



Pollution Minimization Plans and PCB Source Trackdown in Camden City

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ABSTRACT

A PCB source trackdown study was performed in Camden, New Jersey using the sewer collection system of a municipal utility authority (MUA). Sampling and analytical techniques were developed to identify PCB sources using innovative desktop, field and analytical methods including high resolution gas chromatography and mass spectroscopy; the quantitation of 124 separate PCB congeners for source signatures; the use of passive in-situ continuous extraction samplers (PISCES); and the use of electronic data interfaced with a GIS system to geographically isolate potential sources. In addition, PCB immunoassay analyses (ELISA) of street soils were carried out near storm drains in front of suspected facilities. These source identification methods were developed to support Pollution Minimization Plans (PMP), which are permit requirements for discharger facilities in New Jersey, Pennsylvania and Delaware as part of the Delaware Estuary PCB-TMDL. The PMP rules require dischargers to actively seek out, and reduce, PCBs on their facilities footprint which might get into the MUA collection system. This can be problematic, however, for a county-wide MUA with hundreds of miles of pipes and numerous undefined point and non-point sources (i.e., Camden City is a combined sewer outfall (CSO) area where storm run-off can collect PCBs and other contaminants then mix with sewerage in pipes prior to treatment).

KEYWORDS: Aroclor, immunosorbent assays, ELISA, PISCES, PCB, PMP, polychlorinated biphenyl, TMDL, trackdown.

INTRODUCTION

The Delaware Estuary in New Jersey is listed by the new Jersey Department of Environmental Protection (NJDEP) as an impaired waterway due to PCB contamination in fish [1] [2]. Subsequently, in 1998, using a new analytical methodology of high resolution gas chromatography/high resolution mass spectrometry or HRGC/HRMS [3] the Delaware River Basin Commission (DRBC) performed a PCB loadings study on the Delaware Estuary and found PCBs in effluents from five large sewage treatment plants and one industrial facility [4]. Total PCB results ranged from 1.4 to 45.1 ng/L during dry weather, and 2.0 to 20.2 ng/L during wet weather.

Subsequently, in the spring of 2000, ninety-four dischargers (NPDES Permittees) to the Delaware Estuary from three different states were asked to conduct both continuous and stormwater discharge monitoring for eighty-one (81) PCB congeners utilizing Method 1668A. Results indicated that loadings of PCBs to the Delaware Estuary management zones (Figure 1) from point sources were significant and of such magnitude as to cause the water quality standards to be exceeded. The water quality PCB criteria for Zone 3 of the Delaware Estuary (near Camden, New Jersey) is 44.4 picograms per liter. During this year 2000 sampling period the Camden County Municipal Utility Authority (CCMUA) collected three wet weather and three dry weather samples and consistently found all ten homologs of PCBs to be present in their effluent, and with loadings of 819 mg/day, or at levels that exceed ambient water concentrations of PCBs in river by three orders of magnitude [5].



Figure 1. Delaware Estuary Management Areas (Courtesy DRBC)

However, because of the high background levels and ubiquity of PCBs in the environment due to both historical discharges and ongoing approved uses, the Total Maximum Daily Load (TMDL) for Polychlorinated Biphenyls (PCBs) for Zones 2-5 of the Tidal Delaware River estuary [5] stipulates that facilities that discharge to the River, including its tributary streams, must develop and implement a pollution Minimization plan (PMP) which shall include: a list of all known and suspected point and non-point sources of PCBs; a *description of studies used to trackdown PCBs*; a description of actions to minimize the discharge of PCBs; a proposed time frame for PCB load reductions; a method to demonstrate progress; and required PCB monitoring. These required items were subsequently codified in a DRBC Resolution [6] and guidance manual [7].

Yet trackdown of PCBs in a municipal utility authority's collection system is problematic due to the hundreds of miles of piping, the numerous industrial users, and more importantly due to the presence of combined sewers (combined stormwater and sewerage) in Camden City, which adds significant PCB loads from non-point sources and hazardous waste sites due to runoff. A field and lab methodology was therefore needed for MUAs to trackdown PCBs coming into their

collection systems so as to initiate the load reduction strategies as required in the PMP. A cooperative agreement was developed between NJDEP, DRBC and CCMUA to perform a Pilot Trackdown Study. The primary goals of the Pilot Study were to evaluate the most appropriate sampling and analytical techniques for tracking down PCB contamination in CCMUA's Sewer-CSO collection system and to identify potential upland sources of PCBs for follow-up assessment/abatement.

Innovative methods explored in this study included the use of PCB analytical Method 1668a to attain high sensitivity in sampling including quantification of 124 separate PCB congeners as a mean to identify unique source signatures; the use of passive in-situ continuous extraction samplers (PISCES) for sample integration over long time periods (14 days); the use of inexpensive immunoassay techniques for sampling PCBs in street soils; and the use of NJDEP's hazardous waste site's electronic data collection system in conjunction with a geographic information system (GIS) to screen and isolate potential upland sources for further investigatory actions. The Pilot Study was carried out in two phases. Phase 1 involved only in-sewer sampling of wastewater to identify sewersheds with PCB hotspots. Phase 2 followed up on this sampling with additional in-sewer sampling but also with more detailed street soil sampling for PCBs in front of suspect facilities.

PHASE 1: METHODS

Site Selection: The flow of wastewater in any underground piping systems all follow the same engineering hydraulic principals similar to natural stream flows. Water moves from small to progressively larger catchments and merge at key junctions called "*Interceptors*." These Interceptors all have manhole access points for sampling. Fortunately for the Pilot Study the piping and infrastructure of CCMUA's collection system had recently been surveyed and GIS-mapped to delineate five major county basins with multiple in-city sub-basins [8]. In addition, NJDEP adopted technical rules in 1997 for site remediation (NJAC 7:26E) requiring that all entities carrying out hazardous site investigations deliver investigative data in spatial and digital formats including the concentrations of different contaminants (e.g., PCBs). It is called the HazSite database and maintained by NJDEP Site Remediation program (SRP). Finally, CCMUA has a list of industrial users permitted to release wastewater for treatment into its collection system. The SIC codes for these facilities were then cross-checked against industry types known to use of be sources of PCBs [9].

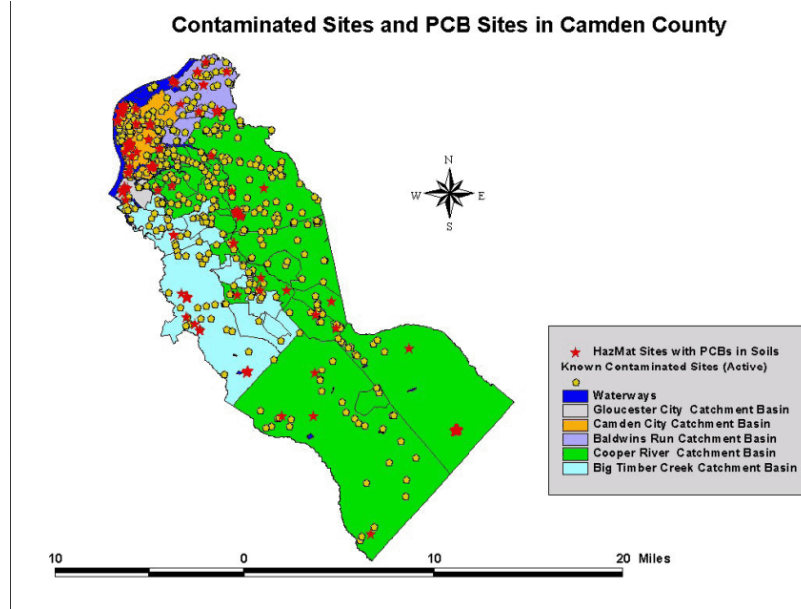


Figure 2. Known Contaminated Sites and PCB Contaminated Sites in Camden County, NJ.

