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Evidence for Widespread Dechlorination of Polychlorinated Biphenyls in Groundwater, Landfills, and Wastewater Collection Systems

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One of the few pathways for environmental transformation of polychlorinated biphenyls (PCBs) is microbial dechlorination under anaerobic conditions, which is reported to occur in contaminated sediments of rivers, lakes and harbors. The goal of this work was to determine whether PCB dechlorination occurs in built waste treatment environments. We analyzed a large database on PCB congener concentrations in effluents and some influents of facilities in the Delaware River Basin. Positive matrix factorization was used to identify the sources of PCBs and to look for evidence of dechlorination. Seven factors were resolved from the data set of 89 congeners in 645 samples. Two of the resolved factors represented dechlorination signals. One of these was dominated by PCBs 4 and 19 and represents an advanced stage of dechlorination of Aroclors to di- and trichlorinated congeners. This dechlorination signal was most prevalent in effluents from sites with contaminated groundwater and from wastewater treatment plants (WWTPs) that serve combined sewers or treat landfill leachate. The other dechlorination signal appeared to represent an intermediate stage of dechlorination, because it was dominated by two coeluting groups of tetrachlorinated congeners: PCBs 44 + 47 + 65 and 45 + 51. This partial dechlorination signal was most prevalent in the 40 WWTPs with separate (sanitary) sewer systems, where it often comprised more than 20% of the PCBs in the effluents. Both dechlorination signals were present in WWTP influents, but were not observed in stormwater runoff, suggesting that dechlorination occurs in sewers. This work represents the first convincing evidence of PCB dechlorination occurring outside of contaminated aquatic sediments or anaerobic digesters. The results suggest that PCBs are dechlorinated by anaerobic bacteria in sewers, landfills, and contaminated groundwater. These two dechlorination signals comprise about 19% of the total loads of PCBs to the Delaware River from the sampled dischargers.

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Introduction

Polychlorinated biphenyls (PCBs) are a worldwide problem due to their toxicity, persistence, and tendency to bioaccumulate. In the U.S., more than 7000 water bodies are impaired by PCB contamination (*1*). The Clean Water Act requires that a total maximum daily load (TMDL) be developed for each of these waterways in order to minimize contamination and improve water quality. The Delaware River was one of the first waterways to receive a TMDL for PCBs (*2*). As part of the effort to characterize the PCB sources to the river, the Delaware River Basin Commission (DRBC) orchestrated the sampling of effluents from most of the major dischargers to the river for measurement of PCBs. In this work, this data set was analyzed using a source apportionment technique called positive matrix factorization (PMF) in order to identify the main components or factors that make up the various sources of PCBs to the river.

This analysis was prompted in part by the recognition that PCB 4 (2-2; numbers before the dash refer to the chlorine positions on ring 1, and the numbers after the dash refer to the chlorine positions on ring 2) was present at high levels in many of the effluent samples, including those from wastewater treatment plants (*3*). PCB 4 has been identified as an indicator that dechlorination has reached an end point in environmental systems (*4–8*). Most reports of anaerobic dechlorination of PCBs occur in deeply buried (anaerobic) sediments that are contaminated with PCBs at levels above about 40 ppm (*9–11*), although it can also be stimulated in sediments with only 2 ppm weathered PCBs (*12*). There appear to be no peer-reviewed reports of dechlorination of PCBs occurring anywhere other than sediments of rivers, lakes, and estuaries, or in laboratories (*13, 14*), although there is some inconclusive evidence of PCB dechlorination occurring in compost (*15*) and landfills (*16, 17*).

The goals of this work were to analyze the discharger data set using PMF in order to identify the main sources of PCBs to the river and to look for evidence of PCB dechlorination in these data.

Methodology. The DRBC required dischargers with National Pollution Discharge Elimination System (NPDES) permits to measure 209 PCB congeners in their effluents via EPA method 1668A. Each discharger collected 2 L of sample which was shipped directly to a contract laboratory. Whole water (dissolved plus particulate) concentrations were reported to DRBC (*18*). Estimated Detection Limits were between 1 and 3 pg L^{-1} on a congener basis. This approach resulted in 605 samples of effluents from 100 dischargers. In addition, 102 influent samples were collected at 20 of these facilities. After trimming the database to exclude congeners and samples with more than 50% nondetects (*18*), the final data matrix contained 89 congeners (or coeluting congener groups) in 645 samples (546 effluent and 99 influent). The resulting database was examined via PMF2 software (YP-Tekniika KY Co., Helsinki, Finland) (*19*). Details of PMF modeling, including criteria for determining the correct number of factors, are provided in the Supporting Information (SI).

Calculation of Loads. The importance of each factor is expressed in terms of the percentage of the total load of all PCBs *from these NPDES-permitted dischargers* to the Delaware River. PCB loads from these dischargers are estimated to represent only about 15% of the *total* loads of PCBs to the river, which also include loads from tributaries, stormwater runoff, and runoff from contaminated sites. Loads were calculated by multiplying the geometric mean concentration

