by multiplying a volumetric flow rate (Table 2) by the geometric mean PCB concentrations (dissolved plus particulate phase). The tributaries considered were the Hudson River at the Federal Dam at Troy, NY, as well as the Mohawk, Wallkill, Raritan, Rahway,

TABLE 2. Loads of Dichloro PCBs to the NY/NJ Harbor during 1998−2001

	flow (L y^{-1})	loads (mg d^{-1})	
	($\times 10^{10}$)	PCB 4	PCB 11
CSOs	12	74	68
stormwater	71	93	470
wastewater effluents	319	1300	1200
tributaries (New York)			
Hudson	742	41000	710
Mohawk	527	440	99
Wallkill	101	41	49
tributaries (New Jersey)			
Elizabeth	2	66	8
Hackensack	5	3	3
Passaic	96	300	150
Rahway	5	5	5
Raritan	105	96	120
total		43000	2900

TABLE 3. Estimated Loads of Dichloro PCBs to the Tidal Delaware River during 2001−2003

	flow (L y^{-1})	loads (mg d^{-1})	
	($\times 10^{12}$)	PCB 4	PCB 11
tributaries			
Delaware at Trenton	8.8	430	350
Schuylkill	2.1	240	110
minor tributaries	1.6	130	91
top 12 dischargers (wastewater treatment plants)			
municipal	0.83	740	170
industrial	0.11	25	21
sum		1600	740

Elizabeth, Passaic, and Hackensack Rivers (see Figure S-1 of the Supporting Information for a map of the area). Flows for these tributaries were total annual discharges averaged over the period 1980−2007 (www.usgs.gov) in order to remove the effect of isolated events such as the drought of 2002. Although there are no systematic trends in tributary discharge over this period, these periodic events cause the average flows to have relative standard deviations of as much as 37%. The stormwater flow was taken from Totten (*8*). The CSO flow was estimated on the basis of data from the Interstate Environmental Commission (http://www.iec-nynjct.org/reports.htm), who report that 12% of total wastewater treatment plant flow in the harbor region is in the form of CSOs, and that New York City's current capture rate for CSOs is 69%. Multiplying these percentages suggests that 3.7% of the total wastewater treatment plant flow is untreated CSO flow into the harbor, corresponding to about 12×10^{10} L y^{-1}. Flows for stormwater and CSOs are highly uncertain, so the flows given in Table 2 should be viewed with caution. Comparing loads of PCB 4 with loads of PCB 11, however, requires only that the same flow rate be used for both congeners.

PCB concentrations in samples from the NY/NJ Harbor were taken from the Contaminant Assessment and Reduction Project (CARP), which measured all 209 PCB congeners via EPA method 1668A in samples collected from 1998−2001. Details of the methodology are available in a variety of reports (*22, 23*) through two Web sites: http://www.state.nj.us/dep/dsr/njtrwp/ and http://www.dec.ny.gov/chemical/23839.html and the raw CARP data are available by request (http://www.carpweb.org/main.html).

A less complete loading assessment was performed for the Delaware River. Again, volumetric flow rates (Table 3) were multiplied by geometric mean PCB concentrations. PCB concentrations were obtained from the database of measurements collected in support of the TMDL for PCBs recently promulgated for the tidal portion of the River. PCBs were measured in samples collected during 2001−2003 via EPA method 1668A. Details of sampling and analysis can be found in the TMDL documents (*21*).

For tributaries, loads were constructed using the same methods used to calculated homologue PCB loads for the TMDL model (*21, 24*). In brief, dry weather flow rates were multiplied by concentrations of PCBs measured in samples collected at these lower flow rates, and wet weather flow rates were multiplied by concentrations of PCBs measured in wet weather samples. Loads were calculated for the Delaware at Trenton and the Schuylkill River as well as the following minor tributaries: Alloways Creek, Big Timber Creek, Brandywine Creek, Chester Creek, Christina River, Cooper River, Crosswicks Creek, Darby Creek, Frankford Creek, Mantua Creek, Neshaminy Creek, Pennsauken Creek, Pennypack Creek, Poquessing Creek, Raccoon Creek, Rancocas Creek, Red Clay Creek, Salem Creek, and White Clay Creek. A map of these tributaries is available in Figure S-2 of the Supporting Information.