The Pilot Study used these datasets in a unique fashion, both as a GIS-screening tool for locating potential discharge points for PCBs coming into the collections system (Figure 2), and for the

selection of Integrator sampling points for delineating sewersheds possibly associated with elevated PCB discharge/runoff to sewers and storm drains. Based on this approach we identified

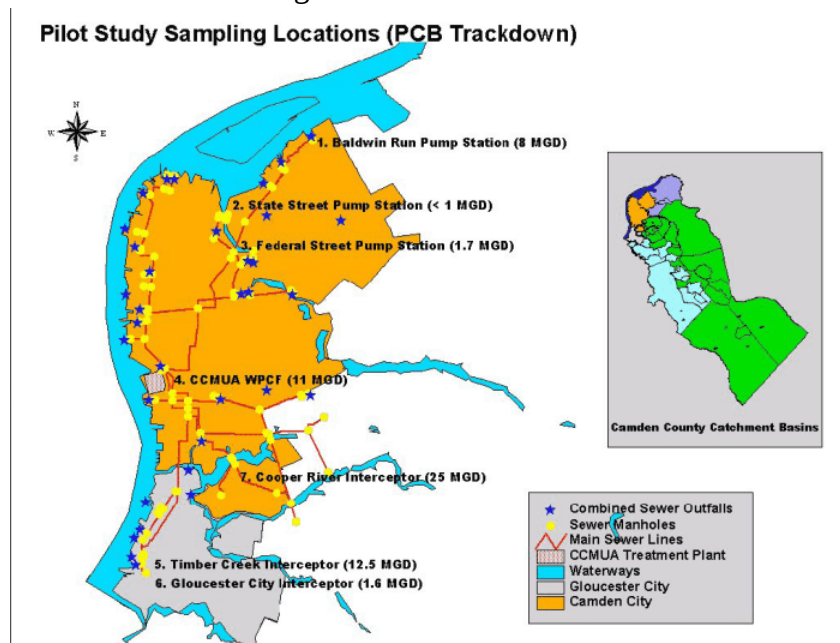


Figure 3. Sewer Sampling Locations - Phase 1

seven interceptor monitoring locations for Phase 1 of the Pilot Study within the municipal boundaries of Camden City (Figure 3), each station draining and representing a separate sub-basin of interest as a potential source of PCBs.

Field Sampling Procedures:
At each interceptor three different types of sampling were performed to gauge accuracy and cost-effectiveness; whole water 24-hour composite samples; single grab samples; and PISCES, a unique 14-day integrated sampling unit which used hexane and a semi-permeable membrane to integrate low concentration organic contaminants over time [10]. Whole water samples were collected using ISCO pump samplers as twenty-four composites on July 7-8, 2003 and grab samples on July 9 and 10, 2003. Sampling was implemented during dry weather in July with no preceding rainfall (i.e., > 0.1 inch of rain with duration of at least an hour within 72 hours of initial deployment). After 24-hours, the composite samples (8 Liters) were retrieved and placed into coolers, a field report and Chain of Custody form completed, then samples were shipped to AXYS Labs. Immediately after the 24-hours composite sample was collected the ISCO pumps were used to pull an additional grab sample (2.5 liter) from each manhole. A field and trip blank were included with each sampling round using nanopure water provided by lab.

PISCES samplers consist of brass pipes, fittings and a semi-permeable membrane filter with hexane as the sampling medium. When submerged in water, dissolved hydrophobic molecules like PCBs pass through the membrane and accumulate in the nonpolar hexane. Two PISCES samplers per station were deployed in parallel [10] with a protective shield placed around them to minimize potential damage to the membrane from debris and turbulent flows in the sewers. Temperature was monitored continuously using Hobo XT temperature sensors and data loggers (every 12–16 min) since the sampling rate of PISCES is strongly influenced by temperature. Temperature data was used to estimate the PISCES sampling rates since PCB uptake is a function of the membrane area and the temperature of the water being sampled [11]. Average temperature values and the membrane area were entered into an equation to estimate the sampling rate. The sampling rate was used to define the equivalent volume of water sampled during deployment, which is then used to calculate the average PCB concentrations in the water during the sampling period.

PISCES samples were collected over a 13 to 14 day deployment (July 9-23, 2003) during dry weather and with no preceding rainfall (i.e., > 0.1 inch of rain with duration of at least an hour within 72 hours of initial deployment), however we did capture a significant rain event during its fourteen day deployment. The two PISCES units per site were then retrieved and decanted into pre-cleaned lab jars onsite. The PISCES units and blanks were filled with the same grade of hexane used by laboratory for sample extractions. Only one of the two PISCES samples was chosen for shipment and PCB analysis by Lab, the other being archived by NJDEP.

Analytical Procedures: All samples were collected, documented with chain of custody provisions, and shipped cold to AXYS analytical laboratories for PCB congener analysis. There they were analyzed for 124 PCB congeners (Table 1) by USEPA method 1668A [3] with slight modifications as performed by an analytical contract lab (AXYS Labs) using HRGC/HRMS. The 124 PCB congeners were selected in consultation with DRBC after a literature review of other PCB congener studies performed in the Delaware River Basin, and comparisons with data sets from DNREC, DRBC, Rutgers and University of Maryland studies. For the PISCES sample analyses (lab grade hexane) the extraction step in Method 1669a proved unnecessary (i.e., PISCES hexane-water exposure essentially mimics lab extraction) and omitted.

PCB IUPAC Congener Numbers for Analysis				
1	32	82	135	181
3	33	83	136	183
4	37	84	137	185
5	40	85	138	187
6	41	87	141	189
7	44	89	146	190
8	45	90	149	191
10	46	91	151	193
11	47	92	153	194
12	48	95	156	195
13	49	97	157	196
14	51	99	158	197
16	52	101	163	198
17	53	105	166	199
18	56	107	167	200
19	60	110	168	201
21	63	114	170	202
22	64	118	171	203
24	65	119	172	204
25	66	123	174	205
26	70	128	176	206
28	74	129	177	207
29	77	130	178	208
30	80	132	179	209
31	81	134	180	

Table 1. Target Analytes for PCB Congeners

The samples were spiked with surrogate standard solution and then dried over sodium sulphate before proceeding with the column chromatography cleanup. All detectable congeners were reported and half the detection limit for non-detected values. The assumption of using ½ DL is justified since most samples exhibited detectable concentrations of PCBs

PHASE 1: RESULTS

Sample analysis by AXYS Labs was performed in two batch loads. Batch 1 showed acceptable QA recoveries and the absence of any quantifiable contamination in field, trip, or lab blanks. Batch 2 however, showed PCB 209 in the procedural blank, therefore this analyte was flagged not quantifiable for all samples in that batch.

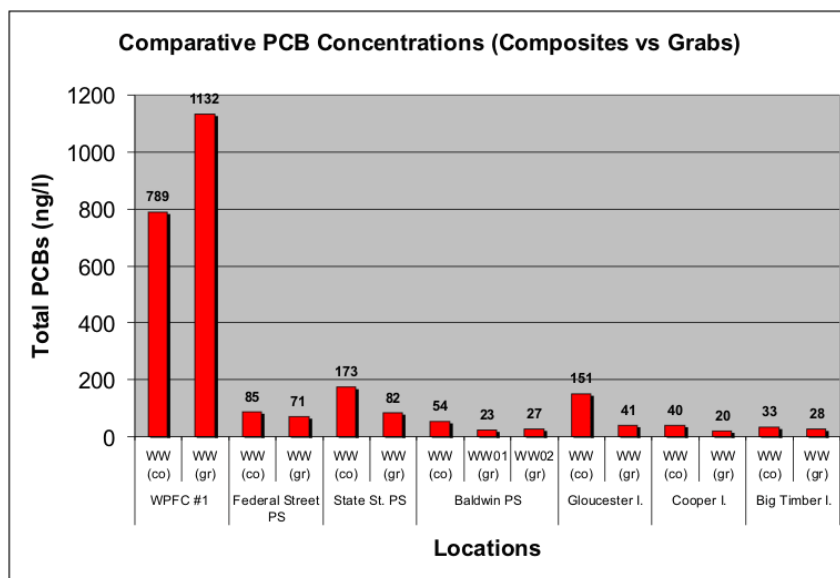


Figure 4. PCB Concentrations for both Grab and 24-Hour Composite Samples

Total PCBs: Analytical results showed quantifiable levels of PCBs at all seven Integrators (Table 2; Figure 4), both urban and suburban sewersheds, and in all sampling media (i.e., 24-hr wastewater composites, grab samples, and PISCES hexane extracts). High concentrations of total PCBs were found in both whole water 24 hr.

composites (Mean: 189 ng/l; Range: 33 ng/l to 784 ng/l) and grab samples (Mean: 41 ng/l; Range: 20 ng/l to 82 ng/l). Fourteen day PISCES hexane

samples also showed consistent high levels of PCBs in the waste stream, although the results were skewed to the lower chlorinated congeners, ostensibly because the more highly chlorinated PCBs tend to adhere to particulates, which do not efficiently cross the PISCES semi-permeable membrane.

