STUDY OF THE LOADINGS OF POLYCHLORINATED BIPHENYLS FROM TRIBUTARIES AND POINT SOURCES DISCHARGING TO THE TIDAL DELAWARE RIVER



### ESTUARY TOXICS MANAGEMENT PROGRAM DELAWARE RIVER BASIN COMMISSION WEST TRENTON, NEW JERSEY

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#### **EXECUTIVE SUMMARY**

Polychlorinated biphenyls (PCBs) have been detected at elevated levels in the sediments and tissues of resident and anadromous fish collected from the Delaware Estuary. Concern regarding these levels has resulted in the issuance of fish consumption advisories by three states covering the entire tidal Delaware River and Bay. The lack of comprehensive and reliable information concerning the sources of PCBs to the estuary and the associated transport pathways has hampered mitigation of the problem. This study focused on two classes of potential sources to the Delaware Estuary; namely, wastewater treatment plants and tributaries.

The results of separate dry weather and wet weather sampling events indicate that wastewater treatment plants and tributaries discharging to the tidal Delaware River are active and significant sources of PCB to the system. Mass loading was significantly greater (up to 60 times) during wet weather conditions than during dry weather conditions. During the wet weather sampling event, 88% to 95% of the PCB loading was associated with combined sewer overflows, with 4% to 9% of the loading contributed by the tributaries and 1% to 3% contributed by point sources. During the dry weather sampling event, point sources contributed  $\sim$  95% of the measured loading of PCBs to the tidal river, with the balance coming from tributary inflow. Independent of weather conditions, the vast majority of PCB loading to the estuary enters DRBC Zone 3, roughly encompassing the reach between the Tacony-Palmyra and Walt Whitman Bridges.

The findings noted above suggest that rainfall acts to significantly increase PCB mass loading to the estuary, presumably due to increased resuspension, erosion and transport of PCBs associated with contaminated upland sediments and/or PCBs associated with sediments otherwise settled out within sewage collection systems.

The study also demonstrates that the current fish contamination problem cannot be attributed solely or predominately to "historic" sediment contamination already in the estuary, as many resource managers have believed. Indeed, the active loading entering the estuary from treatment plants, CSOs, and tributaries is sufficient, independent of the PCB already in estuary sediments, to cause water quality criteria exceedances and associated fish contamination. Of course, treatment plants, CSOs, and tributaries are not original sources of PCBs. Rather, treatment plants and tributaries are merely acting as conduits for PCBs that have been inadvertently or deliberately introduced into sewage collection systems, eroded off of contaminated upland sites, and transported via overland flow into the collection systems and down through tributary watersheds. The treatment plants, in fact, act to significantly reduce the amount of PCB entering the estuary as evidenced by the much lower effluent concentrations in comparison to the influent concentrations. Presumably, much of the PCBs entering the treatment plants is being incorporated into biosolids (sludge), which in turn is then being redistributed back to the environment to an unknown extent. Actions to interrupt this cycle including the systematic identification of significant upland sources of PCBs, enhancement of the Commission's mathematical model of the estuary, and implementation of effective sediment and erosion control practices are recommended.

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#### **INTRODUCTION**

The draft Comprehensive Conservation and Management Plan for the Delaware Estuary Program identifies polychlorinated biphenyls (PCBs) as one of the pollutants of concern in the estuary (U.S. EPA, 1995). Several studies have documented the accumulation of these compounds in fish and shellfish from the Delaware Estuary (Greene and Miller, 1994; U.S. F&WS, 1991 and 1992; Hauge et al., 1990; DRBC, 1988). Pennsylvania, New Jersey, and Delaware, the three states that border the Estuary, have all issued fish consumption advisories based upon PCB contamination, and to a lesser degree, the chlorinated pesticides, DDX and chlordane.

In addition to the human health risks posed to individuals who consume contaminated fish, PCBs also represent an ecological risk to aquatic biota in the Estuary, particularly sediment-dwelling organisms. In a study performed for the Delaware Estuary Program, Costa and Sauer (1994) found that PCBs are far more widespread in sediments than previously indicated and that PCB levels in sediments exceeded the No Observed Effects Level (NOEL) for PCBs at 14 of 16 stations sampled with the highest concentrations measured between Chester, PA and Trenton, NJ. It is important to note that all 16 stations sampled in conjunction with this study were located in non-channel, shoal areas. More recent sampling performed by the U.S. Army Corps of Engineers in connection with the "main channel deepening" project revealed significantly lower levels of PCBs in main channel sediment samples from the estuary in comparison to adjacent shoal samples (Burton, 1997). The shoal areas are nevertheless far more extensive in terms of surface area, and are recognized as important ecological habitat. The higher levels of PCBs in the non-channel areas, the greater areal extent of these areas, and the food web interactions that are known to exist in these areas help to reaffirm the significance of the PCB problem in the estuary.

In order to develop an effective abatement strategy for PCBs in the Delaware estuary, it is important to first have a clear understanding of the factors that control the fate and transport of this contaminant. The figure on the following page presents a conceptual model of PCB movement and transformation in an aquatic system. As indicated in the figure, the concentration of PCB in the water, sediment, and biota of the estuary is a function of highly interconnected physical, chemical, and biological processes. The main processes include: external loading (e.g., treatment plant, CSO, surface runoff, and atmospheric inputs); internal transport (e.g., advection, dispersion, deposition, resuspension, deep burial, and bed load); transfer (e.g., adsorption, desorption, volatilization, diffusion, bioconcentration, and bioaccumulation); and reaction (e.g., decay). When the input rates exceed output and loss rates, concentrations within the system will rise. Eventually, the ability of the system to accommodate or assimilate the contaminant is exceeded and elevated levels are detected. Such is the case for the Delaware Estuary.

The conceptual model just discussed presents a macroscopic view of PCB movement and transformation. PCBs are presented in simple "lumped" terms as sorbed and dissolved chemical. In reality, PCBs are complex mixtures of 209 possible molecules, each having its own unique chemical, physical, and toxicological properties. These properties are, to a large degree, dependent on the number and positioning of chlorine atoms that are bonded to the biphenyl base structure common to all PCBs. As shown in the diagram below, there are ten possible locations on the biphenyl molecule where chlorine atoms may become bonded to biphenyl; these are designated by numbers 2 through 6 on one phenyl ring and 2' through 6' on the other ring. Positions 2, 6, 2', and 6' are also referred to as the ortho positions. If all combinations of chlorine positioning are considered, a total of 209 different PCB molecules (called congeners) are theoretically possible. Only about half of these are thermodynamically stable under normal

### PCBs in a Simple Aquatic Food Chain



environmental conditions. The International Union of Pure and Applied Chemistry (IUPAC) has assigned individual numbers from 1 to 209 to uniquely identify each of the possible PCB congeners.



In the synthesis of PCBs, the hydrogen atoms on the biphenyl molecule are successively substituted by chlorine atoms to yield a variety of compounds with different overall chlorine content. Commercial mixtures of PCBs, known by the trade name Aroclor, were sold based upon their overall level of chlorination. For instance, Aroclor 1254 indicated a PCB mixture with an overall chlorine content of 54%. Each Aroclor mixture contained a different blend of individual PCB congeners. It is now known that certain congeners in commercial PCB mixtures weather more rapidly than others upon release to the environment, resulting in PCB mixtures in the environment that are significantly different than the original product. Because traditional laboratory methods for PCBs rely upon chromatographic pattern matching between the environmental sample and pure Aroclor mixtures, it is not uncommon for laboratories to list PCBs as "non-detected" for severely weathered environmental samples, not because PCBs aren't present, but rather, because the pattern no longer resembles the Aroclor mixtures used as the standard of comparison (Schwartz et al, 1987).

The analytical problem just noted is believed to partially explain the results of a survey of 83 industrial and municipal point sources discharges conducted by the Commission in 1990 and 1991. In that survey, no PCBs were detected in wastewater treatment plant discharges. The survey was conducted using standard analytical methodology (Method 608) with a higher detection limit (e.g., 65 - 500 ng/L) than more sensitive, congener-specific techniques that have recently become available. The study described in this report relied upon the more modern techniques and focused on PCB loading from major wastewater treatment plants, tributaries, and combined sewer overflow. These inputs are depicted as green lines in the conceptual PCB model discussed previously.

The specific objectives of this study were to:

- 1. Identify those specific wastewater treatment plants and tributaries which are sources of PCBs for additional intensive monitoring by NPDES permittees and/or regulatory agencies.
- 2. Estimate mass loadings of PCBs during wet and dry ambient conditions, and determine the relative contribution of municipal wastewater treatment plants and tributaries as sources of PCBs to the tidal Delaware River.

This study was designed as a reconnaissance survey; the results of which could be used to direct additional monitoring and modeling studies, as well as source control activities. It is hoped that this study will eventually lead to a reduction in fish and sediment contamination in the Estuary and a lifting of the current fish consumption advisories.

#### **METHODS**

#### **Sample Collection**

Ten (10) tributaries, six (6) municipal wastewater treatment plants and one (1) industrial treatment plant were selected for sampling under wet and dry weather conditions. Figure 1 depicts the location of the tributaries and treatment plants selected for this study. Table 1 presents the longitude and latitude of each site sampled during the dry weather survey, along with the date and time of collection. Table 2 presents this same information for the wet weather survey. The longitude and latitude of all locations were determined with the aid of a hand held Global Positioning System (GPS). As indicated in Tables 1 and 2, the dry weather survey was conducted in August of 1996, and the wet weather survey was conducted in April and May of 1997.

Tributary sampling sites were selected based upon their relative flow contribution to the estuary and the likelihood of contamination by PCBs. To the extent feasible, the tributary sites were located in close proximity to existing USGS stream gages to allow for the direct computation of pollutant mass loading from measured streamflow and measured PCB concentration. The tributaries sampled are listed below along with their corresponding average flow for the years 1970 to 1995.

| Location   | Average Flow (m <sup>3</sup> /sec) |
|--|------------------------------------|
| Delaware River at Calhoun Street Bridge, Trenton | 204.11                             |
| Schuylkill River at Falls Bridge, Philadelphia   | 35.02                              |
| Upper Christina River at Route 72                | 0.28                               |
| Brandywine Creek at Wilmington                   | 8.46                               |
| Red Clay Creek at Stanton (Route 4)              | 1.13                               |
| White Clay Creek at Stanton                      | 2.02                               |
| Rancocas Creek at Centerton Road                 | 4.67                               |
| Crosswicks Creek at Groveville Road              | 2.30                               |
| Neshaminy Creek at Hulmville                     | 3.02                               |
| Raccoon Creek near Swedesboro                    | 0.74                               |

Grab samples were collected at the above locations when no rainfall had occurred within the previous 5 days, and at the same location no later than 48 hours following a rainfall event equaling or exceeding 0.5". Tributary locations in Delaware were sampled by staff from the Technical Services Section of the Delaware Department of Natural Resources & Environmental Control by immersing a sample bottle directly into the current flow. Other tributary locations were sampled by Commission staff using a 1.2 liter Kemmerer water bottle constructed of Teflon with a stainless steel trip head.

