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DECHLORINATION OF POLYCHLORINATED DIBENZO-P-DIOXINS IN THE
WATERSHED OF THE NEW YORK/NEW JERSEY HARBOR

By

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ABSTRACT OF THE THESIS

Dechlorination of Polychlorinated Dibenzo-p-dioxins in the Watershed of the New

York/New Jersey Harbor

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In this work, data from the Contamination Assessment and Reduction Project (CARP) was used to investigate the dechlorination of polychlorinated dibenzo-p-dioxins and – furans (PCDD/Fs) in the watershed of the New York/New Jersey Harbor. Preliminary investigations using CARP data suggested that *peri* dechlorination of PCDD/Fs occurs in sewer systems. However, the *peri*-lateral dechlorination pathway is more environmentally important since it can remove chlorines in the lateral (2,3,7,8) positions, resulting in products that are considered to be non-toxic. The original CARP data set contains information on concentrations of the 17 2,3,7,8-substituted PCDD/F congeners, so that products of *peri*-lateral dechlorination were not measured. However, during the analysis of these 17 congeners, the data was generated to measure other non-2,3,7,8-substituted congeners that could be products of *peri*-lateral dechlorination. In this work, the archived chromatograms were retrieved from the contract laboratory that conducted the original analysis, and a data set was built containing the concentrations of all of the tetra- through octa- chlorinated PCDD/F congeners. This new data set was analyzed to

discern further evidence that PCDD/Fs are dechlorinated in sewers via the *peri*-lateral pathway that can result in complete elimination of toxicity.

In the first chapter of this thesis, the concentrations of PCDD/Fs within the data set were examined for trends. Results suggested that dechlorination occurred in landfills. The second chapter utilized Positive Matrix Factorization (PMF) analysis on the same data set in an attempt to provide further evidence that PCDD/Fs are dechlorinated in these systems. When compared to EPA's published 2,3,7,8-congener patterns, the sources of PCDD/Fs in the Harbor were identified as: bleached chemical wood pulp and paper mills (1% total mass of data set), wood combustion (3%), Kraft black liquid recovery boilers (4%), and diesel trucks (92%). However, when compared to the New York Academy of Sciences Dioxin report, these results were deemed inaccurate because they did not align with the major PCDD/F sources into the Harbor as represented by the literature.

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Chapter 1

Concentrations of Non-2,3,7,8 PCDD/Fs in the NY/NJ Harbor

1. Abstract

Concentrations of non-2,3,7,8,-polychlorinated dibenzo-*p*-dioxins and -furans (PCDD/Fs) in samples from the Contamination Assessment and Reduction Project (CARP) were obtained by reexamining the original chromatograms. These concentrations are reported and examined for trends. The samples represent a sub-set of the larger CARP database and were classified as surface water, treated effluent from water pollution control facilities (WPCF), sludge from WPCFs, storm water and combined sewer overflows (CSOs), and landfill leachate (treated or untreated). Concentrations and Toxic Equivalency Quotients (TEQ) ranged over several orders of magnitude. In order to identify possible dechlorination of PCDD/Fs at the lateral positions, the percent of the total PCDD/Fs that were non-2,3,7,8-substituted (%P) was calculated by dividing the concentrations of all non-2,3,7,8-substituted congeners within a homologue by the sum of all congeners in that homologue. %P is significantly different ($p < 0.05$) for several of the homologue groups in landfill samples versus the other samples classes. This may indicate that dechlorination occurs in landfills. Further analysis of this data set by Positive Matrix Factorization may help to elucidate possible dechlorination pathways.

1.1. Background

1.1.1. What are PCDD/Fs?

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) are persistent organic pollutants targeted by the Stockholm Convention.² Both are groups of organic polyhalogenated compounds with similar tricyclic planar structures.



Figure 1.1. (a) General structure of polychlorinated dibenzo-*p*-dioxin² and (b) polychlorinated dibenzofuran², where n and m can range from 0 to 4.

Once released into the environment, both groups of compounds are extremely resistant to biodegradation. Although they are typically present in small concentrations, these compounds are considered to be toxic and carcinogenic and they bioaccumulate in humans and wildlife due to their lipophilicity.³ In general, they are hydrophobic and therefore have a tendency to sorb to organic matter. They are also characterized as having low aqueous solubility, especially in cases where the congeners possess a higher number of chlorine substituents attached to their skeletal structure.⁴

1.1.2. Environmental sources of PCDD/Fs

PCDD/Fs have not been synthesized intentionally in mass quantities for a specific purpose outside of a relatively small number of instances of scientific research. Rather,

the largest source of these compounds has historically been as unwanted byproducts released into the environment from various thermal or combustion sources, or from various chemical manufacturing processes.⁴ PCDD/Fs were largely generated unintentionally as side products from the manufacturing of chlorinated chemicals such as various chlorophenoxyacetic acid herbicides, chlorophenols, PCBs, and hexachlorophene.⁵ Furthermore, the synthesis and use of Agent Orange (equal parts 2,4,5-trichlorophenoxyacetic acid and 2,4-dichlorophenoxyacetic acid) during the Vietnam War is thought to have generated approximately 221 to 336 kg of 2,3,7,8-TCDD into the environment, in the form of herbicidal impurities.⁴

An additional source includes the chlorine bleaching of the products in the paper industry, which has been known to release PCDD/Fs into numerous waterways.^{6, 7} Recognized thermal sources for PCDD/Fs include the incineration of municipal and medical waste,⁸ domestic burning, and automobile exhaust.⁴ Furthermore, 2,8-dichlorodibenzo-*p*-dioxin (2,8-DCDD) has been known to be produced via photolysis of triclosan (5-chloro-2-(2,4-dichlorophenoxy)phenol), an antimicrobial additive often detected in surface waters, in sunlight-irradiated surface waters.⁹

Although PCDD/F emissions have displayed a general downward trend in the decades following the 1970s, they remain present in the environment in problematic amounts due to lengthy half-lives. In addition, sites with extremely high contamination concentrations can also serve as secondary PCDD/F sources which allow for the formation of lesser chlorinated, and therefore more mobile, congeners from the degradation of the higher

chlorinated congeners. One such area includes the lower Passaic River and Newark Bay, which received several kg of 2,3,7,8-TCDD, mainly during the manufacture of 2,4,5-T.⁴

1.1.3. General pathways of PCDD/F dechlorination

PCDD/Fs are highly persistent. With the exception of dioxygenases attacking lower chlorinated dioxins,²⁷ virtually the only pathway by which PCDD/Fs can be degraded in the environment is via dechlorination by anaerobic bacteria. Although studies on the microbial reductive dechlorination of PCDD/Fs have been reported, published dechlorination rates range over several orders of magnitude because different environmental conditions cause different rates of dechlorination. In general, however, dechlorination of PCDD/Fs is often too slow in contaminated sediments to significantly impact environmental concentrations of PCDD/Fs. Ideally, for effective bioremediation to occur in an area with an abundance of PCDD/Fs, faster dechlorination is desired. Microbial dechlorination of PCDD/Fs can follow either the *peri*-dechlorination pathway, which removes chlorines at the 1, 4, 6, or 9 positions, producing 2,3,7,8-substituted products, or the *peri*-lateral pathway that removes chlorines at the 2, 3, 7, and 8 positions, resulting in the production of congeners that are not 2,3,7,8-substituted, and are therefore considered to be non-toxic.¹⁰⁻¹³ However, dechlorination is not the only, or even the main, source of PCDD/Fs.

1.1.4. PCDD/Fs in the New York/New Jersey Harbor

PCDD/Fs, especially the most toxic congener, 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD), are a particular problem in the New York-New Jersey Harbor. The Health of the Harbor Report¹⁴ notes that dioxin concentrations found in estuary sediments were

above the EPA Guidance Value from approximately 1950 to 1980 in the Newark Bay and Lower Passaic regions. The same was discovered of the NY/NJ Harbor region from 1950 to 1990. The lower 17 miles of the Passaic River, from Dundee Dam to Newark Bay, have been the most heavily impacted by contamination of dioxin due to several decades of urbanization and industrialization.¹⁵ In particular, this stretch of the River is notorious for contamination with 2,3,7,8-TCDD, which came in large part from the Diamond Alkali Superfund site.²⁸

1.1.5. The Contamination Assessment and Reduction Project (CARP)

The Contamination Assessment and Reduction Project (CARP) was developed in 1997 for the purpose of identifying the sources of sediment contamination in the NY/NJ Harbor. In 1992, sediment dredging showed that nearly 85% of the material was contaminated to the point of unsuitable use, and the available disposal methods would cause remediation efforts to be prohibitively expensive. To investigate affordable alternatives for contamination reduction, a \$30 million commitment from regional agencies was provided to form the CARP workgroup.¹⁶

The CARP program was ambitious in scope and was notable for utilizing the newest, best methods of sample collection and detection for its time. These chemicals, which are damaging to human health even in small concentrations, were tested within this project although they are typically present below detection levels for conventional analytical chemistry methods. Furthermore, the magnitude of the project required the development of innovative field and laboratory methods in order to minimize variability brought about

by the use of multiple sampling teams, labs, and sampling locations.^{17, 18} The PCDD/F laboratory testing method was developed in 1994¹⁹ and the method for PCBs was created in 1999²⁰ by the U.S. EPA. CARP began sampling in 1999,¹⁶ therefore they were required to develop their own methods for testing certain compounds. For instance, they developed their own high-resolution GC/MS method for PAHs because of the lack of already available procedures.¹⁸

1.2. Introduction

In previous work, the CARP data for various Water Pollution Control Facilities (WPCFs) were used to demonstrate that PCDD/Fs are dechlorinated in the sewers of the CARP study area,¹ but this investigation was limited to the 2,3,7,8-CDD/F congeners and so could only demonstrate dechlorination at the peri positions. Here we report concentrations of non-2,3,7,8-PCDD/F congeners from a sub-set of the CARP samples in order to look for evidence of lateral dechlorination. In order to identify patterns indicative of dechlorination, it is helpful to look at past studies in which all of the PCDD/F congeners have been measured. Unfortunately, previously published studies containing reported concentrations and/or percentages of non-2,3,7,8-CDD/Fs are relatively scarce. Therefore, the aim of this chapter is to build upon those studies and to provide further data on concentrations of non-2,3,7,8-PCDD/Fs in environmental samples.

Barkovskii and Adriaens¹⁰ studied the microbial dechlorination of PCDDs in dioxin-contaminated Passaic River sediments under laboratory-induced methanogenic conditions over a period of 7 months. Initial concentrations of 2,3,7,8-TCDD were 62.3 ± 12.5

nmol/L (or 0.6 ± 0.1 $\mu\text{g}/\text{mg}$ of total cell protein). After 7 months of incubation, this congener was reductively dechlorinated, resulting in a 30% decrease in concentration to 43.6 ± 6.2 nmol/L (or 0.24 ± 0.04 $\mu\text{g}/\text{mg}$ of total cell protein). This also resulted in the formation of the following non-2,3,7,8-substituted congeners: 9.8 ± 2.8 nmol of triCDD per L and 9.7 ± 1.4 nmol of 2-monoCDD per L. In sediments that were freshly spiked with a mixture of highly chlorinated (hexa- through octa-) CDDs, 82 nmol/L of 1,2,3,4,6,7,9-heptaCDD dechlorinated to a total of 3.6 nmol/L of five different hexaCDD isomers, three of which were non-2,3,7,8-substituted (1,2,3,4,6,7-; 1,2,4,6,7,9-; and 1,2,3,4,6,8-). This study suggests that lateral dechlorination of CDDs is possible in Passaic River sediment. Since the Passaic River is part of the CARP study area, this suggests that lateral dechlorination of PCDD/Fs may occur elsewhere in the harbor, and quantification of the non-2,3,7,8-CDD/F congeners should be useful in identifying dechlorination processes.

Gaus et al.²¹ examined dated estuarine sediment cores in Queensland, Australia to develop a better understanding of unusual PCDD congener profiles (i.e. profiles characterized by very high OCDD and very low PCDFs). The lateral- to peri-lateral to peri- dechlorination ratios for various lake and river sediment cores were as follows: ~34:2:1 for the bottom of Mississippi Lake, 4:1:1 for the Hinchinbrook River area, and ~4:2:1 for both a core from Mississippi River and a core from Mississippi Lake. The peri-lateral dechlorination products in this case were 1,2,3,6,7,9-/1,2,3,6,8,9-HxCDD.

These studies provide clues as to which PCDD/F congeners may be indicators of dechlorination. The purpose of this chapter is to present the concentrations of all PCDD/F congeners with 4 or more chlorines in the Contaminant Assessment and Reduction Project (CARP) samples from the NY/NJ Harbor and to investigate these concentrations for trends that might be indicative of dechlorination. In order to do this, the peri-lateral (non-2,3,7,8-substituted) congeners are presented as the percent of total PCDD/Fs for each homologue group (%P).

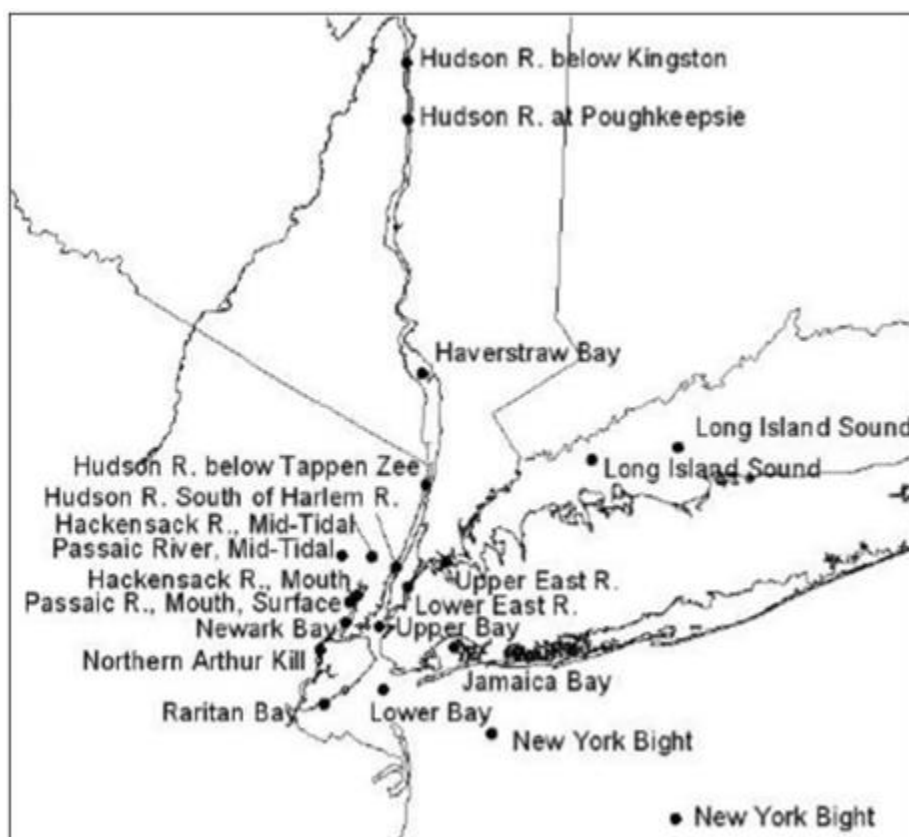


Figure 1.2. Centroids of 20 ambient sampling stations.¹⁷

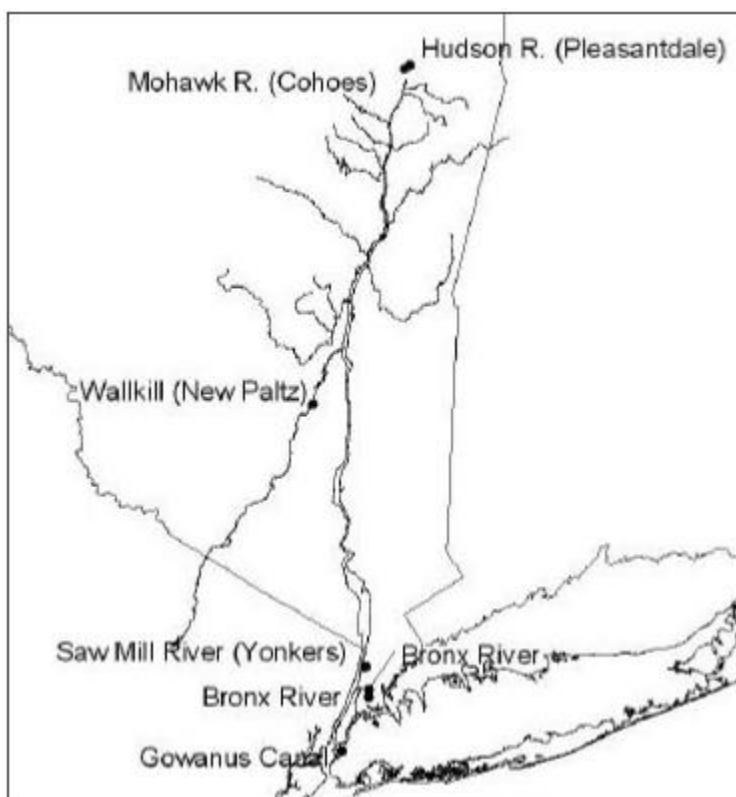


Figure 1.3. Locations of sampling points on 3 major and 3 minor tributaries.¹⁷

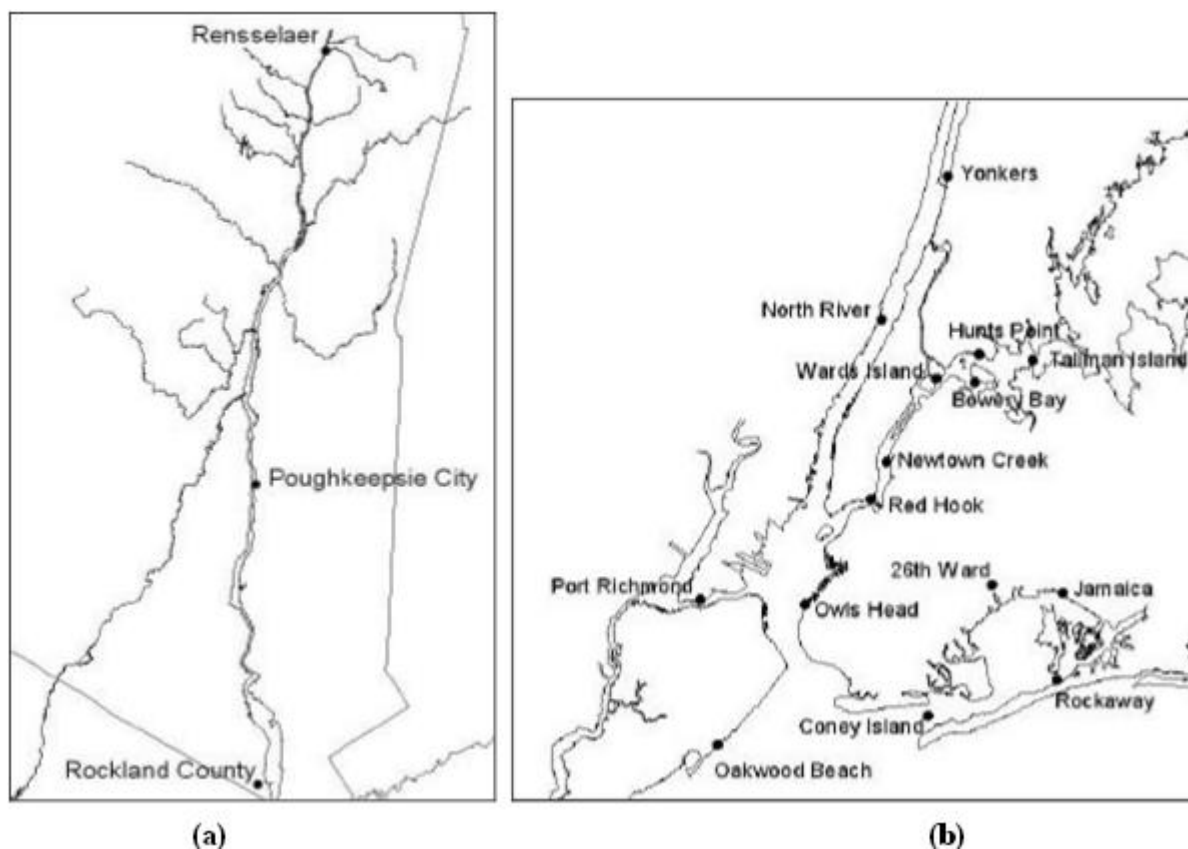


Figure 1.4. (a) Locations of upstate WPCFs, and (b) locations of NYC area WPCFs.¹⁷