For point discharges, the geometric mean concentration was multiplied by the average of the daily reported flows from the discharger during the period of sample collection (9/1/2001 to 3/31/2003). Point discharge loads were calculated for the top 12 discharges (by flow). These 12 accounted for about 88% of the total flow of all 75 dischargers sampled.

Using these data sets, two approaches were developed to investigate the possibility that PCB 11 arises primarily from dechlorination of heavier congeners. PCB 4 is a characteristic dechlorination end product in Hudson River sediments (*18*). If PCB 11 arises primarily from the dechlorination of heavier congeners, it would be prevalent in areas with high Aroclor PCB concentrations and notable levels of dechlorination activity such as the Upper Hudson River. Therefore the first approach was to use PCB 4 as an indicator of dechlorination activity and assume that if PCB 11 arises primarily from dechlorination, it will have a similar loading pattern and will be strongly correlated with PCB 4 in these two data sets. PCB 4 provides a good comparison to PCB 11 because both are dichloro PCB congeners and therefore have similar physical−chemical properties, suggesting that their transport and partitioning in the environment are similar. A box and whisker plot of these ratios is presented in Figure S-3 of the Supporting Information.

The second approach is to look for an association between PCB 11 and its precursors. Although microbially mediated reductive dechlorination of PCBs can remove chlorines at the ortho, meta, and para positions, removal of ortho chlorines is much less common (*25*). The most logical precursors for PCB 11 are therefore congeners that contain chlorines at the 3 and 3′ positions but have no chlorines in the ortho positions. Only three congeners meet these requirements: 3,3′,4,4′-tetrachlorobiphenyl (PCB 77), 3,3′,4,4′,5-pentachlorobiphenyl (PCB 126), and 3,3′,4,4′,5,5′-hexachlorobiphenyl (PCB 169). These three congeners are not very abundant in the Aroclors, comprising much less than 1% of any individual Aroclor (*26*). Thus it is possible that in areas of high Aroclor PCB concentration, PCB 4 concentrations could be high due to meta and para dechlorination, yet PCB 11 concentration remains low due to the inability of the bacteria to remove chlorines at the ortho position and the relative lack of these three congeners as precursors. For this reason, the second method of determining whether PCB 11 arises primarily from dechlorination is to look for its possible precursors in the PCB signal. Outside of the Upper Hudson River, PCB dechlorination tends to be slow and typically does not occur to a great extent. In fact, the TMDL models for the NY/NJ Harbor and the Delaware River assume that no degradation of PCBs occurs (*21, 22*). We therefore assume that if PCB 11 arises primarily from dechlorination in areas outside of the Upper Hudson River, its concentrations would not exceed those of its parent congeners, PCBs 77, 126, and 169.

Results

Concentrations of PCB 11 in Consumer Goods. PCB 11 concentrations in consumer goods sampled during 2008 ranged from nondetect to 38 ppb (Table 1). These levels are many orders of magnitude lower than the levels of ∑PCBs found in carbonless copy paper in 1972, when Kuratsune and Masuda (*27*) reported PCB concentrations as high as 64.7 mg g^{-1}. Two samples of each material were extracted, but they are not duplicates. For example, the newspaper and magazine samples were different mastheads printed on different days. The cereal boxes were from the same brand of cereal with a distinctive yellow box, but the boxes were obtained about 3 months apart. The plastic bags were obtained from a local grocery store several months apart. PCB 11 was below the detection limit of about 0.25 ppb in the GFF blanks as well as in samples of white copy paper and one of the manila envelopes. Thus PCB 11 is associated with color, especially yellow, printing. PCB 11 was by far the dominant PCB congener detected in the color samples. Most other PCB congeners were below detection limit.

The detection of these levels of PCB 11 in consumer goods is problematic. The use of PCBs in carbonless copy paper was banned due to concerns that they could be readily transferred to human skin during handling (*27*). It remains unclear to what extent PCB 11 is capable of leaching out of these materials, but given that paper and cardboard are easily shredded, especially when wet, it is certain that PCB 11 from these types of materials can contribute to particle-phase PCB concentrations in ambient waters.