Table 2. PCB Results and Loadings for 24 Hour Composite Water Samples Collected at Pump Stations and Interceptors Served by CCMUA (Phase I - 2003)*

Location	Area Served	Total PCBs, pg/L	Flow, mgd**	PCB Load, g/day	% of Total Load
Baldwin Run Pump Station PS	Northeast Camden and Pennsauken	53,839	8.0	1.63	4%
State St. PS	Northeast Camden Industrial Area	173,466	1.0	0.66	2%
Federal St. PS	Pavonia Yards	85,373	1.7	0.55	1%
Main Influent CCMUA +	Waterfront (West) & South Camden	798,081	11.0	30.94	77%
Cooper River	Camden County (East)	40,107	25.0	3.80	9%
Big Timber	Camden County (West)	32,763	12.5	1.60	4%
Gloucester City	Gloucester City	151,088	1.6	0.92	2%
TOTAL	--	--	60.8	40.04	100%

* 24 hr whole water composite samples analyzed by EPA Method 1668A.

** Estimated flows from CCMUA's CSO Modeling Report (CH2M Hill 1999).

+ Main Influent CCMUA sampling point includes loads from State St and Federal St pump stations. The pump station loads were subtracted from the actual WPCF loading to derive the

West & South Camden loading [i.e., actual WPCF loading of 33.23 g/day minus the sum of the State St (1.63 g/day) and Federal St pump stations (0.66 g/day)].

PCB Congener Patterns: PCBs are a mixture of up to 209 distinct congeners making the laboratory analysis particularly challenging. Most PCBs were commercially produced in the United States as standard mixtures bearing the brand name Aroclor. The reaction and separation conditions for production of each Aroclor favor the synthesis of certain congeners, giving each Aroclor a unique signature or pattern based on its congener composition [12]. No Aroclor contains all 209 congeners; in fact, 110–120 congeners typically account for over 95% of the total mass in each Aroclor.

An analysis of PCB congener patterns in this study suggests varied potential sources since there are differences in PCB congener profiles between Integrators and sewersheds. For example, the Federal Street Integrator (Figure 5a) has an overwhelming makeup of the lower chlorinated PCB congeners (i.e., mono-, di- and tri-chlorinated) whereas the main influent Interceptor to CCMUA's treatment plant (Figure 5b), which receives flow from the Federal Street Integrator, is depauperate in these lower chlorinated PCBs but enriched with the more chlorinated PCB congeners.

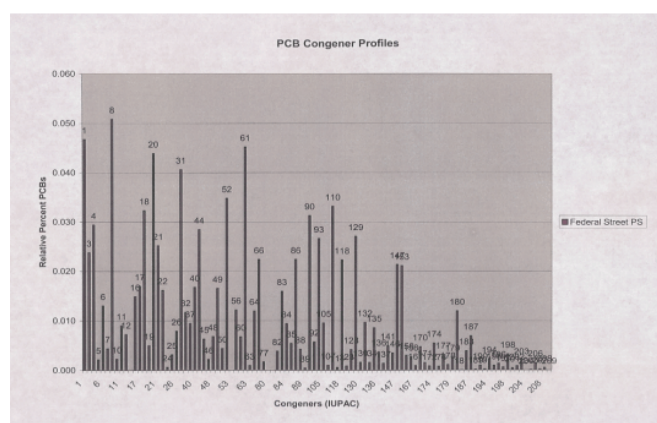


Figure 5a. PCB Congener Profile for Federal Street Interceptor

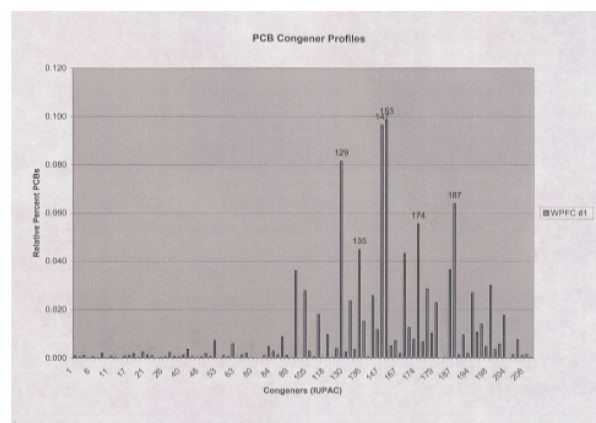


Figure 5b. PCB Congener Profile for Main Influent Interceptor CCMUA

Homologs/Aroclors: Historical attempts at isolating PCB source signatures have looked at the Aroclor distributions of PCB homologs [12]. That is the grouping of PCB congeners into chlorinated homolog groups (i.e., grouping congeners into 10 classes by degree of biphenyl chlorination) and to compare these with known distributions of homologs in Aroclors [12]. For example, the Aroclor-based distribution of PCB homologs at the Federal Street Integrator with its collection of lower chlorinated congeners (Figure 6a) resembles a mixture of Aroclors A1242 and A1248 whereas wastewater from main influent Interceptor to CCMUA's treatment plant (Figure 6b) appears looks more like Aroclor 1260.

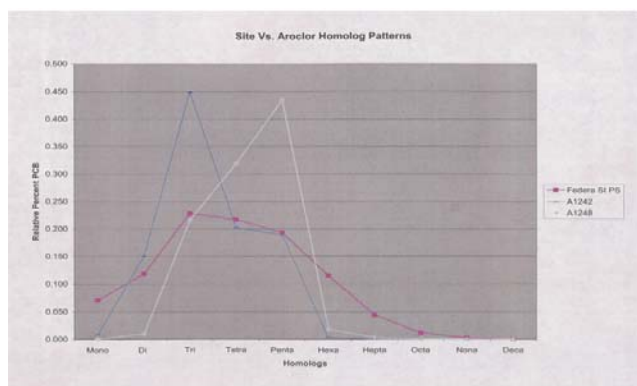


Figure 6a. PCB Homologs as Aroclors at the Federal Street Pump Station

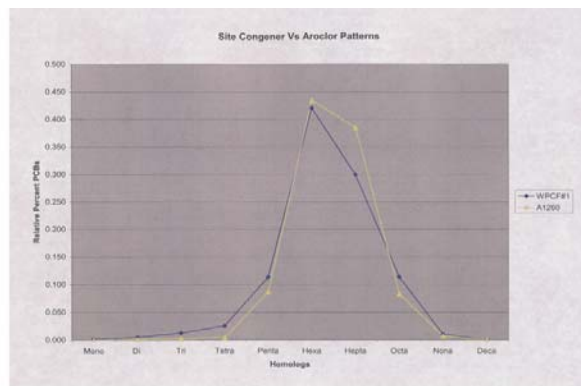


Figure 6b. PCB Homologs as Aroclors at the Main Influent CCMUA

PISCES: PISCES results are reported in ng/sample (since they integrate over a period of 14 days) but were converted to ng/l [10], which allows an estimate of the amount of PCBs in the surrounding water, if certain physical features are known (i.e., temperature). PISCES PCB results in both the hexane fraction and the estimated water quantities also show consistent levels of PCBs in the waste stream although congener results for PISCES were skewed more to the lower chlorinated PCBs, since the higher chlorinated PCBs tend to adhere to particulates which do not cross the PISCES sampling membrane efficiently.

PHASE 1: DISCUSSION

Concentration of PCBs were found and quantified in CCMUA wastewater at all sampling locations (i.e., both urban and suburban) and in all sampling media (i.e., wastewater composites, grabs samples, and PISCES hexane) potentially from varied sources (i.e., as indicated by differences in PCB congener profiles and homolog distributions between sampling sites and associated waste streams). The whole water sampler has the advantage of collecting total PCBs (i.e., PCBs both soluble and attached to suspended solids) whereas PISCES only collects PCBs that diffuse through its semi-permeable membrane (i.e., dissolved/soluble). This somewhat limits PISCES utility in potential source identification (i.e., congener pattern recognition). This is somewhat offset by the advantage of PISCES in its ability to integrate PCB concentrations over an extended sampling period (e.g., 7 to 10 days).

Higher concentrations of PCBs were found in 24-hr whole water composites versus grab samples. However, quantifiable levels in the grab samples at an order of magnitude above the analytical detection limits indicates that the more expensive and time consuming 24-hour composites may not be necessary. At least for a quick source trackdown result, when a yes-or-no answer as to the presence of PCBs in the sample is more indicative of nearby sources than actual quantitation.