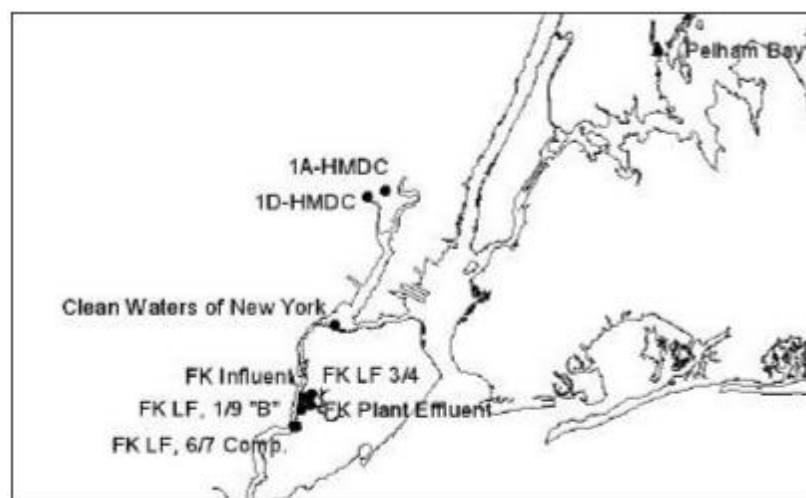


Figure 1.5. Locations of industrial effluents and leachates sampled by CARP.¹⁷

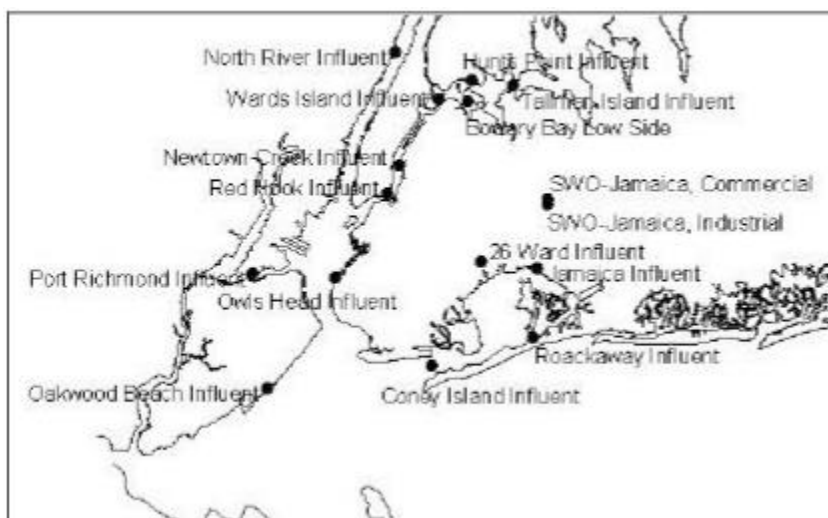


Figure 1.6. Locations of the CSO and SWO sampling sites.¹⁷

1.3. Methods

1.3.1. CARP

CARP was conducted under a Quality Assurance Project Plan (QAPP) approved by the US EPA. Details of sample collection and analysis are available in the CARP reports.¹⁶⁻¹⁸

Procedures are briefly summarized here. Maps of the sample locations are provided in figures 1.2 to 1.6. For this analysis, data collected by the New York State Department of Environmental Conservation were used. [Note that the New Jersey data available through CARP were not used because a different contract laboratory was utilized for sample analysis.] Most of the sampling was conducted using a trace organics platform sampler (TOPS), which was developed explicitly for the CARP program. The TOPS was a flexible sampling platform that allowed the separate collection of the particulate and ‘dissolved’ fractions of each water sample by passing the water through a glass cartridge filter (1.0 micron nominal porosity) and then through a column packed with XAD-2 resin. The contaminants captured on the filter were considered to be in the particle phase,

while those captured in the XAD-2 resin were designated as ‘dissolved’ even though very small particles can pass through the filter. The problem of accurately quantifying the dissolved and particle phase concentrations of very hydrophobic analytes such as PCBs and PCDD/Fs is inherent in water sampling. In addition, both phases were not always analyzed. Especially for PCDD/Fs, often only the particle phase was analyzed based on the assumption that the dissolved phase concentration was negligible. In some cases, a whole water sample was collected, in which the total water column concentration (dissolved plus particle) was measured. Luckily, the distinction between dissolved and particle phase concentrations is not relevant in the present work, which investigates *percentages* of concentrations rather than *absolute* concentrations. It should also be noted that PCDD/F analysis was performed on samples that were largely obtained from the TOPS, and extracts were obtained from 0.7 micron glass fiber filters and XAD-2 resin. A small number of samples were also obtained from sludges, hexane, whole water grab samples, and sediments.

Samples which were collected from landfills were obtained from leachate collection systems in order to determine the approximate leachate quality from various treatment systems. It should be noted that, while leachate was largely collected within these contained systems, on occasion it escaped into surface waters. For instance, although the leachate from the New Jersey Meadowlands Commission was treated at the Passaic Valley Sewerage Commissioners WPCF located in Newark, it was also determined that a small amount flowed directly into the Passaic River. An estimated “4.2 mgd of untreated leachate may be entering into the Harbor area surface waters from both states”¹⁷.

Therefore, only the glass fiber filtered water was processed in this set of samples, because the escaped leachate was entering the surface waters through diffusion. Therefore, it was not possible to approximate the particle bound phase of the transport, rendering it useless to collect data on particulate organic carbon or total suspended solids from leachate samples.

For ambient water column samples, a 100 mesh Nytex plankton net helped to strain out large zooplankton from the collected samples. When collecting the samples using TOPS, the volume of water which passed through the XAD columns or filter for the sample volume was adjusted manually in the field. For sampling at locations which were considered to be tidal ambient sites (locations excluding Long Island Sound and the New York Bight), the average time period for sample collection was 5.6 hours over the duration of a portion of the tidal cycle. NOAA gauges determined the high and low tides at the Narrows, Battery, Kings Point, and Kill van Kull locations.¹⁷ PCBs, chlorinated pesticides, PCDD/Fs, PAHs, cadmium, and mercury were analyzed in most CARP samples. Dissolved organic carbon (DOC), suspended sediment (SS), and particulate organic carbon (POC) were also measured as accessory parameters. PCDD/F samples were obtained and quantified strictly from suspended material recovered by filters.

Some XAD samples were analyzed for PCDDs, however most measurements were below detection limit. Some whole water samples were also analyzed for the PCDDs. In order to examine the efficiency of PCDD/F capture on XAD, quality control tests which

consisted of metering (releasing in regulated amounts) chemical surrogates of PCDDs into water streams was conducted near the end of the project.¹⁷

PCDD/Fs were quantified by EPA method 1613.¹⁹ For the PCDD/Fs, the minimum detection limit for the sample set was 0.01 pg/L, the maximum detection limit was 459 pg/L, and the average detection limits ranged from 0.44 pg/L to 23.41pg/L. The contract laboratory (Axys Analytical Services, British Columbia, Canada) reported concentrations of the 17 2,3,7,8- substituted PCDD/F congeners and the concentrations of each of the PCDD/F homologues. In order to do this, Axys quantified the non-2,3,7,8-substituted PCDD/F congeners, but then reported only the sum, not the concentrations of the individual congeners. Thus, our task was to extract the concentrations of the non-2,3,7,8-substituted PCDD/F congeners from the data packages.

1.3.2. Obtaining data packages and transcribing them into Excel

Because we were interested in sewers and landfills, we identified data packages that contained samples from WPCFs, landfills, and CSOs using the CARP Microsoft Access database. We sent the work group numbers of the desired samples to Axys Analytical Services (British Colombia, Canada), and Axys attempted to find the corresponding data packages in their physical archive. When they could be found, Axys sent us the entire data package for the work group, which included a group of samples all analyzed in the same run. Thus the chromatograms obtained included the ones we requested along with any others present in the same analytical run. Therefore the data presented here is not representative of the CARP data set as a whole: it is heavily weighted in CSO, WPCF,

and landfill samples, but includes some samples classified as ambient surface water, trackdown samples (labeled TRK and mostly representing storm water from separate storm sewers), indefinite samples (labeled INDEF and representing landfill leachate from the Fresh Kills landfill), and some WPCF sludge samples.

The original PCDD/F chromatograms contained information on the concentrations of both the 2,3,7,8-substituted and the non-2,3,7,8-substituted PCDD/F congeners with four to eight chlorines. The calculated concentrations of these congeners were provided on the chromatogram. These sample packages, which are now over 10 years old, were presented in the form of pdf files that were scanned from printouts that contained hand-written notes. Because of this, data packages could not be exported directly onto a spreadsheet, nor could optical character recognition be used on them. Thus, the information from these packages were transcribed manually into an Excel spreadsheet and combined with the existing CARP data available on the CARP CDs.¹⁶ Data was checked to ensure that any concentration information met data quality criteria, including the correct ratio of quantifying and confirming ion abundances and detection limits (these were also provided in the data packages provided by Axys). There were several unidentified peaks detected. These are labeled as “unknown” in Appendix A. Not all peaks were resolved, resulting in several coeluting PCDD/F congeners that have very similar vapor pressures.

1.3.3. Comparing to MS Access Database

To ensure accuracy, the octachlorodibenzo-p-dioxin (OCDD) concentrations provided in the original chromatograms were checked against their corresponding values provided in

the CARP Microsoft Access database. When concentrations were reported as mass per sample, the database values matched the OCDD concentrations provided on the chromatograms. However, in several cases when concentrations were expressed in fg/L obtained from XAD columns, the OCDD value in the database failed to match its corresponding value as presented in its chromatogram. When the value from the chromatogram was changed to units of fg/L by dividing the original pg/sample unit by the sample volume (L), the two numbers still did not match. During correspondence with Axys labs [Georgina Brooks, personal communication, July 5, 2013], it was determined that the CARP personnel had made an error when entering the concentration (fg/L) values into the database. The workup sheets in the data package indicated that the XAD columns in question were extracted and then the raw extract was gravimetrically split, with an approximately 68% portion used to measure PCDD/Fs. Since the dioxin surrogates were only spiked into the 0.68 portion of raw extract, the Axys results were corrected for the approximately 32% that was removed prior to dioxin analysis. This correction was done during quantification by the OpusQuan software via application of the "F2" factor of approximately 1.47.

Unfortunately, when CARP personnel entered these values into the database, it appears that they erroneously applied the correction factor a second time. Therefore, for these XAD samples, these database values are erroneous, whereas their corresponding OCDD values (and by extension, concentrations of all other PCDD/Fs) on the chromatograms appear to be correct. Luckily this has little effect on our analysis, since we primarily

focus on the filter samples. In addition, the erroneous correction factor has no impact on the *relative* concentrations of the analytes, on which we focus.

The resulting spreadsheet of sample concentrations was organized into several different categories. Furans and dioxins were separated from each other, which were then separated into congeners that were non-2,3,7,8-substituted and those which were 2,3,7,8-substituted. These were then separated further by homologues, and then by sample location class, which was indicated on the CARP database. The data were lumped together as follows: ambient water samples which include surface water (major tributaries (7 samples), minor tributaries (10 samples) and ambient non-kills (1 surface water sample)); sludge (12 samples); WPCF (i.e. treated effluent, 41 samples); storm water samples (storm water overflows (2 samples), trackdown samples (usually collected in storm sewers, 2 samples), and combined sewer overflows (22 samples)); and landfill samples (landfill leachate or treated effluent from the Fresh Kills landfill leachate treatment plant (9 samples) and indefinite samples (6 samples)). The indefinite samples were combined with the landfill samples because their GPS coordinates indicated that they were obtained from the Fresh Kills landfill. These landfill sampling points were located around the landfill mounds, and the leachate was collected using a system of trenches and pumps.¹⁷ It should be noted that none of the sludge samples were from the Fresh Kills landfill leachate treatment plant, so there is no overlap between the landfill and sludge classes.

1.3.4. Determination of %P and Statistical Analyses

The percentage of peri (as opposed to lateral) chlorines on a dioxin or furan can be an indicator of peri-lateral dechlorination. Dechlorination reactions result in the loss of mass, but not in total molar concentration. Therefore, reporting concentrations of congeners at various stages of dechlorination as molar percentages is preferable.²²

Furthermore, reporting results as percentages allows for focus on the changes in PCDD/F composition via dechlorination by neutralizing sample-specific properties, such as pollution level.²³ The resulting value provides the percentage of 2,3,7,8-substituted PCDD/Fs in each sample set, thereby illustrating the likely dechlorination pathway of that compound within its particular sample location. Sample sets with lower percentage values imply a higher yield of non-toxic products, with fewer chlorines in the lateral positions. Because the peri-dechlorination pathway has been studied before, comparisons of the results can be made alongside values in existing literature.

The concentration of each analyte (with the exception of the sludge samples) was obtained by dividing by the sampled volume. Because the sludge samples were solids, they were divided by grams of dry weight per sample. To obtain the percentage of the non-2,3,7,8-substituted congeners (%P) within the sample location class for each homologue (homologue designations are as follows: TCDD = tetrachloroDD, PeCDD = pentachloroDD, HxCDD = hexachloroDD, HpCDD = heptachloroDD, OCDD = octachloroDD, TCDF = tetrachloroDF, PeCDF = pentachloroDF, HxCDF = hexachloroDF, HpCDF = heptachloroDF, OCDF = octachloroDF), the amount of non-2,3,7,8-substituted congeners was divided by the summation of all of the congeners (both

2,3,7,8- and non-2,3,7,8-substituted) in each case, as demonstrated by the following equation:

$$\%P = \frac{P}{P+L} \quad (\text{Equation 1})$$

Here, P is the sum of the concentration of the non-2,3,7,8-substituted congeners, whereas P+L refers to the total homologue concentration (peri plus lateral). Although this method for calculating the percentage of peri-lateral dechlorination has not been published widely, existing literature demonstrates a similar method of obtaining the percentages for other peri- or lateral- PCDD/F dechlorination pathways.^{13, 24-25} For instance, an average mol% ratio for 1,2,3,4,6,7,8-HpCDF and 1,2,3,4,6,8,9-HpCDF congeners was determined by Liu et al. by dividing one over the sum total of both.¹³

To examine whether the %P for each homologue, at each location, and for each class of samples were significantly different from each other, unpaired two-sample students t-tests were conducted using SigmaPlot. This program automatically conducted the preliminary f-test for each t-test to determine whether the comparable sample sets were of equal or unequal variance. P-value results less than or equal to 0.05 (95% confidence) were used to designate a statistically significant difference between the two data sets.

1.4. Results

1.4.1. General notes/comments about data set

Concentrations of all PCDD/Fs with four or more chlorines are listed in Appendix 1. The 2,3,7,8-substituted congeners accounted for approximately 52% of the mass for the PCDFs and about 87% of the mass for the PCDDs in this data set. Approximately 67% of

the mass for the 2,3,7,8-CDFs are due to OCDF, and about 90% of the 2,3,7,8-CDDs are attributed to OCDD. Figure 1.7 illustrates the overall variation of sample concentrations within the data set, broken down by sample class. Some of the analytical results are summarized in table 1.1.

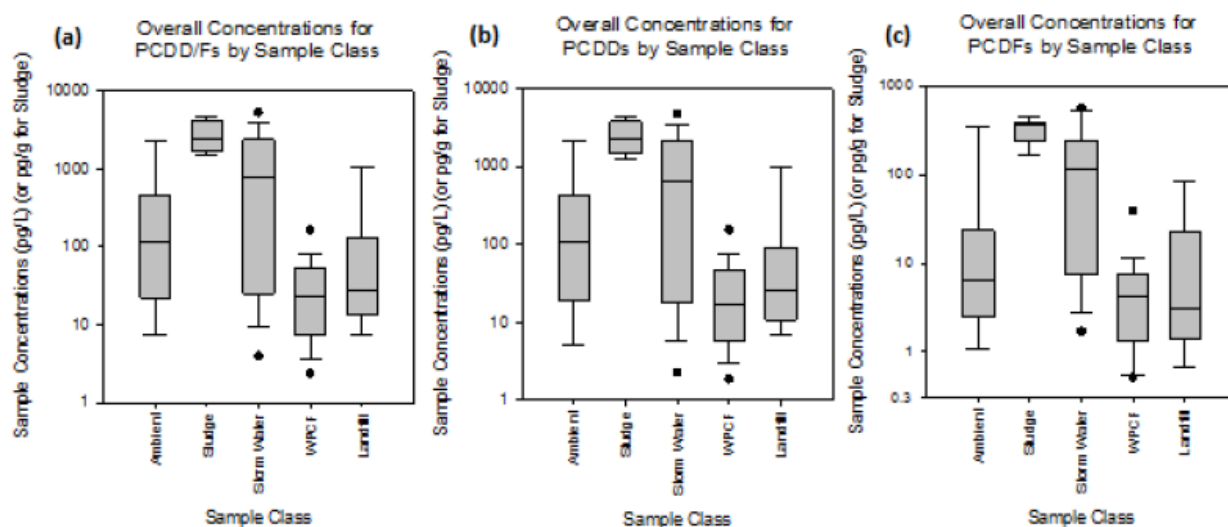


Figure 1.7. Overall concentrations within sample class for (a) PCDDs and PCDFs combined, (b) PCDDs only, and (c) PCDFs only.

Table 1.1. Average, maximum, and standard deviation values of sample concentrations within the larger congener classes across all water and sludge samples.

Congener class	Concentration		
	Average	Maximum	Standard Deviation
Non-2378-CDFs (water) (pg/L)	41	1435	151
Non-2378-CDFs (sludge) (pg/g)	126	177	43
2378-CDFs (water) (pg/L)	38	1016	117
2378-CDFs (sludge) (pg/g)	206	295	56
Non-2378-CDDs (water) (pg/L)	63	1545	181
Non-2378-CDDs (sludge) (pg/g)	297	621	166
2378-CDDs (water) (pg/L)	422	8674	1133
2378-CDDs (sludge) (pg/g)	2325	3913	993
OCDF (water) (pg/L)	22	437	58
OCDF (sludge) (pg/g)	152	226	43
OCDD (water) (pg/L)	378	7852	1016
OCDD (sludge) (pg/g)	2129	3618	907

For all of the water samples, the highest concentrations of 2,3,7,8- and non-2,3,7,8-CDD/F were present in the storm water samples followed by the ambient water samples. Within the non-2,3,7,8-substituted PCDF water sample subset, it appears that the congeners which are particularly abundant, in order of increasing value, are 1,3,4,6,8/1,2,4,6,8-PeCDF (the “/” indicates congeners that coelute and are quantified together), 1,3,4,6,7,8/1,2,4,6,7,8-HxCDF, and 1,2,3,4,6,8,9-HpCDF. The most abundant congeners for the 2,3,7,8-substituted PCDFs were OCDF, followed by 1,2,3,4,6,7,8-

HpCDF. The most prevalent congeners within the non-2,3,7,8-substituted PCDD water sample subset were 1,2,3,6,7,9/1,2,3,6,8,9-HxCDD, 1,2,4,6,8/1,2,4,7,9-PeCDD, and 1,2,3,4,6,7,9-HpCDD. For the 2,3,7,8-substituted PCDDs, the most abundant congeners were OCDD, followed by 1,2,3,4,6,7,8-HpCDD.