A simple calculation illustrates the potential of these PCB 11-containing materials to affect surface water quality. An average cereal box such as those measured in Table 1 weighs about 90 g and therefore contains about 0.27 μg of PCB 11. If the cardboard of the box is assumed to be similar to the type of organic carbon usually encountered in the environment (an assumption which is debatable *28*−*30*), then the organic carbon−water partition coefficient (K_{oc}) can be used to estimate the volume of water that one cereal box can contaminate. Hansen et al. (*31*) report a value for log K_{oc} for PCB 11 of 4.84. Using this value, one cereal box can contaminate nearly 7000 L of water at a level of 20 pg L^{-1}, the average PCB 11 concentration in the ambient waters of the Delaware River.

PCB 11 in the NY/NJ Harbor. In constructing the loads from wastewater treatment plants, concentration data from the two wastewater treatment plants known to receive effluents from pigment manufacturers were excluded (although their flow was included in the total flow). In these two plants, PCB 11 concentrations in the effluents ranged from 5 to 116 ng L^{-1}. In effluents from the other plants, PCB 11 ranged from 0.0016 to 9.4 ng L^{-1}. As noted above, the load of PCB 11 from these two plants into the NY/NJ Harbor was calculated to be on the order of 100 kg y^{-1} (nearly 300 g d^{-1}) at the time these samples were collected. In comparison, the loads presented in Table 2 are small.

The main loads of PCB 11 to the harbor come from wastewater treatment plant effluents, stormwater, and the Hudson River. In contrast, by far the main source of PCB 4 to the harbor is the Hudson River, which is known to be contaminated with PCBs, mostly in the form of Aroclor 1242 (*14*). Indeed, the correlation coefficient between PCB 4 and PCB 11 concentrations in the CARP data set is poor (R^2 < 0.01). Extensive dechlorination of PCBs occurs in the Upper Hudson, resulting in high concentrations of PCB 4 in these waters. In samples from the Hudson River at Waterford, NY, near the site of documented PCB dechlorination, PCB 4 concentrations range from 0.9 to 7.5 ng L^{-1}, and PCB 4 comprises about 20% of ∑PCBs in the dissolved plus particle phases, despite comprising only about 4.7% of Aroclor 1242 (*26*). PCB 11 concentrations at this location range from 0.016 to 0.073 ng L^{-1}. PCB 11 represents about 1.2% of ∑PCBs in these samples and <0.1% of Aroclor 1242 (*26*). The ratio of PCB 11 to PCB 4 in these samples ranges from 0.004 to 0.2, with an arithmetic mean of 0.012 and a relative standard deviation (RSD) of 54%. The values appear to be normally distributed, and the geometric mean (0.011) is very similar to the arithmetic mean. In these samples it is probable that PCB 11 arises primarily from the dechlorination of higher molecular weight PCBs.

Downstream of the Hudson River in the NY/NJ Harbor this pattern is not observed. For example, in the CSO and stormwater samples, the ratio of PCB 11 to PCB 4 is much larger and more variable, ranging from 0.2 to 9 with an arithmetic mean of 1.7 (RSD = 110%). These values appear to be log-normally distributed, with a geometric mean of 1.1 and a geometric standard deviation of 0.4. Absolute PCB 11 concentrations in these samples range from 0.071 to 2.1 ng L^{-1}. The average and the maximum concentrations of PCB 11 in these samples are higher than the average and maximum concentrations of PCB congeners that could potentially be precursors to PCB 11 (PCBs 77, 126, and 169). Thus, in the area of arguably the highest PCB dechlorination activity in the world (the upper Hudson River), concentrations of PCB 11 are lower than in samples of stormwater and CSO effluents from the harbor downstream. It is difficult to imagine a scenario in which extensive degradation and dechlorination of PCBs occurs in the stormwater−wastewater collection system, resulting in PCB 11 concentrations that are higher than those of a characteristic dechlorination end product, PCB 4, and higher than those of the possible precursors of PCB 11. In fact, the TMDL model of the NY/NJ Harbor assumes that degradation of PCBs in this system is negligible (*32*). This suggests that PCB 11 in samples collected in the NY/NJ Harbor is not a product of dechlorination, and that its sources are different from the sources of PCB 4.