Comparing the results of the three methods ; 24-hr composites, grab samples and PISCES we can see that they all can be used to identify PCBs in a MUA waste stream. The benefits of each approach however must be weighed against the logistical aspects and the disadvantages for the second and possibly more critical goal of source identification.

The PISCES sampling advantage, of long-term media integration, is offset by the difficulty of deployment (i.e., keeping a bulk sampler in place within a confined turbulent pipe) and its limited ability to identify the more highly chlorinated PCB congeners (i.e., usually transported on suspended solids).

The 24-hr composite samples which include both the aqueous and particulate wastewater fractions allow the most confidence in quantitative analytical results and congener patterns that may be more complete. This approach may also add significantly to any follow-up trackdown activities anticipated, since it's more complete and time integrated congener patterns may be the best means to match with upland soils, sediments or aqueous samples once a candidate site has been identified through HazSite/GIS screening.

Grab samples, on the other hand, based on comparison with 24-hr composite samples taken concurrently are also good at identifying the presence of PCBs in wastewater. This approach allows a quick and less expensive mode of sampling, and a more practical means of identifying PCB presence in wastewater and the relative patterns of PCB congeners.

The pattern of lower chlorinated PCB congeners found at the Federal Street Interceptor are unusual in the open environment since they tend to volatilize off quickly. Their presence in the wastewater sample may be indicative of a recent discharge or perhaps a by-product of the pumping process itself. But interestingly, PCBs found at the downstream main influent Interceptor to CCMUA's treatment plant had the higher chlorinated congeners, perhaps indicative of volatilization along the pipes and vent routes through central Camden, and/or indicative of other sources through the intervening sewersheds.

It should be noted however, that the value of chemical fingerprinting, using either homolog or congener analysis, is problematic since PCBs exposed in the environment have been shown to change over time due to weathering where chemical and physical transformations alter the composition of a sample. Weathering may be due to differences in congener volatilization, partitioning, chemical transformation, photo-degradation, biodegradation, or bioaccumulation [13]. Therefore PCB pattern-recognition based on weathered Aroclors may make it difficult to match one environmental sample against another. Specific congener analysis shows more promise.

Finally, although the mass-balance, or loadings, of PCBs to CCMUA were not a primary goal in this PCB source trackdown study, we felt it worthwhile to compute the loadings from these different sewer-sheds as a means to prioritize future trackdown investigations since small, cumulative source concentrations in a larger flow may far outweigh in significance a higher concentration in a more decreased flow (Table 1). The largest PCB load is at the Integrator at CCMUA's main treatment plant, which integrates all of Camden City's urban flows. It has 77 % of the PCB load whereas North Camden, in contrast, has relatively less (State St. = 2%; Federal St. = 1 %). Yet these two North Camden flows merge at the main plant in fluent yet account for only a small fraction of that load. Seventy-four percent of the PCB load must therefore come from somewhere in the intervening city blocks. Surprisingly the Cooper River Interceptor, primarily a suburban flow, has the next highest PCB load (9 %) and should not be ignored in future trackdown activities.

PHASE 2: INTRODUCTION

Phase 1 results revealed levels of PCBs at all sewer sampling locations and sampling media potentially from varied sources. Geographic analysis of sewer results indicated a concentration of potential PCB sources in the industrialized south-central area of Camden. In Phase 2 we decided to further evaluate desktop trackdown methods and innovative field methods to close in on the sources. This included an innovative field method using PCB immunoassays kits, approved for use by both NJDEP [14] [15] and USEPA [16] [17], and known to be quick, inexpensive and accurate. Our approach was to document suspect PCB sources within the central Camden sewersheds identified in Phase 1 from readily accessible regulatory datasets and then to sample street soils at storm drains in front of the suspected PCB source facilities.

And although the number of samples per site is limited in this approach, it is acceptable as per USEPA guidelines that direct, “When the objective of a sampling event is to simply determine whether a suspected facility is contaminated, a limited number of samples from properly chosen field locations will yield more useful information [18] [19]. For the soils study, site-selection criteria for suspected PCB-related facilities in Camden City were developed based on a number of factors including: 1.) documented positive PCB results onsite; 2.) industry types known to use PCBs (e.g. hydraulic fluids, gas pipelines, electrical transformers, paper and pulping); and 3.) facilities possibly secondarily contaminated with PCBs (e.g. metal recycling, concrete and aggregate processing, drum reconditioning).

Using these criteria we culled potential PCB contaminated sites from multiple regulatory lists or databases including: NJDEP’s Known Contaminated Sites List (KCSL); NJDEP Division of Water Quality NPDES point and non-point discharger files; USEPA’s CERCLIS and NPL lists of Superfund sites; NJDEP’s HazSite database (i.e., KCSL positive for PCBs and under investigation); CCMUA’s list of facilities discharging into their collection system screened for SIC codes of industries known to generate or use PCB contaminated materials [9]; NJDEP Enforcement Program (i.e., in 2004 NJDEP Camden Strike Force performed synchronized onsite inspections at hundreds of targeted facilities issuing notices of violation); NJDEP Hotline discharge/spill reports; USEPA TSCA Database of PCB Transformers; federal Toxics Reduction Inventory (TRI) data of PCB emissions; personal communications - Camden City Engineer, United Water, CCMUA, DRBC.

PCB sampling using immunoassay (IA) techniques were developed in the 1990s [20] [21] and enzyme-linked immunosorbent assay (ELISA) kits are commercially available for screening PCB contamination in water and soils [17] [22]. These methods are inexpensive and have a fast turnaround time. NJDEP’s Field Sampling Procedures Manual [15] and Field Analysis Manual [14] recommend immunoassays for site screening, delineation; characterization and monitoring when organic compounds such as PCBs, pentachlorophenol, and total petroleum hydrocarbons are the known contaminants of concern. But only with confirmation analysis in accordance with NJDEP’s ‘Technical Requirements for Site Remediation’ [23]. USEPA also recommends integration of IA techniques into a project plan [16] to cut costs and decrease time spent in the field, especially if the project requires fast turnaround field analyses at low costs to perform site activities such as hot spot screening, plume delineation, and/or removal/remedial site clean-up [17].

PHASE 2: METHODS

Soil Collection: Soil samples were collected in accordance with NJDEP Field Sampling Procedures Manual [15] and the USEPA's guidance for PCB spills [18]. Discrete biased samples were collected in front of suspected sites, which meets with FSPM recommendations that "sampling conducted in potentially contaminated areas of concern be biased to suspected areas of greatest contamination based on professional judgment, site history, stressed vegetation, soil discoloration, odor, etc." All surface debris, such as vegetation and rocks, were first removed from the surface before sampling and soil scraped from a 10 cm. x 10 cm. area to a depth of about 1 cm. with a trowel to yield about 100 g of soil [18]. Sampling trowels were pre-cleaned, individually packaged, rigid polyvinyl, one trowel per soil sample. Disposable gloves were changed between each sample location and soil collected as surficial scrapes and placed in lab-grade, zip-lock bags, labeled and stored upright in coolers for transport back to the NJDEP lab where they were refrigerated until ELISA analysis.

ELISA-PCB Spectrophotometry Analysis: Enzyme-linked immunosorbent assays (ELISA) are a biological quantitation process, whereby a stationary antibody is engineered to react with a contaminant of interest (e.g., PCBs, PAHs, dioxins), bind to an enzyme-conjugate, complex by fixation to a membrane (via filtration and/or magnetic force), then catalyzed via a color-agent reaction inversely proportional to the amount of contaminant present [22]. The colored product is then measured using UV/Visible spectrophotometry and quantified against a standard curve of known contaminant concentration.

The SDI RaPID Assay for total PCBs includes a Kit with extraction solvent, reagents, diluent, analyzer and accessories. The analysis is a two-step process involving solids extraction with methanol followed by immunological analysis, which can process 49 samples at a time along with three controls and six standards [22]. The color reaction is read against a calibration curve at 450 nm on the photometer and measured against a PCB (Aroclor 1254) standard concentration curve established with pre-measured standards of 0.0 ppm PCBs, 0.25 ppm PCBs, 1.0 ppm PCBs and 5.0 ppm PCBs. Manufacturer specifications recommend a data quality objective for establishing each standard curve (before each sample run) at a correlation coefficient of $r = 0.990$ for all assays and a %CV of 10% or between standard duplicates.

The quantifiable range of ELISA detection for PCBs in soils (as Aroclor 1254) using this methodology is from 0.05 ppm to 10.0 mg/kg (ppm). In addition, to assess the relative accuracy and reproducibility of the runs we did standard QA duplicate analysis (20%) for each set, but also did one complete duplicate analyses of all samples in a run using the same standardized curve on the spectrophotometer.

