WASTEWATER CONTAMINANTS MEASURED TO SUPPORT THE NEW JERSEY TOXICS REDUCTION PROGRAM – PART 1: PROGRAM OVERVIEW AND PAH PROFILES

Bo Liu[1], Gregory S. Durell[1], Deirdre T. Dahlen[1], Mary E. Schrock[2], Mick DeGraeve[3], and Dennis McCauley[3]

1 Battelle Memorial Institute, 397 Washington Street, Duxbury, MA 02332, USA
2 Battelle Memorial Institute, 505 King Ave., Columbus, OH 43201, USA
3 Great Lakes Environmental Center, 739 Hastings St, Traverse City, MI 49684, USA

Introduction

Sediments in the New York-New Jersey (NY-NJ) Harbor have become contaminated with toxics to the extent that dredged materials cannot be disposed of safely. This inability to remove accumulated sediments from ship channels and berthing areas is becoming an economic impact on the Harbor region, which has the potential to become worse over time. The NY-NJ Harbor Estuary Program Comprehensive Conservation and Management Plan[1] (HEP CCMP) identified at least fifteen chemicals (or classes of chemicals) of concern, including polychlorinated biphenyls (PCBs), dioxins/furans, chlorinated pesticides, polycyclic aromatic hydrocarbons (PAHs), and metals[2]. As a result of these two circumstances, the Contaminant Assessment Reduction Program (CARP) was initiated by the Port Authority of NY-NJ to, among other things, determine current loadings of key contaminants to the Harbor estuary, relate current inputs of contamination to historical inputs, and identify potential sources of contamination that may warrant management actions. The toxic chemicals discharged to NY-NJ Harbor originated from uncontrolled industrial and municipal sources, distant sources through atmospheric deposition and rivers, and local sources such as municipal and industrial wastewater treatment facilities, combined sewer and storm water outfalls, and rainfall-induced runoff (non-point sources). In addition, the Harbor sediments, which preferentially bind many toxic chemicals, act as a continuing source as they are resuspended and transported throughout the system by both natural and man-made means[2].

Twelve publicly owned treatment works (POTWs) in New Jersey discharge about 610 million gallons of treated wastewater per day to the NY-NJ Harbor estuary. This accounts for about 30% of the total wastewater volume discharged by treatment facilities to the Hudson River Basin below Troy Dam. POTWs treat residential sewage and wastewater from a variety of industrial operations. A number of industrial wastewater treatment facilities also discharge directly to the Harbor. Limited studies in the past have shown that discharges from POTW can contain measurable (and sometimes significant) concentrations of some of the chemicals of concern[2].

Combined sewer overflow systems (CSOs) transport both untreated sanitary sewage and storm water. The capacity of POTWs can be insufficient during wet weather events, and in those cases CSO flows are diverted directly to the Harbor. There are approximately 730 CSOs in the NY-NJ Harbor area, including 239 in New Jersey[2]. These CSOs may also be significant sources of some chemicals of concern. Likewise, discharges from storm water outfall systems (SWOs), and direct (non-point source) runoff from the land during wet weather events, are not treated and can contribute to the problem of toxic chemicals in the Harbor.

There are significant information gaps in the understanding of POTWs, CSOs, and SWOs as sources of contamination to the Harbor, because there have been few toxics monitoring programs, and because inadequate analytical methods have been used historically. The analyses conducted for the CARP Program focus on detection of trace amounts of the chemicals of concern, and were used to improve the understanding of the relative importance of these discharges so that well informed management actions can be implemented to eliminate/reduce the input of these toxic chemicals to the NY-NJ Harbors.

The objective of our effort is to determine PAH, PCB, dioxin/furan, and pesticide concentrations in POTW effluent and CSO/SWO samples collected by Great Lakes Environmental Center (GLEC) and the Passaic Valley Sewerage Commissioners (PVSC) from New Jersey locations that discharge to the NY-NJ Harbor area. The results of PAH analyses are presented in this paper, and results of dioxin/furans, PCBs and chlorinated pesticides are presented in a companion paper.

Methods and Materials

Four seasonal sets of POTW samples were collected in 2000 and 2001 by GLEC/PVSC at twelve NJ POTWs (Figure 1). Additionally, samples were collected at five SWOs and five CSOs during heavy rain conditions. POTW samples were 24 hr composites, while SWO/CSO samples were collected over a period of approximately 0.5 hr. Field duplicate and field blank samples were also collected during each sampling event.