The fact that the largest loading categories for PCB 11 are wastewater treatment plant effluents and stormwater is consistent with a chemical that arises from nonpoint sources. Most of the sewers in the NY/NJ Harbor region are combined sewers such that wastewater influents include debris that is washed off of impervious surfaces. This debris can be expected to include discarded newspapers and other printed material. We hypothesize that PCB 11 could enter stormwater and wastewater treatment plant influents via these types of consumer goods, thereby contributing to the particle-phase PCB 11 levels. We further hypothesize that PCB 11 desorbs from these products and thereby enters the dissolved phase. Because PCB 11 has a higher aqueous solubility ($10^{-2.331}$ mol m^{-3}) and lower octanol−water partition coefficient ($10^{5.020}$ L kg^{-1}) than heavier PCB congeners (*33*), a larger fraction of its mass will exit the plant via the effluent.

PCB 11 in the Delaware River. Investigating PCB 11 dynamics in the NY/NJ Harbor is somewhat problematic because of the presence of pigment manufacturers in the watershed. In contrast, there are no known producers of diarylide yellow pigments in the Delaware River watershed. There are a few small pigment manufacturers in the area, but none that are listed in the Toxics Release Inventory (*34*) for releases of 3,3′-dichlorobenzidine, 3,3′-dichlorobenzidine dihydrochloride, and 3,3′-dichlorobenzidine sulfate, the key intermediates in the synthesis of pigments associated with PCB 11. As in the harbor, the TMDL model for PCBs in the tidal Delaware River assumes that degradation of PCBs in this system is negligible (*21*), and the correlation between concentrations of PCB 4 and PCB 11 in the Delaware River is poor (R^2 < 0.01). The ratio of PCB 11 to PCB 4 in the ambient waters of the Delaware River ranges from 0.1 to 22, with an arithmetic mean (RSD) of 1.3 (167%) and a geometric mean of 0.69. PCB 11 concentrations in the ambient waters of the Delaware River ranged from nondetect to 0.2 ng L^{-1}. The tributary loads of PCBs 4 and 11 (Table 3) generally follow the flows of the tributaries.

In samples from dischargers, a category which includes wastewater treatment plants, PCB 11 concentrations ranged from nondetect to 20 ng L^{-1}. Of the 75 discharger effluents sampled, only one contained the kind of high concentrations of PCB 11 observed in the two plants from the NY/NJ Harbor that receive wastewater from pigment manufacturers (i.e., > 5 ng L^{-1}). This one discharger was a paper mill south of Philadelphia that produces tissue products and is permitted for stormwater discharges. Two samples of stormwater from this mill contained 5.4 and 20 ng L^{-1} PCB 11. Excluding these two samples, the highest PCB 11 concentration observed in the dischargers was 1.7 ng L^{-1}. The highest PCB 11 concentrations were generally measured in effluents from industrial outfalls, although a municipal outfall from the city of Trenton, NJ, had one of the highest PCB 11 concentrations at 0.7 ng L^{-1}. As in the harbor, the concentrations of PCB 11 were higher than the concentrations of its precursors (PCBs 77, 126, and 169) in more than 90% of the discharger samples.

The loads from the top 12 point dischargers (by flow) total nearly 200 mg d^{-1} for PCB 11. These 12 dischargers are all wastewater treatment plants, 4 of which treat industrial effluents, with the other 8 being municipal plants. Most of the discharger load of PCB 11 comes from the municipal plants, largely due to their higher flow.