High Resolution GC–High Resolution MS Analysis: A subset of ten (10) soil samples, identified by ELISA as positive for PCBs were submitted for confirmatory laboratory analysis using high resolution HRGC/HRMS. The analytical methodology used was USEPA Method 1668A [3] with slight modifications as performed by AXYS Labs, the same contract lab used for wastewater in Phase 1.

PHASE 2: RESULTS

ELISA Results

Total PCBs: Two hundred and seven Camden City locations were screened using desktop methods on readily accessible datasets to determine whether they could be sources of PCBs to streets, sewers and storm drains. Each site was windscreen-surveyed by car to assess locational accuracy, the presence of nearby storm drains, and positioning within a GIS-based sewershed from CCMUA's detailed CSO maps [24]. Of these candidate sites 98 sites were selected for sampling in March of 2006. Including the quality assurance samples (duplicates and blanks) 134 separate ELISA PCB analyses were performed.

As referenced above, sampling locations were biased towards suspected PCB source sites, so it wasn't surprising to find PCBs present in sixty-five (65) % of street soils analyzed (Figure 7). Overall the mean total PCB concentration for all 98 samples was 0.5 ppm (Range: 0.05 ppm (detection limit) to 5.16 ppm PCBs). Background Samples were taken in municipal parks and private cemeteries throughout Camden and the surrounding suburbs. All background samples were less than the DL of 0.05 ppm. Removing all background sites and just including samples from in front of suspect source facilities results in a mean total PCB concentration of 0.6 ppm.

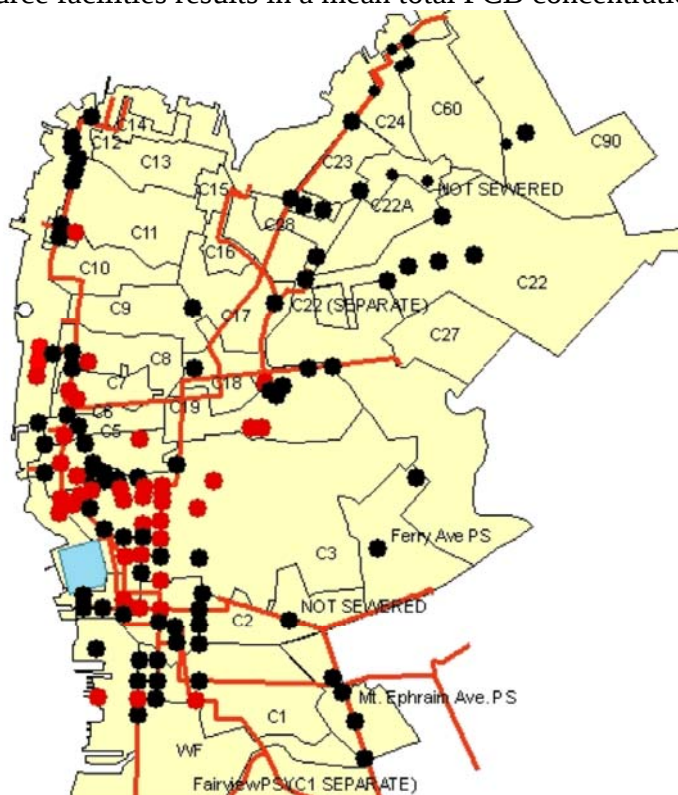


Figure 7. PCB Sampling Locations in Street Soils for Camden NJ

(Red dot indicates PCB level greater than NJDEP Residential Soil Cleanup Criteria of 0.49 mg/kg using ELISA Method)

Eleven of the sites had electrical transformers present. Only two were labeled as PCB Transformers (i.e., >500 ppm PCBs), which collectively showed a mean PCB concentration of 0.3 ppm (Range: 0.05 ppm to 0.91 ppm). A comparison of 2006 PCB soil results with a set of soil samples collected and archived from Phase 1 (2004) showed slightly higher PCB levels with

a mean of 0.8 ppm PCBs (Range: 0.05 ppm to 6.2 ppm). The 2004 results, however, were based on fewer samples (only 17 sites).

Soil samples were primarily in the silt to fine-silt particle size (i.e., soils winnowed by erosion and street runoff to a storm drain's edge). Moisture content was not analyzed but sampling took place in March of 2006 when there was only 0.91 inches rain (4th driest on record). It had been the driest month since 1966 and less than a quarter of normal Philadelphia March precipitation of 3.81 inches (US National Weather Service: Philadelphia - March 31, 2006). Therefore, after a month long drought, the water content of soils was assumed to be negligible and samples extremely dry. Data quality objectives were met for all ELISA sample runs of both 2004 and 2006 data with % Coefficients of Variation (CV) less than 10% for all standards replicates and a correlation factor (r) 0.990 for all assay regressions.

Industrial Source Categories: Sites results were clustered by industry source category (Table 3). In general, known contaminated sites and metal reclamation industries appear as the most likely sources of PCBs to nearby street soils and storm drains. Decreasing PCB concentration in street soils by source categories using ELISA include: 1. HazMat sites (known contaminated sites) 2. junkyards; 3. metal shredders; 4. aluminum smelters; 5. paper & pulping; 6. transportation facilities; 7. gas pipelines; 8. drum cleaning; 9. metal manufacturing; 10. manufacturing – general; 11. waste management; 12. electrical transmission; 13. aggregate processing (concrete); 14. landfills; and 15. background sites (cemeteries and city parks).

Table 3. PCB ELISA Results (mg/kg) in Street Soils Grouped by Industry Type

Rank	Industry Source Type	PCBs (n)*
1.	HazMat (Contaminated Sites)	1.60 (5)
2.	Metal Scrap – Junkyards	1.41 (10)
3.	Metal Scrap – Shredders	0.50 (3)
4.	Meal Scrap – Smelters	0.47 (4)
5.	Paper & Pulping	0.42 (1)
6.	Transportation	0.42 (8)
7.	Gas Plant - Pipeline	0.40 (3)
8.	Drum Cleaning – Reconditioning	0.38 (10)
9.	Metal – Manufacturing	0.35 (3)
10.	Manufacturing - General	0.26 (15)
11.	Waste Management	0.24 (5)
12.	Electrical Transmission (Substations)	0.16 (7)
13.	Aggregates	0.05 (4)
14.	Landfill	0.05 (2)
15.	Background (Parks, Cemeteries)	0.05 (18)

* mean concentration; n = number samples

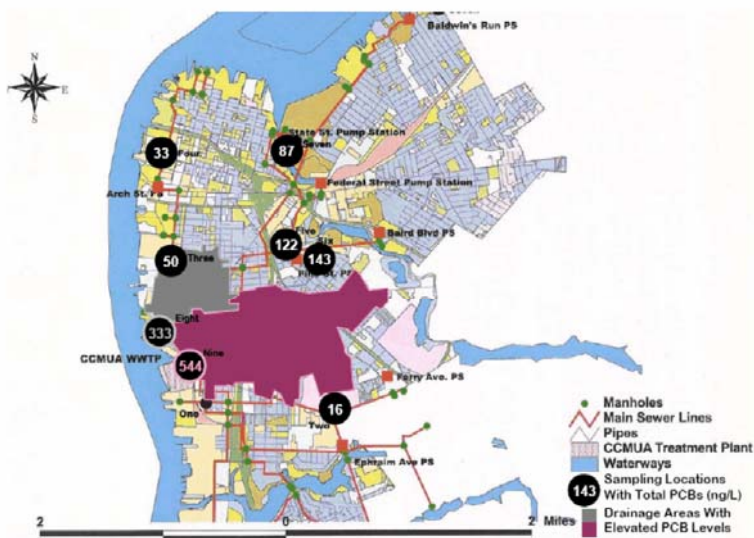


Figure 4. Whole Water Total PCB Concentrations by Sewer Sampling Location for Phase 2 of CCMUA's PCB Trackdown and Drainage Areas With Elevated PCB Levels

Figure 8. PCB Results (HRGC/HRMS) for Sewersheds in Central Camden

refined this spatial analysis to indicate contamination at the sub-sewershed or neighborhood level (Figure 9a). Our results indicate the following sub-sewer sheds as potential sources of PCBs: C3-1, C3-2, C3-11, C3-12, C5-1, C7-1, C8-2, C19-2 and C19-3 (Figure 9b).