Concentrations in the sludge samples are expressed as grams per dry weight (units are in pg/g instead of pg/L). For the non-2,3,7,8-substituted PCDFs, the list of most abundant congeners is the same as for water samples: 1,2,3,4,6,8,9-HpCDF followed by 1,3,4,6,7,8/1,2,4,6,7,8-HxCDF followed by 1,3,4,6,8/1,2,4,6,8-PeCDF. Likewise, the most abundant 2,3,7,8-substituted PCDF congeners for sludge in order of increasing abundance were OCDF followed by 1,2,3,4,6,7,8-HpCDF. The most abundant congener within the non-2,3,7,8-substituted PCDD sludge sample subset was 1,2,4,6,8/1,2,4,7,9-PeCDD followed by 1,2,3,4,6,7,9-HpCDD. The congener abundance of the 2,3,7,8-substituted PCDD sludge samples also mirrored those of the water samples, with the most abundant congeners being OCDD, followed by 1,2,3,4,6,7,8-HpCDD.

1.4.2. %P

Each box-and-whisker plot depicting the %P by homologue was logarithmically transformed, because the data appears to be log-normally distributed (Figures 1.8 to 1.9).²³ For the TCDFs, the median %P within each data set for all sample classes were similar to each other, ranging from approximately 0.86 to about 0.89, with the ambient class possessing the highest median %P. The WPCF class possessed the greatest range of %Ps within this particular homologue. For the PeCDFs, the %P for the landfill class was

slightly lower than the other classes, and the range for its %P values was also wider, encompassing both the highest and the lowest %P for the subset of data for the homologue. In the plot for the HxCDFs, storm water appears to have the highest %P, whereas the landfill class has the lowest. For the HpCDFs, the %Ps were generally alike throughout the five classes, although the WPCF class possessed the greatest range of values (it contained the lowest value within its sample set). For furans, the %P values for the ambient and sludge classes are similar to each other. Within the PeCDF and HxCDF homologues, the %P for the landfill class is the lowest, and it is highest for the WPCF and storm water classes.

The %P for the PCDD homologues displayed greater variation by sample class. Within the TCDDs, WPCF contained the highest %P and the lowest was found in the ambient class. The %P for the landfill class was the highest in the PeCDD, HxCDD, and HpCDD homologues (although in the HpCDDs, the %P for the ambient class was also nearly identical to that of the landfill class). The %P for the WPCF class was the lowest percent for the HpCDDs, HxCDDs, and the PeCDDs. In addition, it should be noted that the storm water %P was only slightly higher than that of the WPCF class in every homologue, with the exception of the TCDDs (in which it was slightly lower). Furthermore, when comparing PCDFs to PCDDs, it appears that the %P for landfills was lower in the PCDF plots, and it was the reverse in the PCDD plots.

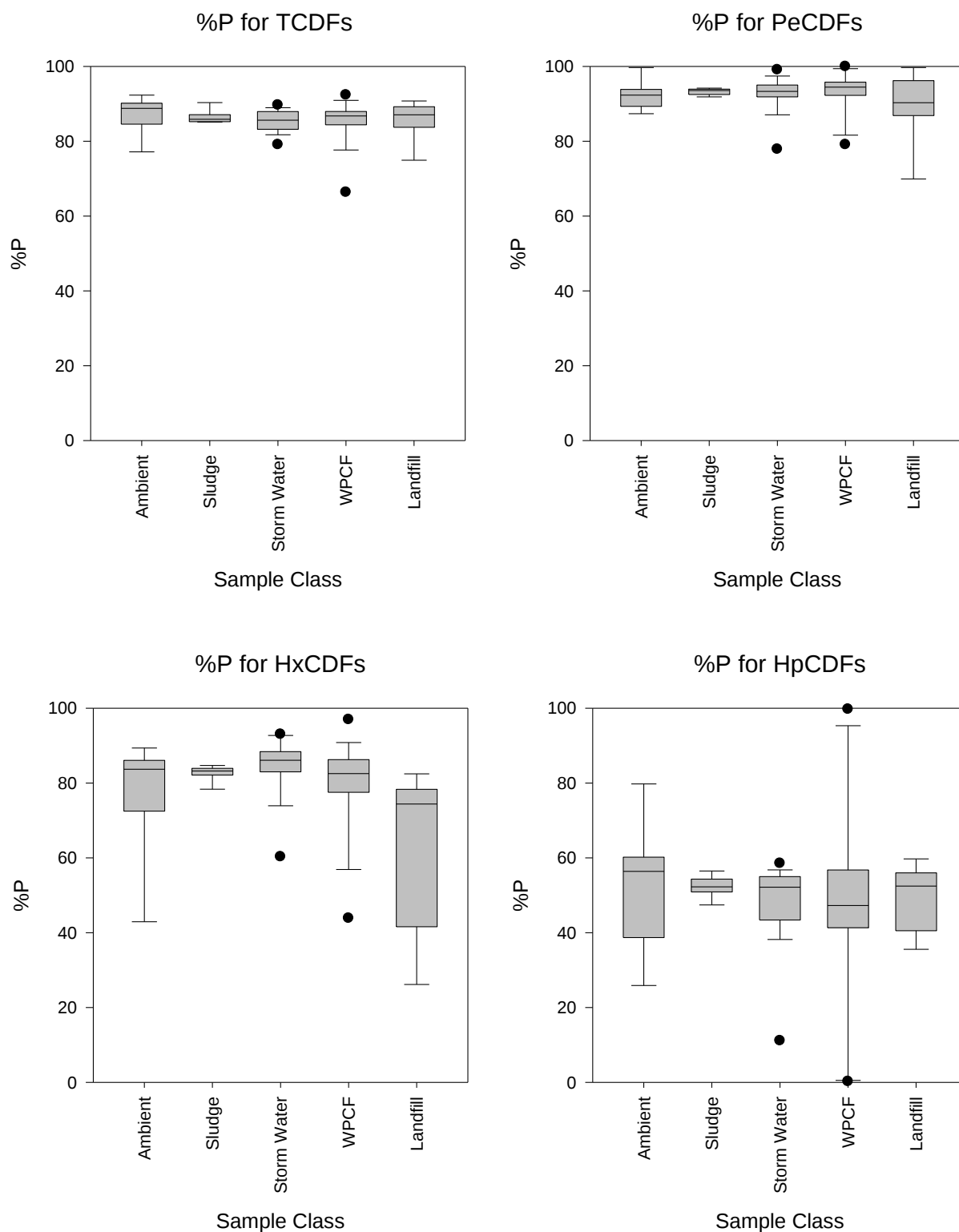


Figure 1.8. %Ps for sample classes within the CDF homologues available in the CARP data set. Bars within the boxes denote the median value within the data subset. Boxes

display the 25th and 75th percentiles, bars at the end of each whisker represent the minimum and maximum values, and dots indicate the 5th and 95th percentile outliers.

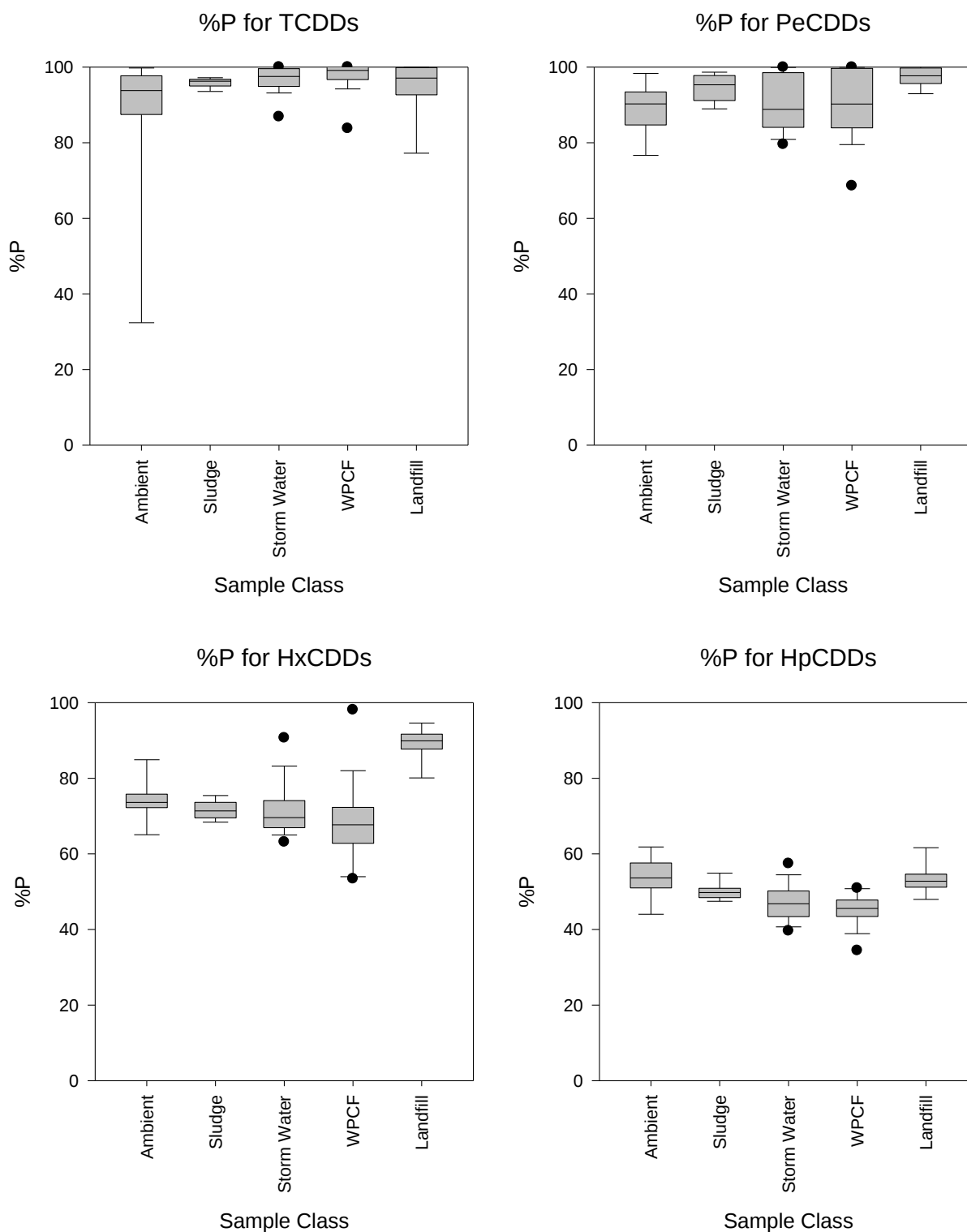


Figure 1.9. %Ps for sample classes within the CDD homologues available in the CARP data set. Bars within the boxes denote the median value within the data subset. Boxes

display the 25th and 75th percentiles, bars at the end of each whisker represent the minimum and maximum values, and dots indicate the 5th and 95th percentile outliers.

1.4.3. Student's t-test

A Student's t-test was conducted to identify whether the %P values for each homologue within each class of samples were significantly different from each other. Within the furan data subset, the %Ps for the TCDFs and HpCDFs displayed no significant difference between their respective classes. However, for the PeCDFs, the landfill and WPCF classes were significantly different from each other, with a p-value of approximately 0.025. Within the HxCDFs, the landfill class was significantly different from the sludge, storm water, and WPCF classes, with p-values of 0.0091, 0.00017, and 0.0088, respectively.

The %P values for the dioxins displayed a greater difference between classes overall. For the TCDDs, the ambient class was significantly different from the storm water and WPCF classes, with p-values of approximately 0.022 and 0.0022, respectively. For the PeCDDs, the landfill %P values were significantly different from all of the other classes, and the ambient class was also significantly different from the sludge class. The landfill class was significantly different from all of the other classes within the HxCDDs. The HpCDDs exhibited the greatest amount of difference between classes: ambient values were significantly different from storm water and WPCF, sludge was different from WPCF values, and the landfill class was significantly different from the sludge, storm water, and WPCF classes. In general, then, the landfill class was most often significantly

different from the other classes across several homologues for both CDFs and CDDs.

This may indicate that dechlorination of PCDD/Fs occurs in the Fresh Kills landfill. This was expected, since our previous analysis showed that the Fresh Kills landfill samples contained the highest proportions of PCB dechlorination products when compared to all of the other WPCFs in the CARP data set.¹

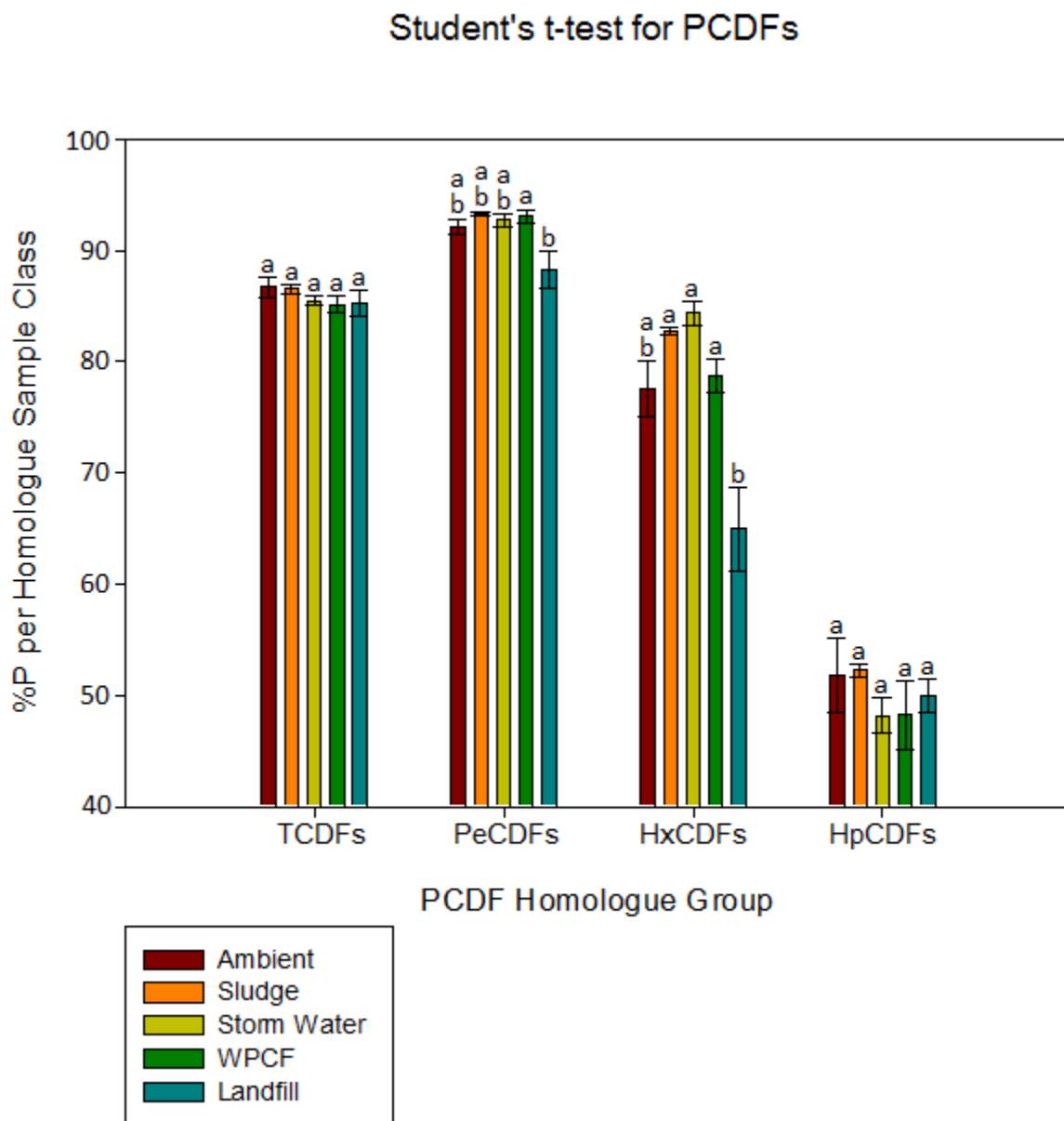


Figure 1.10. Student's t-test for PCDF homologues. Average %Ps for each sample class are plotted, and 95% confidence interval error bars are displayed. Bars with letters differing from each other within each homologue group indicate a difference between sample classes with a p value of <0.05 .

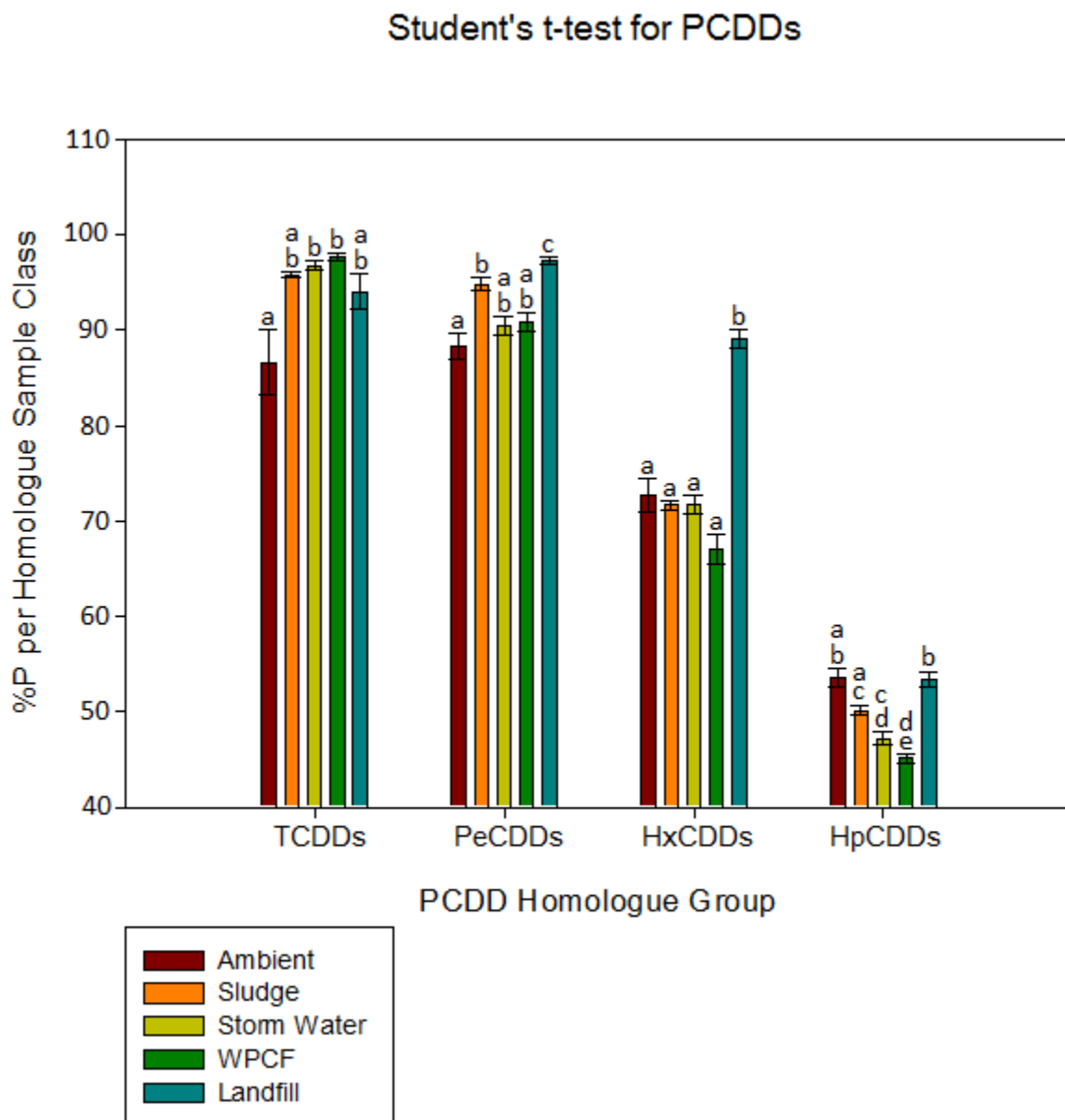


Figure 1.11. Student's t-test for PCDD homologues. Average %Ps for each sample class are plotted, and 95% confidence interval error bars are displayed. Bars with letters differing from each other within each homologue group indicate a difference between sample classes with a p value of <0.05 .