The estimated loads of PCB 11 to the Delaware River presented in Table 3 do not include three loading categories that were included in the TMDL model for PCBs: CSOs,

contaminated sites, and nonpoint sources, a category dominated by stormwater inputs. Loads from these three categories could not be estimated for PCB 11 because the necessary data are not available. Thus the total load of PCB 11 to the Delaware River is likely to be greater than the sum of all the estimated loads presented in Table 3. Loads from contaminated sites and nonpoint sources are significant for other PCBs. On the basis of the stormwater load calculated for the NY/NJ Harbor, PCB 11 loads from stormwater are likely to be significant in the Delaware River as well. Even without these loads, the total of the loads presented in Table 3 is about 740 mg d^{-1}, which is nearly twice the TMDL for the ∑PCBs in the Delaware River (380 mg d^{-1}). PCB 11 is therefore a significant problem in the Delaware River, a watershed which is not known to harbor any diarylide yellow pigment manufacturers. To the extent that the Delaware River can be considered a typical urbanized watershed, we find this result suggests that PCB 11 may be an obstacle to implementing PCB TMDLs in other regions of the United States.

Discussion

Relatively little is known about the toxicity of PCB 11. Because it is not substituted in the ortho positions, it may exhibit dioxin-like toxicity. PCB 11 reportedly produces neurochemical effects in rat cerebellar granule cells (*35*). Because it is less hydrophobic than heavier PCB congeners, it may be expected to have less bioaccumulation potential (*36*). It is likely to be less persistent in the environment than heavier PCBs because it is likely to partition to a greater extent into the gas phase, where it is subject to relatively fast reactions with the hydroxyl radical (*37*). It is also likely to be more susceptible to aerobic biodegradation (*38, 39*). Nevertheless, here we have provided evidence that loads of PCB 11 to waterways in the United States are likely to be significant and therefore must be addressed in order to implement PCB TMDLs. We have also presented evidence that the main source of PCB 11 in two typical urban watersheds is not dechlorination of heavier congeners, and we have demonstrated that PCB 11 is present in paper and cardboard materials that may be easily shredded and therefore can contribute to the particle-phase PCB 11 burden in ambient waters. We hypothesize that PCB 11 can also be released from these materials to the dissolved phase. Our results suggest that the sources of PCB 11 in urban watersheds are different from the sources of the Aroclor PCB congeners, and therefore control strategies designed to lower the loads of most other PCB congeners to urbanized surface waters are not likely to be successful in lowering PCB 11 loads. We recommend that monitoring programs should measure all 209 PCB congeners in at least a subset of samples and should measure PCB 11 in all samples. Because PCBs in the United States and in many other countries are regulated as the sum of all 209 congeners, PCB 11 appears to be a significant problem that will require further study.

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Supporting Information Available