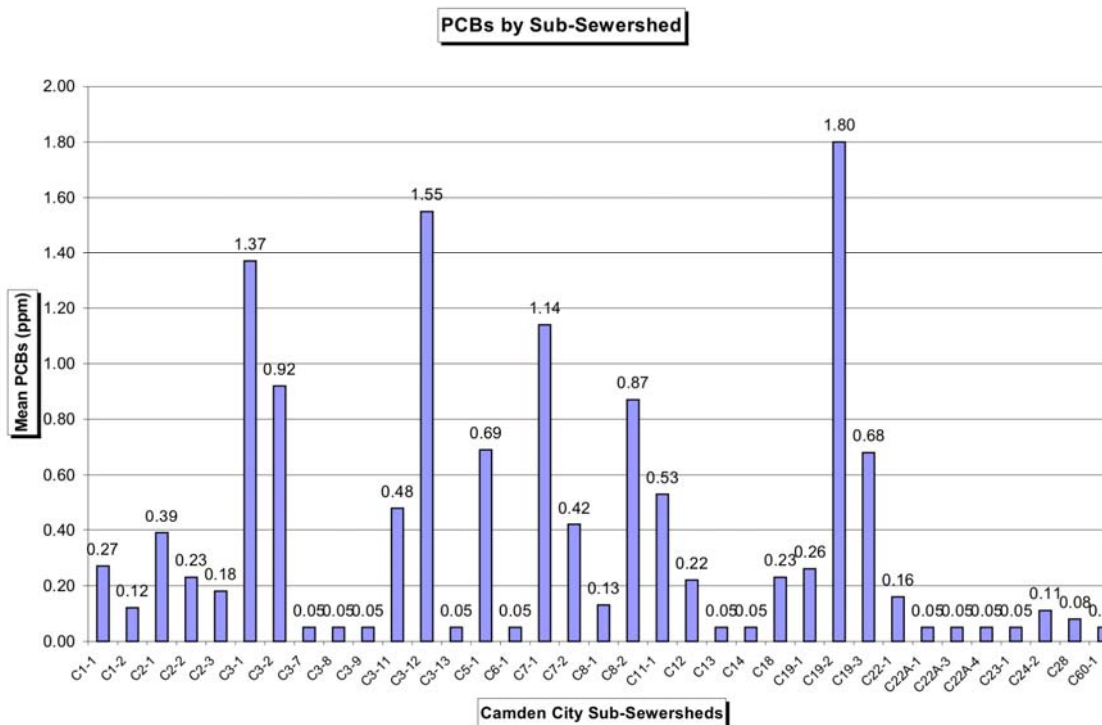


Figure 9a

Sewer Sheds: The spatial distribution of Camden's upland PCB soil results is in agreement with the results based on wastewater in Phase 1. In 2004 we identified sewersheds C3, C5, C6, and C7 within Central Camden as major potential sources of PCBs to CCMUA's collection system (Figure 8). In Phase 2, using ELISA and soils at the inlets of storm drains we further

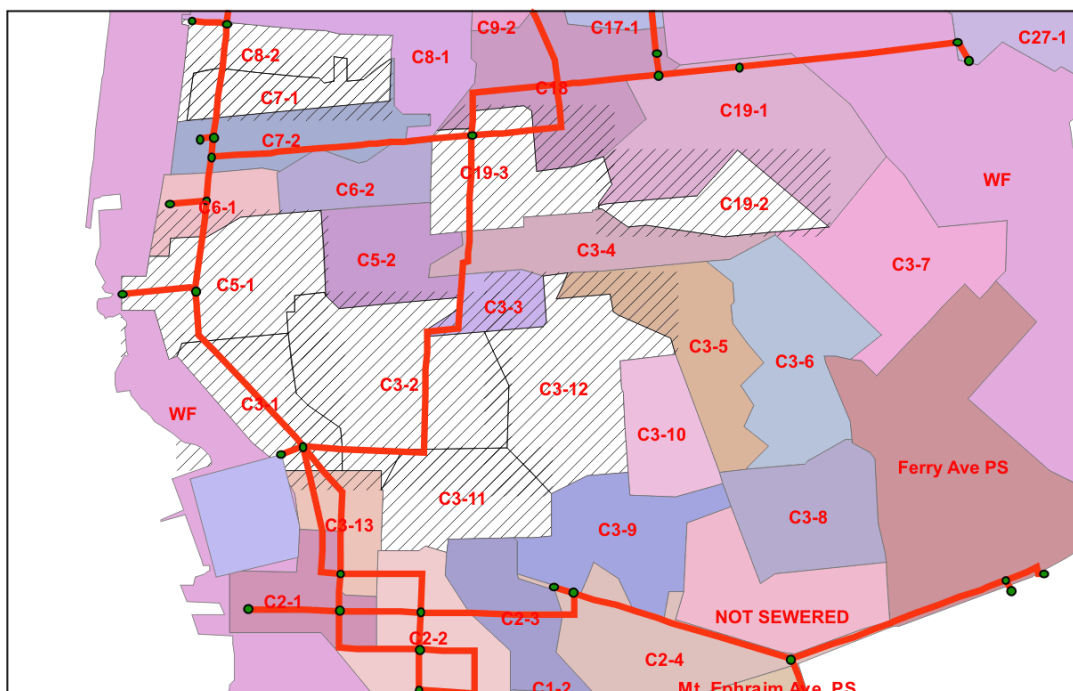


Figure 9b. PCBs in Soils by Sewershed in Central Camden (ELISA)

High Resolution GC/HRMS Results

High resolution GC/HRMS analysis of the ten selected soil samples confirms the utility of using ELISA (a semi-quantitative approach) for PCB trackdown purposes. If ELISA showed PCBs to present, then HRGC/HRMS results confirmed it (Figure 10). As expected HRGC/HRMS results were more accurate and differed in concentration, especially at the upper range of acceptable ELISA-SDI Kit quantitation. That is, ELISA typically underestimated the total PCBs at the upper end of the range.