Wastewater samples were also collected under both wet and dry conditions at six NPDES municipal discharges that contribute the largest input of wastewater to the estuary. In addition, a dry weather sample

was collected from an industrial discharge that formally received PCB-contaminated wastewater from the pretreatment system for an onsite hazardous waste site. The facilities sampled, their location and design effluent flow were:

| Name   | Effluent Flow<br>(m <sup>3</sup> /sec) | Location<br>(River Mile) |
|--|--|--------------------------|
| City of Philadelphia Northeast Water Pollution Control Plant | 9.198                                  | 104.20                   |
| City of Philadelphia Southeast Water Pollution Control Plant | 5.241                                  | 96.70                    |
| City of Philadelphia Southwest Water Pollution Control Plant | 8.760                                  | 90.70                    |
| Camden County Municipal Utilities Authority                  | 3.504                                  | 97.93                    |
| Delaware County Regional Water Quality Control Authority     | 1.927                                  | 80.70                    |
| City of Wilmington Wastewater Treatment Plant                | 4.310                                  | 71.76                    |
| Monsanto Corporation   | 0.054                                  | 79.00                    |

During the dry weather survey, municipal wastewater samples were collected by the staff of the Annapolis Field Office, U.S. Environmental Protection Agency, Region III. During the wet weather survey, municipal wastewater samples were collected by personnel from Ogden Environmental and Energy Services, Inc. under contract to the Commission. The coordinates of each sampling location are listed in Table 1 and depicted in Figure 1. Table 1 contains the date and time that each sample was collected during the dry weather survey. Table 2 contains the date and time that each sample was collected during the wet weather survey.

Wastewater samples consisted of 24 hour composite samples of the final effluent from each municipal treatment during both wet and dry conditions, and 24 hour composite samples of the influent to each plant under wet weather conditions. All samplers were activated manually by field crews. During the wet weather survey, effluent samplers were activated after the influent samplers based upon the hydraulic retention time of the facility in an attempt to monitor the same parcel of water. The samples were collected using automated ISCO samplers equipped with Teflon tubing and stainless steel strainers. The strainers were positioned to sample near the mid-depth of the wastewater flow. The samplers were calibrated to sample every 60 minutes during both the dry and wet weather surveys. The wastewater from the industrial facility was sampled by Commission staff using a single grab sample.

Specific quality assurance procedures were employed to assess and account for possible PCB contamination associated with sampling equipment and laboratory sources. Sample bottles consisted of pre-cleaned I-Chem amber glass bottles with Teflon-lined caps supplied by the analytical laboratory. One liter bottles were used for all tributary samples as well as trip and equipment blanks. For wastewater samples collected using automatic samplers, 2.5 liter bottles were used directly in the samplers, eliminating the need for transfer from the bottles normally provided with the samplers. Trip blanks were provided by the analytical laboratory and carried by each field team during both the dry and wet weather surveys. These blanks consisted of reagent grade water provided by the laboratory in 1 liter sample bottles from the same batch used in the surveys. Equipment blanks were prepared by Commission staff by pouring reagent grade water provided by the laboratory into the Kemmerer sampler, and collecting the water directly from the sampler

into a 1 liter amber glass bottle. Equipment blanks were prepared by field crews at the municipal wastewater plants by pumping 1 liter of reagent grade water provided by the laboratory through the sampler and into a 1 liter amber glass bottle. No equipment blanks were needed by the DNREC field crew since the tributary samples collected in Delaware were obtained by directly submerging the sample bottle in the tributary flow without the aid of a sampling device.

All sampling equipment that came in contact with ambient or wastewater samples was decontaminated prior to use at each sampling location by rinsing first with methanol followed by methylene chloride, then another rinsing with methanol. Several deionized water rinses completed the decontamination procedure. This procedure was modified for the tubing used in the peristaltic pump in the ISCO samplers by eliminating the methylene chloride rinse.

Upon collection, samples were stored in a cooler packed with wet ice and generally returned to the respective offices of the sampling crew where they were stored in a refrigerator at  $4^{\circ}$ C until shipment to the analytical laboratory. Wastewater samples collected by EPA Region III staff were transferred to Commission staff shortly after collection and returned to the Commission's offices. Samples were shipped overnight to the analytical laboratory.

#### Laboratory Analysis

Sample analysis was performed by the Chemical Sciences Department of Midwest Research Institute (MRI) under contract to the Commission. All samples were received intact by the laboratory, and were extracted within the required 14 day holding time. Eighty-one (81) targeted PCB congeners were analyzed using High Resolution Gas Chromatography / High Resolution Mass Spectrometry (HRGC/HRMS) to achieve low nanogram per liter (parts per trillion) detection limits (Table 3). These particular congeners were selected based upon their coplanar chemical structure, their presence as principal components in commercial Aroclor mixtures, and their detection in previous monitoring conducted in the Estuary. Sample preparation, extraction, and analysis procedures used by the laboratory are discussed in detail in Section 2 of the Appendix. Briefly, quality assurance procedures included the use of method blanks, duplicate field and laboratory samples, matrix spikes and <sup>13</sup>Carbon-labeled PCB surrogates, and d<sub>6</sub> tetra-PCB internal standards. Carbon-13 labeled surrogates included congener numbers 3, 15, 47, 138, 202, and 209; representing the mono, di, tetra, hexa, octa and decachlorobiphenyls.

#### Adjustment of PCB Concentrations Based Upon Equipment and Blank Contamination

PCB congener data were reported by the laboratory for three different types of samples: ambient or wastewater samples, trip blanks, and equipment blanks. PCB results for collected samples may include contamination from the source being sampled, laboratory contamination, and/or contamination from the sampling equipment, if such equipment were used. PCB results for the trip blanks reflect contamination originating solely from the laboratory. Results for the equipment blanks reflect contamination that may be associated with the sampling equipment plus contamination that might have been in the laboratory water that was used to rinse the equipment and prepare the equipment blank. Contamination sources were minimized by having the analytical laboratory provide the water used in both the trip blanks and for preparing the equipment blanks.

In those situations where the source sample was collected with the aid of a sampling device, it was necessary to subtract out any contamination that may have been introduced into the sample bottle from the

sampling equipment and/or the laboratory water. This adjustment was made by subtracting the congenerspecific equipment blank result from the congener-specific sample result. The adjusted result thereby reflects PCB contamination solely attributable to the source being sampled, independent of contamination associated with the sampling equipment and/or laboratory water.

In those situations where the sample was collected directly into a bottle without the aid of a sampling device, the adjusted result for the sample was calculated by subtracting the appropriate trip blank result. Again, this adjustment was performed on a congener-by-congener basis.

#### **Estimation of PCB Loading**

The mass loading of PCB congeners to the tidal Delaware River during both surveys was estimated by multiplying the flow of the tributary or point source times the sum of the concentrations of the 81 congeners in the respective sample. This list of congeners has been shown to represent over 95% of the total PCB present in environmental samples (MRI, 1995; MRI, 1997; MRI, 1998). Total PCB concentrations were computed as the sum of all detected PCB congeners, with non-detects assumed to be zero. Mass loading analyses are useful for comparing sources and accounting for the variable flows of each source to the estuary. Each of the tributaries sampled was located close to a U.S. Geological Survey hydrological station that provided continuous flow monitoring. Each point source also provided flow data for both of the dry and wet weather surveys. Flow measurements at the municipal wastewater treatment plants are generally conducted at the influent to each plant. Therefore, loading estimates at the effluent were based on influent measurements.

Estimates of the loadings from combined sewer overflows (CSOs) associated with the collection systems of the cities of Philadelphia, Camden, and Wilmington and the Delaware County Regional Authority were obtained by assuming that the influent PCB concentrations to the wastewater treatment plants during the wet weather survey were representative of the concentrations in the respective CSOs. The validity of this assumption depends upon the design of the collection systems of trunk and interceptor sewers, and whether the concentration measured at the influent to the treatment plant is representative of the concentration of PCBs in the individual CSOs. Estimated overflows from the City of Philadelphia CSOs during the wet weather survey in May 1997 were graciously provided by the Philadelphia Water Department (Marengo, 1998). Since comparable overflow estimates for the May 1997 survey were not readily available for the Camden, DELCORA, and Wilmington systems, a different approach was necessary for those overflows. Using overflows projected for a 5-year design storm for all of the systems (NJDEP, 1994), including the Philadelphia CSOs, an average ratio between the May 1997 Philadelphia overflows and their corresponding 5-year storm overflows was first determined. This ratio was then multiplied by the respective 5-year storm overflows associated with the Camden, DELCORA, and Wilmington systems. This procedure resulted in an estimated CSO overflow for Camden, DELCORA, and Wilmington during the May 1997 wet weather survey.

Loadings from CSOs during the dry weather survey were assumed to be zero.

#### **Toxicity Equivalency Factors for PCBs**

Polychlorinated dibenzo-*p*-dioxins (PCDDs or dioxins), polychlorinated dibenzofurans (PCDFs or furans), and selected coplanar polychlorinated biphenyls (coplanar PCBs) are a group of structurally-related organic compounds containing 2 benzene rings and numerous chlorine substitution patterns. Figure 2 illustrates

the similarity in the structure of 2,3,7,8 - tetrachloro-dibenzo-p-dioxin (2,3,7,8 - TCDD) and coplanar PCBs. In general, these compounds have low water solubility, high octanol-water partition coefficients, low vapor pressure and tend to bioaccumulate in fatty tissue of animals and humans. They are very stable in the environment.

Not only do these compounds have similar physicochemical properties, but they are also known to exert similar toxic responses (e.g., immunotoxicity, carcinogenicity, and endocrine toxicity). Strong evidence exists to suggest that certain dioxins, furans, and coplanar PCBs follow a common receptor mediated physiological mechanism of toxicity (Safe 1990; Safe, 1994). This observation has led to the so-called "toxicity equivalency" approach for assessing the cumulative risk of these compounds.

In applying the toxicity equivalency approach, 2,3,7,8-TCDD is taken as the most toxic representative of the entire class of dioxin-like compounds. Other dioxin-like compounds in the class (including certain coplanar PCBs) are assigned toxicities relative to that of 2,3,7,8-TCDD. As a means of normalizing the relative toxicities, 2,3,7,8-TCDD is assigned a toxicity equivalency factor (TEF) of 1 and the other dioxin-like compounds are assigned TEF values less than 1 based on the results of *in vivo* and *in vitro* studies. The biochemical response typically used to assign TEFs is the degree of induction of the liver enzyme, aryl hydrocarbon hydroxylase (AHH).

Operationally, the toxicity equivalents (or TEQs) of an environmental sample containing dioxin and dioxinlike compounds is computed using the following equation:

$$TEQ = \sum_{i} (TEF_{i} \times C_{i})$$

where:

 $TEF_i = Toxicity$  Equivalency Factor for the *i*th member in the dioxin and dioxin-like family, and

 $C_i = Concentration of the ith member.$ 

In situations where dioxins and furans are not measured in the sample but dioxin-like coplanar PCBs are, it is common for TEQs to be referred to as "AHH-Active PCB," rather than "PCB TEQs." Since this study did not measure dioxins and furans, we adopt the convention in this report of expressing the PCB contribution to TEQs as AHH-Active PCB.

TEFs for selected coplanar PCBs were based upon the recommendations of an international panel of experts that met in December 1993 as a part of a consultation by the World Health Organization - European Centre for Environment and Health (WHO-ECEH) and International Programme on Chemical Safety (IPCS), (Ahlborg et al, 1994). That consultation resulted in interim TEFs for 3 non-ortho substituted PCB congeners, 8 mono-ortho substituted PCB congeners, and 2 di-ortho substituted PCB congeners. Those TEFs are listed in the following table.

|            | С         |                       |         |  |  |
|------------|-----------|-----------------------|---------|--|--|
| РСВ Туре   | IUPAC No. | Structure             | TEF     |  |  |
| Non-ortho  | 77        | 3,3',4,4'-TCB         | 0.0005  |  |  |
|            | 126       | 3,3',4,4',5-PeCB      | 0.1     |  |  |
|            | 169       | 3,3',4,4',5,5'-HxCB   | 0.01    |  |  |
| Mono-ortho | 105       | 2,3,3',4,4'-PeCB      | 0.0001  |  |  |
|            | 114       | 2,3,4,4',5-PeCB       | 0.0005  |  |  |
|            | 118       | 2,3',4,4',5-PeCB      | 0.0001  |  |  |
|            | 123       | 2',3,4,4',5-PeCB      | 0.0001  |  |  |
|            | 156       | 2,3,3',4,4',5-HxCB    | 0.0005  |  |  |
|            | 157       | 2,3,3',4,4',5'-HxCB   | 0.0005  |  |  |
|            | 167       | 2,3',4,4',5,5'-HxCB   | 0.00001 |  |  |
|            | 189       | 2,3,3',4,4',5,5'-HpCB | 0.0001  |  |  |
| Di-ortho   | 170       | 2,2',3,3',4,4',5-HpCB | 0.0001  |  |  |
|            | 180       | 2,2',3,4,4',5,5'-HpCB | 0.00001 |  |  |

Note that the procedure described above will underestimate total toxicity equivalents since dioxins and furans were not measured as part of this study.