Three figures and two tables. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) United Nations Environment Program *Final Act of the Conference of Plenipotentiaries on The Stockholm Convention on Persistent Organic Pollutants*; United Nations Environment Program: Geneva, Switzerland, 2001; p 44.
(2) Herbst, W.; Unger, K. *Industrial Organic Pigments: Production, Properties, Applications*. Wiley VHC: New York, 1993.
(3) *Polychlorinated Biphenyls (PCBs) Manufacturing, Processing, Distribution in Commerce, and Use Prohibitions*; 40 Code of Federal Regulations; Environmental Protection Agency: Washington, DC, 1979; Part *761.31* (g).
(4) Savastano, D. The Pigment Report: Although 2006 was a year of improvement, pigment manufacturers are coping with a wide variety of challenges, including raw material pricing and supply issues and overcapacity. *Ink World* , March 2007.
(5) Rastogi, S. C. Investigation of isomer specific polychlorinated biphenyls in printing inks. *Bull. Environ. Contam. Toxicol.* **1992**, *48*, 567–571.
(6) Vanderhoff, J. W. Rheology and Dispersion of Printing Inks. In *Pigment Handbook*, Patton, T. C., Ed; John Wiley & Sons: New York, 1973; Volume*III*, Characterization and Physical Relationships.
(7) Litten, S.; Fowler, B. I.; Luszniak, D. Identification of a novel PCB source through analysis of 209 PCB congeners by US EPA modified method 1668. *Chemosphere* **2002**, *46*, 1457–1459.
(8) Totten, L. A. Present Day Sources and Sinks for Polychlorinated Biphenyls (PCBs) in the Lower Hudson River Estuary. In *Pollution Prevention and Management Strategies for Polychlorinated Biphenyls in the New York/New Jersey Harbor*; Panero, M., Boehme, S., Munoz, G., Eds.; New York Academy of Sciences: New York, 2005.
(9) King, T. L.; Yeats, P.; Hellou, J.; Niven, S. Tracing the source of 3,3′-dichlorobiphenyl found in samples collected in and around Halifax Harbour. *Mar. Pollut. Bull.* **2002**, *44*, 590–596.
(10) Du, S.; Wall, S. J.; Cacia, D.; Rodenburg, L. A. Passive air sampling for polychlorinated biphenyls in the Philadelphia, U.S.A. metropolitan area. *Environ. Sci. Technol.* **2009**, *43*, 1287–1292.
(11) Hu, D.; Martinez, A.; Hornbuckle, K. C. Discovery of non-Aroclor PCB (3,3′-Dichlorobiphenyl) in Chicago air. *Environ. Sci. Technol.* **2008**, *42*, 7873–7877.
(12) Choi, S.; Baek, S.; Chang, Y.; Wania, F.; Ikonomou, M.; Yoon, Y.; Park, B.; Hong, S. Passive air sampling of polychlorinated biphenyls and organochlorine pesticides at the Korean Arctic and Antarctic research stations: Implications for long-range transport and local pollution. *Environ. Sci. Technol.* **2008**, *42*, 7125–7131.
(13) Du, S.; Belton, T. J.; Rodenburg, L. A. Source apportionment of PCBs in the tidal Delaware River. *Environ. Sci. Technol.* **2008**, *42*, 4044–4051.
(14) Hudson River PCBs Site, New York, Record of Decision. U.S. Environmental Protection Agency: Washington, DC, 2002, http://www.epa.gov/hudson/d_rod.htm#record.
(15) Quensen, J. F.; Boyd, S. A.; Tiedje, J. M. Dechlorination of four commercial polychlorinated biphenyl mixtures (Aroclors) by anaerobic microorganisms from sediments. *Appl. Environ. Microbiol.* **1990**, *56*, 2360–2369.
(16) Quensen, J. F.; Tiedje, J. M.; Boyd, S. A. Reductive dechlorination of polychlorinated biphenyls by anaerobic microorganisms from sediments. *Science* **1988**, *242*, 752–754.
(17) Fish, K. M.; Principe, J. M. Biotransformations of Aroclor 1242 in Hudson River test tube microcosms. *Appl. Environ. Microbiol.* **1994**, *60*, 4289–4296.
(18) Brown, J. F.; Wagner, R. E.; Feng, H.; Bedard, D. L.; Brennan, M. J.; Carnahan, J. C.; May, R. J. Environmental dechlorination of PCBs. *Environ. Toxicol. Chem.* **1987**, *6*, 579–593.
(19) Brown, J. F.; Bedard, D. L.; Brennan, M. J.; Carnahan, J. C.; Feng, H.; Wagner, R. E. Polychlorinated biphenyl dechlorination in aquatic sediments. *Science* **1987**, *236*, 709–712.
(20) Brown, J. F.; Wagner, R. E.; Bedard, D. L.; Brennan, M. J.; Carnahan, J. C.; May, R. J.; Tofflemire, T. J. PCB transformations in upper Hudson sediments. *Northeastern Environ. Sci.* **1984**, *3*, 167–179.
(21) Fikslin, T. J.; Suk, N. *Total Maximum Daily Loads for Polychlorinated Biphenyls (PCBs) For Zones 2−5 of the Tidal Delaware River*; Report to the U.S. Environmental Protection Agency Rgions II and III; Washington, DC, 2003.
(22) *A Model for the Evaluation and Management of Contaminants of Concern in Water, Sediment, and Biota in the NY/NJ Harbor Estuary: Contaminant Fate & Transport & Bioaccumulation Sub-Models*; Contamination Assessment and Reduction Project (CARP); Hudson River Foundation: New York, 2007.