1.4.4. Correlations between congener concentrations

A simple way to determine which PCDD/F congeners are correlated with each other in terms of concentration is to calculate the R^2 value for each one to one correlation (Tables 1.2 and 1.3). This can quickly indicate patterns in the data set that will be explored in more detail by using factor analysis techniques (in this case, Positive Matrix Factorization; see Chapter 2). In tables 1.2 and 1.3, the values are color coded with high correlations in green and low correlations in red. This allows a visual indication of patterns within the data matrix. For example, the group of green in the lower portion of table 1.3 suggests that the 2,3,7,8-substituted CDDs are well correlated with each other (with the exception of 2,3,7,8-TCDD).

For the non-2,3,7,8-substituted CDFs, the R^2 values for the entire set (with all of the homologues combined) displayed a wide range of variation, from 0.04-1.00. Generally, R^2 values decrease with increasing chlorination. The R^2 values for the TCDFs range from 0.05-0.96, with the majority of values falling within the 0.71-0.95 range. The most well-correlated peaks were 1,2,7,8-TCDF, 1,3,4,9/1,2,6,7-TCDF, 2,3,6,7-TCDF, and 3,4,6,7/1,2,6,9-TCDF. This indicates that these non-2,3,7,8 congeners may come from the same source(s). The 3 least well-correlated peaks overall included 2,4,6,8-TCDF, 1,2,6,8/1,4,6,7/1,4,7,8-TCDF, and 1,3,6,9/1,2,3,7-TCDF. This demonstrates that there are at least two distinct groups of TCDF congeners coming from at least two sources. The R^2 for the PeCDFs ranged from 0.04-0.99, with the 3 least well-correlated peaks being 1,2,4,8,9/1,2,6,7,9/1,2,3,6,9-PeCDF, 1,2,3,4,9-PeCDF, and 1,2,3,8,9-PeCDF. Again, these are a group of non-2,3,7,8-CDFs that covary and therefore may arise from the same

source(s). For the HxCDFs, the R^2 values ranged from 0.03-1.00, with the majority of values falling below a 0.60 threshold. The two peaks that contained the majority of the values above this number were 1,2,4,6,7,9-HxCDF and 1,2,3,4,6,7-HxCDF, both non-2,3,7,8 congeners. The R^2 for the two peaks within the HpCDF homologue category ranged from 0.02-0.91, with 1,2,3,4,6,8,9-HpCDF being less well-correlated to the %P than 1,2,3,4,6,7,9-HpCDF.

The R^2 values for the entire set of 2,3,7,8-substituted PCDFs ranged from 0.02-0.99, and they were less well-correlated on the whole to the %P than the non-2,3,7,8-CDFs. Similar to the non-2,3,7,8-CDFs, they also exhibited a pattern in which increased chlorination yielded generally lower R^2 values across homologues. The R^2 values ranged from 0.27-0.98 for the TCDFs, 0.15-0.97 for the PeCDFs (with 2,3,4,7,8-PeCDF being the most well-correlated peak and 1,2,3,7,8-PeCDF being the least), 0.12-0.99 for the HxCDF, 0.04-0.95 for the HpCDFs, and 0.02-0.97 for OCDF (with the majority of the values within this congener falling below 0.50).

For the PCDDs, the R^2 values were generally higher throughout the entire data subset than for the PCDFs, although the 2,3,7,8-chlorinated congeners were higher within this subgroup. For the non-2,3,7,8-substituted PCDDs, the R^2 ranged from 0.03-0.99. For the TCDDs, this range was also 0.03-0.99, with many of the values being above 0.45. However, there were two peaks in which the values were consistently below 0.20: 1,2,3,7/1,2,3,8-TCDD and 1,2,8,9-TCDD. The R^2 values for the PeCDDs ranged from 0.01-0.98, with the least well-correlated peaks being 1,2,4,6,8/1,2,4,7,9-PeCDD and

1,2,3,6,8-PeCDD. For the HxCDDs, the range was from 0.05-0.95, with the majority of the values falling within the middle of that range. For the sole peak representing HpCDD, the R^2 ranged from 0.11-0.95, with the majority of the values falling below 0.50.

The overall R^2 range for the 2,3,7,8-PCDDs was between 0.04-0.98. Within this subset, as the homologue increased in chlorination, the resulting R^2 range also tended to increase as a whole. The TCDDs contained relatively low values, ranging from 0.04-0.50. The R^2 range for the PeCDDs was 0.12-0.91, with approximately 60% of those values falling below the 0.50 level. The HxCDDs ranged from 0.06-0.98, the HpCDDs ranged from 0.09-0.98, and the OCDD peak ranged from 0.09-0.95. The latter 2 peaks representing the HpCDD and OCDD homologues contained the highest amount of R^2 values over 0.50 out of any individual peaks within this particular subset of data.

[illegible]

Table 1.3. Correlation coefficients (R^2) between the 35 PCDD congeners included in the data matrix for analysis. 2,3,7,8-CDDs are on the bottom/right. Homologues are color coded in the top row: blue = TCDDs, purple = PeCDDs, maroon = HxCDDs, yellow = HpCDDs, teal = OCDD.

	1368	1379	1369	1247/1248/1378/1469										1246/1249	1268	1478	1234/1236/1269										1237/1238	1239	1278	1289	12468/12479										12469	12368	12478	12379	12369	12467/12489										12347	12346	12367	12389	124679/124689										123468	123679/123689										123469	1234679	2378	12378	123789/123467										123478	123678	1234678	OCDD
1368		0.99	0.52	0.64	0.64	0.44	0.48	0.76	0.17	0.35	0.38	0.03	0.02	0.47	0.03	0.28	0.11	0.39	0.57	0.40	0.53	0.43	0.35	0.33	0.43	0.23	0.23	0.17	0.38	0.20	0.14	0.25	0.17	0.13	0.16																																																															
1379			0.45	0.58	0.62	0.43	0.47	0.71	0.16	0.33	0.37	0.03	0.01	0.39	0.03	0.28	0.10	0.35	0.55	0.41	0.54	0.42	0.35	0.30	0.45	0.22	0.23	0.17	0.37	0.20	0.14	0.26	0.16	0.13	0.16																																																															
1369				0.81	0.67	0.50	0.57	0.77	0.16	0.37	0.36	0.08	0.21	0.71	0.26	0.23	0.36	0.47	0.45	0.34	0.40	0.39	0.23	0.40	0.38	0.28	0.25	0.16	0.22	0.21	0.17	0.11	0.22	0.15	0.13																																																															
1247/1248/1378/1469					0.76	0.68	0.77	0.92	0.08	0.56	0.63	0.09	0.04	0.79	0.08	0.47	0.19	0.67	0.72	0.46	0.52	0.65	0.52	0.58	0.49	0.43	0.42	0.31	0.37	0.42	0.35	0.27	0.35	0.26	0.29																																																															
1246/1249						0.58	0.71	0.84	0.05	0.42	0.45	0.05	0.05	0.65	0.08	0.32	0.20	0.53	0.60	0.54	0.68	0.59	0.39	0.40	0.58	0.29	0.32	0.20	0.30	0.27	0.23	0.16	0.23	0.17	0.19																																																															
1268							0.65	0.65	0.16	0.49	0.67	0.26	0.11	0.40	0.19	0.52	0.32	0.54	0.58	0.47	0.46	0.63	0.53	0.53	0.55	0.45	0.51	0.38	0.35	0.55	0.45	0.33	0.43	0.32	0.37																																																															
1478								0.81	0.03	0.50	0.66	0.13	0.04	0.56	0.08	0.48	0.21	0.67	0.65	0.58	0.63	0.68	0.60	0.49	0.61	0.37	0.43	0.29	0.36	0.45	0.35	0.30	0.31	0.23	0.31																																																															
1234/1236/1269									0.07	0.52	0.58	0.07	0.03	0.74	0.07	0.43	0.19	0.66	0.73	0.62	0.72	0.68	0.54	0.52	0.63	0.38	0.40	0.26	0.42	0.37	0.30	0.25	0.31	0.22	0.25																																																															
1237/1238										0.07	0.10	0.14	0.45	0.03	0.48	0.10	0.44	0.06	0.09	0.02	0.02	0.07	0.05	0.11	0.05	0.12	0.09	0.11	0.14	0.10	0.08	0.10	0.13	0.09	0.09																																																															
1239											0.52	0.07	0.04	0.45	0.07	0.43	0.15	0.40	0.55	0.29	0.30	0.56	0.45	0.45	0.36	0.35	0.37	0.30	0.23	0.40	0.34	0.27	0.31	0.24	0.30																																																															
1278												0.20	0.07	0.46	0.13	0.84	0.27	0.73	0.79	0.39	0.34	0.79	0.83	0.80	0.46	0.72	0.76	0.65	0.49	0.82	0.74	0.57	0.69	0.57	0.67																																																															
1289													0.11	0.02	0.15	0.22	0.15	0.08	0.06	0.09	0.05	0.10	0.14	0.14	0.16	0.15	0.18	0.11	0.05	0.25	0.18	0.10	0.17	0.11	0.10																																																															
12468/12479														0.02	0.98	0.08	0.88	0.05	0.03	0.03	0.01	0.06	0.02	0.12	0.07	0.15	0.13	0.14	0.04	0.12	0.11	0.06	0.18	0.15	0.11																																																															
12469															0.05	0.33	0.11	0.58	0.63	0.30	0.35	0.51	0.36	0.52	0.28	0.35	0.31	0.22	0.25	0.26	0.24	0.20	0.26	0.19	0.22																																																															
12368																0.13	0.94	0.10	0.07	0.06	0.03	0.11	0.05	0.18	0.13	0.22	0.19	0.20	0.08	0.19	0.18	0.09	0.24	0.20	0.15																																																															
12478																	0.24	0.62	0.71	0.35	0.27	0.75	0.82	0.80	0.41	0.79	0.82	0.77	0.45	0.89	0.83	0.68	0.79	0.70	0.76																																																															
12379																		0.21	0.20	0.19	0.13	0.26	0.17	0.31	0.29	0.35	0.33	0.31	0.17	0.32	0.30	0.18	0.37	0.31	0.26																																																															
12369																			0.69	0.44	0.43	0.73	0.65	0.68	0.40	0.57	0.59	0.48	0.49	0.58	0.53	0.41	0.52	0.42	0.46																																																															
12467/12489																				0.50	0.50	0.90	0.80	0.71	0.51	0.60	0.62	0.52	0.50	0.61	0.56	0.51	0.53	0.45	0.54																																																															
12347																					0.91	0.56	0.49	0.31	0.88	0.27	0.35	0.20	0.41	0.30	0.25	0.17	0.23	0.18	0.19																																																															
12346																						0.56	0.43	0.26	0.83	0.19	0.26	0.12	0.38	0.22	0.17	0.13	0.15	0.10	0.12																																																															
12367																							0.86	0.71	0.58	0.64	0.70	0.56	0.47	0.69	0.64	0.51	0.60	0.50	0.55																																																															
12389																								0.69	0.50	0.65	0.71	0.59	0.50	0.76	0.70	0.57	0.63	0.53	0.60																																																															
124679/124689																									0.41	0.95	0.93	0.86	0.42	0.84	0.85	0.67	0.90	0.83	0.82																																																															
123468																										0.38	0.48	0.31	0.38	0.41	0.36	0.24	0.35	0.29	0.28																																																															
123679/123689																											0.97	0.95	0.37	0.86	0.90	0.71	0.98	0.95	0.88																																																															
123469																												0.93	0.40	0.91	0.93	0.71	0.96	0.92	0.88																																																															
1234679																													0.31	0.85	0.89	0.77	0.95	0.98	0.95																																																															
2378																														0.41	0.35	0.31	0.34	0.27	0.30																																																															
12378																															0.95	0.71	0.89	0.79	0.82																																																															
123789/123467																																0.62	0.95	0.86	0.86																																																															
123478																																	0.68	0.71	0.75																																																															
123678																																		0.95	0.89																																																															
1234678																																			0.91																																																															
OCDD																																																																																																		

1.4.5. TEQ values

The seventeen 2,3,7,8-substituted PCDD/F congeners are the focus of regulatory effort due to their toxicity and the effect that they have on humans and wildlife.²⁶ Toxic equivalency factors (TEFs) are published by the World Health Organization to indicate an order of magnitude of estimated toxicity of the various 2,3,7,8-substituted PCDD/F congeners in comparison with the most toxic PCDD/F congener, 2,3,7,8-

tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD). To obtain the toxic equivalency quotient (TEQ) for each congener, the mass concentration was multiplied by the congener's 2005 World Health Organization TEF values for humans and mammals (Table 1.4).²⁶

Table 1.4. WHO-TEF values for 1998 and 2005 for mammals.²⁶

Congener	WHO-TEF ²⁶	
	1998	2005
2,3,7,8-TCDD	1	1
1,2,3,7,8-PeCDD	1	1
1,2,3,4,7,8-HxCDD	0.1	0.1
1,2,3,6,7,8-HxCDD	0.1	0.1
1,2,3,7,8,9-HxCDD	0.1	0.1
1,2,3,4,6,7,8-HpCDD	0.01	0.01
OCDD	0.0001	0.0003
2,3,7,8-TCDF	0.1	0.1
1,2,3,7,8-PeCDF	0.05	0.03
2,3,4,7,8-PeCDF	0.5	0.3
1,2,3,4,7,8-HxCDF	0.1	0.1
1,2,3,6,7,8-HxCDF	0.1	0.1
1,2,3,7,8,9-HxCDF	0.1	0.1
2,3,4,6,7,8-HxCDF	0.1	0.1
1,2,3,4,6,7,8-HpCDF	0.01	0.01
1,2,3,4,7,8,9-HpCDF	0.01	0.01
OCDF	0.0001	0.0003

Then, to obtain the TEQ for each sample, which is expressed as equivalents of 2,3,7,8-TCDD, the TEQs for each congener are summed. TEQ values ranged from 0.0044 pg/L (sample 1SPL02808 collected from the 26th Ward WPCF, Figure 1.4b) to 118 pg/L (sample 1SPL03082, an ambient water sample collected from the Mohawk River at Cohoes, Figure 1.3).

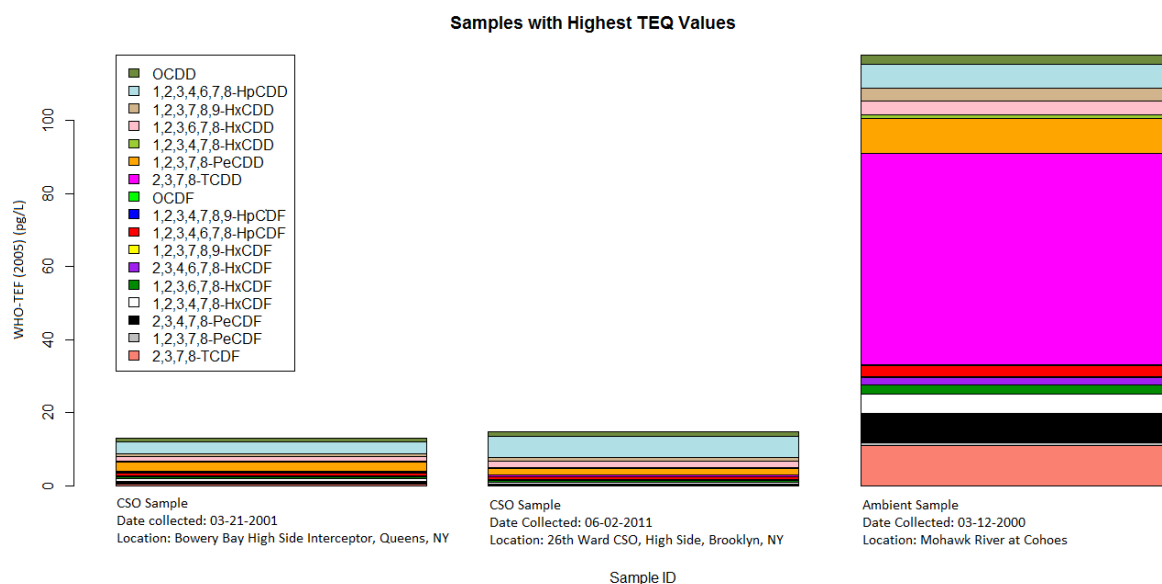


Figure 1.12. Three samples from data set with highest TEQ values. Toxicity contribution is examined by each individual PCDD/F homologue within each sample.

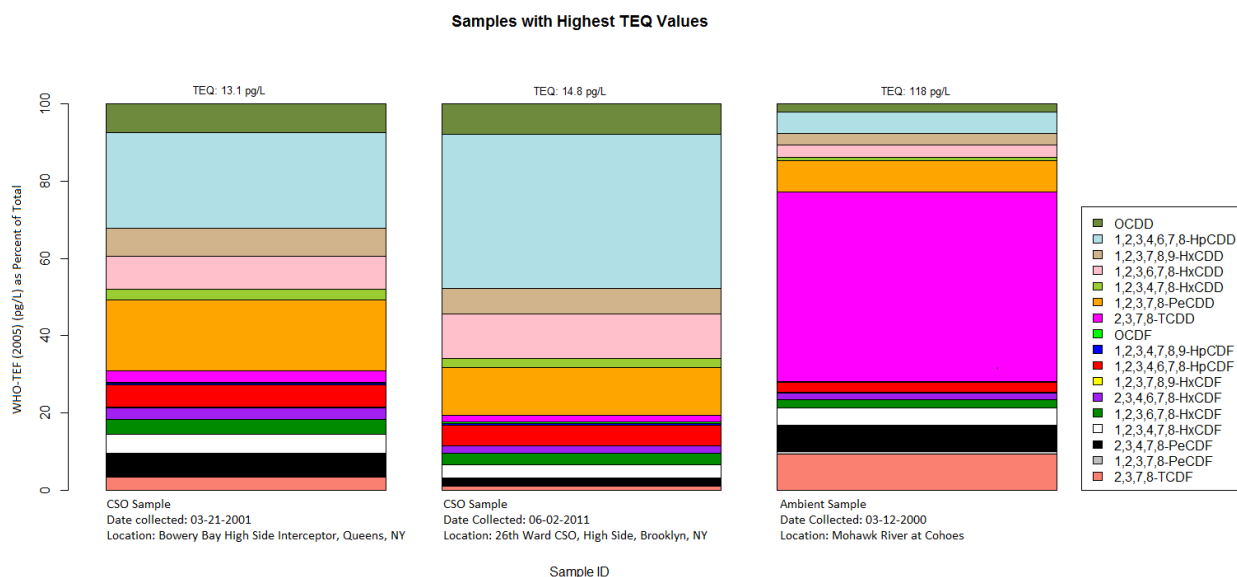


Figure 1.13. Three samples from data set with highest TEQ values. Toxicity contribution is examined by each individual PCDD/F homologue within each sample in terms of percent of total.