#### **Statistical Analyses**

For purposes of this report, PCB congener results that were reported as non-detected values were assigned concentrations of zero. It is expected that this handling of non-detected values will have the effect of biasing summary statistics slightly downward in comparison to alternative techniques of dealing with non-detects (e.g., substitution of one-half the detection limit, substituting the detection limit, or using maximum likelihood estimators).

The non-parametric Sign Test (Gilbert, 1987) was used to determine if the total PCB congener concentrations and loadings were significantly different between the dry and wet weather surveys. This test is an analogue to the parametric paired T-test, but does not require that the observations of the populations be normally distributed or that the variances of the populations are equal. Specifically, we tested the null hypothesis that the median difference between wet-dry weather data pairs was zero. A one-sided test was performed such that the alternative hypothesis was that the wet weather values tended to exceed their corresponding dry weather values. A level of significance, alpha, for all comparisons was set at 0.005 (i.e., 99.5 %). Categories compared included total PCB concentrations from the wet versus dry weather surveys; total PCB mass loadings from the wet versus dry weather surveys; AHH-Active PCB mass loadings from the wet versus dry weather surveys. Data were pooled across DRBC zones and source categories in order to

increase the power of the test. This treatment resulted in a total of 21 complete data pairs for the categories compared.

Several statistical analyses were used to determine if the PCB concentrations at each sampling location were correlated with total solids. For the purpose of these analyses, only data from the tributary locations were utilized since the solids levels in the effluent samples are influenced by the solids removal efficiency at each facility. These analyses included analysis of covariance with log PCB concentration and percent solids as continuous variables, and precipitation condition as the covariate class variable. Linear, curvilinear, and polynomial regression techniques were also used to assess possible relationships between PCB concentration and solids.

#### Assessing the Risk of PCBs

The risk to aquatic life, and human health from the ingestion of water or fish taken from the estuary can be estimated by comparing the mass loadings calculated from the data obtained during this study to an estimate of mass of PCBs that can be assimilated by the Delaware River Estuary. The latter estimate was developed by determining the net advective flow of the tidal river at the design conditions appropriate for the aquatic life and human health water quality criteria, and assuming no fate processes or sediment interactions were operative. The one-dimensional water quality model of the estuary (DELTOX) that was developed by the Commission was used to estimate the net downstream flow in each of the four zones of the tidal Delaware River (Zones 2 - 5) under average tidal conditions. The model was run for a 60 day simulation period, and the net downstream flow within each zone was then calculated as the average of the net flow entering and leaving the zone over the simulation period. The product of this net advective flow and the water quality criterion represents an estimate of maximum amount that can be assimilated on a daily basis. This value called the assimilation capacity is not a Total Maximum Daily Load, or TMDL since the many complexities associated with the fate and transport of hydrophobic contaminants such as PCBs have not been considered in its development.

#### RESULTS

The measured concentration of each of the 81 congeners in a sample was adjusted if detectable levels of the congener were found in the trip or equipment blank associated with the sample. Since the water used in both the trip blanks and equipment blanks originated in the analytical laboratory, the adjustment involved the subtraction of the equipment blank results if the sample was associated with such a blank; or if no equipment blank was associated, then the trip blank results associated with the sample were subtracted from the sample result. Given the levels of PCB congeners found in the trip blanks and the similar levels found in some equipment blanks, it appears that the contamination in the equipment blanks is due to the laboratory water rather than the sampling equipment or environment.

The laboratory method blanks demonstrated acceptable results for both the dry and wet weather surveys. No detections were observed in the three blanks analyzed with the dry weather samples. Detections were observed in the 6 blanks analyzed with the wet weather samples; however, only one congener (2, 4, 4'-trichlorobiphenyl) exceeded a value of 0.5 ng/l (Appendix, Tables 8 and 9). Method spike (20 ng/l) recoveries were biased low (~ 65%) for the dry weather samples, but were excellent for the wet weather samples (> 85% and < 103%) for all but 5 congeners which demonstrated > 74% (Appendix, Tables 10 and 11). Precision as measured by the relative standard deviation between the matrix spike duplicates was also excellent (< 10.0 for the dry weather and < 20.0 for the wet weather samples), and indicated good method reproducibility between method batches. Surrogate spike recoveries in the samples were generally within the control limits of 50% to 150% with the mean recovery for the six congeners ranging between 63.1% and 70.7% for the dry weather survey and 94.8% and 106.2% for the wet weather survey (Appendix, Tables 12 and 13). Precision as measured by the duplicate laboratory and field samples were within the 35% relative percent difference (RPD) criteria for three of the four sets of duplicates (Appendix, Table 14). The other set happened to be associated with a field replicate that was also duplicated in the laboratory. The mean concentrations of the two sets were 50.2 and 47.0 ng/l.

#### **Dry Weather Survey**

The dry weather survey of tributaries and point source discharges was conducted between August 20 and 22, 1996. Trip blank samples associated with the dry weather survey had undetected congener concentrations with the exception of one sample that had a concentration of 3.9 ng/l. Four of seven equipment blanks collected by the DRBC and EPA Region III field crews had undetectable concentrations of congeners. PCB concentrations in the other three blanks ranged between 2.3 and 4.1 ng/l. Table 4 summarizes the adjusted total concentration of the 81 congeners in each sample collected during the dry weather survey in August 1996. Figures 3 and 4 depict the relative concentrations at each tributary and point source during this survey, respectively. Prior to and during the survey, precipitation and river flow were low (Table 5). The mean river flow at Trenton on the day of collection was 4400 cfs, while the mean flow of the Schuylkill River was 1030 cfs. The normal mean flow for each tributary for August is 4550 cfs and 1340 cfs, respectively. The only precipitation that was recorded in the week prior to the survey occurred on August 16 when 0.28 and 0.39 inches of rain was recorded at Philadelphia Airport and Wilmington, respectively.

The tributaries generally had lower concentrations than at the treatment plant effluents during the dry weather survey (Figure 3 & 4). The relative loading of PCB congeners from tributaries and point sources indicated that point sources contributed 95.4% of the loading to the estuary during the survey (Table 6, Figures 5 and 6). Tributaries did not contribute any toxicity equivalents or TEQs during this survey (Table 4).

#### Wet Weather Survey

The wet weather survey of tributaries and point source discharges was conducted on April 29 and 30, 1997. Due to an error by the contractor's field crew, wastewater samples collected on April 29 - 30 were discarded, and another sampling event was conducted at the wastewater treatment plants on May 26 - 27 (Table 2). Trip blank samples associated with the wet weather survey all had low but detectable congener concentrations. The concentrations ranged from 0.77 to 1.38 ng/l. The six field blanks collected during the wet weather survey also demonstrated low levels of contamination, ranging between 1.57 and 5.48 ng/l. The adjusted total concentration of the 81 congeners in each sample collected during the wet weather survey is summarized in Table 4.

Prior to and during the tributary portion of the survey, precipitation and river flow were higher than that observed in August 1996 (Table 5). The mean river flow at Trenton on the day of collection was 11,400 cfs, while the mean flow of the Schuylkill River was 3310 cfs. The normal mean flow for each tributary for April is 23,320 cfs and 4263 cfs, respectively. 1.22 inches of rain were recorded at Philadelphia Airport on April 27 and 28, while 0.67 inches of rain were recorded at Wilmington. During the wastewater treatment plant portion of the survey, precipitation was slightly less than that observed during the April sampling survey with 1.10 and 0.26 inches of rain recorded at Philadelphia Airport and Wilmington, respectively.

Concentrations were higher in the tributary samples during the wet weather surveys (Figure 3), but concentrations in the wastewater effluents were similar to that observed during the dry weather survey (Table 4, Figure 4). Significantly higher PCB concentrations were observed in the wastewater influent samples (Figure 7). Concentrations ranged from a low of 11.0 ng/l to 1509 ng/l (i.e., 1.5 ppb). The highest concentrations were observed in the influents to the City of Philadelphia's Southeast Plant and Southwest Plant. Despite the elevated levels in the influents to the wastewater plants during the wet weather survey, significant percent removals were observed at most of the plants (Table 7). Percent reductions at the two plants with the highest PCB influent concentrations were 98.7 and 97.3%. The lowest percent reduction of 68.2% was observed at the Wilmington facility.

The relative mass loading of PCBs and TEQs also differed between the two surveys. Loadings of approximately 30 grams per day were observed at the two largest tributaries to the estuary during the wet weather survey compared to zero loading during the dry weather survey (Figure 8, Table 4). While no TEQ loading was observed from the tributaries during the dry weather sampling, all but one tributary had loadings of TEQs. As with total PCBs, the two largest tributaries to the estuary had the greatest loading (~ 500 µg/day), while two tributaries of the Christina River (Upper Christina River and Red Clay Creek) had the next highest loading (~ 60 µg/day). Similar loadings of both total PCB and TEQs was observed at the wastewater treatment plant effluents (Figure 9). Estimated loadings of PCBs and TEQs from CSOs exceeded both the loading from tributaries and treatment plant effluents by one to two orders of magnitude (Table 6, Figure 10). The loading from all CSOs combined was 2020 grams per day of PCBs and 28,815 µg/day of TEQs compared to 25 grams per day of PCBs and 259 µg/day of TEQs for the wastewater effluents, and 84 grams per day of PCBs and 1218 µg/day of TEQs for all tributaries combined.

The distribution of the loads to the estuary varied depending on the source and weather conditions (Table 8 and 9). During the dry weather survey, 57% of the PCB loading from tributaries was to Zone 5. During the wet weather survey, only 24% of the loading was to Zone 5 with 43% entering Zone 2. In addition, the loading of TEQs from tributaries was split rather evenly between Zones 2 and 4. The distribution of

loads from the point sources was more uniform with the majority of the PCB and TEQ loading entering Zone 3. The distribution of the CSO loads for both PCBs and TEQs was predominantly ( $\sim 75\%$ ) to Zone 3.

#### **Statistical Comparisons**

The results of the non-parametric Sign Test are contained in Table 10. The results indicate that the concentrations and loadings of both PCBs and TEQs during the wet weather survey are significantly greater than the corresponding concentrations and loadings during the dry weather survey. The results of the analysis of covariance of the effect of precipitation and percent solids on PCB concentration at tributary sampling locations is presented in Table 11. The results indicate that while precipitation significantly effects the PCB concentration at each location, the relationship between PCB concentration and percent solids is not statistically significant. Neither linear, curvilinear or polynomial analyses of the relationship with percent solids were found to be statistically significant.

#### **Risk Assessment for PCBs**

The capacity for the estuary to assimilate total PCBs will vary depending on the net advective flow and the controlling water quality criteria in that portion of the estuary. The net advective flow in the four zones of the estuary established by the DRBC in their water quality regulations, the applicable water quality criteria, and resulting assimilation capacity (AC) in grams per day are listed in Table 12. While the chronic aquatic life criteria for each zone is the same, the criteria for the protection of human health from carcinogenic effects varies because Zones 3 and 4 are not designated for use as a potable water source. The criteria in Zones 4 and 5 are based upon exposure due to the consumption of fish only. The lower criterion in Zone 5 is due to the higher consumption rate used to establish the criterion (37 versus 6.5 grams per day in Zone 4). As indicated in the table, human health criteria are governing for PCBs in the estuary with total PCB loads ranging from approximately 0.2 to 1 grams per day.