POTW and CSO/SWO effluent samples were analyzed for PAHs following Battelle methods[3], described in detail in the project specific Final Quality Assurance Project Plan. Briefly, effluent water samples were filtered using pre-baked Whatman GF/F filters (0.7 µm, 142 mm diameter; Whatman) prior to extraction. The samples were also spiked with labelled surrogate internal standard (SIS) compounds, and analyzed by isotope dilution using high-resolution gas chromatography/low-resolution mass spectrometry, with the mass spectrometer operating in selected ion monitoring mode (HRGC/LRMS-SIM). For the first POTW event the filter and filtrate sample extracts were analyzed separately. For all other sampling events, the filter and filtrate extracts were combined for a total sample analysis. A rigorous QA/QC program was applied, including the analysis of field blanks, equipment blanks, field duplicate, method blanks, laboratory control spikes, matrix spikes and matrix spike duplicates, and standard reference material samples.

Figure 1. Sampling Locations

Filtrate samples were serially extracted using separatory funnel extraction technique. Filters (particulate phase) were serially extracted using extended physical shaking/agitation followed by sonication. Filtrate and filter extracts were subject to 20 g alumina column cleanup and copper treatment. Labeled recovery internal standards (RIS) were spiked into the extract prior to analysis. Analysis by HRGC/LRMS-SIM was carried out using an Agilent 5973N LRMS equipped with an Agilent 6890N GC and a 0.25 mm i.d. 60 m DB-5 column (0.25 µm stationary phase). A six level calibration was analyzed before any sample extract, with the lowest level near the detection limit, and the range of the calibration encompassing the expected concentration range of the samples (0.005 to 5.0 µg/mL). A continuing calibration was analyzed every 12 hours. An independent check standard (ICS; different source from initial calibration standards) was analyzed with every initial calibration. The achieved analytical minimal level (ML) for the target PAH compounds was ~1.3 ng/L. This is in contrasted with a reported detection limit as high as 5000 ng/L using standard EPA CLP-SOW methods.

Results and Discussion

The PAH extraction efficiency for dissolved and particulate phases at POTW site 4 in sampling event #1 is presented in Figure 2. Labelled surrogate compounds were recovered very well, and generally with similar efficiency from both the dissolved and suspended phase of the same original effluent sample in POTW sampling event #1. Therefore, extracts from the dissolved and suspended phases of the samples were combined in the rest of sampling events and analyzed to determine total contaminant concentrations.

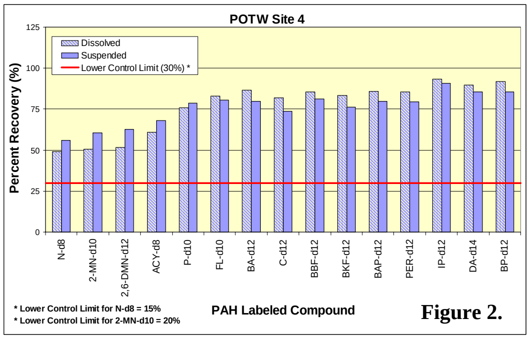

Figure 2.

Figure 3 presents the total PAH concentration for the different sample phases for six selected POTWs. The majority of the PAHs were associated with the dissolved phase; the dissolved phase contained from 70% (POTW site 6) to 85% (POTW site 9) of the overall amount of PAH.

Figure 4 presents the individual PAH compound distribution between the dissolved and suspended phases in the effluent from POTW site 9. Most of the target PAH compounds were detected in the samples. The PAH distribution was similar for most samples, and was dominated by the more polar naphthalene (N) and alkylated naphthalene compounds (C1-N, C2-N, C3-N and C4-N). The dissolved phase contained higher concentrations of the lower molecular weight (MW) PAHs than the suspended phase samples. The mid-MW PAH compounds were detected at similar concentrations in dissolved and suspended phase samples, while the high MW PAH were consistently detected at higher concentrations in suspended phase samples (Figure 4).

Samples collected at POTW sites 2, 3, 6, 9 and 10 consistently contained considerably higher concentrations of parent N relative to its alkyl homologues, whereas samples from POTW sites 7 and 12 contained relatively higher concentrations of the alkyl homologues, suggesting input of relatively fresh petroleum product(s). Parent and alkylated naphthalenes and phenanthrenes (2/3-ring PAHs) were the dominant PAHs in samples from all 12 POTWs, CSO sites 2, 3, and 4, and

SWO sites 1, 2, 4 and 5. However, 4/5-ring PAHs were dominant in samples from SWO site 3 and CSO sites 1 and 5, suggesting primarily pyrogenic sources.