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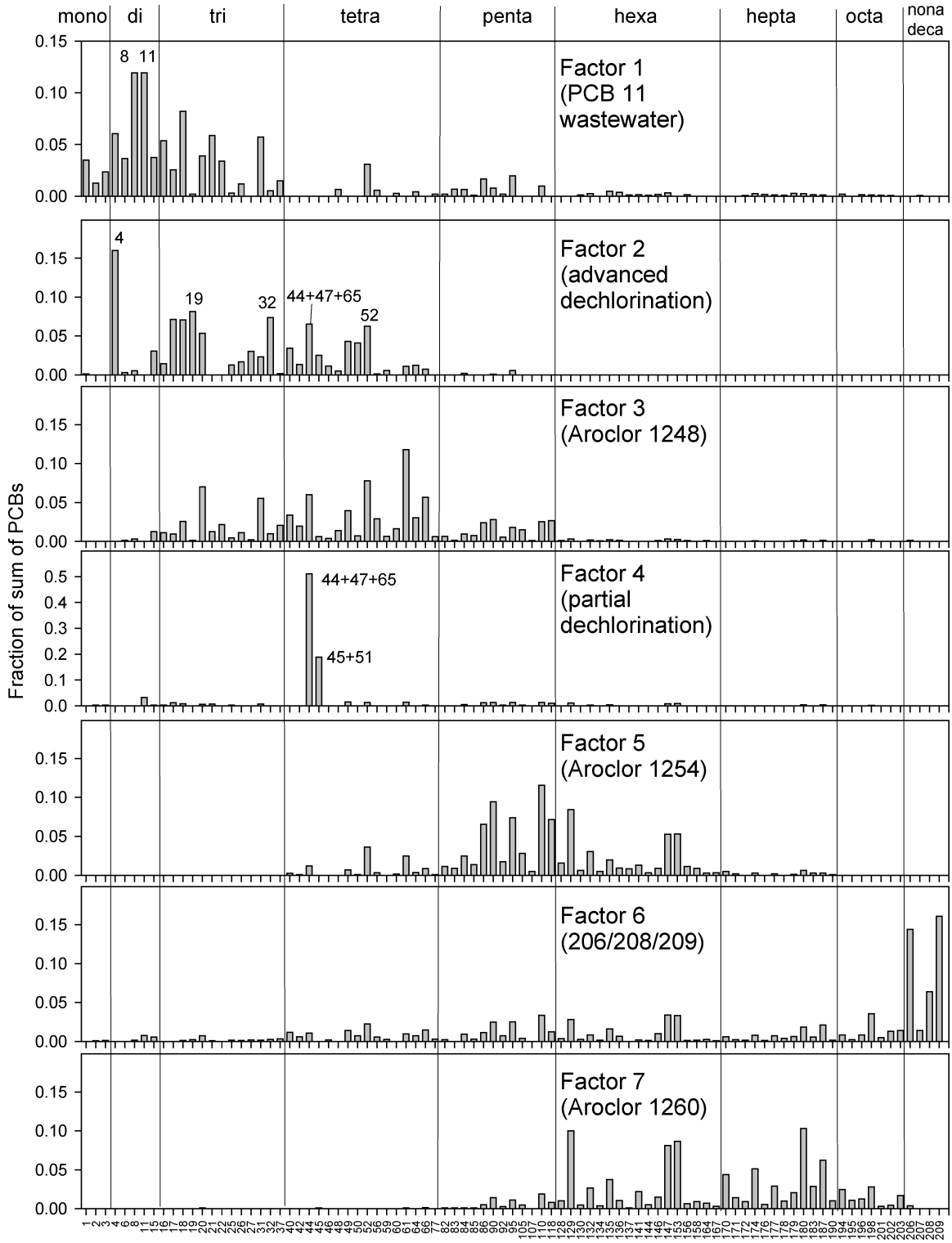

FIGURE 1. Congener profiles of the seven resolved factors.

of each factor for each discharger by the discharger's flow rate as reported to the DRBC (*2*).

Results

The concentrations of ∑PCBs in the effluent samples ranged from 0.047 to 6800 ng L^{-1} and are presented by discharger category in SI Figure S-1. Seven factors were resolved from the data set. Three factors resembled Aroclors, two represented non-Aroclor congener patterns, and two were dechlorination signals (Figure 1).

Non-Aroclor Factors. Factors 1 and 6 appear to represent non-Aroclor PCB congener signatures. Factor 1 contains the most PCB 11 (3-3) of any factor. PCB 11 is the dominant congener in this factor, constituting 12% of ∑PCBs. In previous work (*18*), we concluded that PCB 11 was a tracer for wastewater treatment plant (WWTP) effluents and combined sewer overflows in the ambient waters of the Delaware River. PCB 8 also comprises about 12% of factor 1. Hu and Hornbuckle (*20*) observed that PCB 8 and 11 were associated with commercial paint pigments. Factor 1 com-

prises 6.7% of the NPDES PCB loads, and is prevalent in a wide variety of effluents (SI Figure S-1), probably because many of the NPDES permits are for stormwater runoff, regardless of the SIC code of the discharger. Thus we hypothesize that factor 1 is related to stormwater runoff.

Factor 6 contains a characteristic PCB 206/208/209 signal produced inadvertently during the production of titanium tetrachloride (*21*) observed throughout the Delaware River and concentrated near Wilmington, DE (*18, 22*). These three congeners make up 37% of the PCB mass in this factor. Factor 6 bears no resemblance to any of the Aroclors, even when these three congeners are removed from the correlation. Factor 6 constitutes 1.5% of the total NPDES loads.

Aroclor Factors. Factors 3, 5, and 7 appear to represent Aroclors 1248, 1254, and 1260, respectively, with corresponding R^2 values ranging from 0.81 to 0.97 (*23*). The high correlation coefficients indicate that these Aroclors have undergone insignificant weathering. These three factors constitute 25%, 27%, and 21% of the NPDES loads, respectively.

Dechlorination Factors. Factors 2 and 4 appear to be dechlorination signals. Factor 2 is rich in low molecular weight *ortho*-substituted congeners, especially PCB 4 (2−2, 16% of the sum of PCBs) and PCB 19 (26−2, 8%). Other congeners that are reported in the literature as markers of dechlorination are present in factor 2 including PCBs 1 (2), 25 (24−3), 26 (25−3), 32 (26−4), and 49 (24−25) (*24, 25*). Congeners with five or more chlorines make up just 1.2% of this factor. Since *ortho* dechlorination, though possible, is not as prevalent or as major a pathway as *meta* and *para* dechlorination (*26, 27*), this factor appears to represent an *advanced dechlorination* PCB signal, that is, none of the original Aroclor profile remains. This factor contains virtually no PCB 11 (0.00002%), further supporting our conclusion in a previous publication (*3*) that dechlorination of heavier PCB congeners is not a significant source of PCB 11. Based on the differences in average molecular weight, conversion of Aroclors 1260, 1254, and 1248 to factor 2 would require a 30%, 23%, or 9% reduction in mass, respectively.

Factor 2 constitutes 14.8% of the total NPDES loads. This factor is abundant across many industry classes, due to its presence in effluents from contaminated sites across many industries. This factor constitutes more than 5% of the sum of PCBs in effluents from 10 of the 46 WWTPs in the data set and in discharges from several industrial facilities. Factor 2 is therefore widespread throughout the Delaware River basin.

Factor 4 also appears to be a dechlorination signal. It is dominated by two groups of coeluting congeners. PCBs 44 + 47 + 65 (23−25, 24−24, 2356, respectively) make up 51% of factor 4, while PCBs 45 + 51 (236−2, 24−26, respectively) constitute 19% (Figure 1). PCBs 47 (24−24) and 51 (24−26) are documented intermediate dechlorination products via process N (*24, 25, 27–29*). PCBs 44 (23−25) and 45 (236−2) similarly contain multiple chlorines in the *ortho* positions and could be dehalogenation products from process P or N, respectively (*8*). In contrast, PCB 65 (2356) contains four chlorines on one ring, and is therefore not present in the Aroclors (*23*) and is not likely to be a dechlorination product or major component of the chromatographic peak in this instance. Congeners with five or more chlorines make up about 15% of factor 4. Thus we conclude that Factor 4 represents an intermediate stage of dechlorination.

Magar et al. (*25*) found similar congener patterns in PCB fingerprints of sediment cores from the Lake Hartwell Superfund site in South Carolina using polytopic vector analysis. Their end member 3 (EM3) was dominated by PCBs 4 (2-2) and 19 (26-2), and they similarly interpreted it as a signal of nearly complete dechlorination. EM3 was dominant in the oldest and deepest sediments, which also tended to have the highest ∑PCB concentrations. Similar to the present work, they observed a second dechlorination end member (EM4), and hypothesized that it represented an intermediate dechlorination pattern because of the accumulation of PCBs 47 (24-24) and 51 (24-26) (among others).