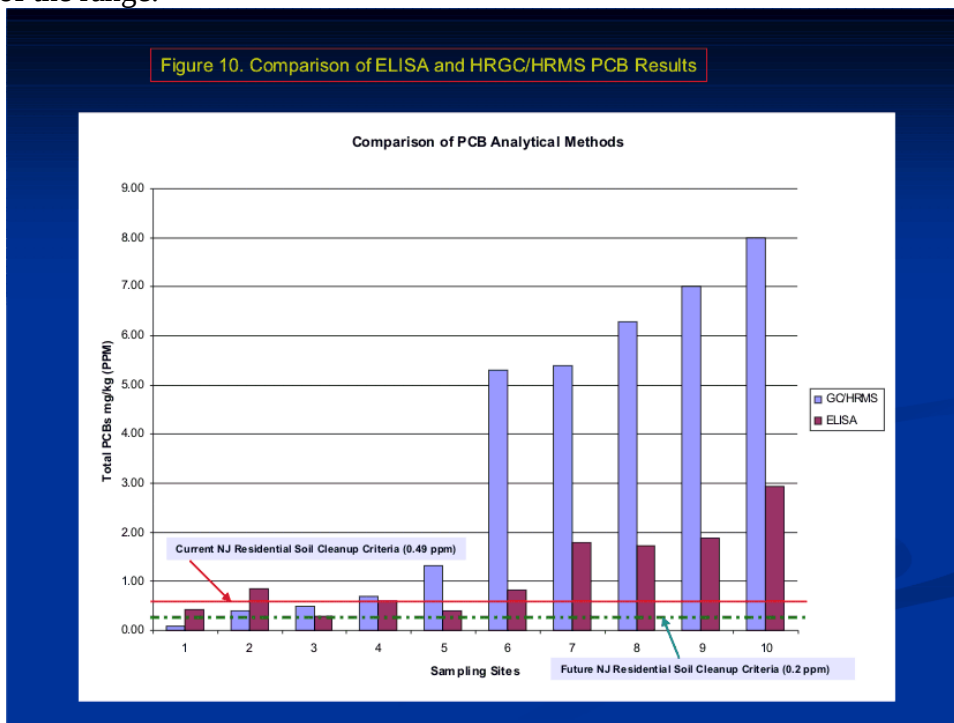


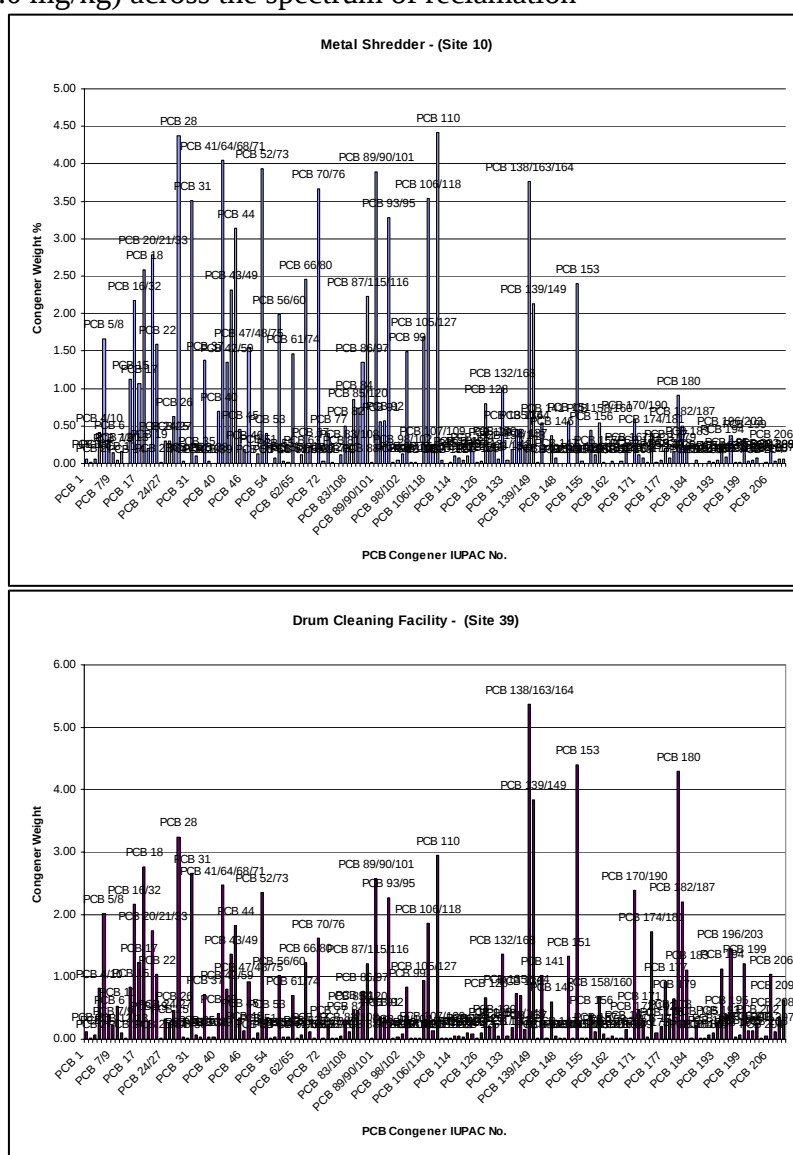
Figure 10

In fact, the increased accuracy of the ELISA at the low to mid-range of its manufacturer's estimated accuracy is in keeping with observations that immunoassay tests are analogous to carbon adsorption which has a saturation point [20]. That is, it performs like an enzyme-mediated reaction, starting off quickly and linearly but then as the reactions approaches enzyme saturation it becomes asymptotic (the reaction curve flattens out). Therefore linearity lies at the low concentration range and sensitivity is greater in this area than in the higher range. The low-to-mid range ELISA results are therefore more accurate and reproducible with the GC/MS results. However, for trackdown purposes this should not be a hindrance since as long as the method accurately shows the presence of PCBs at the lower range where it is more difficult to detect, it is more likely to avoid false negatives.

The ten HRGC/HRMS analyses also confirmed the ELISA findings for prioritizing industrial sources (Table 3 and Figure 10). In general, the highest PCB levels were associated with scrap metal processing (i.e., Range: 5.3 mg/kg to 8.0 mg/kg) across the spectrum of reclamation operations (i.e., shredders, automobile shredder residue (fluff) processing, and port storage/ship loading

operations). One soil sample collected near a known contaminated site (No. 148 at 5.4 mg/kg PCBs) was also high. The two secondary aluminum smelters (Nos. 22 and 165) were an order of magnitude lower in PCBs than the bulk scrap metal sites and slightly higher than the drum reconditioning site (No. 85) and the abandoned paper recycling facility (No. 39).

Congener-Homolog Patterns: As discussed above, the HRGC/HRMS analysis allows the grouping PCB congeners into chlorinated congener and homolog groups for comparison with each other and with known distributions of homologs in Aroclors [12]. Soils from in front of metal processing facilities differed in congener profile (Figure 11a) from those non-metal processing industries such as drum cleaning (Figure 11b). Looked at from a PCB homolog basis, all of the metal reclamation industry samples were similar and looked like Aroclor 1248 (Figure 12). Aroclor 1248 was sold by Monsanto primarily for use in vacuum pumps, hydraulic fluids, as a plasticizer in resins and rubber and as an adhesive [25] but not extensively in electrical transformers and capacitors but was.



Figures. PCB Congener Profiles in Street Soils near (11a) Automobile Metal Shredder and (11b) Drum Cleaning Facility

In contrast, the homolog patterns for the other soil samples (i.e., gas pipeline, paper pulping, manufacturing and drum cleaning) are shifted towards the higher chlorinated homologs with peaks at the penta-chlorinated PCBs. This pattern is indicative of Aroclor 1254 and 1260 which had broader usage in over fourteen major industry groups including electrical transmission and industrial applications [12]. However, as noted in Phase 1, the value of chemical fingerprinting in wastewater or soils using homolog or congener analysis is somewhat problematic. The composition of Aroclors in the environment has been shown to change over time due to weathering where chemical and physical transformations alter the composition of a sample.

Transport Study: Due to the concentration of metal reclamation facilities in such a small geographic area and the likely-hood that truck traffic might re-mobilize and redistribute PCB contaminated street dusts, we gridded out a three block by ten block area within Camden's Water Front South and sampled using ELISA analyses (Figure 13). Waterfront South encloses a number of potential PCB sources including a Superfund site; an automobile shredder facility; and an automobile shredder residue (ASR) processing facility. Results show elevated levels of PCBs in street dusts but especially those roads traveled by trucks loaded with ASR or 'fluff' and moving from the metal shredder on Atlantic Avenue to the ASR-processing facility on Sixth Street. Elevated PCB levels for our study were defined as being greater than NJDEP's 2006 Residential Soil Cleanup Criteria (RSCC) of 0.49 ppm PCBs (Note: the RSCC for PCBs subsequently was reduced to 0.20 ppm PCBs in 2008).

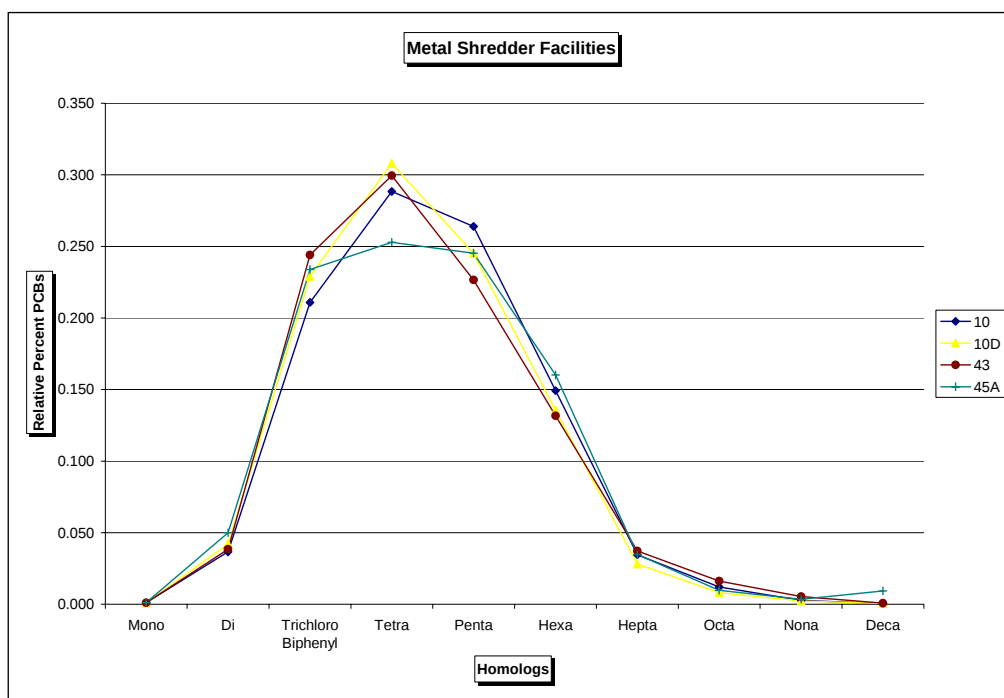


Figure 12. Aroclor Homolog Profiles of Metal Shredder Facilities in



PHASE 2: DISCUSSION

The primary objectives of the Camden PCB trackdown study was to develop methods and identify PCB sources to storm drains and combined sewer outfalls (CSOs) in order to abate PCB transport to the Delaware River, thereby decreasing bioaccumulation in foodfish and decreasing risk to human consumers. To that end we narrowed down the universe of potential PCB sources in CCMUA's collection system from a county-wide range of potential sources and municipalities to just a few specific neighborhoods, industry types and streets in Camden City (77% of PCB load). However, it should be noted that it's problematic that a PCB street soil sample taken in front of a suspected facility is definitively related to that one site. There is much weathering and transport of soils in city streets and PCB sources could only be proven with onsite sampling of the facility in question.