The three samples with the highest TEQ values (increasing in value) were 1SPL02733, 1SPL02795, and 1SPL03082. 1SPL02733 was obtained from a CSO in Bowery Bay in the Jamaica section of Queens, New York, in Steinway near Rikers Island (refer to Figure 1.6). 1SPL02795 was obtained from a CSO of the 26th Ward sewage treatment plant in Brooklyn, NY from the High Side (Refer to Figure 1.6). 1SPL03082 was an ambient surface water collected from the Mohawk River at Cohoes (Refer to Figure 1.3).^{16, 17}

The Mohawk River Sample contained the highest TEQ value, due to a high TEF value of approximately 57 pg/L for the 2,3,7,8-TCDD congener which was approximately 49% of the total TEQ value for that sample. The highest TEQs for the two CSO samples were due to the 1,2,3,4,6,7,8-HpCDD congener, with values of about 3.3 pg/L (about 25% of total TEQ) for the Bowery Bay sample and 5.9 pg/L (49% of total TEQ) for the 26th Ward sample. Thus, the samples displaying the highest toxicities, the TEQ was dominated by dioxin congeners, rather than furans.

In general, WPCF samples have lower TEQ values, whereas storm water has the highest overall TEQ (Figures 1.14 and 1.15). 1,2,3,4,6,7,8-HpCDD is generally the largest contributor to the overall TEQ across all sample classes, followed by 1,2,3,7,8-PeCDD.

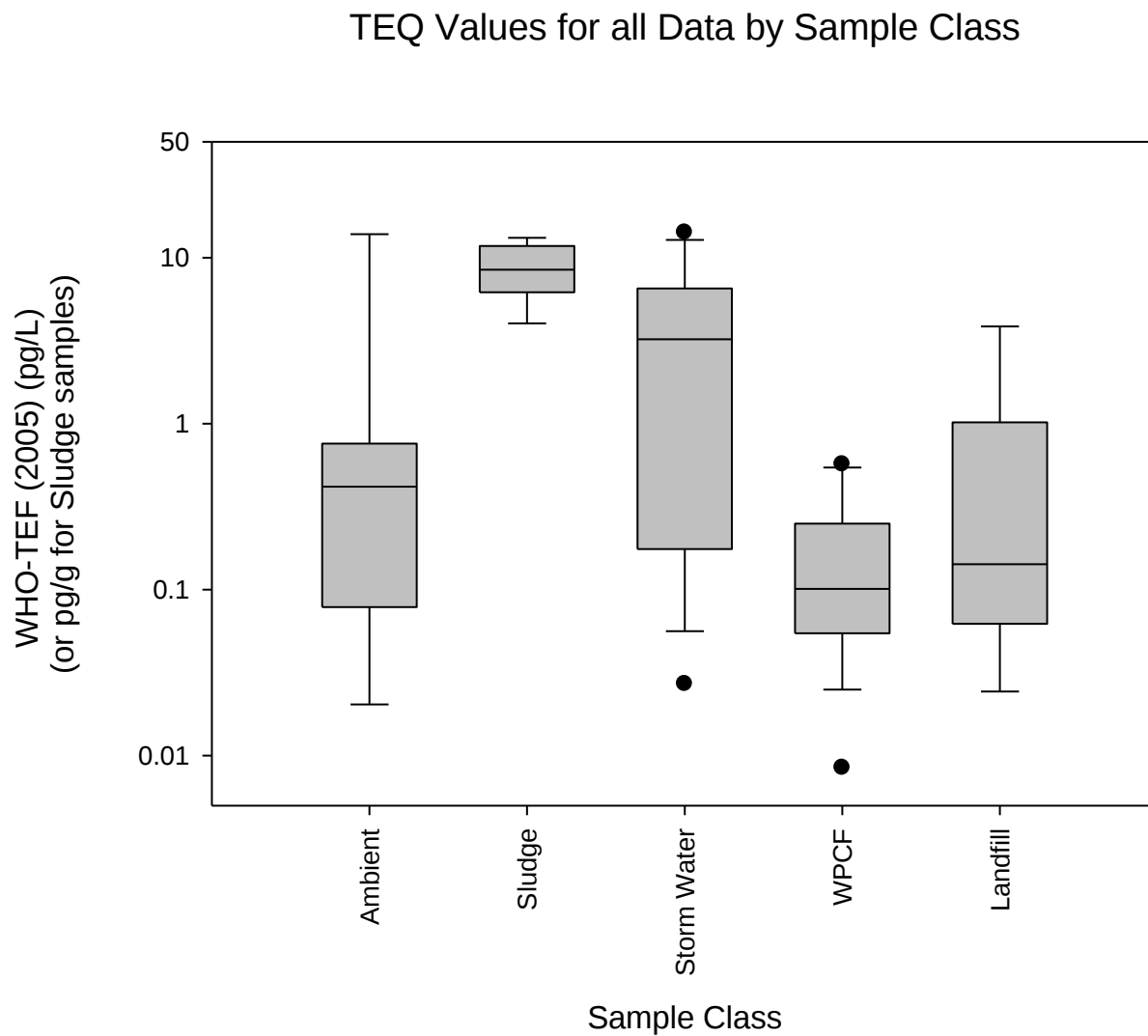


Figure 1.14. TEQ values for all data by sample class.

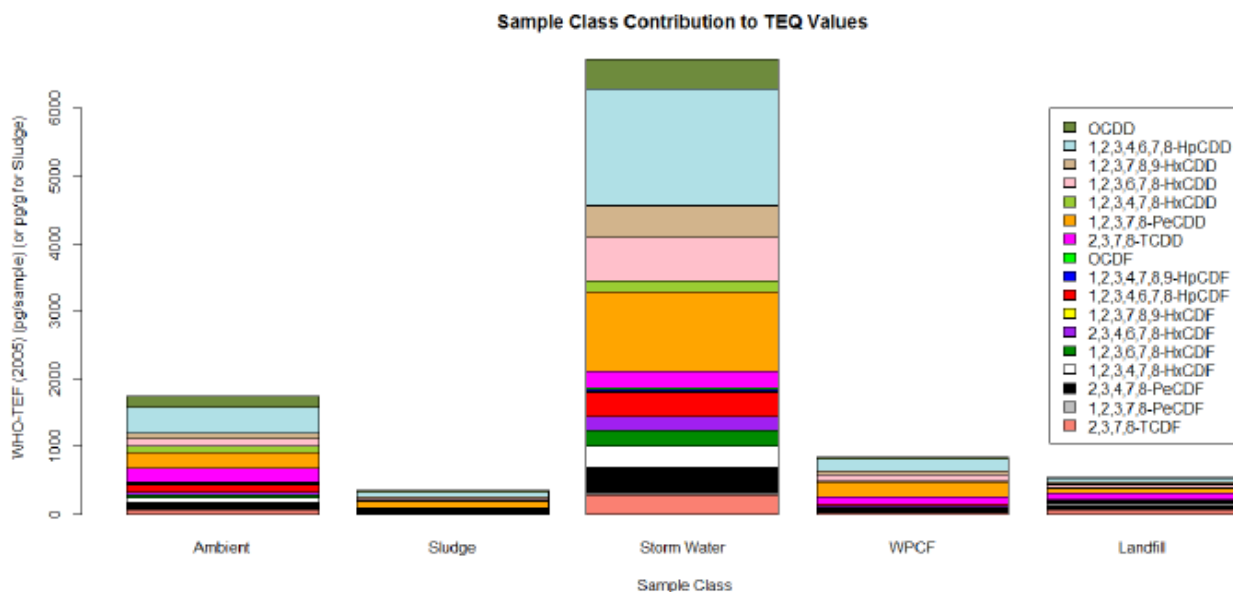


Figure 1.15. Sample class contribution to TEQ values.

1.5. Discussion

This chapter used various statistical analyses on the CARP data set to examine the possible evidence of *peri*-lateral dechlorination of PCDD/F congeners within the New York/New Jersey Harbor Watershed. Additionally, this study also intended to counterbalance the lack of studies reporting the concentrations or percentages of the dechlorination of non-2,3,7,8 PCDD/F congeners. While it seems that a great deal of *peri*-lateral dechlorination did not occur within our specific data set overall, several trends were nevertheless recognized from the results of our analyses. Generally, in the instances where the amount and presence of this pathway of dechlorination was of note, much of it was present in landfills, and the most toxic sample concentrations were found in CSOs or sewers.

Two out of the three laboratory samples with the highest TEQ values, and therefore the highest toxicity, were obtained from CSOs in two separate boroughs of New York City. This aligns with previous studies suggesting that dechlorination of PCDD/Fs does indeed occur in sewers,¹ and it also implies that it would be beneficial for detoxifying existing sediments within these particular sample locations. When examining the %P in the box-and-whisker plots in addition to the student's t-tests, it seems that landfill samples are most likely have significantly different %P relative to the other sample classes. This may indicate dechlorination occurs in the Fresh Kills landfill, which is not surprising since our previous analysis¹ showed that dechlorination of PCBs in the Fresh Kills landfill was extensive.

Within the original data set, the concentrations of non-2,3,7,8-CDD/Fs were far lower than those of the 2,3,7,8-CDD/Fs. The greatest concentrations of non-2,3,7,8-PCDD/Fs in the data set were in the storm water samples, which contained the CSO samples. Within the original non-2,3,7,8-substituted PCDD/F water sample subset, heavier homologues are more abundant than lighter homologues (HpCDD/Fs congeners are more abundant than HxCDD/Fs, which are more abundant than PeCDD/Fs, and so on). It should also be noted that, in general, %P was greater for the CDF samples than for the CDDs. These differences could be attributed to several possible sources: varying dechlorination rates due to the slight differences in compound structures between furans and dioxins, the numerous environmental variables affecting samples collected from site to site, or even differing dates during which the samples were collected (in general, it would be assumed

that samples collected at later dates would allow for greater time for dechlorination processes to occur).

One of the drawbacks to these results is that it does not provide a complete snapshot of potential *peri*-lateral dechlorination of PCDD/F congeners within the Harbor. Because the CARP data set only provided the concentrations of the 17 tetra- through octa-chlorinated non-2,3,7,8 congeners, potentially valuable information regarding the mono-through tri-chlorinated congeners was ignored because it was unavailable. A larger and more complete data set including these missing congeners may provide further evidence of dechlorination.

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Chapter 2

Analysis of the PCCD/F data matrix using Positive Matrix Factorization

2. Abstract

The purpose of this study was to analyze the CARP-obtained PCDD/F data set via Positive Matrix Factorization (PMF) to look for evidence of PCDD/F dechlorination by bacteria at both the peri and lateral positions. Previous published studies illustrated a relationship between PCDD/F dechlorination products and PCB dechlorination products, suggesting that PCDD/Fs are indeed dechlorinated at the peri positions. Data on tetra- through octa- chlorinated PCDD/F congeners sampled from various sites in the NY/NJ Harbor from the CARP Project were obtained from Axys Analytical Services in British Columbia, and were manually inserted into an Excel spreadsheet to build a PMF matrix. Duplicate, negligible, and samples which skewed results to yield inaccurate results were discarded, yielding a PMF data matrix of 117 samples and 84 PCDD/F congeners. A four-factor model was chosen based on the following criteria: stability of PMF matrices, positive and significant coefficients in the multiple linear regression, independent G space plots, model fit based on R^2 values, and meaningful and interpretable results. When compared to the 2,3,7,8-congener patterns published by the EPA, the sources of PCDD/Fs in the Harbor were identified as: bleached chemical wood pulp and paper mills (1% total mass of data set), wood combustion (3%), Kraft black liquid recovery boilers (4%), and diesel trucks (92%). However, when compared to the New York Academy of Sciences Dioxin report, these results seem inaccurate.

2.1. Introduction

Finding evidence of dechlorination in the CARP data set described in Chapter 1 requires a method that can detect even small changes in congener patterns that might result from dechlorination. This type of problem is ideal for factor analysis. Several studies have used factor analysis, specifically Positive Matrix Factorization (PMF), to reveal evidence of dechlorination of PCBs, BDEs, and PCDD/Fs.¹⁻⁹

PMF is a source apportionment factor analysis method that allows only positive correlations. As a result, PMF conserves mass and is ideal for a data set in which one congener may be dechlorinated to form another. Our earlier work² suggested that PCDD/Fs are dechlorinated at the peri positions by showing a correlation between PCB dechlorination products and PCDD/F dechlorination products. The purpose of this chapter is to analyze the PCDD/F data set described in Chapter 1 (and presented in Appendix 1) via PMF to look for evidence of dechlorination of PCDD/Fs by bacteria at both the peri and lateral positions.

2.2. Methods

2.2.1. Background on PMF

PMF2, the PMF software which was developed by Paatero and Tapper¹⁰, is a statistical factor analysis method which is based on the law of conservation.³ Sources of particular compounds can be identified based on congener pattern profiles, and their percent distributions from these sources can be generated. The PMF model in its simplest form is comprised of an observation data matrix, X , which is the product of its various congener

source profile output patterns (F), and the percent contribution of each of these sources to the total sample distribution (G):

$$X = GF + E \quad (\text{Equation 2-1})$$

where E is the variation in the data matrix that is not explained by G and F, i.e. the residue or remainder. Within the PMF program, the data points are associated with their corresponding error values, so that the data points which are below detection limits or are completely missing are given far less weight. To accurately estimate the error matrix for PMF, different uncertainty values were calculated for each data point for each sample using the following equation:

$$s_{ij} = t_{ij} + u_{ij} \sqrt{\max(|x_{ij}|, |y_{ij}|)} + v_{ij} \max(|x_{ij}|, |y_{ij}|) \quad (\text{Equation 2-2})$$

where t_{ij} represents the detection limit for a particular sample or analyte, u_{ij} denotes the Poisson distribution, v_{ij} represents the surrogate recoveries (which illustrate the precision or uncertainty of measurement), x_{ij} represents the observed data value, and y_{ij} denotes the modeled value.¹⁰ Thus three matrixes are entered into the PMF software: the concentration matrix, the uncertainty matrix, and the Limit of Detection (LOD) matrix.

The PMF program cannot, by itself, determine the “correct” number of factors. This must be determined by the user. The PMF results will be erroneous if an incorrect number of factors is chosen. Our laboratory has investigated many permutations of the

concentration, uncertainty, and LOD matrixes and suggested several methods of determining the correct number of factors. The correct number of factors should: (1) be stable with respect to several runs starting with different seed values given essentially the same answer (low RSD of the G matrix), (2) contain factors that all contribute in a positive and significant way to the measured concentrations (i.e. a multiple linear regression (MLR) with the measured sum of analytes as Y and the G matrix factors as the X variables should show positive and significant ($p < 0.05$) coefficients for all factors), (3) contain factors that are independent of each other as evidenced by wide scatter in the G-space plots, (4) reproduce the data well (high R^2 values for the correlation of measured and modeled concentrations of the analytes), and (5) be physically meaningful and interpretable.

2.2.2. Information on CARP data set

Data on tetra- through octa- chlorinated PCDD/F congeners sampled from various sites in the NY/NJ Harbor from the CARP Project were obtained from Axys Analytical Services in British Columbia, as described in Chapter 1. These sample packages, which were over 10 years old, were provided in the form of scanned pdf files. It should be noted that not all of the samples were used in the PMF matrix. Dissolved phase (XAD) samples with minimal amounts and concentrations were discarded because they always sorted out into their own separate factor. Furthermore, each XAD sample would ideally be added to the corresponding filter sample to obtain a 'whole water' concentration, yet the corresponding filter was not always available.

Thus, those sample amounts in the dissolved phase which were present in small amounts – typically those found in the “GRW” labelled samples from the laboratory data – were assumed to be negligible. The majority of these discarded XAD samples were obtained from surface water locations, with most of them categorized as ambient water samples (this included a combination of ambient non-kill samples, ambient clean samples, and ambient Hudson samples). Within this particular subsection of the data set, the majority were the 36 ambient non-kill samples. Here, the smallest discarded amount was for sample 1SPL00293, an ambient clean water sample from New York Bight Apex on January 29, 1999. It had a sample concentration of 0.0070 pg/L, and it was an XAD sample of 913 L with a mass of 6.41 pg/sample. The largest discarded sample within this category was 1GRW04213, which was an ambient Hudson sample obtained from the Hudson River at Poughkeepsie. Its concentration was 994 pg/L, and it was an XAD sample of 111 L, with a mass of 110000 pg/sample. However, most of the discarded sample concentrations within this category were below 1 pg/L.

Outside of these ambient water samples, the surface water category with the greatest amount (percentage-wise) of discarded samples was within the category of major tributaries, with 42 samples being discarded. Here, the sample with the smallest concentration was 1GRW00331, with a concentration of 0.082 pg/L obtained from Hudson River (Waterford) on April 1st, 1999. It had a sample weight of 333 L, and a mass of 27.4 pg/sample amount. The discarded sample with the largest concentration within this very same category was 1GRW04650, obtained on February 28, 2000 from

the Hudson River (Waterford). It had a weight of 21 L, a mass of 560 pg/sample, and a concentration of 27 pg/L.

It should be noted that none of the CSO, trackdown, or stormwater overflow samples were discarded. Furthermore, none of the sludge samples were discarded within this process, because they were solid instead of liquid samples. Additionally, a small amount (3 samples) of those discarded were landfill samples, and many were WPCF samples.

A complete list of samples used in the PMF matrix is provided in Appendix 2. Table 2.1 provides a complete list of analytes used within the initial PMF run. All of these analytes were included in the final PMF run (none were discarded from the data matrix) resulting in the factor profiles presented later in this chapter.

Table 2.1. Complete list of PCDD/F congeners used within the PMF runs. Those containing the “/” symbol indicate coeluted congeners.

14 TCDFs	15 PeCDFs	14 HxCDFs
1368	13468/12468	123468
1468	13678	134678/124678
2468	12368/12478/13467/13478/12467	134679
1247/1347/1378/1346/1246	13479/14678	124679
1367/1348/1379/1248	12479/13469	124689
1268/1467/1478	23468/12469/12347/12346	123467
1369/1237	12348	123478
2368	12378	123678
2467/1238/1236/1469/1678/1234	12367	123479
1278	12678/12379	123469/123679
1349/1267	12489/12679/12369	123689
2378/2348/2347/2346/1249/1279	23478	234678
2367	23467	123789
3467/1269	12349	123489
	12389	
4 HpCDFs	OCDF	
1234678		
1234679		
1234689		
1234789		
13 TCDDs	12 PeCDDs	6 HxCDDs
1368	12468/12479	124679/124689
1379	12469	123468
1369	12368	123679/123689
1247/1248/1378/1469	12478	123469
1246/1249	12379	123478
1268	12369	123678
1478	12467/12489	
1234/1236/1269	12347	
1237/1238	12346	
2378	12378	
1239	12367	
1278	12389	
1289		

3 HpCDDs	OCDD
123789/123467	
1234679	
1234678	

2.2.3. PMF data matrices

The concentration matrix consisted of mass concentrations of each PCDD/F congener within each sample. Typically, data points which are below detection limit (BDL) are either replaced with one-half of the LOD, or they are multiplied by a random number between zero and the detection limit.¹⁰ Measurements of BDL in which the LOD values were not available were replaced with the minimum detected concentration divided by 5. Out of the entire LOD concentration matrix, 2653 data points were BDL whereas the remaining 7175 were not. Thus, approximately 27% of the data points within the LOD concentration matrix were BDL.