Our results thus correspond well with the current understanding of microbial PCB dechlorination (*8*). The two dechlorination factors may represent two different dechlorination regimes that occur in series. The first regime dechlorinates heavy PCBs with PCB 47 and 51 as the main products (factor 4). This regime presumably involves removal of flanked chlorines, so that the end products lack flanked chlorines. Removal of flanked or doubly flanked chlorines occurs in all dechlorination processes, but is stipulated for more highly chlorinated congeners in processes P, H, H′, and N (*8*). The second regime dechlorinates these intermediate products more fully, with PCB 4 and 19 as the main products. This regime would therefore involve removal of unflanked chlorines in the *meta* and *para* positions from lightly chlorinated congeners (dechlorination processes M, Q, and LP) (*8*).

Influent vs Effluent Samples. In order to determine whether dechlorination is occurring during processing by the facilities in the database, influent concentrations of factors 2 and 4 were compared to effluent concentrations (Table 1; see also SI Table S-2). Of the 20 facilities for which both influent and effluents were sampled, 18 displayed similar or higher concentrations of factors 2 and 4 in their influents than in their effluents, suggesting that passing through the facility had either no effect on the PCB concentrations of these factors or actually removed lightly chlorinated PCBs from the water. It is difficult to generalize from this limited sample, but it appears that dechlorination does not occur within most facilities.

Only two facilities had higher concentrations of factors 2 and 4 in their effluents than in their influents: the former U.S. Steel plant at Fairless Hills, PA (PA0013463), and the Repauno facility in Gibbstown, NJ (NJ0004219). Both of these are Superfund sites being managed under the Resource Conservation Recovery Act (RCRA). At Fairless Hills, factor 2 comprised as much as 67% of the PCBs in the effluent, while factor 4 comprised up to 11%. Factor 2 concentrations averaged 0.9 ng L^{-1} in the influent and 138 ng L^{-1} in the effluent. Similarly, the concentration of factor 4 averaged 0.02 ng L^{-1} in the influent and 13 ng L^{-1} in the effluent. At the Repauno facility, the pattern was the same, with the concentrations of factors 2 and 4 increasing by factors of 12 and 3.5, respectively, from influent to effluent. Clearly, substantial dechlorination is occurring at these sites.

Four of the 20 facilities for which influents were sampled were WWTPs (SIC code 4952): Pennsville Sewerage Authority, Penn's Grove WWTP, Gloucester County Utilities Authority, and Delaware County Regional Water Quality Control Authority (DELCORA). At these four plants, the dechlorination signals (factors 2 and 4) are already present in the influent, suggesting that dechlorination occurred upstream of the treatment plant. These four WWTPs remove as much as 98% of the ∑PCBs in their influents, in agreement with other studies (*30–32*) including a 1998 study by the DRBC (*33*). Unfortunately, these earlier studies did not measure PCBs 4, 19, 47, and 51, which are the congeners most useful for the detection of evidence of dechlorination.

Evidence for Dechlorination in Sewers. As noted above, factors 2 and 4 are already present in the influents of the four WWTPs for which influents were sampled. Also, many of the industrial dischargers in the database are permitted for stormwater runoff, and these runoff samples contained little dechlorination signal. In 41 samples of stormwater runoff from areas throughout the Delaware River Basin such as commercial/industrial parking lots, Factor 2 comprised just 1.7 ± 3.0% and Factor 4 constituted 1.0 ± 1.4% of ∑PCBs.

TABLE 1. Concentrations of the Dechlorination Signals (Factors 2 and 4) in Influents and Effluents[a]

NPDES			factor 2				factor 4			
			influent		effluent		influent		effluent	
permit #	SIC code[b]	location	ng/L	% ∑PCBs	ng/L	% ∑PCBs	ng/L	% ∑PCBs	ng/L	% ∑PCBs
DE0000051	2816	Edgemoor, DE	0.11	2.7%	0.20	0.5%	0.043	1.0%	0.030	0.1%
DE0000256	2911	Delaware City, DE	0.084	2.9%	0.058	2.6%	0.058	2.0%	0.044	2.0%
NJ0004669	2631	Pennsauken, NJ	0.88	21%	0.57	4.1%	0.19	4.6%	0.27	2.0%
NJ0004995	4911	Hamilton, NJ	0.041	3.1%	0.036	3.3%	0.26	20%	0.16	14%
NJ0005029	2911	Paulsboro, NJ	0.48	10%	0.060	0.1%	0.14	2.9%	0.046	0.1%
NJ0005100	2869	Deepwater, NJ	0.10	2.1%	0.21	2.4%	0.057	1.1%	0.30	3.4%
NJ0005401	2911	Westville, NJ	0.26	7.2%	0.010	1.0%	0.030	0.8%	0.0082	0.8%
NJ0025411	4911	Hancock's Bridge, NJ	0.014	0.4%	0.15	7.0%	0.018	0.6%	0.018	0.9%
PA0011533	2911	Philadelphia, PA	0.52	6.5%	0.023	5.5%	0.042	0.5%	0.0027	0.6%
PA0011657	4911	Philadelphia, PA	0.26	2.6%	0.24	13%	0.023	0.2%	0.019	1.0%
PA0012629	2911	Philadelphia, PA	0.33	12%	0.0042	1.0%	0.029	1.0%	0.0023	0.5%
PA0012637	2911	Trainer, PA	0.23	5.9%	0.10	1.2%	0.15	4.0%	0.042	0.5%
PA0013714	4911	Eddystone, PA	0.53	38%	0.39	8%	0.064	4.6%	0.033	0.6%
PA0057088	4911	Fairless Hills, PA	1.8	29%	0.56	37%	0.0018	0.0%	0.0010	0.1%
NJ0004219	**2819**	**Gibbstown, NJ**	**0.52**	**11%**	**6.5**	**26%**	**0.092**	**2.0%**	**0.32**	**1.3%**
PA0013463	**3312**	**Fairless Hills, PA**	**0.87**	**5.6%**	**138**	**57%**	**0.016**	**0.1%**	**13**	**5.6%**
NJ0021598	4952	Pennsville, NJ	0.12	1.1%	0.043	0.6%	2.9	27%	1.3	17%
NJ0024686	4952	Gloucester County, NJ	0.38	1.5%	0.092	3.7%	13	52%	1.6	64%
PA0027103	4952	Delaware County, PA	1.3	11%	0.039	5.4%	0.72	6.0%	0.0028	0.4%
NJ0024023	4952	Penn's Grove, NJ	0.13	1.8%	0.033	0.7%	4.0	56%	1.3	29%

[a] Values in bold indicate facilities for which the effluent concentration is much larger than the influent concentration. [b] Standard Industrial Classification code. 2816 = inorganic pigments; 2911 = petroleum refining; 2631 = paperboard mills; 4911 = electric services; 2869 = industrial organic chemicals, not elsewhere classified; 2819 = industrial inorganic chemicals, not elsewhere classified; 3312 = steel works, blast furnaces (including coke ovens), and rolling mills; 4952 = sewerage systems.