A comparison of the ACs with the loading of PCBs and TEQs during the dry and wet weather surveys is presented in Table 13. This comparison indicated that the loadings of PCBs during dry weather did not exceed the assimilation capacity based upon the chronic aquatic life criteria, but did exceed the capacity based upon human health criteria in 3 of the four zones of the estuary (Figure 11). TEQ loadings did not exceed the TEQ-based capacity in three of the four estuary zones during dry weather. During wet weather, the assimilation capacity for both total PCB and TEQs was exceeded based upon human health criteria in all zones, particularly in Zones 3 and 4. The aquatic life AC was exceeded only in Zones 3 and 4 during wet weather.

#### DISCUSSION

The results of this study indicate that both tributaries and municipal wastewater treatment plants are active sources of PCBs to the tidal Delaware River. Concentrations of PCBs were generally higher in the municipal treatment plants effluents compared to the tributaries during both the dry and wet weather surveys. The highest concentrations were observed in the effluent samples from the Philadelphia SE plant during both surveys.

Tributary samples exhibited several differences between the surveys. No PCB congeners were detected in the two major tributaries to the estuary, the Delaware and Schuylkill Rivers, during the dry weather survey. There was also no loadings of the AHH-Active PCB congeners from any tributary during the dry weather survey as evidenced by the zero loadings of TEQs. During the wet weather survey, the highest concentrations of both congeners and TEQs were observed in two of the tributaries to the Christina River, Upper Christina and Red Clay Creek. Despite the low concentrations of PCBs and TEQs observed, the greatest loading of PCBs was from the Delaware and Schuylkill Rivers due to their higher flow. This indicates that more of the highly chlorinated and more toxic PCB congeners are present during the wet weather, and suggests that transport of these more hydrophobic compounds is facilitated by the higher solids concentrations during wet weather events. Solids concentrations were 7 to 11 times higher in the Delaware and Schuylkill Rivers samples collected during the wet weather survey compared to the dry weather survey (Appendix, Table 3). Congener distributions also differed between the two surveys. Triand tetrachlorobiphenyls were the dominant homolog group observed during the dry weather survey (Figure 12).

The concentration and mass loading of PCBs and TEQs from the wastewater treatment plant effluents was similar during both the dry and wet weather surveys (Figures 4 and 9). The greatest loading of PCBs during both surveys was from the City of Philadelphia's Southeast Plant. This facility had by far the highest influent concentration of PCBs (1509 ng/l). The high influent concentrations were reportedly due to an illegal discharge of transformer fluid into the interceptor serving the plant. This event affected not only this facility, but also the Southwest facility which processes wastewater from the city's sludge recycling facility. The Southwest facility also appears to be receiving PCBs from other sources. Separate samples were collected at the influent channels to the Southwest plant. The low level sample included the sludge recycling facility, the Lower Schuylkill East Side interceptor and Cobbs Creek Low Level interceptor. The concentration of PCBs in this sample was 539.2 ng/l. The high level sample included the Southwest Main Gravity interceptor, and had a PCB concentration of 339.7 ng/l. The higher TEQs associated with the latter sample also suggest a separate source of PCBs to this plant. The City of Wilmington facility ranked third in PCB concentration during the dry weather survey and second during the wet weather survey. Effluent from the DELCORA facility and Northeast facility were the lowest during both surveys.

Congener distributions in the wastewater effluent samples did show differences between the two surveys. Tetra- and pentachlorobiphenyls were the dominant homolog groups observed during the dry weather survey, while penta-, hexa-, and heptachlorobiphenyls dominated during the wet weather survey (Figure 13). In addition, octa-, nona- and decachlorobiphenyls were only detected during the wet weather survey. Similar to the tributary results discussed above, the greater proportion of highly chlorinated congeners during the wet weather survey may be associated with the greater solids evident in these samples.

The highest PCB and TEQ concentrations were observed in the wastewater influent samples. The concentrations were from 1 to 3 orders of magnitude greater than the concentrations observed in the

tributary samples during either the dry or wet weather surveys. Assuming that these concentrations are representative of concentrations in the CSOs, the combined sewer overflows, particularly those associated with the interceptor systems of the Southeast and Southwest plants of the City of Philadelphia, are significant sources of PCBs. Since the high concentration of PCBs in the influent to the Southeast plant may have resulted from the illegal discharge into one of the trunk sewers in the collection system for this plant, the mean concentration of PCBs in the influent to the Southeast plants was used to estimate the loading from the CSOs associated with the Southeast plant. A loading of 760.6 grams/day of PCBs from CSOs associated with the Southeast plant was calculated, reducing the contribution of CSOs during wet weather to 87.5% from 94.9% (Table 6, Figure 6).

The congener distributions in the influent samples were similar to that observed in the wet weather effluent samples, with penta-, hexa-, and heptachlorobiphenyls dominating the congener mixture (Figure 14).

A similar study targeting 71 PCB congeners was conducted at 26 wastewater treatment plants discharging to the New York/New Jersey Harbor Estuary in 1994 and 1995 (Durell and Lizotte, 1998). Effluent concentrations in all 26 plants was similar during two dry weather sampling events, ranging between 11 and 55 ng/l. During two wet weather sampling events, influent concentrations were higher, ranging between 53 and 408 ng/l. Thus similar concentrations were observed in dry weather effluent samples and wet weather influent samples during both the New York/New Jersey Harbor Estuary and Delaware River Estuary studies. An analysis of the annual contribution wastewater treatment plant effluents and combined sewer overflows to the mass loading of PCBs to the NY/NJ Harbor was also presented. No flow and duration data were available for this analysis which indicated that wastewater effluent contribute almost 97% of the mass loading on an annual basis.

The distribution of congeners in environmental samples has implications for the source, age and potential impact of these compounds. The degree of chlorination is known to influence the volatility, degradation rate, and affinity for lipids (Brown et al, 1985). Congeners containing few chlorine atoms are more likely to degrade at a faster rate due to their greater volatility and susceptibility to biodegradation by aerobic bacteria. Therefore, their presence in environmental samples may indicate a more recent release. The distribution of congeners also significantly influence the degree of bioavailability. Stange and Swackhamer (1994) reported that the accumulation of PCB congeners in three species of freshwater phytoplankton was congener-specific. Mono- to tetrachlorobiphenyls with a log octanol water partition coefficient less than 6.0 were rapidly associated and accumulated by phytoplankton, but species-specific differences were noted. In contrast, the bioaccumulation of higher-chlorinated congeners was not linear, possibly due to their association with dissolved organic compounds or a difficulty in crossing the algal membrane. Gerstenberger et al (1997) observed significant differences in the accumulation of 89 PCB congeners between Great Lakes fish species. Lower trophic level species such as carp and whitefish had greater proportions of tri- and tetrachlorobiphenyls, while walleye and lake trout had greater proportions of penta-, hexa- and heptachlorobiphenyl. Sericano et al (1992) reported that oysters from Galveston Bay, Texas accumulated the more highly toxic tetra- (No. 77), penta- (No. 126) and hexa- (No. 169) coplanar congeners in as little as 30 days.

Information is available on the distribution of PCB congeners in the sediments and biota of the Delaware River Estuary. Costa and Sauer (1994) analyzed 51 PCB congeners from four sections of the estuary representing various levels of contamination by point and non-point sources. These sections roughly correspond to Zones 3 to 6. Higher concentrations of total PCBs were found in sections corresponding to Zones 3 and 4 (median values of 128 and 179.5 ng/g, respectively), but these were not statistically different from concentrations in the lower two sections (median values of 89 and 65 ng/g, respectively)

(Greene, 1994). In this study, 79% of the PCB loading during the dry weather survey was to Zones 3 and 4, while 96% of the loading during the wet weather survey was to these two zones. The distribution of congeners was also different between the sections corresponding to Zones 3 & 4 and the two sections further downriver. Hepta- and octachlorobiphenyls were more prevalent in the upriver sections with lower chlorinated congeners predominating in the downriver sections. Fish tissue samples of two species from five locations in the tidal river portion of the estuary have been collected since 1991 by the Commission. In 1996, these samples were analyzed for 74 PCB congeners. Peak concentrations of total PCBs were observed in the samples collected at the Tacony-Palmyra Bridge in Zone 3. The congener distribution was similar in both species with penta-, hexa- and heptachlorobiphenyls predominating. Approximately 10% of the PCBs in the tissue samples consisted of highly chlorinated octa- to decachlorobiphenyl congeners, and detectable levels of the more toxic coplanar congeners 77, 126 and 169 were found.

The results of the analysis which indicated that the wet weather loading of PCBs exceeded the assimilation capacity (AC) for the estuary was not surprising. Fish consumption advisories have been issued by all three states bordering the estuary, and are still in effect. This analysis did indicate, however, that with the exception of loadings to Zone 2 during dry weather, the human health-based ACs are exceeded throughout the estuary regardless of the amount of precipitation. During the wet weather survey, the loading in all zones of the estuary exceeded the AC by 2 to 5 orders of magnitude. Additionally, the ACs based upon chronic impacts to aquatic life are exceeded in Zones 3 and 4 only during the wet weather survey. It should be noted that the ACs consider PCBs to be a conservative substance, and do not consider degradation of PCBs or the contribution of PCBs adsorbed to the sediment. Since significant levels of PCBs have been reported in estuary sediments (Costa and Sauer, 1994; Burton, 1997), the ACs estimated using the net advective flow calculations may actually overestimate the assimilation capacity for the estuary.

The finding of PCBs in the influent and effluent of the six wastewater treatment plants was not unexpected, although the magnitude of the concentrations was surprising. While the manufacture and use of PCBs were prohibited by law in the late 1970s, the removal of existing electrical equipment containing PCBs was not required by Federal regulations (40 CFR Part 761.20 and Part 761.80). Exemptions are included in the regulations for totally-enclosed items such as electrical transformers, capacitors, switches and circuit breakers; and a number of products with PCB levels less than 50 ppm. PCB-containing equipment will continue to be removed from service in the next decade as it reaches the end of its useful life. Improper disposal of this equipment can be expected to threaten the aquatic life of the estuary, and human health through consumption of water and fish.

#### RECOMMENDATIONS

The results of this study indicate the need for additional steps to mitigate of the impact of PCBs on aquatic life and human health. Barriers exist, however, to developing a comprehensive approach to identifying and mitigating sources of PCBs. The barriers include the perception among both regulators and the public that PCBs are a "historical" pollutant that is no longer manufactured and is therefore not currently entering the environment. This perception is erroneous since the Toxic Substances Control Act did not require the removal of PCBs from its extensive use in electrical equipment and also contained numerous exceptions for small quantities and specific uses. The retirement of this equipment will require diligence to ensure that it does not enter the environment. Another barrier involves the analytical methods used to detect and quantify PCBs. The traditional method focused on the commercial mixtures of PCBs called Aroclors, and had a higher detection limit than the congener-specific method used in this study. PCB congeners degrade at different rates resulting in a distribution of congeners that differs from the commercial mixtures. This may result in laboratory reports of "undetected Aroclors" when PCB congeners are present. The lack of an official U.S. EPA methodology also hampers the use of congener-specific methods in regulatory requirements. Many environmental investigation and remediation activities required by federal and state statutes still utilize the Aroclor methodology.

A final barrier to mitigating the impact of PCBs on the environment is the failure to consider some pathways by which PCBs enter the environment. Remedial activities at hazardous waste facilities and abandoned waste sites often use cleanup standards that may not protect nearby aquatic environments. A soil cleanup standard of 50 parts per million is commonly used in the Superfund program when the ambient water quality standard is typically in the part per quadrillion level. Remedial investigations need to consider the transport of such "cleaned soil" into adjacent water bodies and the cleanup of contaminated sediments to levels that will not contribute to aquatic life and human health impacts.