In order to construct the LOD matrix, LOD values for certain homologues for each sample at various collection dates were extracted and obtained from the CARP database in the form of an Excel spreadsheet. These values were assumed to be representative of the entire homologue within that particular sample. For samples with two or more LODs per homologue, the numbers were averaged for that particular category.

An (x,3x) uncertainty matrix was used: the uncertainty for the detected concentrations was equal to the RSD of the surrogate recoveries for that analyte (x), and three times this uncertainty (3x) was applied to all measurements BDL. Due to the way surrogates are assigned in EPA Method 1613, the uncertainty was the same for all congeners in the

same homologue. No surrogate recoveries were available for the pentachlorodioxin homologue, thus an arbitrary value of 0.25 was assigned because it fell within the range of the uncertainty values for the other homologues (0.22 to 0.40).

2.2.4. Preliminary PMF runs and selection of final data matrix

Conducting PMF analysis is an iterative process in which several data matrixes are investigated until a stable and robust solution is obtained. The initial data matrix contained 135 samples and 84 analytes. This matrix was pared to remove duplicate samples, resulting in a matrix of 127 samples and 84 analytes. In order to ensure greater accuracy of results, OCDD was removed. OCDD is the most abundant congener in the data set in virtually all samples, which causes it to sort into all resolved factors.

Removing compounds such as OCDD that are dominant in the data matrix is common in factor analysis,^{9, 11} although in our earlier investigation of the PCDD/F CARP data, OCDD was kept in the data matrix.² This yielded a 127 by 83 matrix.

Analysis of this 127 by 83 data matrix displayed a great disparity amongst the various seed runs and high overall relative standard deviation (RSD) of the G matrix at all numbers of factors. PMF results from many iterations of this basic data set resolved four factors as source profiles: motor vehicle emissions (74% of the mass in the data set), emissions from secondary aluminum smelters (smelting refers to metal refining in furnaces of various facilities¹⁵) (11% of the mass of the data set), pine resin (7% of the mass of the data set), and atmospheric deposition (8% of the mass in the data set). When examining these source profiles in greater detail, however, the results seemed

uncharacteristic of actual sources to the Harbor. For instance, although the presence of pine resin emissions may be due to house fires, backyard household waste combustion, forest fires,¹⁶ and perhaps even from pitch pine (the primary tree found in the New Jersey Pine Barrens¹⁷), it is unlikely that pine resin is an important PCDD/F source for the Harbor as a whole, and is not helpful in the quest to identify a possible dechlorination signal.

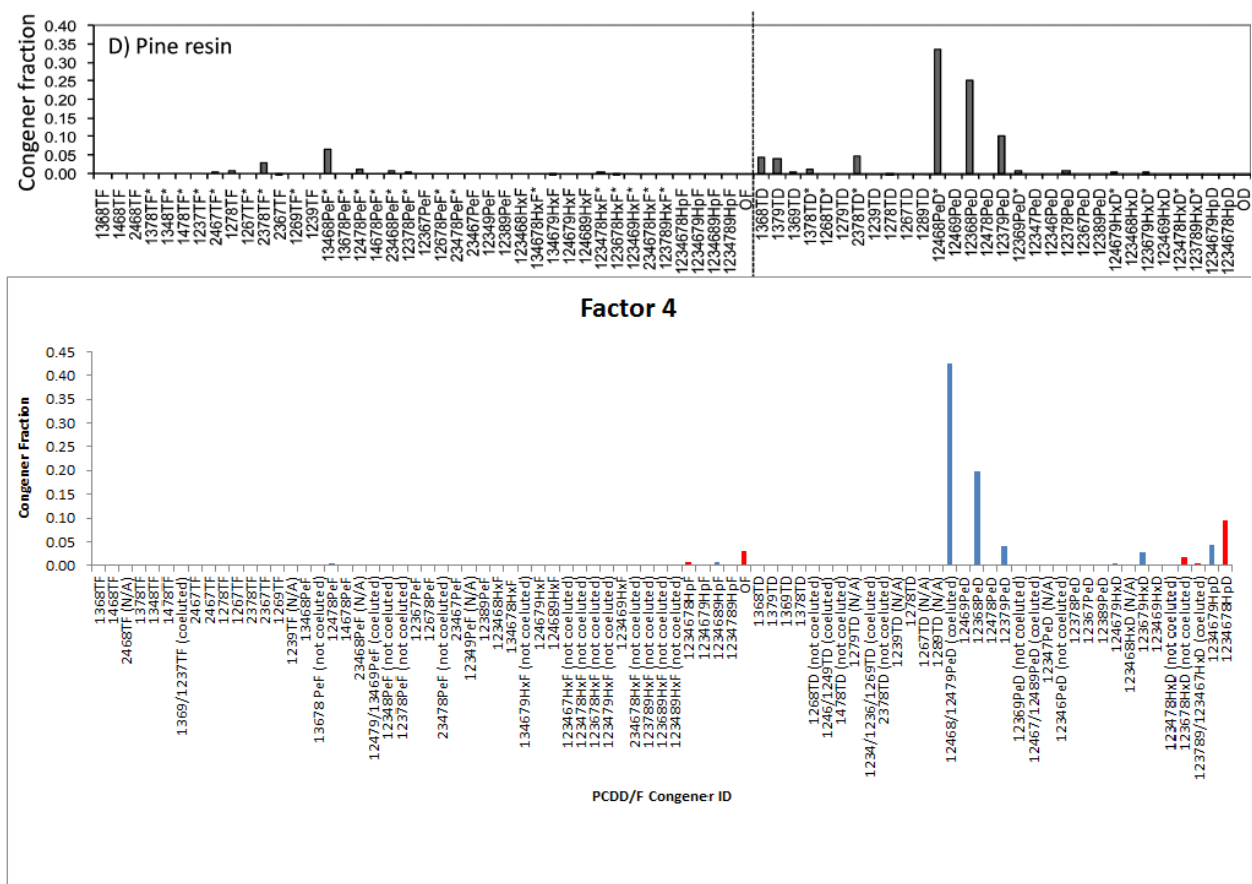


Figure 2.1. (a) Sundqvist et al.'s Data Profile for pine resin,¹³ and (b) Factor 4 displaying the source profile for pine resin as a result of the 127 by 83 data matrix. Similarities between the two profiles include 1,2,4,6,8-PeCDD as the dominant peak (although in our Factor 4 results, this peak is simultaneously coeluted with 1,2,4,7,9-PeCDD), followed by 1,2,3,6,8-PeCDD. Although the ratios of other peaks contain slight differences, both profiles also have a peak present at 1,2,3,7,9-PeCDD.

It was determined that the congener pattern similar to pine resin¹³ was the dominant contributor to six of the samples (1SPL02576 (collected from ST004 at the North River WPCF on 01-25-2001), 1SPL02665 (collected from ST011 at Jamaica WPCF on 02-15-2001), 1SPL02785 (collected from ST001 at Newtown Creek WPCF on 05-21-2001), 1SPL02400 (collected from ST007 at Owls Head WPCF on 08-23-2000), 1SPL02416 (collected from ST015 at Tallman Island WPCF on 09-06-2000), and 1SPL02527 (collected from ST024 at Poughkeepsie (C) WPCF on 12-05-2000), all of which were obtained from WPCFs). The PCDD/F fingerprint thought to be associated with pine resin was rich in 1,2,4,6,8/1,2,4,7,9-PeCDD, 1,2,3,6,8-PeCDD, and 1,2,3,7,9-PeCDD. Therefore these six samples and four more that were not well explained by the model were removed from the data matrix. Furthermore, it was found that OCDD did not disproportionately skew the PMF results, so it was added back into the PMF matrices. This yielded a final data set of matrices with dimensions of 117 by 84, which was subsequently analyzed via the PMF program.

2.3. Results

2.3.1. Selection of the correct number of factors

Four factors were resolved from this data matrix of 117 samples and 84 congeners. The criteria for selection of the four factor model followed the criteria outlined above.

Criteria 1: The RSD of the G matrix when 3 or 4 factors were requested was below 10% (Table 2.2), indicating that the model was stable in these particular conditions. When

more than four factors were requested, however, the model solution became unstable with an RSD value of the G matrix of greater than 80%.

Criteria 2: A multiple linear regression (MLR) of the G matrix versus the measured sum of analytes in each sample was performed. The 6-factor model contained one negative coefficient, and the majority of the coefficients possessed insignificant p values. The 5-factor model contained all positive coefficients, however the majority of them were not significant. For the 4-factor model, one of the coefficients was negative, but it was simultaneously the only value considered to be insignificant. Lastly, for the 3-factor model, all coefficients were positive but most were insignificant. Out of the 3- to 6-factor models which were obtained from the PMF results (and especially when deciding between the 3- and 4-factor models as a result of Criteria 1 above), it seems that the 4-factor model is the most plausible candidate or factor that may contribute significantly to the model solution.

Table 2.2. Resulting Q Plot for Factors 3-6.

Number of Factors	Theoretical Q	Actual Q	RSD G
3	9225	10436.18	0.2%
4	9024	8724.23	0.4%
5	8823	8013.071	85.1%
6	8622	7303.503	83.3%

Criteria 3: The G-space plots indicated that the factors of the four factor model were independent of each other. Once the top 10 most concentrated samples were removed

from the master data set, the G-space plots displayed no correlation between the measured and modeled concentrations (i.e. they were not dependent on each other).

Criteria 4: The four factor model was able to reproduce the measured data as illustrated in Figure 2.2. There is a large improvement in the model fit for 1,2,3,7/1,2,3,8-TCDD when moving from the three-factor to the four-factor model. When comparing the five-factor model to the four-factor model, it is evident that the model fit for several of the pentadioxin homologues is better with the latter four-factor model.

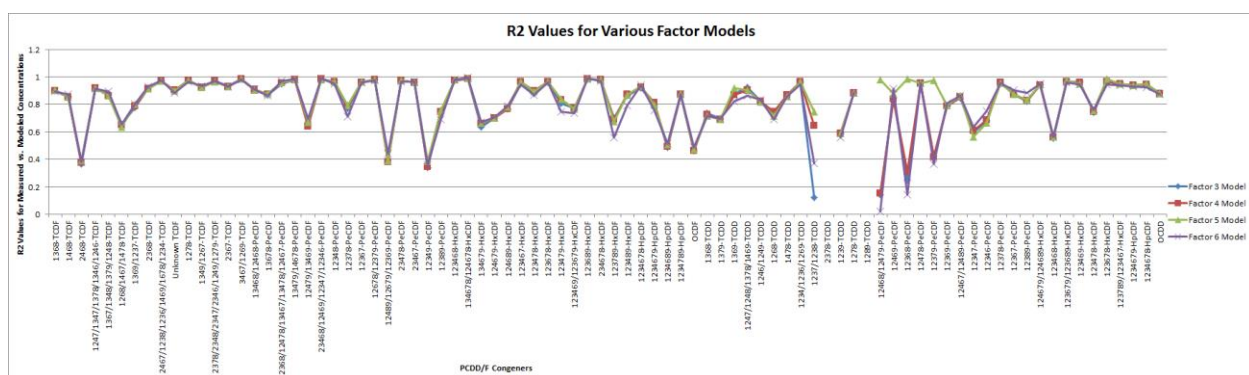


Figure 2.2. R^2 values for factor models 3 through 6. Congeners 2,3,7,8-TCDD and 1,2,8,9-TCDD were not included in this figure because they were not well represented by the PMF model.

For the four factor model, the R^2 values of the measured versus modeled concentrations were greater than 0.8 for 53 of the 84 congeners. The R^2 was greater than 0.6 for another eighteen congeners. Ten congeners displayed R^2 values less than 0.6: 2,4,6,8-TCDF (0.376), 1,2,4,8,9/1,2,6,7,9/1,2,3,6,9-PeCDF (0.379), 1,2,3,4,9-PeCDF (0.344), 1,2,3,4,6,8,9-HpCDF (0.492), OCDF (0.462), 1,2,3,9-TCDD (0.588), 1,2,4,6,8/1,2,4,7,9-

PeCDD (0.158), 1,2,3,6,8-PeCDD (0.310), 1,2,3,7,9-PeCDD (0.416), and 1,2,3,4,6,8-HxCDD (0.558).

Criteria 5: The results of the four factor model were physically meaningful and interpretable, as described below.

2.3.2. Interpretation of the resolved factors

The four PCDD/F source fingerprints resulting from the final PMF run are shown in Figure 2.4, where the 2,3,7,8-substituted congeners are highlighted in red. The contribution of each factor is presented four ways in figure 2.3: the contribution to the total mass, the total mass excluding OCDD (which by itself accounted for 92% of the mass of the total output), the mass of the 2,3,7,8-substituted congeners, and the TEQ. Factor 4, which is dominated by OCDD, accounts for the largest share of mass from all four viewpoints. Factor 1 explains only a small fraction of the total mass but makes a relatively large contribution to the total TEQ. Factors 2 and 3 likewise make a small contribution to total mass, but they contain a large proportion of all of the 2,3,7,8-substituted congeners.

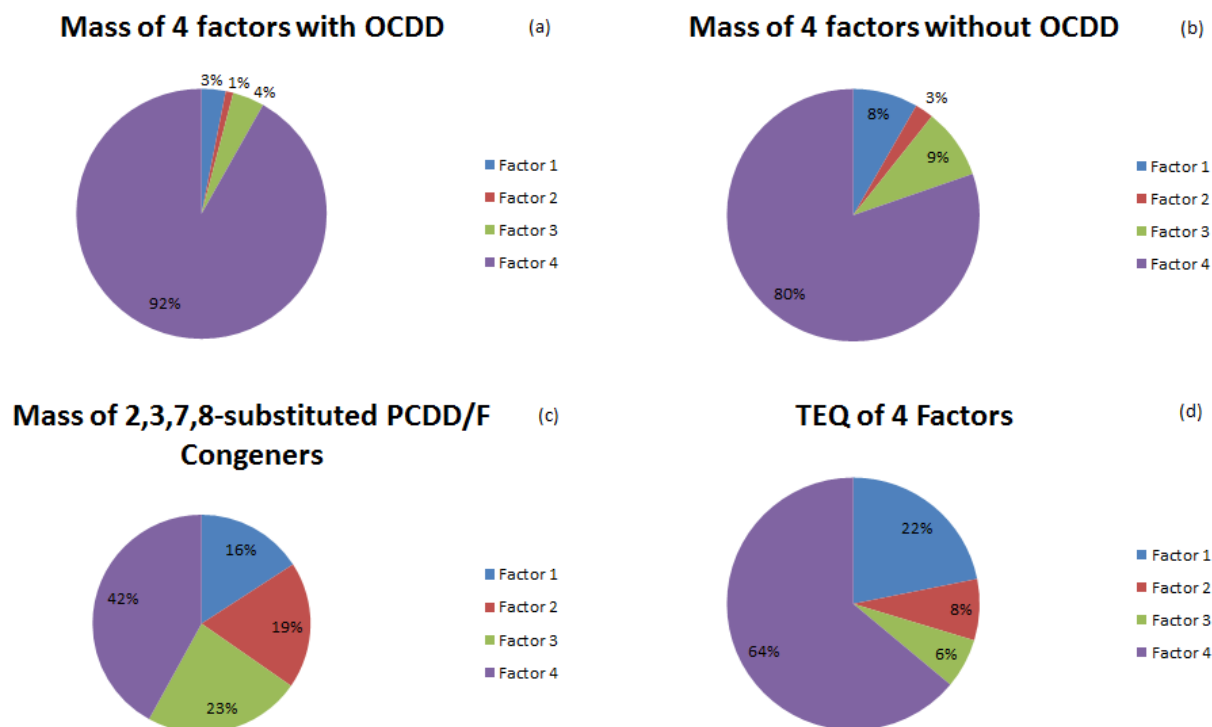


Figure 2.3. Percentages within data set of (a) mass of each factor with OCDD, (b) mass of each factor excluding OCDD, (c) mass of each factor when examining 2,3,7,8-substituted PCDD/Fs exclusively, and (d) each factor's contribution to overall TEQ.

Associating the various factors with specific sources or source types is complicated by the fact that very few published studies have measured all of the PCDD/F congeners (most measure only the 2,3,7,8-congeners).^{3,12,13} These previous studies were used to aid our identification of factors wherever possible, keeping in mind that they were often obtained in different geographic locations and sometimes used different analytical methodologies producing different coelution patterns that can complicate comparisons across data sets. In addition, the 2,3,7,8-congener patterns associated with many types of PCDD/F sources published by the US EPA¹⁴ were used to identify sources.

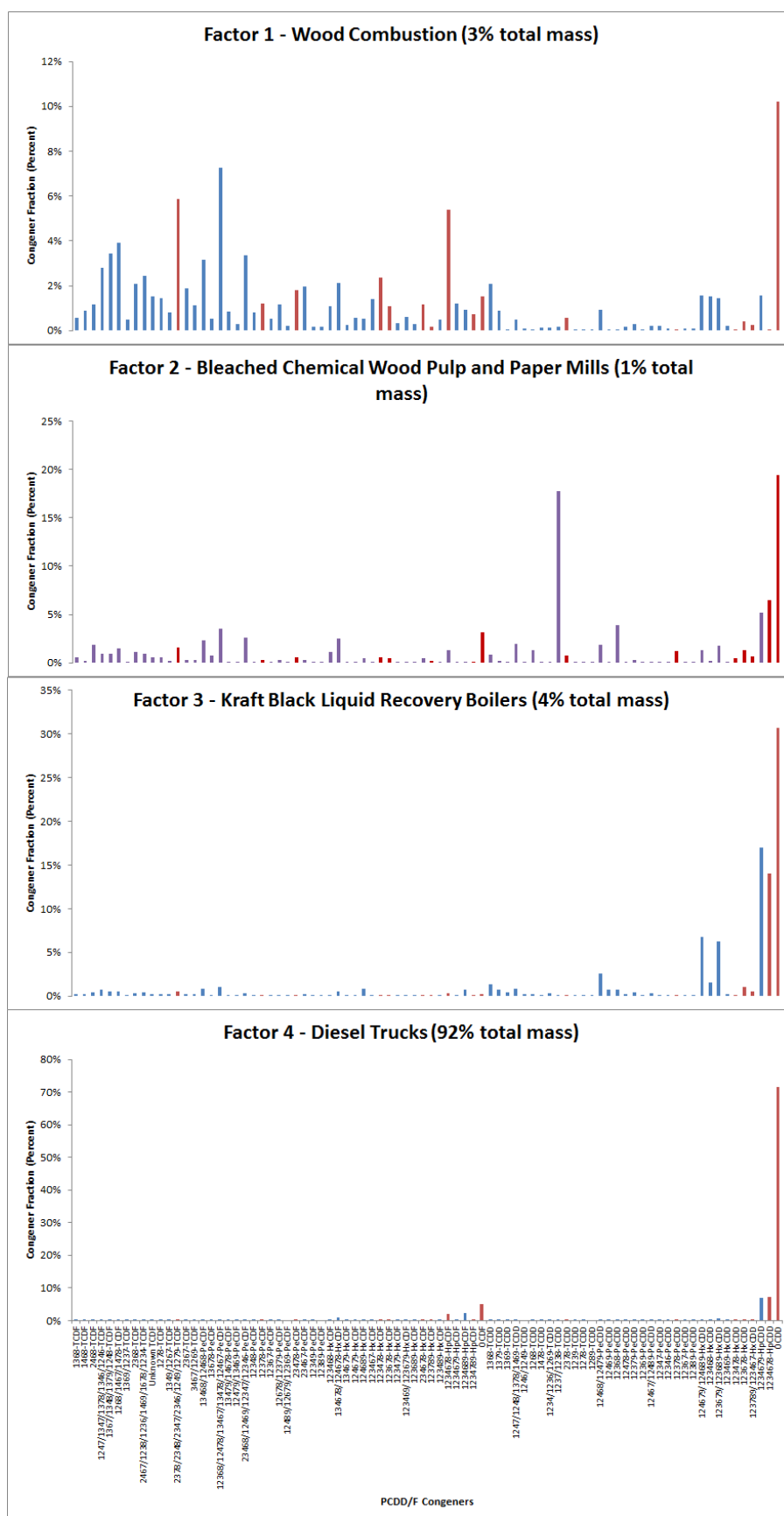


Figure 2.4. Congener fingerprints of the four factors resolved from the final PMF analysis. 2,3,7,8-congeners are highlighted in red.