Taken together, these results suggest that the dechlorination occurs after the stormwater (and presumably wastewater) enters the collection system and before it reaches the WWTP. We hypothesize that PCB dechlorination occurs in the sewage collection system. Sewers contain anaerobic zones which support sulfidogenesis and methanogenesis (*34*). To date members of the Chloroflexi, including *Dehalococcoides* (*27, 35, 36*), and *Dehalobacter* (*37*) have been implicated in dechlorination of PCBs. Members of the *Dehalococcoides* are commonly detected in contaminated groundwater (*38, 39*) and municipal anaerobic digester sludge (*40*). Members of the *Dehalobacter* and *Desulfitobacterium* were detected in unsaturated soils (*41*) and a nondehalogenating strain of *Desulfitobacterium* was isolated from human feces (*42*). Thus it is possible that diverse dehalogenating bacterial communities could be established in sediments in sewers either directly from waste inputs, from soil particles carried in stormwater runoff into combined sewers, or by introduction of groundwater and aquifer sediments via infiltration.

The sewage collection and treatment system may therefore be thought to consist of an anaerobic "pretreatment" zone (the sewer), followed by an aerobic treatment plant (e.g., activated sludge). This is precisely the treatment scheme that has been suggested by Brown et al. (*5*) to be ideal for the treatment of PCB contamination, since dechlorination in the anaerobic zone produces congeners that are more amenable to oxidative degradation in the aerobic zone.

The data set includes effluent data from 46 WWTPs. Of these, only six serve areas with combined sewers. These six also are the largest plants (by flow) in the database: all three of the Philadelphia Water Department's sewage treatment plants, and the Wilmington, DE; Camden, NJ; and DELCORA plants. The other 40 plants serve areas with exclusively separate (sanitary) sewers. Figure 2 demonstrates that factor 2 (the advanced dechlorination signal) is most prevalent at the six largest plants with combined sewer systems, where it comprises between 4% and 32% of the PCB mass in the effluents. Thus plants with combined sewers tend to exhibit the highest fractions of factor 2. We speculate that this may be because combined sewers are more likely to develop methanogenic zones than separate sanitary sewers (*34*), and further, these sewers could have been extensively seeded with dehalogenating bacteria via soil particles in runoff. Factor 2 is also remarkably prevalent (24% of ∑PCBs) in the effluent from the WWTP in Exeter Township, PA. At this plant, about 20% of the total flow is leachate from five landfills, suggesting that dechlorination may be occurring inside the landfills (see below). In contrast to these seven plants, the effluents of many of the other WWTPs in the database contain essentially no factor 2.

Factor 4 (the partial dechlorination signal) is particularly prevalent in WWTP effluents, where it sometimes comprises more than 70% of ∑PCBs. A greater preponderance of force mains (as opposed to gravity mains) in the sewershed is significantly ($p < 0.05$) correlated with increased amounts (% of ∑PCBs) of factor 4 in the WWTP's effluent (SI Figure S-2). This may be because force mains necessarily exclude air, allowing the sewage to become anaerobic (usually sulfidogenic), while gravity mains contain air that allows the sewage to maintain aerobic conditions most of the time (*34*). The absence of factor 4 in some effluents could also be caused by an absence of high molecular weight Aroclors in the sewage, which are necessary to provide the starting congeners that produce PCBs 47 and 51 upon dechlorination.

Because of their high flow rates, WWTPs are some of the largest contributors of factors 2 and 4 to the river. The five largest WWTPs contribute about 650 g yr^{-1}, or about 70% of the total mass of factor 2 discharged to the river. The numbers are even more dramatic for factor 4: WWTPs contribute 270 g yr^{-1} or 91% of all the factor 4 discharged to the river.

Evidence for Dechlorination in Groundwater. As noted above, a small number of facilities contain high proportions of factor 2 in their effluents, including the General Chemical facility in Claymont, DE; Bridgeport Disposal in Bridgeport, NJ; the former Navy Yards in Philadelphia, PA; and the U.S. Steel facility in Fairless, PA. PCBs in effluents from the General Chemical site are comprised almost entirely (92−98%) of factor 2. This facility appears to have inadvertently created

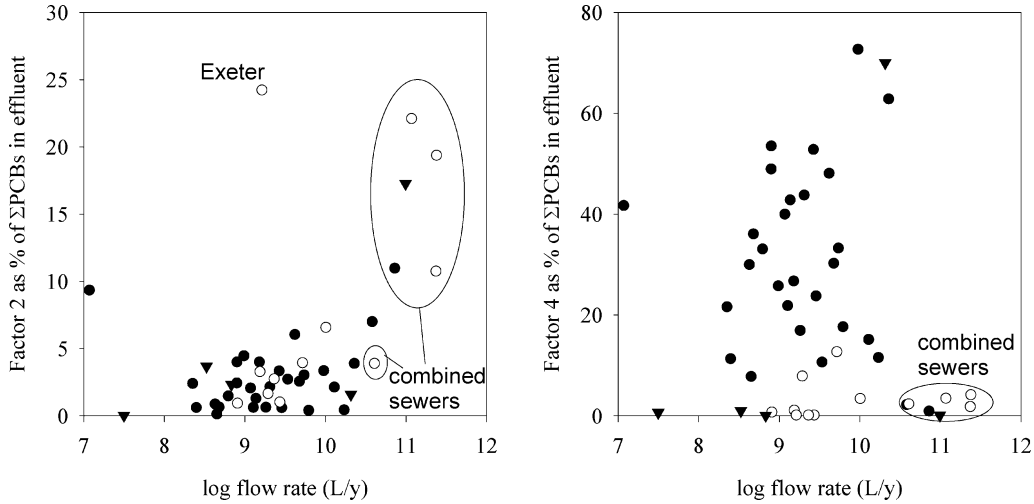

FIGURE 2. The percent of (a) fraction 2 (the advanced dechlorination signal) and (b) factor 4 (the partial dechlorination signal) in the effluents of the WWTPs plotted as a function of the log of the flow rate for each plant. The location of each plant is shown by symbol: filled circles for NJ, open circles for PA, and filled triangles for DE.

the most efficient bioreactor for the dechlorination of PCBs in the world. Similarly, in effluents from Bridgeport Disposal, factor 2 constitutes 84−90% of the PCBs. In addition to these sites, factor 2 comprises at least 10% of ∑PCBs in the effluents from another 13 active and inactive facilities, only some of which have been identified as RCRA sites. Factor 4 is, by contrast, much less abundant at these facilities, suggesting that dechlorination has gone nearly to completion at these sites, or that it proceeds primarily by the regime that produces di- and tri- chlorobiphenyls.