Additional information and data are necessary, however, before appropriate source reductions are developed that will eventually result in the lifting of the current fish consumption advisories. The following actions are therefore recommended in priority order:

- 1. Enhance the mathematical model of the Delaware Estuary to incorporate a sediment transport submodel, a food chain submodel, and loadings of PCB-contaminated sediment/soil from non-point sources such as Superfund Sites. This effort will permit the evaluation of source reduction scenarios.
- 2. Increase public awareness that PCBs are a *current* and not a historical threat to the health of the biota and users of the estuary.
- 3. Encourage proper disposal of electrical equipment containing PCBs, and practices that minimize erosion of PCB-contaminated soil and sediment.
- 4. Conduct additional monitoring for PCBs using low level, congener-specific analytical methods to identify sources and improve loading estimates. Monitoring should be conducted at municipal and industrial point sources (including Combined Sewer Overflows) during both dry and wet weather periods, at head of tide of tributaries to the estuary, and to determine the contribution of PCBs from airborne sources.

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### Table 1: Sample Tracking Information for Dry Weather Survey, August 1996

| Location                                   |          | Sample<br>Number | Date<br>Collected | Sample<br>Type          | Collection<br>Time   | Latitude       | Longitude       |
|--|----------|------------------|-------------------|-------------------------|----------------------|----------------|-----------------|
| Upper Christina River<br>at Route 72       | Ambient  | 201061           | 20-Aug-96         | Grab                    | 09:35 AM             | 39 38.120      | 75 53.660       |
| Lower Brandywine Creek                     | Ambient  | 201062           | 20-Aug-96         | Grab                    | 10:30 AM             | 39 45.640      | 75 33.347       |
| White Clay Creek<br>at Stanton             | Ambient  | 201063           | 20-Aug-96         | Grab                    | 11:15 AM             | 39 42.421      | 75 39.137       |
| Red Clay Creek<br>at Stanton (Rt. 4)       | Ambient  | 201064           | 20-Aug-96         | Grab                    | 11:40 AM             | 39 42.930      | 75 38.497       |
| DNREC Trip Blank                           | Ambient  |                  |                   | Grab                    |                      | -              | -               |
| DRBC Trip Blank                            | Ambient  | 203086           | 20-Aug-96         | Grab                    | 10:10 AM             | -              | -               |
| DRBC Field Blank                           | Ambient  | 201087           | 20-Aug-96         | Grab                    | 10:10 AM             | -              | -               |
| Delaware River at<br>Calhoun Street Bridge | Ambient  | 201090           | 20-Aug-96         | Composite of<br>3 grabs | 02:20 PM<br>02:40 PM | 40 13 09.98429 | 9 74 46 43.246  |
| Neshaminy Creek                            | Ambient  | 201091           | 20-Aug-96         | Grab                    | 03:35 PM             | 40 08 29.45929 | 9 74 54 45.311  |
| Schuylkill River at                        | Ambient  | 201092           | 20-Aug-96         | Grab                    | 05:05 PM             | 40 00 30.09610 | ) 75 11 50.463  |
| (Duplicate)                                | Ambient  | 201093           | 20-Aug-96         | Grab                    | 05:10 PM             |                |                 |
| Raccoon Creek                              | Ambient  | 201085           | 20-Aug-96         | Grab                    | 10:10 AM             | 39 45 19.39394 | \$ 75 19 00.393 |
| Rancocas Creek                             | Ambient  | 201088           | 20-Aug-96         | Grab                    | 11:45 AM             | 39 59 51.30542 | 2 74 52 20.803  |
| Crosswicks Creek                           | Ambient  | 201089           | 20-Aug-96         | Grab                    | 12:40 PM             | 40 10 01.97007 | 74 40 38.355    |
| Monsanto Corp.                             | Effluent | 201096           | 21-Aug-96         | Grab                    | 02:15 PM             | 39 48 22       | 75 24 24        |

| Treatment Plant Trip Blank | -           | 201078 | 20-Aug-96              | Grab           | -                    | -          | -          |
|----------------------------|-------------|--------|------------------------|----------------|----------------------|------------|------------|
| DELCORA                    | Effluent    | 201052 | 20-Aug-96<br>21-Aug-96 | Time Composite | 11:50 AM<br>11:50 AM | 39 49 25   | 75 23 23   |
|                            | Field Blank | 201055 | 20-Aug-96              | Grab           | 11:20 AM             |            |            |
| Philadelphia SW            | Effluent    | 201053 | 20-Aug-96<br>21-Aug-96 | Time Composite | 03:00 PM<br>03:00 PM | 39 52 13   | 75 13 13   |
|                            | Field Blank | 201055 | 20-Aug-96              | Grab           | 01:40 PM             |            |            |
| Philadelphia SE            | Effluent    | 201058 | 20-Aug-96<br>21-Aug-96 | Time Composite | 03:20 PM<br>08:20 PM | 39 54 25.7 | 75 08 8.1  |
|                            | Field Blank | 201077 | 20-Aug-96              | Grab           | 03:00 PM             |            |            |
| Philadelphia NE            | Effluent    | 201056 | 20-Aug-96<br>21-Aug-96 | Time Composite | 12:00 PM<br>11:00 AM | 39 59 7.7  | 75 04 43   |
|                            | Field Blank | 201059 | 20-Aug-96              | Grab           | 11:10 AM             |            |            |
| Wilmington                 | Effluent    | 201051 | 20-Aug-96<br>21-Aug-96 | Time Composite | 10:20 AM<br>10:20 AM | 39 43 49   | 75 30 25   |
|                            | Field Blank | 201054 | 20-Aug-96              | Grab           | 09:55 AM             |            |            |
| Camden County MUA          | Effluent    | 201079 | 21-Aug-96<br>22-Aug-96 | Time Composite | 01:15 PM<br>01:15 PM | 39 55 21.7 | 75 07 41.4 |
|                            | Field Blank | 201060 | 20-Aug-96              | Grab           | 01:40 PM             |            |            |

| Location                                   |             | Sample<br>Number | Date<br>Collected      | Sample<br>Type              | Collection<br>Time   |
|--|-------------|------------------|------------------------|-----------------------------|----------------------|
| Upper Christina River<br>at Route 72       | Ambient     | 203094           | 28-Apr-97              | Grab                        | 10:21 AM             |
| Lower Brandywine Creek                     | Ambient     | 203095           | 28-Apr-97              | Grab                        | 11:01 AM             |
| White Clay Creek<br>at Stanton             | Ambient     | 203096           | 28-Apr-97              | Grab                        | 11:43 AM             |
| Red Clay Creek<br>at Stanton (Rt. 4)       | Ambient     | 203097           | 28-Apr-97              | Grab                        | 11:33 AM             |
| DNREC Trip Blank                           | Ambient     |                  |                        | Grab                        | -                    |
| DRBC Trip Blank                            | Ambient     | 203093           | 15-Apr-97              | Grab                        | -                    |
| DRBC Field Blank                           | Ambient     | 202826           | 29-Apr-97              | Grab                        | 10:00 AM             |
| Delaware River at<br>Calhoun Street Bridge | Ambient     | 202827           | 29-Apr-97              | Composite of 3 grab samples | 10:15 AM<br>10:30 AM |
| Neshaminy Creek                            | Ambient     | 202828           | 29-Apr-97              | Grab                        | 11:30 AM             |
| Schuylkill River at<br>Falls Bridge        | Ambient     | 202829           | 29-Apr-97              | Grab                        | 12:35 PM             |
| Raccoon Creek                              | Ambient     | 203090           | 29-Apr-97              | Grab                        | 02:35 PM             |
| Rancocas Creek                             | Ambient     | 203091           | 29-Apr-97              | Grab                        | 03:50 PM             |
| Crosswicks Creek                           | Ambient     | 203092           | 29-Apr-97              | Grab                        | 04:40 PM             |
| Camden County MUA                          | Influent    | 201098           | 29-Apr-97              | Composite of 2 grab samples | 12:00 AM<br>12:00 AM |
| Wilmington                                 | Influent    | 201099           | 26-May-97<br>27-May-97 | Time Composite              | 09:05 AM<br>09:05 AM |
| Wilmington                                 | Field Blank | 201099A          | 05-May-97              | Grab                        | 03:25 PM             |
| Treatment Plant Trip Blank                 | -           | 203373           |                        | Grab                        |                      |
| DELCORA                                    | Effluent    | 203362           | 26-May-97<br>27-May-97 | Time Composite              | 12:25 PM<br>12:25 PM |
| Philadelphia SE                            | Effluent    | 203363           | 26-May-97              | Time Composite              | 01:50 PM             |

# Table 2: Sample Tracking Information for Wet Weather Survey,April - May 1997

|                                |                |        | 27-May-97              |                | 01:50 PM             |
|--------------------------------|----------------|--------|------------------------|----------------|----------------------|
| Philadelphia SE                | Influent 2     | 03364  | 26-May-97<br>27-May-97 | Time Composite | 09:55 AM<br>09:55 AM |
| Philadelphia SE                | Field Blank 20 | )3364A | 05-May-97              | Grab           | 03:15 PM             |
| Philadelphia SW                | Effluent 2     | 03365  | 26-May-97<br>27-May-97 | Time Composite | 01:30 PM<br>01:30 PM |
| Philadelphia SW<br>Low Level   | Influent 2     | 03366  | 26-May-97<br>27-May-97 | Time Composite | 08:50 AM<br>08:50 AM |
| Philadelphia SW                | Field Blank 20 | )3366A | 05-May-97              | Grab           | 11:00 AM             |
| Philadelphia SW<br>High Level  | Influent 2     | 03367  | 26-May-97<br>27-May-97 | Time Composite | 09:00 AM<br>09:00 AM |
| Philadelphia NE                | Effluent 2     | 03368  | 26-May-97<br>27-May-97 | Time Composite | 03:00 PM<br>03:00 PM |
| Philadelphia NE<br>Influent #2 | Influent 2     | 03369  | 26-May-97<br>27-May-97 | Time Composite | 11:05 AM<br>11:05 AM |
| Philadelphia NE<br>Influent #1 | Influent 2     | 03370  | 26-May-97<br>27-May-97 | Time Composite | 11:55 AM<br>11:55 AM |
| Philadelphia NE                | Field Blank 20 | )3370A | 05-May-97              | Grab           | 11:00 AM             |
| Wilmington                     | Effluent 2     | 03371  | 27-May-97<br>28-May-97 | Time Composite | 02:40 PM<br>02:40 PM |
| DELCORA                        | Influent 2     | 03372  | 26-May-97<br>26-May-97 | Time Composite | 10:06 AM<br>08:06 PM |
| DELCORA                        | Field Blank 20 | 3372A  | 05-May-97              | Grab           | 12:50 PM             |