2.3.3. Factor 4

Factor 4, which is by far the largest mass in the data set at 92%, is probably associated with motor vehicle emissions. The 2,3,7,8-congener pattern of this factor resembles the EPA's published pattern for diesel trucks (Figure 2.5). For instance, in both the EPA diesel truck signature and factor 2, OCDD is extremely abundant: it comprises 65% of the profile mass in the former and 72% of the profile mass in the latter. This is followed by 1,2,3,4,6,7,8-HpCDD, which is 14% of the mass of the EPA diesel emissions and 7% of the mass in our generated profile. OCDF is also a small peak (4% in the EPA data and 5% in the Factor 4 profile), followed by 1,2,3,4,6,7,8-HpCDF (4% in the EPA profile and 1.9% in Factor 4). The remaining congeners are present in extremely small amounts which are similar to each other.

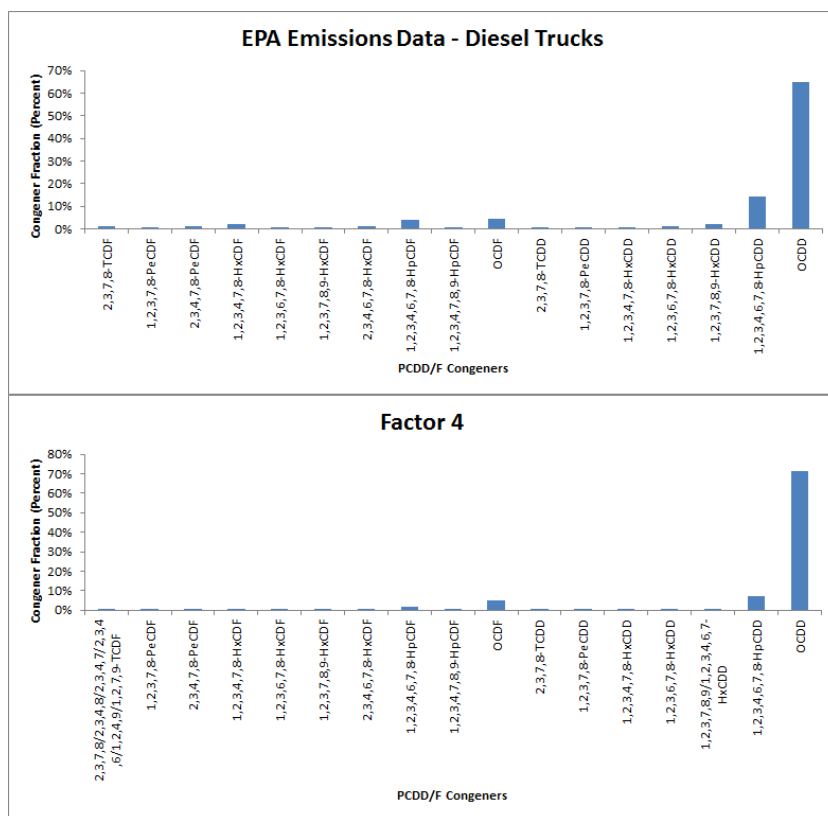


Figure 2.5. (a) EPA Emissions Data Profile for diesel trucks¹⁴, and (b) Factor 4.

In addition, Figure 2.6 illustrates the correlations between factor 4 and the EPA emissions relevant to all motor vehicles. Diesel trucks display the highest R^2 when compared to factor 4, with a value of 0.994. (It should be noted however, that in our data set, 1,2,3,4,7,8,9- HpCDF coelutes with 1,2,3,4,6,7-HpCDF. In the EPA emissions profiles, 1,2,3,4,7,8,9-HpCDF is resolved separately.) This could be attributed to specific characteristics of the region, such as greater urbanization.

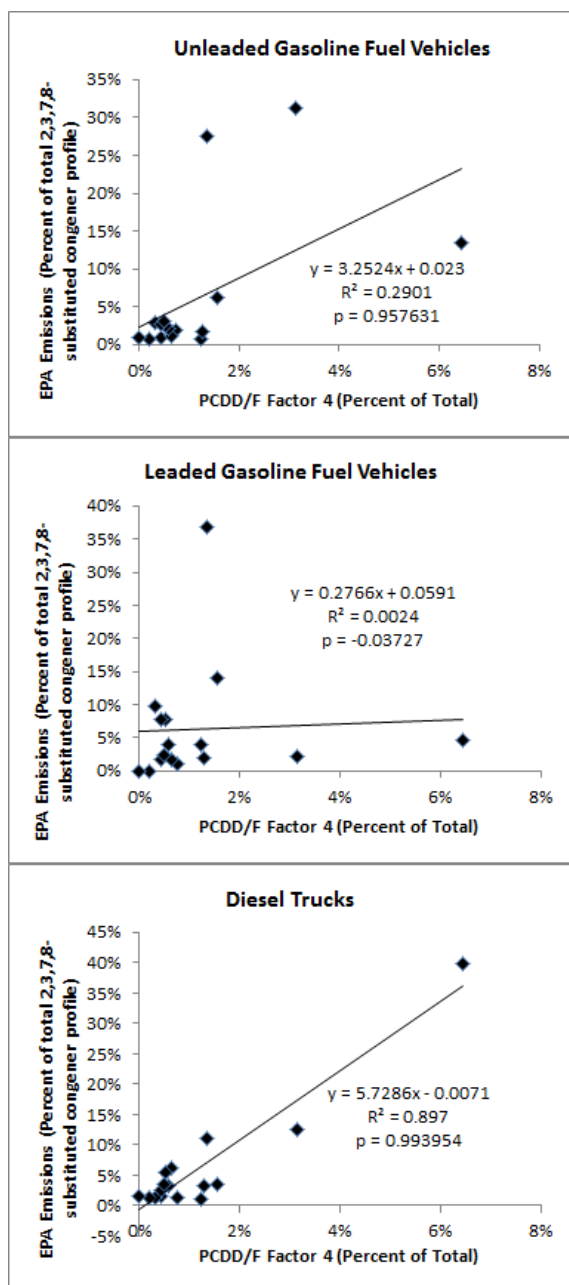


Figure 2.6. Correlations between PCDD/F factor 4 and EPA fingerprints/emissions¹⁴ associated with vehicles of all types.

The assignment of Factor 4 as motor vehicle emissions is sensible, since an earlier assessment suggested that combustion sources are the dominant sources of PCDD/Fs in the New York/New Jersey Harbor. This area is located in one of the most densely

populated, largest metropolitan areas in the United States. Vehicle emissions are typically more concentrated in urban regions with dense populations.¹⁵ Uncontrolled burning is known to be an important source of PCDD/Fs across the US. However, in New Jersey open burning has been banned by law for many years. New York State passed an open-burn ban in 2009, after the CARP data was collected. However, open burning was banned in most urban areas of NY before the time of CARP data collection. Furthermore, accidental fires (both garbage-related and structural fires) may also factor into this uncontrolled burning source.¹⁵

2.3.4. Factor 3

Factor 3 was the second largest mass at 4% within the data set and the most difficult to identify, because it did not match other congener profiles found in the literature to a great degree. However, it bears some resemblance to the EPA 2,3,7,8-congener profile for emissions from Kraft Black Liquid Recovery Boilers (Figure 2.7). In both factor profiles, OCDD is by far the most abundant congener, appearing with a mass of 73% in the EPA emissions profile and 31% in the generated factor profile. The next common most prevalent congener found in both profiles was 1,2,3,4,5,7,8-HpCDD, which was 8% of the mass in the EPA data and 14% of the mass in the Factor 3 profile. It should be noted, however, that the EPA source profile for Kraft Black Liquid Recovery Boilers contains 8% OCDF, whereas the amount of OCDF in Factor 3 is 0%. Aside from the difference in the mass of OCDF, the amount of the remainder of the congeners in both factor profiles was little to none.

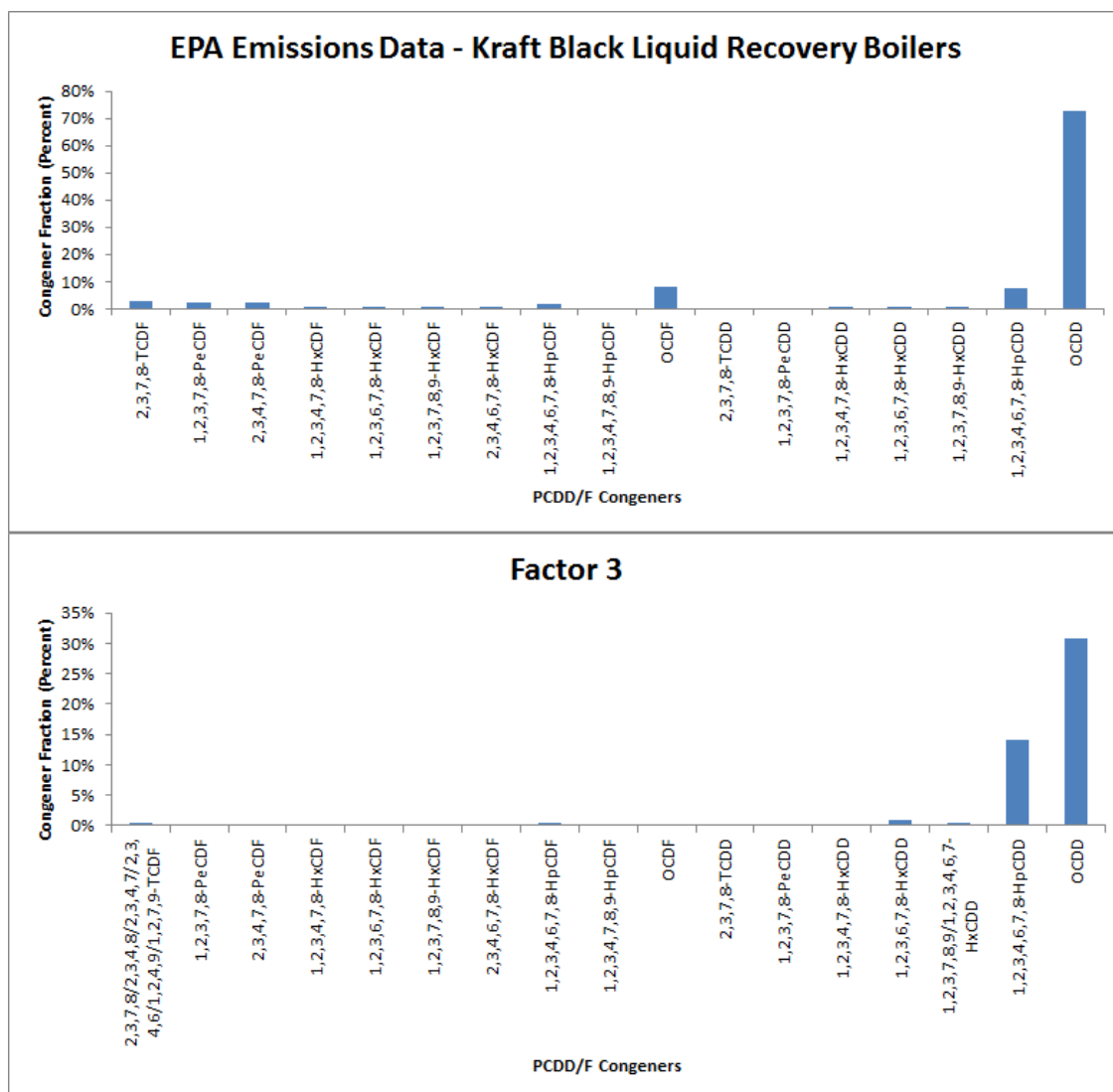


Figure 2.7. (a) EPA Emissions Data Profile for Kraft Black Liquid Recovery Boilers,¹⁴ and (b) Factor 3.

Instead of the paper production process as described in Factor 2, Factor 3 focuses specifically on the recovery boilers, which are used to recycle pulping chemicals, within the Kraft process of pulping. Black liquor is the waste sludge from the paper pulping process,²¹ consisting of a mixture of pulping chemicals, water, and wood biomass.²² It is burned in recovery boilers in order to generate heat and electricity for the paper plant.

Typically, concentrated black liquor accumulates massive ash deposits on heat-transfer surfaces.²¹ Concentrations of fly ash in flue gas may range from 10-15 g/Nm.²³

Additionally, recovery boilers are also able to be used to destroy other waste products such as gases from the pulping process or sludge from biological water treatment.²¹

The NJ/NY Harbor Watershed contains 36 paper and pulp mills, with 14 of them located in NJ and 22 located in NY. Factor 3 is particularly dominant amongst landfill samples collected within the data set. The waste products produced by the Kraft process in the recovery boilers are often disposed of directly into landfills. For instance, in the United States, nearly 51% of sludge from paper mills is disposed of in surface impoundments such as landfills¹⁵, and fly ash is also disposed of in landfills.^{21, 23}

Initially, it was assumed that it was possible that Factor 3 may be associated with dechlorination, because its congener pattern is unique in that the amount of 1,2,3,4,6,7,9-HpCDD is larger than that of 1,2,3,4,6,7,8-HpCDD. This could have potentially meant either that (1) dechlorination of OCDD occurs at the lateral position such that less 1,2,3,4,6,7,8-HpCDD is produced, or (2) peri dechlorination of OCDD does produce 1,2,3,4,6,7,8-HpCDD, but it is subsequently rapidly dechlorinated. Under option 2, if 1,2,3,4,6,7,8-HpCDD were further dechlorinated at the peri positions, several 2,3,7,8-substituted CDDs would be formed, but these were less pronounced (fewer red bars in figure 2.4). However, no 2,3,7,8-TCDD is observed in Factor 3 (although it should be noted that 2,3,7,8-TCDD is one of the species that was not well represented by the PMF model, so this may not be credited with too much meaning). Under option 1, which

could have been a possibility, lateral dechlorination of OCDD produces 1,2,3,4,6,7,9-HpCDD, and all subsequent dechlorination products are not 2,3,7,8-substituted. Under both scenarios, little or no 2,3,7,8-substituted CDDs accumulate, and as a result toxicity associated with CDDs is reduced.

If factor 3 represented the dechlorination of PCDD/Fs, we would expect that it would be most abundant in samples in which the PCB dechlorination signal was also the most pronounced, especially considering that bacterial strains which are capable of dechlorinating PCBs are also capable of dechlorinating PCDD/Fs.²⁵⁻²⁷ A previous study which used PMF to examine the dechlorination of PCBs within the CARP data set in addition to a data set obtained from the Delaware River Basin Commission (DRBC) suggested the presence of two different PCB dechlorination signals (figure 2.8). One was an “advanced” dechlorination signal, characterized by the dominance of PCB 4 (2,2'-dichlorobiphenyl), which typically indicated that dechlorination had gone to completion. The other was a “partial” dechlorination signal, since it was dominated by two coeluting groups of tetrachlorinated congeners: PCBs 44+47+65 and 45+51.²

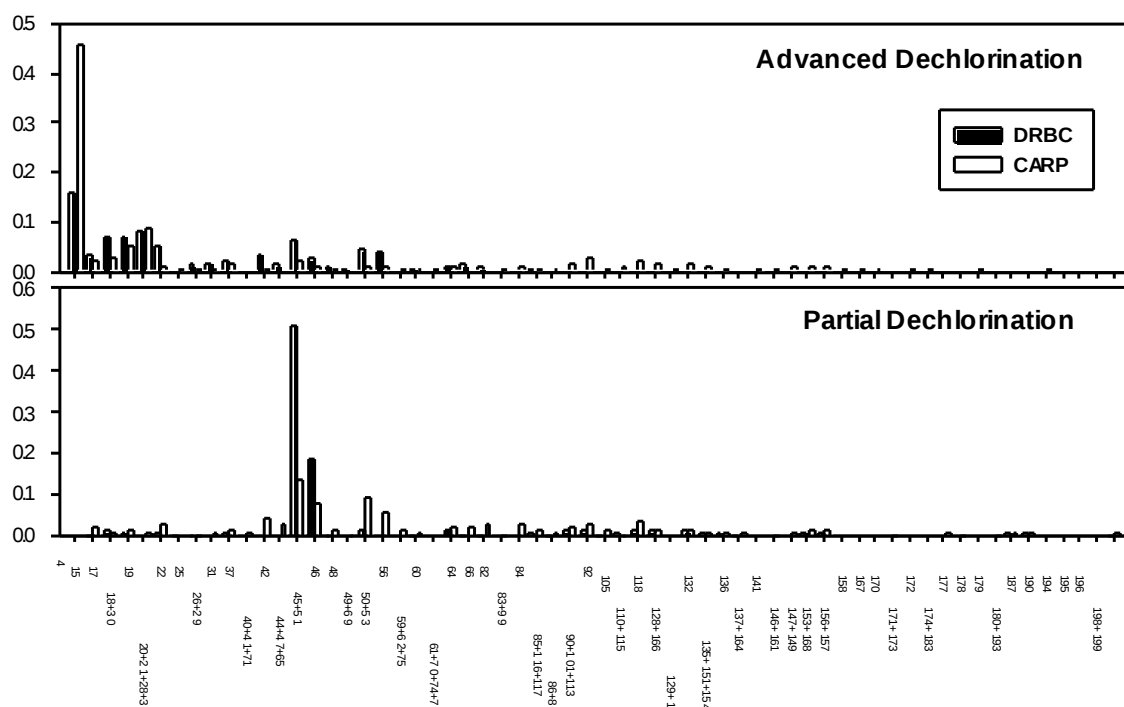


Figure 2.8. Comparison of the advanced and partial dechlorination factors isolated from the DRBC and CARP databases.²

To test this, we compared the abundance of factor 3 to the abundance of the PCB dechlorination signals (advanced, partial, and the sum of the two) in the subset of samples that were included in our original examination of PCB dechlorination.² This was done two ways. In the first, the factors were expressed as a percent of total concentration in the sample. In the second, the percent of total concentration was used to calculate the rank order and a Pearson's rank order correlation was performed. These correlations yielded no evidence that Factor 3 could represent a dechlorination signal. For the correlation on a percent of total concentration basis, the best correlation ($R^2 = 0.47$) is between factor 3 and the sum of the partial and advanced PCB dechlorination factors.

This correlation is significant only when samples from the Fresh Kills Landfill are included. If factor 3 represented microbial dechlorination, we would expect it to be abundant in samples of wastewater influent and effluent as well.

Previous research indicated that PCBs are extensively dechlorinated both in sewers and landfills,² therefore it would be likely that evidence of PCDD/F dechlorination would display similar patterns. Both sewers and landfills display several characteristics suitable for the existence of thriving anaerobic bacteria colonies which could be responsible for the dechlorination of PCBs and PCDD/Fs: they maintain high temperatures year round, they are anaerobic, and they are continuously fed with carbon and nutrients.