Most of these facilities have been identified as contaminated sites under the RCRA where contaminated groundwater is discharged into the river (see the SI for details). These sites share some common features. First, at many of these sites, PCBs are not one of the contaminants of primary concern (CPCs). The main CPCs are often hydrocarbons such as polycyclic aromatic hydrocarbons (PAHs), fuel oil, and volatile organic compounds (VOCs). In some cases, CPCs include halogenated compounds, such as tetrachloroethylene, and metals, including arsenic and lead. From this information, we conclude that dechlorination of PCBs occurs in the groundwater, where hydrocarbons speed the transition to methanogenic conditions and provide an energy source for dechlorinating bacteria. Further, presence of other organohalides has been shown to stimulate dechlorination of PCBs (*43–46*).

Evidence for Dechlorination in Landfills. A sample of effluent from the Grows landfill leachate treatment plant had the highest concentration of factor 2 in the entire data set at about 306 ng L^{-1}. As a result, factor 2 accounted for about half of the ∑PCBs in this sample. Three other samples of effluent from this plant contained 0.6 to 1.6 ng L^{-1} of factor 2. As described above, the abundance of factor 2 in the effluent of the Exeter Township WWTP also provides evidence that PCBs are dechlorinated in landfills, since landfill leachate comprises 20% of this plant's flow (*47*).

The Contamination Assessment and Reduction Project (CARP) database also contains evidence of dechlorination of PCBs in landfills. CARP measured all 209 PCB congeners via EPA method 1668A in samples of water, sediment, and biota (*48*). The CARP landfill leachate samples contain high concentrations of PCBs 1, 4, and 19. These three congeners represent as much as 27%, 69%, and 17% of ∑PCBs in these samples, respectively.

Implications. This analysis was made possible by an unprecedented data collection effort by the DRBC. The key to the success of this analysis was the standardized protocols developed by the DRBC including analytical and reporting requirements for all 209 congeners and the achievement of very low detection limits. For purposes of detecting dechlorination, PCB congeners 4, 19, 47 (44 + 47 + 65), and 51 (45 + 51) are the most useful and should be included in any studies attempting to detect evidence of PCB dechlorination.

PCBs from unweathered Aroclors (factors 3, 5, and 7) account for about 73% of the PCBs discharged to the river from the NPDES outfalls. Factors 1 and 6, which represent non-Aroclor or weathered Aroclor sources, represent about 8% of the total loads. The dechlorination factors (factors 2 and 4) represent about 19% of the loads of PCBs to the river from these dischargers. About 75% of the loads of these dechlorinated congeners come from WWTPs, highlighting the important role that WWTPs and sewage collection systems play in controlling water pollution. It is surprising that "persistent" chemicals such as PCBs should be undergoing such extensive transformation, especially since this dechlorination appears to be happening outside of anaerobic sediments, which were previously assumed to be the major environments where measurable PCB dechlorination could occur. This analysis suggests that PCBs undergo dechlorination in a variety of environments.

The data indicate that dechlorination of PCBs is occurring in contaminated groundwater, landfills, and sewage collection/treatment systems. These three systems share some features. First, all are usually or frequently anaerobic, with redox conditions ranging from sulfidogenic to methanogenic. Second, the concentrations of PCBs are relatively high at ng L^{-1} levels or higher in the water column. Third, these systems all contain a significant carbon source. Fourth, in at least the landfill and sewage collection systems, nutrients such as N and P are plentiful. There seems to be no lack of dechlorinating bacteria ready to colonize any location that provides these favorable conditions. Some of the bacterial strains and mixed cultures that have been identified as PCB dechlorinators are capable of dechlorinating other compounds, including chlorinated ethylenes, chlorobenzenes, and polychlorinated dibenzo-*p*-dioxins and -furans (*36, 49–54*). Thus these compounds and other halogenated compounds such as brominated diphenyl ethers may be degraded in landfills, contaminated groundwater, and sewers. Significant cocontamination with metals in landfills and at some of the contaminated sites does not seem to hinder the biological dechlorination of PCBs.

Microbially mediated in situ dechlorination of PCBs is currently an emerging treatment option for contaminated

sediments, but has not yet been implemented on a large scale. This analysis suggests that it is already being inadvertently and very successfully employed for the remediation of PCBs in groundwater and landfills, and that it is a significant and sometimes dominant process affecting the fate of PCBs in sewage collection systems.

Acknowledgments

L.A.R. dedicates this work to her father on this 70th birthday. S.D. is supported by SERDP Grant Number ER-1492. Thanks to Nicole Oseagulu for compiling the data in Supporting Information Figure S-2.

Supporting Information Available

Additional information including two figures and one table. This material is available free of charge via the Internet at http://pubs.acs.org.

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Evidence for widespread dechlorination of polychlorinated biphenyls in groundwater, landfills, and wastewater collection systems

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Supporting Information

Twelve pages

Two tables

Two figures

PMF

PMF defines the sample matrix as product of two unknown factor matrices with a residue matrix:

$$X = GF + E \quad (1)$$

The sample matrix (X) is composed of n observed samples and m chemical species. F is a matrix of chemical profiles of p factors or sources. The G matrix describes the contribution of each factor to any given sample, while E is the matrix of residuals. The PMF solution, i.e. G and F matrices, are obtained by minimizing the objective function Q through the iterative algorithm:

$$Q = \sum_{i=1}^{n}\sum_{j=1}^{m}(e_{ij} / s_{ij})^2 \quad (2)$$

Q is the sum of the squares of the difference (i.e. e_{ij}) between the observations (X) and the model (GF), weighted by the measurement uncertainties (s_{ij}).

PMF computes the error estimate (S_{ij}) for each data point (X_{ij}) based on the data point and its original error estimate. The present study utilizes the EM = -14 error model [1]. Uncertainty values were calculated from the standard deviations of surrogate recoveries. As in previous work [2], below detection limit values were replaced with a random number between zero and the detection limit, and these values were assigned three times the normal uncertainty.