| PARAMETER       | STRUCTURE       | DETECTION<br>LIMIT | QUANTITATION<br>LIMIT <sup>a</sup> |
|-----------------|-----------------|--------------------|------------------------------------|
| PCB Congeners ( | IUPAC Number)   |                    |                                    |
| 8               | 2, 4'           | 0.25 ng/l          | 1.25 ng/l                          |
| 18              | 2, 2', 5        | 0.25 ng/l          | 1.25 ng/l                          |
| 22              | 2, 3, 4'        | 0.25 ng/l          | 1.25 ng/l                          |
| 28              | 2, 4, 4'        | 0.25 ng/l          | 1.25 ng/l                          |
| 31              | 2, 4', 5        | 0.25 ng/l          | 1.25 ng/l                          |
| 33              | 2', 3, 4        | 0.25 ng/l          | 1.25 ng/l                          |
| 37              | 3, 4, 4'        | 0.25 ng/l          | 1.25 ng/l                          |
| 42              | 2, 2', 3, 4'    | 0.50 ng/l          | 2.50 ng/l                          |
| 44              | 2, 2', 3, 5'    | 0.50 ng/l          | 2.50 ng/l                          |
| 47              | 2, 2', 4, 4'    | 0.50 ng/l          | 2.50 ng/l                          |
| 49              | 2, 2', 4, 5'    | 0.50 ng/l          | 2.50 ng/l                          |
| 52              | 2, 2', 5, 5'    | 0.50 ng/l          | 2.50 ng/l                          |
| 60              | 2, 3, 4, 4'     | 0.50 ng/l          | 2.50 ng/l                          |
| 64              | 2, 3, 4', 6     | 0.50 ng/l          | 2.50 ng/l                          |
| 66              | 2, 3', 4, 4'    | 0.50 ng/l          | 2.50 ng/l                          |
| 70              | 2, 3', 4', 5    | 0.50 ng/l          | 2.50 ng/l                          |
| 74              | 2, 4, 4', 5     | 0.50 ng/l          | 2.50 ng/l                          |
| 77 <sup>ь</sup> | 3, 3', 4', 4    | 0.50 ng/l          | 2.50 ng/l                          |
| 80              | 3, 3', 5, 5'    | 0.50 ng/l          | 2.50 ng/l                          |
| 81 <sup>b</sup> | 3, 4, 4', 5     | 0.50 ng/l          | 2.50 ng/l                          |
| 82              | 2, 2', 3, 3', 4 | 0.50 ng/l          | 2.50 ng/l                          |
| 84              | 2, 2',3, 3', 6  | 0.50 ng/l          | 2.50 ng/l                          |
| 86              | 2, 2', 3, 4, 5  | 0.50 ng/l          | 2.50 ng/l                          |
| 87              | 2, 2', 3, 4, 5' | 0.50 ng/l          | 2.50 ng/l                          |
| 91              | 2, 2', 3, 4', 6 | 0.50 ng/l          | 2.50 ng/l                          |
| 92              | 2, 2', 3, 5, 5' | 0.50 ng/l          | 2.50 ng/l                          |
| 95              | 2, 2', 3, 5', 6 | 0.50 ng/l          | 2.50 ng/l                          |
| 97              | 2, 2', 3', 4, 5 | 0.50 ng/l          | 2.50 ng/l                          |
| 99              | 2, 2', 4, 4', 5 | 0.50 ng/l          | 2.50 ng/l                          |
| 101             | 2, 2', 4, 5, 5' | 0.50 ng/l          | 2.50 ng/l                          |

# TABLE 3: Target Analytes, Detection and Quantitation Limits for PCB Congeners

| PARAMETER        | STRUCTURE              | DETECTION<br>LIMIT | QUANTITATION<br>LIMIT <sup>a</sup> |
|------------------|------------------------|--------------------|------------------------------------|
| 105              | 2, 3, 3', 4, 4'        | 0.50 ng/l          | 2.50 ng/l                          |
| 110              | 2, 3, 3', 4', 6        | 0.50 ng/l          | 2.50 ng/l                          |
| 114              | 2, 3, 4, 4', 5         | 0.50 ng/l          | 2.50 ng/l                          |
| 118              | 2, 3', 4, 4', 5        | 0.50 ng/l          | 2.50 ng/l                          |
| 119              | 2, 3', 4, 4', 6        | 0.50 ng/l          | 2.50 ng/l                          |
| 120              | 2, 3', 4, 5, 5'        | 0.50 ng/l          | 2.50 ng/l                          |
| 123              | 2', 3, 4, 4', 5        | 0.50 ng/l          | 2.50 ng/l                          |
| 126 <sup>b</sup> | 3, 3', 4, 4', 5        | 0.50 ng/l          | 2.50 ng/l                          |
| 127              | 3, 3', 4, 5, 5'        | 0.50 ng/l          | 2.50 ng/l                          |
| 128              | 2, 2', 3, 3', 4, 4'    | 0.50 ng/l          | 2.50 ng/l                          |
| 132              | 2, 2', 3, 3', 4, 6     | 0.50 ng/l          | 2.50 ng/l                          |
| 135              | 2, 2', 3, 3', 5, 6'    | 0.50 ng/l          | 2.50 ng/l                          |
| 136              | 2, 2', 3, 3', 6, 6'    | 0.50 ng/l          | 2.50 ng/l                          |
| 137              | 2, 2', 3, 4, 4', 5     | 0.50 ng/l          | 2.50 ng/l                          |
| 138              | 2, 2', 3, 4, 4', 5'    | 0.50 ng/l          | 2.50 ng/l                          |
| 141              | 2, 2', 3, 4, 5, 5'     | 0.50 ng/l          | 2.50 ng/l                          |
| 146              | 2, 2', 3, 4', 5, 5'    | 0.50 ng/l          | 2.50 ng/l                          |
| 149              | 2, 2', 3, 4', 5', 6    | 0.50 ng/l          | 2.50 ng/l                          |
| 151              | 2, 2', 3, 5, 5', 6     | 0.50 ng/l          | 2.50 ng/l                          |
| 153              | 2, 2', 4, 4', 5, 5'    | 0.50 ng/l          | 2.50 ng/l                          |
| 156              | 2, 3, 3', 4, 4', 5     | 0.50 ng/l          | 2.50 ng/l                          |
| 157              | 2, 3, 3', 4, 4', 5'    | 0.50 ng/l          | 2.50 ng/l                          |
| 158              | 2, 3, 3', 4, 4', 6     | 0.50 ng/l          | 2.50 ng/l                          |
| 166              | 2, 3, 4, 4', 5, 6      | 0.50 ng/l          | 2.50 ng/l                          |
| 167              | 2, 3', 4, 4', 5, 5'    | 0.50 ng/l          | 2.50 ng/l                          |
| 168              | 2, 3', 4, 4', 5', 6    | 0.50 ng/l          | 2.50 ng/l                          |
| 169 <sup>b</sup> | 3, 3', 4, 4', 5, 5'    | 0.50 ng/l          | 2.50 ng/l                          |
| 170              | 2, 2', 3, 3', 4, 4', 5 | 0.75 ng/l          | 3.75 ng/l                          |
| 171              | 2, 2', 3, 3', 4, 4', 6 | 0.75 ng/l          | 3.75 ng/l                          |
| 174              | 2, 2', 3, 3', 4, 5, 6' | 0.75 ng/l          | 3.75 ng/l                          |
| 177              | 2, 2', 3, 3', 4', 5, 6 | 0.75 ng/l          | 3.75 ng/l                          |
| 178              | 2, 2', 3, 3', 5, 5', 6 | 0.75 ng/l          | 3.75 ng/l                          |
| 179              | 2, 2', 3, 3', 5, 6, 6' | 0.75 ng/l          | 3.75 ng/l                          |
| 180              | 2, 2', 3, 4, 4', 5, 5' | 0.75 ng/l          | 3.75 ng/l                          |

| PARAMETER | STRUCTURE                         | DETECTION<br>LIMIT | QUANTITATION<br>LIMIT <sup>a</sup> |
|-----------|-----------------------------------|--------------------|------------------------------------|
| 183       | 2, 2', 3, 4, 4', 5', 6            | 0.75 ng/l          | 3.75 ng/l                          |
| 185       | 2, 2', 3, 4, 5, 5', 6             | 0.75 ng/l          | 3.75 ng/l                          |
| 187       | 2, 2', 3, 4', 5, 5', 6            | 0.75 ng/l          | 3.75 ng/l                          |
| 189       | 2, 3, 3', 4, 4', 5, 5'            | 0.75 ng/l          | 3.75 ng/l                          |
| 190       | 2, 3, 3', 4, 4', 5, 6             | 0.75 ng/l          | 3.75 ng/l                          |
| 191       | 2, 3, 3', 4, 4', 5', 6            | 0.75 ng/l          | 3.75 ng/l                          |
| 194       | 2, 2', 3, 3', 4, 4', 5, 5'        | 0.75 ng/l          | 3.75 ng/l                          |
| 195       | 2, 2', 3, 3', 4, 4', 5, 6         | 0.75 ng/l          | 3.75 ng/l                          |
| 196       | 2, 2', 3, 3', 4, 4', 5', 6        | 0.75 ng/l          | 3.75 ng/l                          |
| 198       | 2, 2', 3, 3', 4, 5, 5', 6         | 0.75 ng/l          | 3.75 ng/l                          |
| 200       | 2, 2', 3, 3', 4, 5', 6, 6'        | 0.75 ng/l          | 3.75 ng/l                          |
| 201       | 2, 2', 3, 3', 4', 5, 5', 6        | 0.75 ng/l          | 3.75 ng/l                          |
| 203       | 2, 2', 3, 4, 4', 5, 5', 6         | 0.75 ng/l          | 3.75 ng/l                          |
| 205       | 2, 3, 3', 4, 4', 5, 5', 6         | 0.75 ng/l          | 3.75 ng/l                          |
| 206       | 2, 2', 3, 3', 4, 4', 5, 5', 6     | 1.00 ng/l          | 5.00 ng/l                          |
| 207       | 2, 2', 3, 3', 4, 4', 5, 6, 6'     | 1.00 ng/l          | 5.00 ng/l                          |
| 208       | 2, 2', 3, 3', 4, 5, 5', 6, 6'     | 1.00 ng/l          | 5.00 ng/l                          |
| 209       | 2, 2', 3, 3', 4, 4', 5, 5', 6, 6' | 1.25 ng/l          | 5.00 ng/l                          |

a - Quantitation limits are estimated at 5 times the detection limit. b - Coplanar congener.

|  |              | DRY WEATHER                   |                        |                |                          |                  | WET WEATHER                   |                        |                          |                          |                  |
|--|--------------|-------------------------------|------------------------|----------------|--------------------------|------------------|-------------------------------|------------------------|--------------------------|--------------------------|------------------|
| SOURCES  |              | Concentration                 |                        | Mass Loading   |                          |                  | Concentration                 |                        | Mass Loading             |                          |                  |
|  | DRBC<br>Zone | # of<br>Congeners<br>Detected | Total<br>PCB<br>(ng/L) | TEQs<br>(ng/L) | Total<br>PCB<br>(gm/day) | TEQs<br>(ug/day) | # of<br>Congeners<br>Detected | Total<br>PCB<br>(ng/L) | TEQs<br>(ng/L)           | Total<br>PCB<br>(gm/day) | TEQs<br>(ug/day) |
| TRIBUTARIES                                    |              |                               |                        |                |                          |                  |                               |                        |                          |                          |                  |
| Upper Christina River                          | 5            | 4                             | 2.01                   | 0              | 0.06                     | 0                | 27                            | 10.97                  | 1.21E-04                 | 5.37                     | 59.38            |
| Brandywine Creek                               | 5            | 1                             | 0.80                   | 0              | 0.74                     | 0                | 16                            | 2.19                   | 1.28E-06                 | 5.26                     | 3.07             |
| White Clay Creek                               | 5            | 2                             | 0.68                   | 0              | 0.15                     | 0                | 19                            | 3.08                   | 2.60E-05                 | 3.99                     | 27.26            |
| Red Clay Creek                                 | 5            | 0                             | 0                      | 0              | 0                        | 0                | 36                            | 9.96                   | 1.11E-04                 | 5.48                     | 60.95            |
| Raccoon Creek                                  | 4            | 8                             | 5.01                   | 0              | 0.26                     | 0                | 5                             | 1.06                   | 0                        | 0.17                     | 0                |
| Rancocas Creek                                 | 2            | 1                             | 0.68                   | 0              | 0.46                     | 0                | 14                            | 2.18                   | 1.43E-05                 | 2.29                     | 15.05            |
| Crosswicks Creek                               | 2            | 0                             | 0                      | 0              | 0                        | 0                | 17                            | 1.76                   | 3.62E-05                 | 1.76                     | 36.34            |
| Delaware River                                 | 2            | 0                             | 0                      | 0              | 0                        | 0                | 8                             | 1.08                   | 1.76E-05                 | 30.18                    | 490.97           |
| Neshaminy Creek                                | 2            | 0                             | 0                      | 0              | 0                        | 0                | 12                            | 1.57                   | 1.77E-05                 | 1.54                     | 17.37            |
| Schuykill River<br>Schuykill River (Replicate) | 4            | 0<br>0                        | 0<br>0                 | 0<br>0         | 0<br>0                   | 0<br>0           | 22<br>No repli                | 3.42<br>cate collect   | 6.27E-05<br>ted during W | 27.68<br>Vet Weather S   | 508.09<br>urvey  |
| POINT SOURCE EFFLUE                            | NTS          |                               |                        |                |                          |                  |                               |                        |                          |                          |                  |
| Camden County MUA                              | 3            | 22                            | 23.16                  | 0.00006        | 4.85                     | 13.35            | No sample due to fire         |                        |                          |                          |                  |
| Wilmington                                     | 5            | 24                            | 16.43                  | 0.00023        | 6.08                     | 83.31            | 34                            | 11.87                  | 0.00021                  | 4.12                     | 74.28            |
| DELCORA  | 4            | 2                             | 1.43                   | 0              | 0.15                     | 0                | 15                            | 2.02                   | 0.00002                  | 0.19                     | 2.25             |