Trackdown Methods: When used in conjunction with a careful desktop review of readily available datasets and with a GIS-based data, ELISA can be a powerful tool for tracking down non-point sources of PCBs to MUAs. Conjoined with the in-sewer wastewater sampling it allows a means to reduce the universe of potential PCB sources, contaminated sewersheds, and industrial users to a manageable size for follow-up sampling and/or regulatory action as a part of a TMDL-related "Pollution Minimization Plan." Reduced costs are also a positive factor. Whereas typical GC-ECD or HRGC/HRMS PCB analysis can range in costs from \$700 to \$1,000; an individual ELISA test may cost as little as \$35 per sample. The secondary utility of

using ELISA in a trackdown investigation is its immediacy (i.e., real time, in-situ results) rather than waiting 2 weeks for samples at a lab.

Other trackdown studies have also found PCBs in street soils near suspect facilities including investigations in Buffalo, NY [26] [27]; Savannah, GA [28], New Bedford, MA [29] [30] and Catalonia, Spain [31]. The PCB levels found in Camden City street soils were some of the highest recorded (See Table 4).

Table 4. Comparison of PCBs in Sanitary Wastewater and Urban Soils					
		Wastewater		Soils	No. Congeners
		Mean ng/l (ppt)	Range ng/l (ppt)	Range ng/g (ppb)	
Camden NJ¹	(24-hr comp)	189	33 – 784		124
Phase 1					
Camden NJ		41	20 – 82		124
Phase 1					
Camden NJ²				50 – 5,160	NA
Phase 2 (ELISA)					
Camden NJ				100 – 8,000	209
Phase 2 (GC/MS)					
Buffalo NY	- Grab (2.4 L)	< 0.2 (nd)*	101 - 268 ng/g (ppb)*	53 – 1,700	27
Study³					
Savannah GA⁴				1 – 88	25
NY-NJ MUA		110	26 – 1,096 (low flow)		71
Study⁵ (24 hr comp)⁺			44 – 773 (hi flow)		
Catalonia Spain⁶				0.6 – 12	7
Montreal Canada⁷	4.3				13
Delaware	??		11 – 1,509 (hi flow)**		81
Estuary⁸ (24-hr Comp)					
New York Harbor⁹			24 – 630		

**All aqueous phase = non-detectable; measurable PCBs were on particulate fraction.*
***60 ng/l at CCMUA influent.; 1,509 ng/l associated with PCB spill in Philadelphia*

¹ Belton et al. 2005

² Belton et al. 2007 (This study)

³ Loganathan et al. 1997

⁴ Loganathan et al. 1997

⁵ Durell and Lizotte 1998; + data mean and range from 26 MUAs in NY and NJ

⁶ Schuhmacher et al. 2004

⁷ Pham and Proulx 1997

⁸ DRBC Report 1998; data composite from seven MUAs

⁹ Linden Roselle Report 2007

Non-Point Sources: It should be recognized that many of the facilities identified as potential PCB sources are not regulated by the MUAs directly (i.e., through NJDEP Pretreatment Rules), since they do not have direct industrial piping or connections to the MUAs collection system. Secondary contamination of the CSO system probably occurs via stormwater runoff or fugitive air emissions associated with onsite activities (e.g., shredding metal).

For PMP purposes this does not allow a meaningful way to reduce PCB loadings as part the TMDL process. That is, unless other regulatory programs and environmental laws can be brought to bear (e.g., contaminated sites, State Spill Act and Superfund; metal recyclers, NPDES Non-Point Source permits). These programs, which focus on best management practices for on-site reduction of emissions rather than command-and-control approaches (i.e., effluent limits) may require novel cross-cutting adaptive management practices by legislators and regulators.

Metal Reclamation Facilities: Our analysis has shown that metal reclamation facilities can be significant sources of PCBs to streets soils, storm drains and the surrounding communities. A recent study by the Belgium Government confirmed elevated concentration of PCBs in both stack and fugitive emissions from scrap metal shredder-plants but also in the surrounding soils [32]. This resulted in regulations to initiate action plans for reducing PCBs focusing on diffuse (fugitive) sources by limiting the formation and emission of dust through good housekeeping and improved process manipulation. Many other studies have also identified automobile shredder residue (ASR) as a source of PCBs to the environment [25] [33] [34] [35] [36] [37] [38]. ASR also contains high levels of heavy metals including cadmium, chromium, lead, mercury, zinc, nickel and copper [35] [39] [33] [36].

Studies have also linked the transport of PCBs and redistribution of contaminated street dusts to surrounding areas through prevailing wind patterns and vehicular traffic [26] [27] [28]. A possible explanation for the pattern of PCBs found on Waterfront South streets could be localized fugitive emissions from these metal reclamation facilities and weathering of contaminated soils and/or redistribution via prevailing winds and vehicular traffic. For example, the highest levels of soil PCBs in Camden follow major traffic routes to and from the metal processing facilities (Figure 11). This includes the initial shredding at the bottom of Atlantic and Front (by the river); transport of ASR to Sixth St. for mechanical processing; and finally transport of shredder metal from both Atlantic and Sixth Street facilities to the Port where they are stored in large piles and routinely hosed down for dust control and bulk-loaded onto ships.

Of particular interest are the standard operating procedures at the ASR processing facility. All operations are open to the atmosphere with only limited means for reducing fugitive emissions from drums or belts. Visible particulates of ASR are suspended over the site while equipment is operating. In addition, secondary transport may be facilitated by stormwater management plans (as per SPDES Permits). For example the ASR waste piles are stored in the open yet on concrete pads to prevent transport to groundwater. The operators have sealed the onsite storm drains (per NJPDES Stormwater Prevention Plan) to prevent contaminant transport to CCMUA and the Delaware River. The result is standing water and mud contaminated with ASR, which can then be redistributed by truck traffic throughout community. A recent Waterfront South report [40]

estimates that there are almost 8,000 trucks per year entering the SJPC Broadway Shipping Terminal and as high as 77,000 truck trips to local industries in a year.

It could be that for these metal reclamation facilities, the combination of un-clad equipment, fugitive emissions, open piles, sealed drains, and impervious surfaces below the piles (in the absence of swales and catchment basins) facilitates runoff from the site to offsite storm drains (via sheet flow and runoff) and possibly to the surrounding community via dust in prevailing wind and truck traffic.

Known Contaminated Sites: There is a PCB-contaminated property within the study area (Martin Aaron Superfund site), a former drum cleaning and reconditioning facility. Yet, although high levels of PCBs were found in soils at Martin Aaron in 1998 (Range: 0.001 ppm to 77,400 ppm) the surface soil contamination has apparently been significantly reduced in a 1999-2000 emergency removal action [41]. This does not preclude the fact that residual contamination may still be present and possibly redistributed when the site goes to final remedial action in the near future

PMPs and TMDL Implementation: This study was developed to support the Delaware Estuary Phase 1 TMDL process for PCBs which mandates pollution minimization plans and concomitant trackdown activities for NJPDES permitted dischargers. Yet trackdown of PCBs in a municipal utility authority's collection system is problematic due to the hundreds of miles of piping, the numerous industrial users, and more importantly due to the presence of combined sewers (combined stormwater and sewerage) in Camden City, which may add significant PCB loads from non-point sources and hazardous waste sites due to runoff. In addition, many PCB sources identified in the study are not regulated by the MUAs themselves (i.e., via Pre-Treatment rules) but by various NJDEP programs. MUAs will therefore need the Department's help to sort out appropriate management responses for reducing PCB loads, possibly through non-point source management strategies.

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