Number of factors

The correct number of factors was determined to be 7. This number was selected for four reasons. First, it resulted in the best match between the theoretical and calculated Q

values. Second, the resulting 7 factors were easily interpretable. Third, the RSD of the G matrix when 7 factors were requested was 0.47%. When 8 factors were requested, the RSD of the G matrix jumped to 72%, indicating that the PMF software could not generate a stable solution. Fourth, the 7-factor model was able to adequately describe the data set. The R^2 for measured vs. modeled PCB concentrations was 0.986 for the sum of PCBs and was greater than 0.8 for 63 congeners of the 89 congeners (Table S-1). As observed in our previous work [2-3], the R^2 value was generally higher for the heavier congeners and worse for the lighter congeners. This may be because the lighter congeners are more susceptible to volatilization and aerobic degradation than the heavier congeners, and thus likely to exhibit more variable concentrations. The measured vs. modeled R^2 was between 0.5 and 0.8 for an additional 21 congeners. Only five congeners had R^2 values worse than 0.5: PCBs 1 (2), 6 (2-3), 8 (2-4), 11 (3-3) and 45+51 (236-2 + 24-26). Because PCB 11 arises primarily from non-Aroclor sources [4], it is not surprising that it is not well described by the PMF model. When 5 outliers (from MetroMachine and the Amtrak railyard in Wilmington, DE) were excluded, the R^2 for PCB 45+51 increased to 0.79. Two of the congeners that were most useful in identifying the dechlorination signal were PCBs 4 and 19. The R^2 for PCB 4 was 0.62, but rose to 0.88 when the 13 samples with the highest concentrations were excluded. The R^2 for PCB 19 was 0.67 but rose to 0.95 after the removal of two outliers with very high concentrations. For all these outliers, the measured concentration was much higher than the predicted concentration. This occurs when the PMF program is run in robust mode, which down weights outliers.

Table S-1. Congeners included in the PMF model and R^2 values for their measured vs. modeled concentrations.

Congener	Substitution pattern	R^2
1	2	0.09
2	3	0.75
3	4	0.53
4	2-2	0.62
6	2-3	0.27
8	2-4	0.22
11	3-3	0.01
15	4-4	0.69
16	23-2	0.52
17	24-2	0.86
18+30	25-2+246	0.52
19	26-2	0.67
20+28	23-3+24-4	0.87
21+33	234+2-34	0.52
22	23-4	0.71
25	24-3	0.89
26+29	25-3+245	0.88
27	26-3	0.67
31	25-4	0.67
32	26-4	0.76
37	34-4	0.82
40+41+71	23-23+234-2+26-34	0.8
42	23-24	0.72
44+47+65	23-25+24-24+2356	0.86
45+51	236-2+24-26	0.3
46	23-26	0.69
48	245-2	0.82
49+69	24-25+246-3	0.85
50+53	246-2+25-26	0.54
52	25-25	0.93
56	23-34	0.72
59+62+75	236-3+2346+246-4	0.87
60	234-4	0.87
61+70+74+76	2345+25-34+245-4+2-345	0.94
64	236-4	0.94
66	24-34	0.6
77	34-34	0.58
82	234-23	0.97
83+99	235-23+245-24	0.96
84	236-23	0.93
85+116+117	234-24+23456+2356-4	0.94
86+87+97+108+119+125	2345-2+234-25+23-245+234-35+246-34+26-345	1
90+101+113	235-24+245-25+236-35	0.99
92	235-25	0.99
95	236-25	0.9

Table S-1 continued. Congeners included in the PMF model and R^2 values for their measured vs. modeled concentrations.

Congener	Substitution pattern	R^2
105	234-34	0.87
107+124	235-34+24-345	0.9
110+115	236-34	0.98
118	245-34	0.97
128+166	234-234+23456-4	0.94
129+138+160+163	2345-23+234-245+23456-3+2356-34	0.99
130	235-234	0.92
132	234-236	0.97
134+143	2356-23+2345-26	0.96
135+151+154	235-236+2356-25+245-246	0.95
136	236-236	0.94
137	2345-24	0.93
141	2345-25	0.99
144	2346-25	0.94
146	235-245	0.98
147+149	2356-24+236-245	0.97
153+168	245-245+246-345	0.99
156+157	2345-34+234-345	0.98
158	2346-34	0.98
164	236-345	0.73
167	245-345	0.95
170	2345-234	0.87
171+173	2346-234+23456-23	0.99
172	2345-235	0.98
174	2345-236	0.96
176	2346-236	0.93
177	234-2356	1
178	2356-235	1
179	2356-236	0.99
180+193	2345-245	1
183+185	2346-245+23456-25	0.99
187	2356-245	1
190	23456-34	1
194	2345-2345	0.97
195	23456-234	0.99
196	2345-2346	0.93
198+199	23456-235+2345-2356	0.99
201	2346-2356	0.95
202	2356-2356	0.99
203	23456-245	0.99
206	23456-2345	0.95
207	23456-2346	0.68
208	23456-23-56	0.91
209	23456-23456	0.77