# TABLE 4: Total PCB and AHH-Active PCB in Selected Tributaries and Point Source Discharges of the Delaware Estuary

|  |              | DRY WEATHER                   |                          |                       |                          | WET WEATHER             |                                  |  |                                  |                                  |                  |
|--|--------------|-------------------------------|--------------------------|-----------------------|--------------------------|-------------------------|----------------------------------|--|----------------------------------|----------------------------------|------------------|
| SOURCES  |              |                               | Concer                   | ntration Mass Loading |                          | Concentration Mass Load |                                  | oading                                       |                                  |                                  |                  |
|  | DRBC<br>Zone | # of<br>Congeners<br>Detected | Total<br>PCB<br>(ng/L)   | TEQs<br>(ng/L)        | Total<br>PCB<br>(gm/day) | TEQs<br>(ug/day)        | # of<br>Congeners<br>Detected    | Total<br>PCB<br>(ng/L)                       | TEQs<br>(ng/L)                   | Total<br>PCB<br>(gm/day)         | TEQs<br>(ug/day) |
| Philadelphia SW  | 4            | 11                            | 7.49                     | 0.00006               | 5.11                     | 39.21                   | 34                               | 11.92  | 0.00011                          | 8.03                             | 76.14            |
| Philadelphia NE<br>Philadelphia NE (Rep)   | 3            | 0<br>3                        | 0<br>2.25                | 0                     | 0<br>1.65                | 0<br>0                  | 28                               | 5.36   | 0.00004                          | 4.41                             | 32.00            |
| Philadelphia SE  | 3            | 16                            | 45.14                    | 0.00039               | 17.19                    | 149.27                  | 42                               | 20.24  | 0.00019                          | 8.10                             | 74.57            |
| Monsanto Corp.   | 4            | 10                            | 10.27                    | 0                     | 0.04                     | 0                       | Not                              | sampled d                                    | uring Wet W                      | eather Surve                     | у                |
| COMBINED SEWER OVE   | RFLOWS       |                               |                          |                       |                          |                         |                                  |  |                                  |                                  |                  |
| Camden County MUA<br>Camden (Dup)  | 3            |                               | Assume                   | d To Be Ne            | egligible                |                         | 58<br>50                         | 62.76<br>58.14                               | 8.28E-04<br>7.20E-04             | 61.77<br>57.22                   | 814.9<br>708.9   |
| Wilmington<br>Wilmington (Dup)   | 5            |                               | Assume                   | d To Be Ne            | egligible                |                         | 49<br>43                         | 41.62<br>33.09                               | 6.89E-04<br>5.22E-04             | 18.56<br>14.76                   | 307.3<br>233.0   |
| DELCORA  | 4            |                               | Assume                   | d To Be Ne            | gligible                 |                         | 29                               | 11.00  | 9.18E-05                         | 1.27                             | 10.6             |
| Philadelphia SW-Site #1<br>Philadelphia SW-Site #2   | 4            |                               | Assumed To Be Negligible |                       |                          |                         | 63<br>66                         | 339.66<br>539.19                             | 6.69E-03<br>4.82E-03             | 347.17<br>551.11                 | 6839.0<br>4927.1 |
| Philadelphia NE<br>Philadelphia NE (Dup)<br>Philadelphia NE (Rep)<br>Philadelphia NE (Rep-Dup) | 3            |                               | Assumed To Be Negligible |                       |                          | 50<br>52<br>51<br>55    | 35.86<br>64.48<br>41.77<br>52.28 | 3.39E-04<br>3.99E-04<br>3.99E-04<br>5.47E-04 | 47.79<br>85.93<br>55.66<br>69.67 | 451.6<br>532.2<br>531.3<br>729.0 |                  |
| Philadelphia SE  | 3            |                               | Assume                   | d To Be Ne            | gligible                 |                         | 64                               | 1509.09                                      | 2.25E-02                         | 1428.18                          | 21328.5          |

# Table 5: Tributary and Wastewater Treatment Plant Flowsduring the Dry and Wet Weather Surveys(Daily average unless otherwise indicated)

| Location   | Dry Weather<br>20-Aug-96  |                   | Wet Weather<br>04/29/97 |     | Wet Weather<br>26-May-97 |                   |
|--|---------------------------|-------------------|-------------------------|-----|--------------------------|-------------------|
| Upper Christina River  | 12                        | CFS               | 200                     | CFS |                          |                   |
| White Clay Creek   | 89                        | CFS               | 429                     | CFS |                          |                   |
| Red Clay Creek   | 55                        | CFS               | 225                     | CFS |                          |                   |
| Brandywine Creek   | 376                       | CFS               | 980                     | CFS |                          |                   |
| Raccoon Creek  | 21                        | CFS               | 64                      | CFS |                          |                   |
| Rancocas Creek 1,2   | 278                       | CFS               | 430                     | CFS |                          |                   |
| Crosswicks Creek   | 119                       | CFS               | 410                     | CFS |                          |                   |
| Delaware River at<br>Trenton                                 | 4400                      | CFS               | 11,400                  | CFS |                          |                   |
| Neshaminy Creek  | 114                       | CFS               | 401                     | CFS |                          |                   |
| Schuylkill River   | 1030                      | CFS               | 3310                    | CFS |                          |                   |
| Wilmington Effluent  | 97.71                     | MGD               |                         |     | 91.70                    | MGD               |
| DELCORA Influent   | 27.41                     | MGD               |                         |     | 25.30                    | MGD               |
| Camden Influent  | 55.26                     | MGD               |                         |     | 79.58                    | MGD               |
| Philadelphia SW Influent<br>Low Level<br>High Level<br>TOTAL | 16.22<br>115.99<br>180.10 | MGD<br>MGD<br>MGD |                         |     | 16.73<br>178.07          | MGD<br>MGD<br>MGD |
| Philadelphia SE Influent                                     | 100.60                    | MGD               |                         |     | 105.70                   | MGD               |
| Philadelphia NE Influent                                     | 193.52                    | MGD               |                         |     | 217.30                   | MGD               |

1 - Sum of actual data from the North Branch and a value of 76 cfs for the South Branch for July 25, 1996 (instantaneous value measured during water quality sampling)

2 - Sum of actual data from the North Branch and a value of 90 cfs for the South Branch (mean of the instantaneous values measured during water quality sampling on March 25, 1997 and May 27, 1997)

| DRY WEATHE    |                  | EATHER           | WET W               | EATHER           |
|---------------|------------------|------------------|---------------------|------------------|
| SOURCE        | PCBs<br>(gm/day) | TEQs<br>(ug/day) | PCBs<br>(gm/day)    | TEQs<br>(ug/day) |
| Tributaries   | 1.67             | 0                | 83.72               | 1218.48          |
| Point Sources | 34.25            | 285.14           | 24.86               | 259.24           |
| CSOs          | -                | -                | 2019.51             | 28815.23         |
|               |                  |                  | 822.26 <sup>a</sup> |                  |
| TOTAL         | 35.9             | 285.1            | 2128.1              | 30293.0          |
| % Tribs       | 4.6              | 0.0              | 3.9                 | 4.0              |
|               |                  |                  | 9.0 <sup>a</sup>    |                  |
| % Point       | 95.4             | 100.0            | 1.2                 | 0.9              |
|               |                  |                  | 2.7 <sup>a</sup>    |                  |
| % CSOs        | -                | -                | 94.9                | 95.1             |
|               |                  |                  | 88.3 <sup>a</sup>   |                  |

#### TABLE 6: Total PCB and AHH-Active PCB Mass Loading Summary

Note: When laboratory duplicate and/or field replicate sample results were available, the average of the primary and duplicate and/or replicate sample was used in computing mass load.

a - Mass loading from CSOs associated with Philadelpia Southeast plant calculated using the average of the influent concentrations from the Philadelphia Southwest and Northeast plants.

|  | Infl                             | uent   | Effluent            |                | Percent Reduction |             |
|--|----------------------------------|--|---------------------|----------------|-------------------|-------------|
| Facility   | Total PCB<br>(ng/L)              | TEQs<br>(ng/L)                               | Total PCB<br>(ng/L) | TEQs<br>(ng/L) | Total PCB<br>(%)  | TEQs<br>(%) |
| Philadelphia NE<br>Philadelphia NE (Dup)<br>Philadelphia NE (Rep)<br>Philadelphia NE (Rep-Dup) | 35.86<br>64.48<br>41.77<br>52.28 | 3.39E-04<br>3.99E-04<br>3.99E-04<br>5.47E-04 | 5.36                | 3.89E-05       | 88.97             | 90.76       |
| Philadelphia SE  | 1509.09                          | 2.25E-02                                     | 20.24               | 1.86E-04       | 98.66             | 99.17       |
| Philadelphia SW-Site #1<br>Philadelphia SW-Site #2   | 339.66<br>539.19                 | 6.69E-03<br>4.82E-03                         | 11.92               | 1.13E-04       | 97.27             | 98.04       |
| Camden<br>Camden (Dup)   | 62.76<br>58.14                   | 8.28E-04<br>7.20E-04                         | No Sample           | Due To Fire    | -                 | -           |
| DELCORA  | 11.00                            | 9.18E-05                                     | 2.02                | 2.35E-05       | 81.64             | 74.40       |
| Wilmington<br>Wilmington (Dup)   | 41.62<br>33.09                   | 6.89E-04<br>5.22E-04                         | 11.87               | 2.14E-04       | 68.23             | 64.69       |

## TABLE 7: Percent Reduction in Total PCB and AHH-Active PCB Concentrations at Treatment Plants During Wet Weather Sampling Event

Note: When laboratory duplicate and/or field replicate sample results were available, the average of the primary and duplicate and/or replicate sample was used in percent reduction.