(23) *Data Archive: Water, Sediment and Biota Data collected from 1999−2003*; Contamination Assessment and Reduction Project (CARP); Hudson River Foundation: New York, 2007; CD-ROM.
(24) Rowe, A. A.; Totten, L. A.; Cavallo, G. J.; Yagecic, J. R. Watershed processing of atmospheric polychlorinated biphenyl inputs. *Environ. Sci. Technol.* **2007**, *41*, 2331–2337.
(25) Bedard, D. L., Polychlorinated biphenyls in aquatic sediments: Environmental fate and outlook for biological treatment. In *Dehalogenation: Microbial Processes and Environmental Applications*; Haggblom, M. M., Bossert, I. D., Eds.; Kluwer Academic Publishers: Boston, 2003.
(26) Rushneck, D. R.; Beliveau, A.; Fowler, B.; Hamilton, C.; Hoover, D.; Kaye, K.; Berg, M.; Smith, T.; Telliard, W. A.; Roman, H.; Ruder, E.; Ryan, L. Concentrations of dioxin-like PCB congeners in unweathered Aroclors by HRGC/HRMS using EPA Method 1668A. *Chemosphere* **2004**, *54*, 79–87.
(27) Kuratsune, M.; Masuda, Y. Polychlorinated biphenyls in non-carbon copy paper. *Environ. Health Perspect.* **1972**, *1*, 61–62.
(28) Chen, Y.; Knappe, D. R. U.; Barlaz, M. A. Effect of cellulose/hemicellulose and lignin on the bioavailability of toluene sorbed to waste paper. *Environ. Sci. Technol.* **2004**, *38*, 3731–3736.
(29) Wang, X.; Xing, B. Importance of structural makeup of biopolymers for organic contaminant sorption. *Environ. Sci. Technol.* **2007**, *41*, 3559–3565.
(30) Chen, B.; Schnoor, J. L. Role of suberin, suberan, and hemicellulose in phenanthrene sorption by root tissue fractions of switchgrass (*Panicum virgatum*)seedlings. *Environ. Sci. Technol.* **2009**, *43*, 4130–4136.
(31) Hansen, B. G.; Paya-Perez, A. B.; Rahman, M.; Larsen, B. R. QSARs for KOW and KOC of PCB congeners: A critical examination of data, assumptions and statistical approaches. *Chemosphere* **1999**, *39*, 2209–2228.
(32) *HydroQual: A Model for the Evaluation and Management of Contaminants of Concern in Water, Sediment, and Biota in the NY/NJ Harbor Estuary. Contaminant Fate, Transport, and Bioaccumulation Sub-models*; Report prepared for the Hudson River Foundation on behalf of the Contamination Assessment and Reduction Project (CARP); New York, 2007, http://www.carpweb.org.
(33) Paasivirta, J.; Sinkkonen, S. I. Environmentally relevant properties of all 209 polychlorinated biphenyl congeners for modeling their fate in different natural and climatic conditions. *J. Chem. Eng. Data* **2009**, *54*, 1189–1213.
(34) Toxics Release Inventory (TRI) Program. U.S. Environmental Protection Agency. http://www.epa.gov/tri/.
(35) Kodavanti, P. R. S. Neurochemical effects of PCBs: SAR modelling. 15th International Symposium on Chlorinated Dioxins and Related Compounds. *Toxicology* **1995**, *25*, 431–436.
(36) Schwarzenbach, R. P.; Gschwend, P. M.; Imboden, D. M.; *Environmental Organic Chemistry*; Wiley and Sons: Hoboken, NJ, 2003.
(37) Anderson, P. N.; Hites, R. A. OH radical reactions: The major removal pathway for polychlorinated biphenyls from the atmosphere. *Environ. Sci. Technol.* **1996**, *30*, 1756–1763.
(38) Adebusoye, S. A.; Ilori, M. O.; Picardal, F. W.; Amund, O. O. Metabolism of chlorinated biphenyls: Use of 3,3′- and 3,5-dichlorobiphenyl as sole sources of carbon by natural species of Ralstonia and Pseudomonas. *Chemosphere* **2008**, *70*, 656–663.
(39) Vasilyeva, G. K.; Strijakova, E. R. Bioremediation of soils and sediments contaminated by polychlorinated biphenyls. *Microbiology* **2007**, *76* (6), 639–653.

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