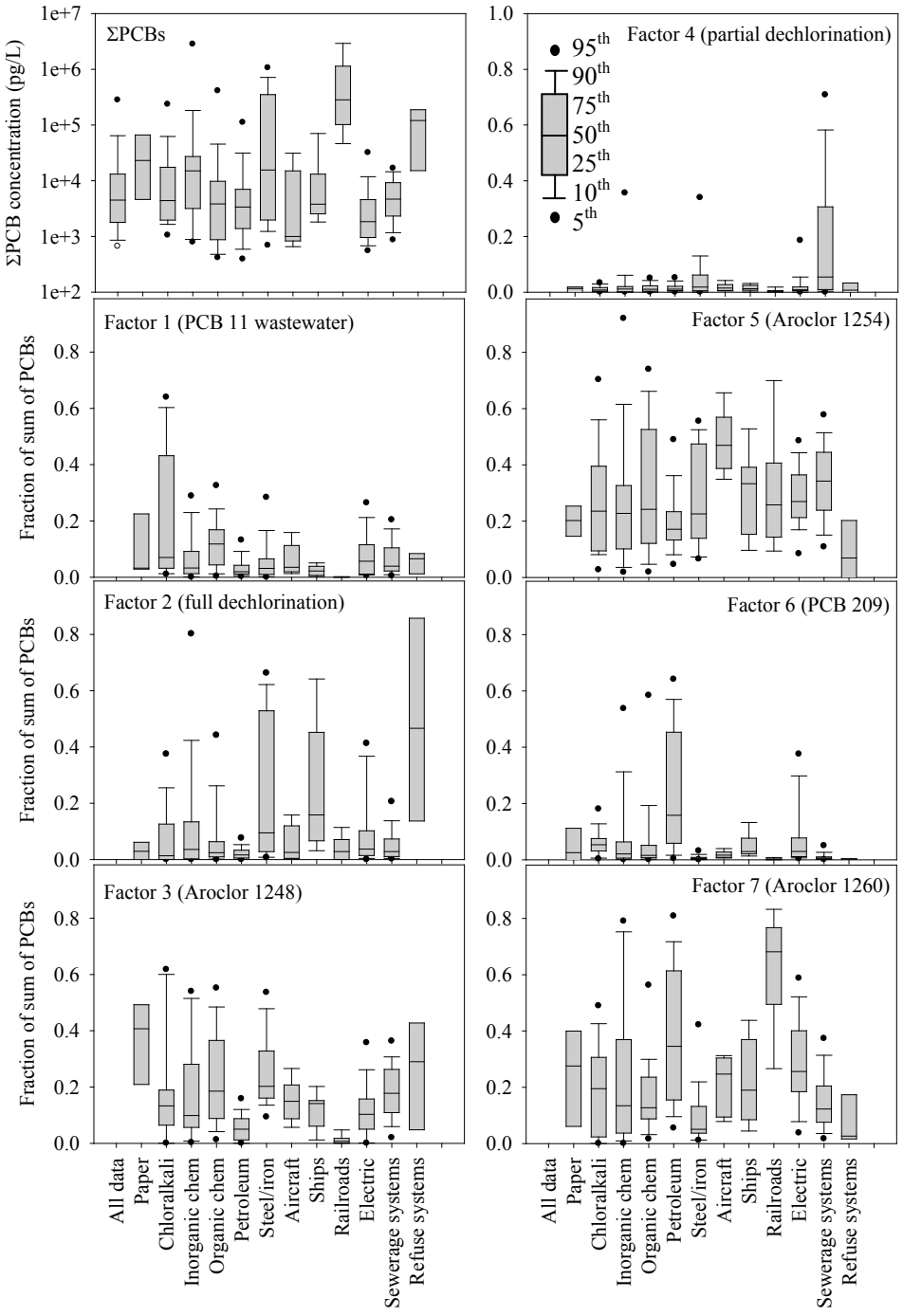

Figure S-1. Box and whisker plots of PCBs in effluents to the Delaware River from NPDES-permitted dischargers. Top left panel presents ΣPCB concentrations in the raw data by category. All other panels depict the fraction of the total PCB concentration that is comprised of each of the factors resolved via PMF analysis. Dischargers are categorized by their SIC (Standard Industrial Classification) codes: paper = 2621 & 2631, chloralkali = 2812, inorganic chem. = 2816 & 2819 & 3221 & 3211, organic chem. =

2821 & 2869, petroleum = 2911 & 5171, steel/iron = 3312 & 3321 & 3399, aircraft = 3721, ships (ship building and repairing) = 3731, railroads = 4011, electric = 4911 & 4931, sewerage systems = 4952, refuse systems = 4953. In cases where the SIC codes were not available from the NPDES permit documents, they were inferred from information about the facility.

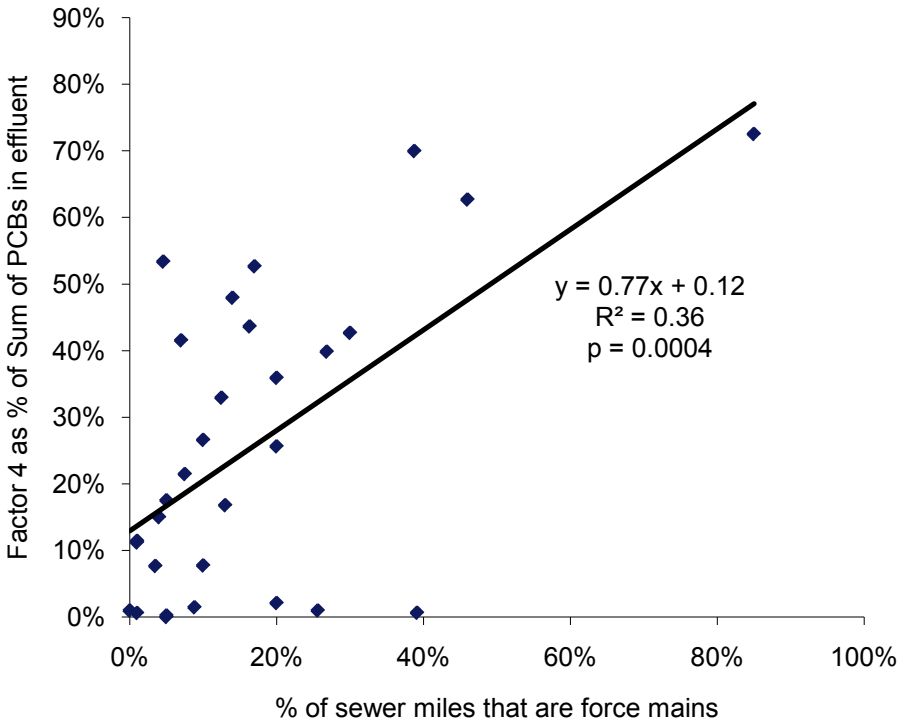

Figure S-2. WWTPs with a higher percentage of force mains in their sewersheds have higher percentages of factor 4, the partial dechlorination factor) in their effluents. Only WWTPs with separate sanitary sewers are plotted. For ten of the 40 plants with separate sanitary sewers, data on the % force mains could not be obtained.

Details on Contaminated Sites

As mentioned in the main text, the US Steel Fairless Works site (NPDES permit number PA0057088; EPA ID # PAD002375376, SIC code 3312) contains a great deal of factor 2 in its effluent (see Table 1). According to the RCRA corrective action documents for this site [5], the main contaminants in the groundwater of this former steel plant are polycyclic aromatic hydrocarbons (PAHs) and tetrachloroethylene. The primary contaminants in the soil are naphthalene and heavy metals, such as arsenic and

lead. Because of the high concentrations of factor 2 in the effluent and the high flow through this facility (4.7×10^9 L y^{-1}), this site discharges the highest load of factor 2 to the river, about 220 g y^{-1} from three outfalls.

The General Chemical facility in Claymont, DE (EPA ID # DED154576698, SIC code 2819) contains one outfall that consists of stormwater and infiltrated groundwater that is treated to adjust pH. This facility manufactured a variety of inorganic chemicals and pesticides, and the primary contaminants of concern at this site are metals and volatile organic compounds [6]. This outfall was sampled five times in dry weather and seven times in wet weather. There is no obvious difference between the wet weather and dry weather samples, all of which contain from 6% to 98% factor 2. Samples with the highest ΣPCB concentrations contained the highest proportions of factor 2. For example, the sample with the highest ΣPCB concentration contained about 120 ng L^{-1} ΣPCBs with 98% of that being factor 2. This suggests that PCB dechlorination is occurring at this site, presumably in the groundwater. In fact, this facility appears to have inadvertently created the most efficient bioreactor for the dechlorination of PCBs in the world. The flow (and therefore the load) from this discharger is negligible, however.

Bridgeport Disposal (EPA ID # NJD053288239, SIC code 4953) is another contaminated site. The EPA documents [7] on the site state: "Contamination occurred from leaks in basins that were used to provide biological breakdown of organic wastes... A fire and explosion that occurred in the facility's tank farm area also released various organic contaminants and polychlorinated biphenyls (PCBs) into the ground. The contaminants in the soil and groundwater include both organics and metals." In the three

samples collected at outfall #1 of this facility, factor 2 comprised 84% to 90% of ΣPCBs. This facility discharges about 19 g y^{-1} of factor 2.