Furthermore, although wastewater in sewers may have a residence time of only days to months, solids reside in sewers for many years. Since PCBs and PCDD/Fs are strongly hydrophobic, most of their mass in sewers is expected to sorb to these sediments, allowing time for the relatively slow process of bacterial reductive dehalogenation to proceed. Similarly, PCDD/Fs and PCBs sorb to solids in landfills and have very long residence times.^{2, 25-27}

When the correlation between factor 3 and the PCB dechlorination signal is examined on a rank-order basis, the coefficient is negative, providing further evidence that the two are independent of each other. In fact, when examining correlations between the PCB dechlorination signal in comparison to all of the factor profiles generated within the results of this study, it was determined that the highest correlation was between factor 2 and the partial PCB dechlorination signal (figure 2.9b). However, even in that case, the

correlation was particularly low, with an R^2 value of approximately 0.29. Overall, then, there is no compelling evidence that factor 3 represents the microbial dechlorination of PCDD/Fs.

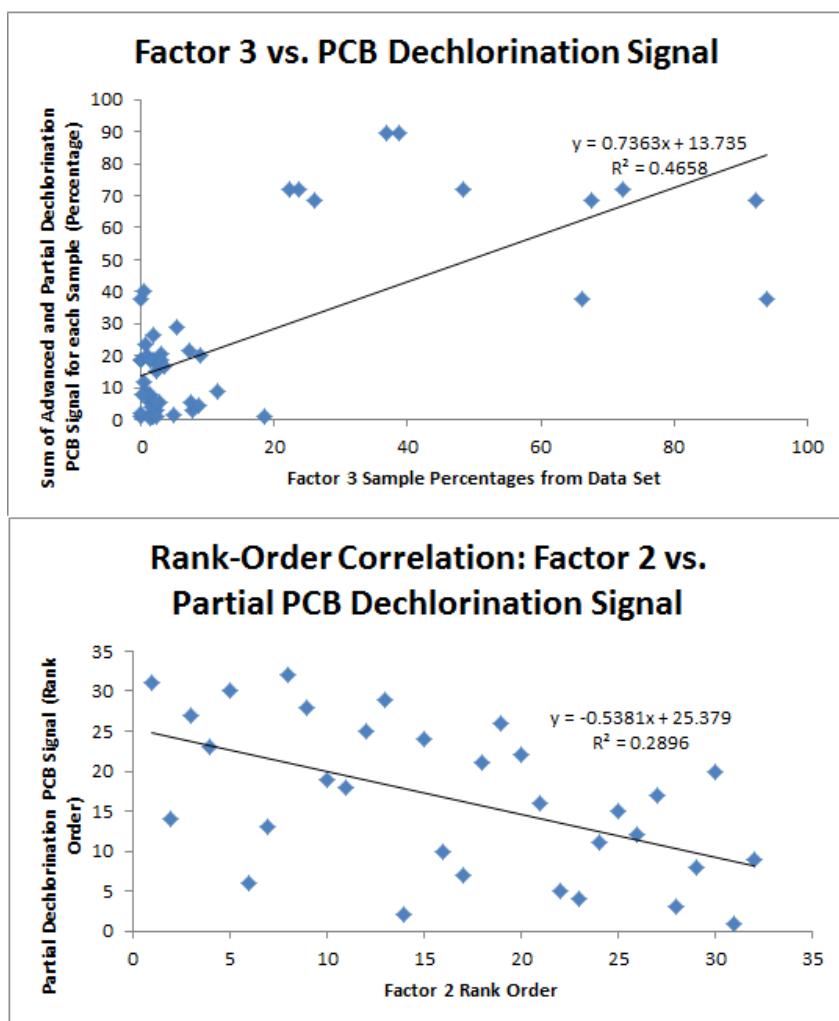


Figure 2.9. (a) represents the correlation between Factor 3 data set percentages and the sum of the advanced and partial PCB dechlorination signal, and (b) represents the rank-order correlation between Factor 2 and the partial PCB dechlorination signal. Both of these figures contain the correlations with the highest R^2 values of their respective data sets.

2.3.5. Factor 1

Factor 1, which represented the third largest mass of the data set (approximately 3% of the mass of all congeners within the PMF output), is likely associated with emissions from wood combustion. EPA's published pattern for these emissions (Figure 2.10) presents numerous similarities with the 2,3,7,8-congener pattern of this factor. In both of the profiles displayed below, common patterns emerge: OCDD is by far the most abundant peak, presenting itself at 10% in the Factor 1 profile and at 36% in the EPA Emissions profile. This was followed by 1,2,3,4,6,7,8-HpCDF which was present at 5.4% in the generated factor profile and 11% in the EPA data set. OCDF is also a prominent peak at 2% in our Factor 1 data and at 7% in the EPA wood burning emissions data (although it should be noted that in the latter profile, it is the fourth most abundant peak only by a small amount).

Furthermore, although there are slight variations in the congener profiles (such as the lack of 1,2,3,4,6,7,8-HpCDD in the resulting Factor 1 profile), the presence of dioxin congeners (with the exception of OCDD) are generally far less than that of the furan congeners in both of the profiles. It should also be noted that the 2,3,7,8-TCDF peak is higher in the PMF factor profile than in the one generated from the EPA emissions data, probably because 2,3,7,8-TCDF coelutes with several other TCDF congeners in this dataset.

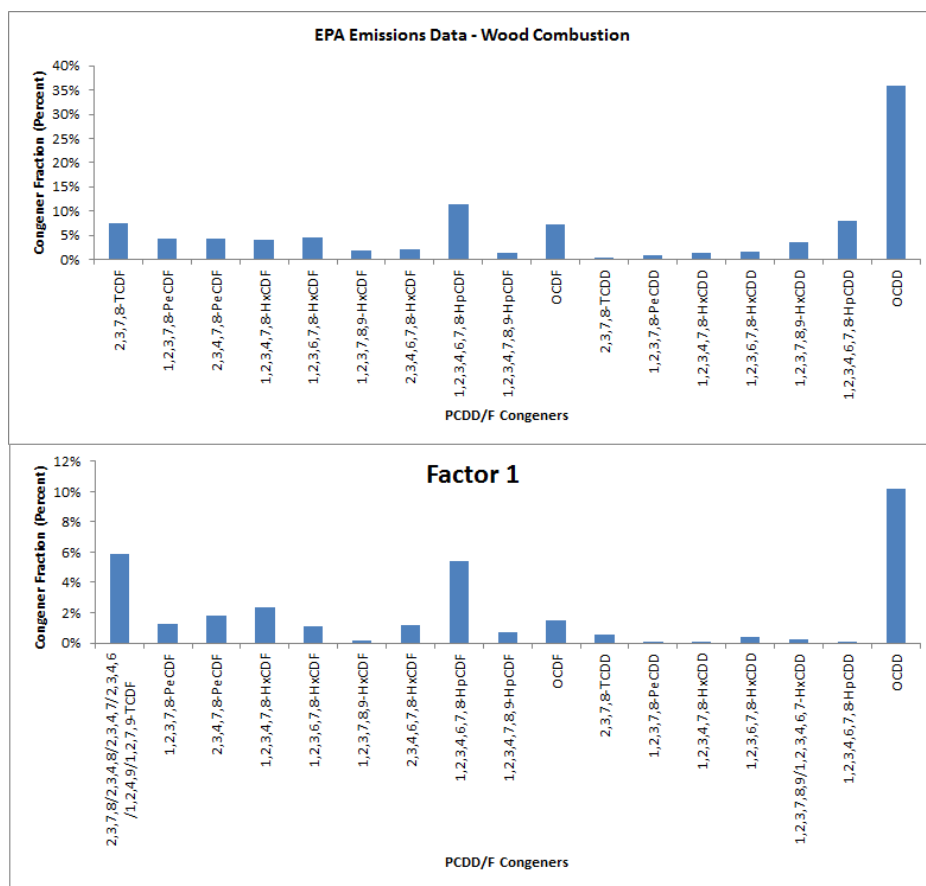


Figure 2.10. (a) EPA Emissions Data Profile for wood combustion,¹⁴ and (b) Factor 1.

Wood combustion from commercial, industrial, and power generating facilities is the largest combustion process, aside from landfill gas combustion and flaring, that releases dioxins into the atmosphere. Wood is burned to produce heat, steam, or electricity. 80% of wood combusted in the United States in 2000 was produced by the industrial sector, largely in the form of paper, lumber, and wood production.¹⁵ In NY and NJ, only untreated, unpainted, and uncontaminated clean wood is permitted for burning because it emits the lowest amount of dioxins. Additionally, salt-laden wood is not burned in this region.¹⁸ The New York Academy of Sciences conducted a thorough review of PCDD/F sources in the NY/NJ Harbor area in 2006. Here, it was determined that out of the wood-

burning facilities operating in NY during the CARP sampling period, the three largest facilities (accounting for approximately half of all wood burned by industrial, power plant, and commercial facilities in NY) are located outside of the Watershed region.¹⁵

Although the type of wood obtained and the type of furnace or boiler used for combustion alter the amount of emissions, it has been generally shown that clean wood releases 0.026-5.1 ng I-TEQ/kg both in the presence and absence of pollution control devices throughout a variety of combustors.¹⁵ Furthermore, minor wood combustion sources within this particular region also include emissions from outdoor boilers.¹⁸

An estimated 1.3-2.3 million T of wood is burned annually in the NY and NJ region, with approximately 50% of this occurring within the Watershed, based upon population distribution. Under the assumption that all the burned wood is definitely clean, total atmospheric emissions are estimated to be 0.01-5 g TEQ/yr, enough to be important to the local atmosphere.¹⁴ It is moderately likely that emissions reach the Harbor because of their proximity to the wood burning source.

Within the PMF output data, it was found that Factor 1 emissions were dominant in storm water samples. In an urban environment, where greater amounts of wood combustion may occur within a concentrated area, there is widespread distribution of dioxins and furans in the atmosphere.¹⁹ Through deposition of such particles, these compounds are found in soils and sediments at low levels in the region. Through wet and dry deposition, dioxins and furans become components of urban runoff through stormwater outfalls

which enter streams, estuaries, and rivers.²⁰ Emissions from wood combustion are also likely to accumulate in larger amounts during the winter, before the snow melt washes off into various storm water collection systems such as storm drains.¹⁹

2.3.6. Factor 2

Factor 2, which represents the smallest mass of 1% within the data set, is likely associated with emissions from the paper industry. The 2,3,7,8-congener pattern of this factor resembles the EPA's published pattern for bleached chemical wood pulp and paper mills (Figure 2.11). OCDD is by far the most abundant peak in both the EPA profile and in Factor 2, consisting of 85% of the mass of the factor profile in the former and 19% mass in the latter. The remaining peaks which are of prominence are 1,2,3,4,6,7,8-HpCDD (5% in the EPA emissions profile and 6.5% in Factor 2), OCDF (5% in the EPA factor profile, 3% in Factor 2), and 2,3,7,8-TCDF (3% in the EPA emissions profile, 2% in the coeluted version in Factor 2). The remainder of the peaks in both profiles are either very small or nonexistent.

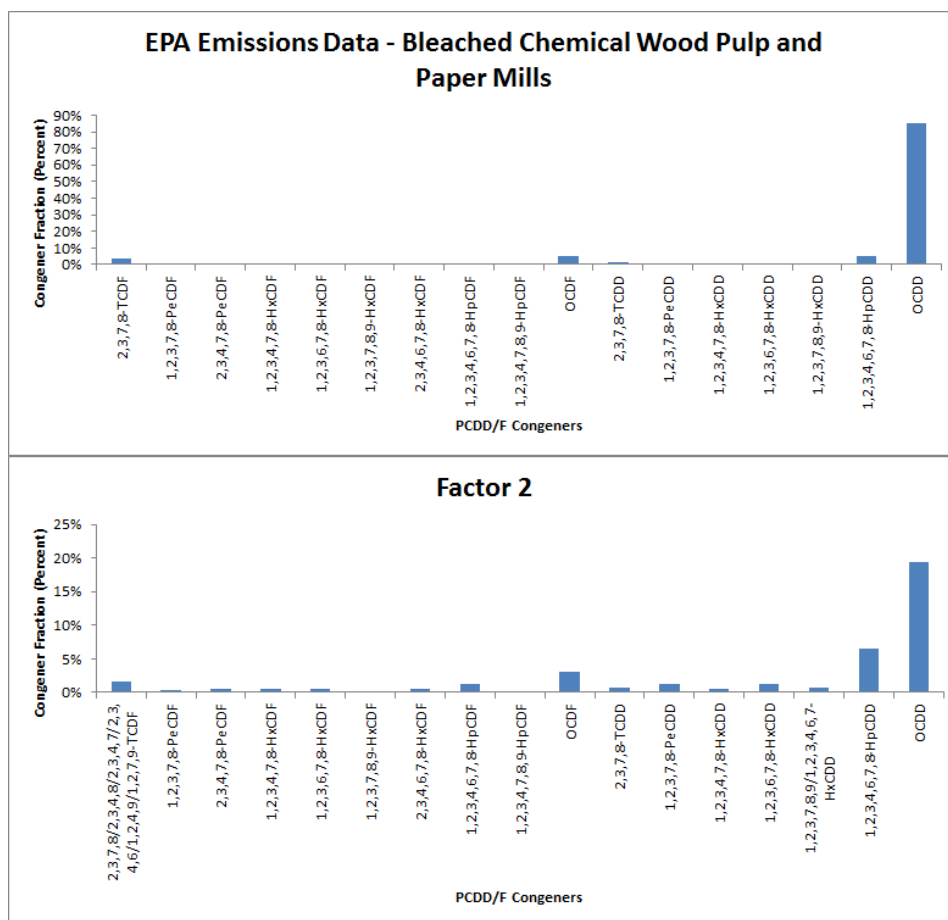


Figure 2.11. (a) EPA Emissions Data Profile for bleached chemical wood pulp and paper mills,¹⁴ and (b) Factor 2.

The paper production process is broken down into several different steps: pulping, washing the pulp, and then bleaching the pulp. The first step, pulping, involves the removal and separation of lignin from cellulose. Lignin is the fiber that binds cellulose wood fibers together. This initial process is typically conducted chemically with various chlorinated compounds via the usage of sulfite or Kraft processes. Next, during the pulp-washing process, the pulp is passed through a series of washers and screens at high temperatures. The resulting liquid contains lignin and the chemicals from the pulping

process, and it is separated from the pulp itself. Finally, the resulting brown pulp product is then bleached in order to produce a white paper product.²⁴

When bleaching with various chlorinated and chlorine-derived chemicals, the likely source of dioxins is due largely to the chlorination of lignin in the initial pulping step. These dioxins are then “found in the bleached pulp (and subsequently in the paper products), sludge, and wastewater effluents”.¹⁵ The amount of dioxins released from bleached pulp in the Watershed is estimated to be approximately 0.006 g TEQ/year. Specifically in New Jersey, discharged waste from paper and pulp mills is directed to Water Pollution Control Facilities, and there are no bleaching mills located within the state.¹⁵ This properly aligns with the corresponding data from the PMF results, because the dominant samples within Factor 2 were prominent amongst WPCFs.

2.4. Conclusions

The crux of what this chapter attempted to achieve was an understanding of both where PCDD/F emissions into the Harbor were generated from as well as how they had arrived to the study site from these sources. However, the aforementioned PMF results were unsuccessful since it was determined that they did not align with the major dioxin sources into the NY/NJ Harbor as represented by the NYAS Report. The top four dioxin emissions sources (in order of abundance from greatest to least) were: PCP-treated wood disposal (483 g TEQ/yr), open burning of residential waste (NY only) (30-173 g TEQ/yr), municipal solid waste incinerators (30-130 g TEQ/yr), and medical waste incinerators (2 g TEQ/yr).¹⁵

One possible explanation for this discrepancy in the comparison of results is that the number of published sources for PMF dioxin emissions profiles was extremely limited. In this particular study, the results from the final successful run which we presented in each corresponding factor subsection above were all compared with one source: the EPA emissions profiles. This lack of available comparable literature alternatives particularly caused confusion in between factors 2 and 3 being attributed to different steps in the paper-making process instead of being identified as two completely separate non-overlapping sources. Justifications for these results needed to be made even if they were not correct in hindsight.

To ensure a more accurate set of results, comparison with a wider pool of literature would be necessary. In addition, even with the available published literature, it was difficult to match up PMF factor source profiles from various studies, primarily because environmental conditions are almost never the same from one geographic location to another, depending on temperature, climate, and so on. Furthermore, the y-axes on the resolved factor profiles for this chapter were not identical with those of the EPA emissions – rather, the percentages and patterns which were observed were relative amounts and peaks as opposed to exact matches. Efforts were not made to renormalize the figures because past literature had not taken this approach either.

Additionally, it should also be noted that although various versions of programs which conduct PMF exist, the PMF2 program which was designed by Paatero and Tapper¹⁰ was the one we selected to use for this project. With version PMF 5.0, which was developed

by the Environmental Protection Agency, PMF runs would either converge or fail to do so completely. This latter option, which occurred frequently with our PMF input data set, resulted in no output whatsoever. With PMF2, however, a solution was always given which could be determined by the program user through his or her own judgement.

One point which this study fails to address is the question of whether matching emissions data with our factor source profiles is even the correct method to study dechlorination in PCDD/Fs. Several problems with this approach arise, namely with the reality that the CARP data is a snapshot in time of collected samples. Therefore, the data set is unable to show transformation occurring by microbes – rather, it illustrates what has happened instead of showcasing a time-lapsed series of data illustrating what could happen. While information about when and where the samples were collected is provided in the database, it is a disadvantage to not know the length of time which the PCDD/Fs have actually been present in the sediments or sample area from which they were obtained because the dechlorination process is pushed forward through time. This point also implies that it is possible that evidence of further dechlorination may have been apparent if samples were only collected at a later date.

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Conclusion

The overall objective of this work was to determine if *peri-lateral* dechlorination of PCDD/Fs, which would yield non-toxic products, occurred in the New York/New Jersey Harbor watershed. Chapter 1 focused on trends in PCDD/F concentrations in certain watershed category areas. Results demonstrated that extensive *peri-lateral* dechlorination did not occur. However, with the amount that did occur, it was suggested that much of it was present in landfills and that the most toxic sample concentrations were found in CSOs or sewers. Chapter 2 used PMF analysis to determine the sources of this PCDD/F contamination in the watershed, however it was later found that the results did not correlate with published emissions of the greatest amounts of PCDD/Fs to the Harbor.

In order to achieve more meaningful results, several recommendations for future research can be made. For instance, obtaining a more comprehensive data set may have helped for Chapter 1. Information regarding the tetra- through octa- congeners were provided within the chromatograms, however data on the mono- through tri- PCDD/F congeners were not included. It is possible that additional *peri-lateral* dechlorination may have occurred elsewhere within the latter category without our knowledge.

For Chapter 2, it would be helpful to compare the PMF-generated factor source profiles to greater pool of published literature sources, if available. Currently, each of the four factor profiles was only successfully matched up with the 2,3,7,8 source profile published by EPA. This may or may not be possible depending on the amount of literature that might be available in the future.

Additionally, because a dechlorination signal specifically for PCBs had previously been published in existing literature,² it might be advisable to combine the data sets for both PCBs and PCDD/Fs before whittling them down and conducting the PMF analysis. This approach has been used to successfully identified PCDD/F dechlorination.^{1, 2} Although this would mean assembling much smaller matrices because of the limited number of samples for which PCB and PCDD/F data were both available, it would ensure for greater accuracy of results. PCBs and PCDD/Fs are structurally similar, and if PCB dechlorination signals have already been verified, it would provide a stronger set of data matrices for the PMF runs.

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