|          | DRY WEATHER |                      |       | WET WEATHER |               |         |         |  |
|----------|-------------|----------------------|-------|-------------|---------------|---------|---------|--|
| ZONE     | Tributaries | <b>Point Sources</b> | Total | Tributaries | Point Sources | CSOs    | Total   |  |
| 2        | 0.46        | -                    | 0.46  | 35.77       | -             | -       | 35.77   |  |
| 3        | -           | 22.87                | 22.87 | -           | 12.51         | 1552.44 | 1564.95 |  |
| 4        | 0.26        | 5.30                 | 5.56  | 27.85       | 8.22          | 450.41  | 486.48  |  |
| 5        | 0.95        | 6.08                 | 7.03  | 20.10       | 4.12          | 16.66   | 40.88   |  |
| TOTAL    | 1.67        | 34.25                | 35.92 | 83.72       | 24.85         | 2019.51 | 2128.08 |  |
| % Zone 2 | 27.54       | 0.00                 | 1.28  | 42.73       | 0.00          | 0.00    | 1.68    |  |
| % Zone 3 | 0.00        | 66.77                | 63.67 | 0.00        | 50.34         | 76.87   | 73.54   |  |
| % Zone 4 | 15.57       | 15.47                | 15.48 | 33.27       | 33.08         | 22.30   | 22.86   |  |
| % Zone 5 | 56.89       | 17.75                | 19.57 | 24.01       | 16.58         | 0.83    | 1.92    |  |

| TABLE 8: | PCB Mass Loading By DR | BC Zone (loading in | i <mark>grams per c</mark> | day) |
|----------|------------------------|---------------------|----------------------------|------|
|----------|------------------------|---------------------|----------------------------|------|

Note: When laboratory duplicate and/or field replicate sample results were available, the average of the primary and duplicate and/or replicate sample was used in computing mass load.

|          | Ι           | DRY WEATHER          |        |             | WET WEATHER   |          |          |  |  |
|----------|-------------|----------------------|--------|-------------|---------------|----------|----------|--|--|
| ZONE     | Tributaries | <b>Point Sources</b> | Total  | Tributaries | Point Sources | CSOs     | Total    |  |  |
| 2        | 0.0         | -                    | 0.0    | 559.73      | -             | -        | 559.73   |  |  |
| 3        | -           | 162.62               | 162.62 | -           | 106.57        | 22651.43 | 22758.00 |  |  |
| 4        | 0.0         | 39.21                | 39.21  | 508.09      | 78.39         | 5893.65  | 6480.13  |  |  |
| 5        | 0.0         | 83.31                | 83.31  | 150.66      | 74.28         | 270.15   | 495.09   |  |  |
| TOTAL    | 0.0         | 285.1                | 285.1  | 1218.5      | 259.2         | 28815.2  | 30293.0  |  |  |
| % Zone 2 | 0.0         | 0.0                  | 0.0    | 45.9        | 0.0           | 0.0      | 1.9      |  |  |
| % Zone 3 | 0.0         | 57.0                 | 57.0   | 0.0         | 41.1          | 78.6     | 75.1     |  |  |
| % Zone 4 | 0.0         | 13.8                 | 13.8   | 41.7        | 30.2          | 20.5     | 21.4     |  |  |
| % Zone 5 | 0.0         | 29.2                 | 29.2   | 12.4        | 28.7          | 0.9      | 1.6      |  |  |

 TABLE 9:
 Mass Loading of AHH-Active PCBs By DRBC Zone (loading in micrograms per day)

Note: When laboratory duplicate and/or field replicate sample results were available, the average of the primary and duplicate and/or replicate sample was used in computing mass load.

| Table 10: | <b>Results of Statistical</b> | <b>Comparisons E</b> | <b>Between Dry</b> | and Wet Weather | Surveys |
|-----------|-------------------------------|----------------------|--------------------|-----------------|---------|
|-----------|-------------------------------|----------------------|--------------------|-----------------|---------|

|                                | Hypot                         |                            |  |
|--------------------------------|-------------------------------|----------------------------|--|
| Categories Being Compared      | H <sub>o</sub> (Null)         | H <sub>a</sub> (Alternate) | Result of Sign Test                    |
| Dry Weather PCB Concentrations | Median Difference Between     | Wet Weather Values Tend to | Accept $H_a$ at alpha = 0.005          |
| vs.                            | Dry-Wet Weather Data Pairs is | Exceed Corresponding Dry   |  |
| Wet Weather PCB Concentrations | Zero                          | Weather Values             |  |
| Dry Weather PCB Mass Loading   | Median Difference Between     | Wet Weather Values Tend to | Accept H <sub>a</sub> at alpha = 0.005 |
| vs.                            | Dry-Wet Weather Data Pairs is | Exceed Corresponding Dry   |  |
| Wet Weather PCB Mass Loading   | Zero                          | Weather Values             |  |
| Dry Weather TEQ Concentrations | Median Difference Between     | Wet Weather Values Tend to | Accept H <sub>a</sub> at alpha = 0.005 |
| vs.                            | Dry-Wet Weather Data Pairs is | Exceed Corresponding Dry   |  |
| Wet Weather TEQ Concentrations | Zero                          | Weather Values             |  |
| Dry Weather TEQ Mass Loading   | Median Difference Between     | Wet Weather Values Tend to | Accept $H_a$ at alpha = 0.005          |
| vs.                            | Dry-Wet Weather Data Pairs is | Exceed Corresponding Dry   |  |
| Wet Weather TEQ Mass Loading   | Zero                          | Weather Values             |  |

# Table 11:Results of Analysis of Covariance of the Effect of Precipitation<br/>and Percent Solids on Total PCB Concentrations in the<br/>Tributaries.

| Dependent Variable: Log <sub>10</sub> (Total PCBs) |                       |                           |                |         |             |  |
|--|-----------------------|---------------------------|----------------|---------|-------------|--|
| MODEL  | Degrees of<br>Freedom | Partial Sum of<br>Squares | Mean<br>Square | F Value | Probability |  |
| Source   |                       |                           |                |         |             |  |
| Weather  | 1                     | 0.40474                   | 0.40474        | 5.52    | 0.0311*     |  |
| Solids   | 1                     | 0.00346                   | 0.00346        | 0.05    | 0.8307      |  |
| Weather*Solids                                     | 1                     | 0.03248                   | 0.03248        | 0.44    | 0.5145      |  |
| Error  | 17                    | 1.24577                   | 0.07328        |         |             |  |
| Corrected Total                                    | 20                    | 2.18697                   |                |         |             |  |

 $R^2 = 0.430$  for overall model.

Data is normally distributed (Shapiro-Wilk W statistic = 0.907,  $\alpha = 0.046$ )

|             | Least Square Means<br>of Log (Conc) | Corresponding<br>Arithmetic Means | Probability for<br>H <sub>0</sub> : Dry = Wet |
|-------------|-------------------------------------|-----------------------------------|---|
| Dry Weather | 0.1864                              | 1.54                              | ž   |
| Wet Weather | 0.6035                              | 4.01                              | 0.0036*                                       |

\* Significant at  $\alpha \le 0.05$ 

# TABLE 12:Net Advective Flow and Applicable Water Quality Criteria for<br/>Total PCBs for Zones 2 to 5 of the Delaware River Estuary.

| Human Health Criteria: Carcinogenic Effects |                                     |                                   |                                      |  |  |
|---|-------------------------------------|-----------------------------------|--------------------------------------|--|--|
| DRBC<br>Zone                                | Water Quality<br>Criteria<br>(ug/L) | Harmonic<br>Mean Flow<br>(m³/sec) | Assimilation<br>Capacity<br>(gm/day) |  |  |
| 2   | 0.0000444                           | 204.16                            | 0.78                                 |  |  |
| 3   | 0.0000444                           | 211.76                            | 0.81                                 |  |  |
| 4   | 0.0000448                           | 242.81                            | 0.94                                 |  |  |
| 5   | 0.0000079                           | 283.67                            | 0.19                                 |  |  |

| Chronic Aquatic Life Criteria |                                     |                                   |                                      |  |  |
|-------------------------------|-------------------------------------|-----------------------------------|--------------------------------------|--|--|
| DRBC<br>Zone                  | Water Quality<br>Criteria<br>(ug/L) | Low Flow<br>(m <sup>3</sup> /sec) | Assimilation<br>Capacity<br>(gm/day) |  |  |
| 2                             | 0.014                               | 67.11                             | 81.18                                |  |  |
| 3                             | 0.014                               | 71.08                             | 85.97                                |  |  |
| 4                             | 0.014                               | 85.18                             | 103.03                               |  |  |
| 5                             | 0.014                               | 118.47                            | 143.30                               |  |  |

| Human Health Criteria: Carcinogenic Effects |   |  |   |  |  |
|---|---|--|---|--|--|
| DRBC<br>Zone                                | Water Quality<br>Criteria in TEQs<br>(ug/L) | Harmonic<br>Mean Flow<br>(m <sup>3</sup> /sec) | TEQ<br>Assimilation<br>Capacity<br>(µg/day) |  |  |
| 2   | 1.30e-08                                    | 204.16   | 229.32                                      |  |  |
| 3   | 1.30e-08                                    | 211.76   | 237.84                                      |  |  |
| 4   | 1.40e-08                                    | 242.81   | 293.70                                      |  |  |
| 5   | 2.40e-09                                    | 283.67   | 58.82                                       |  |  |

TABLE 13:Comparison Between Measured Mass Loadings and Delaware<br/>River Estuary Assimilation Capacity.

|              | Total Polychlorinated Biphenyls           |   |  |  |  |
|--------------|---|---|--|--|--|
| DRBC<br>Zone | Loading During<br>Dry Weather<br>(gm/day) | Loading During<br>Wet Weather<br>(gm/day) | Human Health<br>Assimilation<br>Capacity<br>(gm/day) | Aquatic Life<br>Assimilation<br>Capacity<br>(gm/day) |  |
| 2            | 0.46                                      | 35.77                                     | 0.78   | 81.2   |  |
| 3            | 22.87                                     | 1564.95                                   | 0.81   | 86.0   |  |
| 4            | 5.56                                      | 486.48                                    | 0.94   | 103.0  |  |
| 5            | 7.03                                      | 40.88                                     | 0.19   | 143.3  |  |

| DRBC<br>Zone | PCB TEQs                                  |   |  |  |
|--------------|---|---|--|--|
|              | Loading During<br>Dry Weather<br>(µg/day) | Loading During<br>Wet Weather<br>(µg/day) | Human Health<br>Assimilation<br>Capacity<br>(µg/day) |  |
| 2            | 0.00                                      | 559.73                                    | 229.32   |  |
| 3            | 162.62                                    | 22758.0                                   | 237.84   |  |
| 4            | 39.21                                     | 6480.13                                   | 293.70   |  |
| 5            | 83.31                                     | 495.09                                    | 58.82  |  |





Figure 2: Comparison of molecular models of coplanar PCBs and 2,3,7,8 - TCDD.



Figure 3: Total PCB congener concentrations in tributary samples during the August 1996 dry weather survey and April 1997 wet weather survey.



Figure 4: Total PCB congener concentrations in wastewater treatment plant effluent samples during the August 1996 dry weather survey and May 1997 wet weather survey.





Figure 6: Percent of total PCB loading by source category during the August 1996 dry weather survey and Spring 1997 wet weather survey.



Figure 7: Total PCB congener concentrations in wastewater treatment plant influent samples during the May 1997 wet weather survey.





Figure 9: Total PCB mass loading to the Delaware Estuary from wastewater treatment plants during the August 1996 dry weather survey and May 1997 wet weather survey.





Figure 11: Total PCB mass loading to the Delaware Estuary by DRBC Zone designations during the August 1996 dry weather survey and May 1997 wet weather survey.



Figure 12: Distribution of PCB homolog groups in tributary samples collected during the August 1996 dry weather survey and April 1997 wet weather survey.



Figure 13: Distribution of PCB homolog groups in wastewater treatment plant effluent samples collected during the August 1996 dry weather survey and May 1997 wet weather survey.



Figure 14: Distribution of PCB homolog groups in wastewater treatment plant samples collected during the May 1997 wet weather survey.

### **APPENDIX**

Congener-Specific PCB Analysis for the DRBC Study of the Loadings of PCBs from Tributaries and Point Sources Discharging to the Tidal Delaware River

Midwest Research Institute

[ Available on Request ]