The RCRA corrective action documents [8] for the Repauno site (EPA ID # NJD002373819, SIC code 2819) note that the primary contaminants of concern are nitrobenzene, aniline, diphenylamine, and PCBs. Groundwater at the site is also contaminated with organic compounds, such as nitrobenzene, aniline, benzene, and tetrachloroethylene. The primary source of contamination is a ditch system at which "significant dilution and attenuation of contaminants in groundwater is occurring" [8]. The one wet weather effluent sample collected at this site contained 29 ng L^{-1} factor 2 (52% of ΣPCBs). The rest of the PCBs in the Repauno samples were comprised mostly of Aroclors 1248 and 1254, with less than 4% being Aroclor 1260. At this facility it is therefore most likely that these intermediate-weight Aroclors are the primary substrates for dechlorination.

Aker Philadelphia Shipyard and Metro Machine Corporation (EPA ID # PAR000004846) operate dry docks that were formerly part of the Philadelphia Naval Yard (EPA ID# PA4170022418). As such, they fall under SIC code 3731. Their NPDES permits allow groundwater that infiltrates into the dry docks to be pumped out and discharged into the river. In order to transfer the Philadelphia Naval Yard into private hands, the Department of Defense conducted a cleanup of the site which focused on "PCB transformer site remediation, removal of underground storage tanks and resulting contaminated soil, and removal and off-site disposal of construction debris and blasting grit. A groundwater monitoring program was implemented but no groundwater remediation is planned due to the industrial nature of the site. Groundwater use

restrictions were put in place and all potable water at the complex is supplied by the City of Philadelphia" [9]. At these sites, factor 2 comprised as much as 66% of the ΣPCBs. These two sites together emit about 12 g y^{-1} of factor 2.

Another site of interest is the Amtrak Railyard (SIC code 4011) in Wilmington, DE, an active rail yard that is known to be contaminated with PCBs, which were used in a variety of electrical equipment on the site [10]. Thirteen samples of effluent from this site contain between 13 and 1,033 ng L^{-1} ΣPCBs. Because of these high concentrations, factor 2 only comprises between 0.5% and 14% of the PCBs in these samples, but this still corresponds to concentrations of factor 2 between 1 and 14 ng L^{-1}. Dechlorination is therefore occurring at this site as well, and since Aroclor 1260 comprises about 68% of ΣPCBS here, it is the most probable substrate for dechlorination.

Contaminated sites displaying significant dechlorination thus occur in a wide variety of industries, including railyards (SIC code 4011), refuse systems (4953), shipyards (3731), inorganic chemicals (2819), and steel/iron (3312).

		Influent				Effluent			
		F2		F4		F2		F4	
NPDES number/name		Conc.	%	Conc	%	Conc.	%	Conc	%
DE0000051		n = 11				n = 15			
DuPont Edgemoor	avg	112	2.9%	43	1.0%	204	6.0%	30	0.7%
	stdev	60	1.9%	20	0.3%	298	10%	40	1.3%
DE0000256		n = 6				n = 16			
Delaware City Refinery	avg	84	2.9%	58	2.2%	58	2.7%	44	4.1%
	stdev	39	0.9%	7.2	0.6%	41	1.4%	20	9.2%
NJ0004219		n = 5				n = 6			
Repauno	avg	516	12%	92	2.1%	6471	17%	322	1.7%
	stdev	136	5.0%	16	0.5%	11267	15%	77	0.7%
NJ0004995		n = 8				n = 14			
Mercer Gen. Station	avg	41	4.1%	259	19%	36	3.7%	158	12%
	stdev	18	2.9%	339	23%	21	2.3%	271	19%
NJ0005029		n = 11				n = 7			
Paulsboro Refinery	avg	478	10%	144	3.1%	60	0.2%	46	0.4%
	stdev	247	5.0%	48	1.0%	94	0.4%	40	0.5%
NJ0005100		n = 4				n = 9			
Chambers Works	avg	103	2.0%	57	1.2%	206	2.3%	296	2.8%
	stdev	51	0.6%	15	0.3%	196	0.9%	368	1.2%
NJ0005401		n = 3				n = 4			
Eagle Point Refinery	avg	261	7.3%	30	0.8%	10	0.98%	8	0.7%
	stdev	77	0.7%	9.4	0.04%	14	1.5%	7	0.5%
NJ0021598		n = 1				n = 4			
Pennsville Sewer. Auth.	avg	120	1.1%	2858	27%	43	0.6%	1278	17%
	stdev	NA	NA	NA	NA	14	0.2%	556	8%
NJ0024023		n = 2				n = 2			
Penn's Grove WWTP	avg	130	0.6%	4050	19%	33	0.8%	1312	30%
	stdev	71	0.5%	996	11%	46	1.2%	212	10%
NJ0024686		n = 2				n = 8			
Gloucester County WWTP	avg	383	1.5%	12855	52%	92	4%	1584	63%
	stdev	174	0.5%	178	7%	26	1%	712	15%
NJ0025411		n = 1				n = 10			
Hope Creek Gen. Sta.	avg	14	0.4%	18	0.6%	147	21%	18	1.1%
	stdev	NA	NA	NA	NA	101	19%	22	1.0%
PA0011533		n = 6				n = 4			
Sunoco Girard Point	avg	523	7.9%	42	0.7%	23	4.7%	2.7	0.7%
	stdev	316	3.4%	20	0.4%	21	1.7%	1.6	0.2%
PA0012629		n = 6				n = 3			
Sunoco Point Breeze	avg	326	11%	29	1.1%	4.2	1.5%	2.3	0.6%
	stdev	188	4.2%	17	0.5%	3.9	1.9%	0.79	0.1%
PA0012637		n = 9				n = 46			
Trainer Refinery	avg	226	3.4%	152	2.0%	101	2.5%	83	1.7%
	stdev	98	1.6%	91	0.7%	105	2.8%	72	1.5%
PA0013463		n = 7				n = 16			
USS Fairless	avg	865	30%	16	0.9%	60840	37%	5931	3.5%
	stdev	633	14%	12	0.4%	85658	23%	9275	4.0%
PA0013714		n = 6				n = 3			
Eddystone Gen. Station	avg	527	10%	64	1.1%	392	9.8%	33	0.8%
	stdev	291	7%	29	0.3%	300	5.9%	48	0.7%
PA0027103		n = 3				n = 8			
DELCORA WWTP	avg	1340	3.9%	719	2.2%	39	5.4%	2.8	0.4%
	stdev	819	2.0%	24	0.4%	24	2.9%	2.4	0.3%

Table S-2. Average and standard deviation of the concentration (ng L^{-1}) and % of ΣPCBs for factors 2 and 4 in facilities for which both influent and effluent were measured. n = number of samples.

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