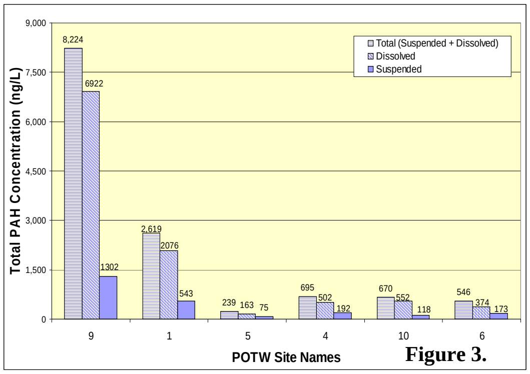

Figure 3.

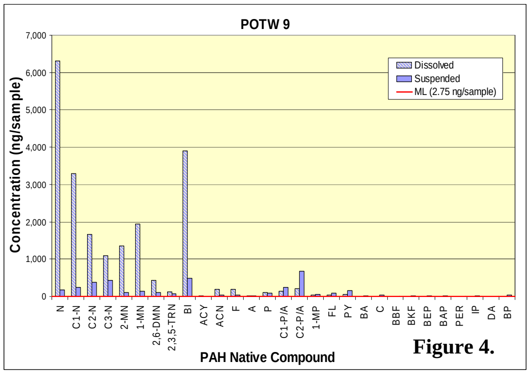

Figure 4.

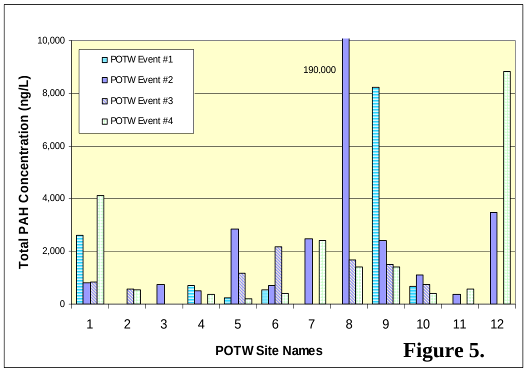

Figure 5.

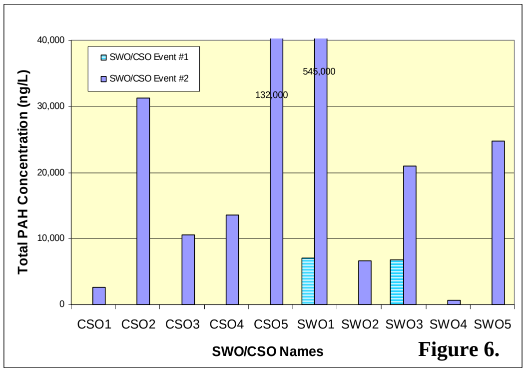

Figure 6.

The total PAH concentrations (dissolved plus suspended phases) from 12 POTW sites and 10 SWO/CSO sites are presented in Figures 5 and 6, respectively. Total PAH in the POTW samples ranged from 201 ng/L to 190,000 ng/L, with most of the samples having concentrations below 4,000 ng/L. The total PAH was generally much higher in the SWO/CSO samples than in the POTW samples. The total PAH in the SWO/CSO samples ranged from 605 ng/L to 545,000 ng/L, with most of the samples having total PAH concentrations above 6,000 ng/L. There was a general trend of decreasing concentrations of PAH from POTW sites 5, 8, 9 and 10 over time. Trends could not be established during the current sampling period for SWO/CSO samples. Additional SWO/CSO sampling events are planned.

References

1. (1996). New York – New Jersey Harbor Estuary Program Including the Bright Restoration Plan, Final Comprehensive Conservation and Management Plan.
2. (1999). New York-New Jersey Harbor Estuary Program, Trackdown Workgroup Meeting, March 5, 1999 – New Jersey Toxics Reduction Workplan.
3. Peven, C.S. and A.D. Uhler. (1993). Sampling and Analytical Methods of the National Status and Trends Program National Benthic Surveillance and Mussel Watch Project. Pp. 141-161, Volume IV. NOAA Technical Memorandum NOS ORCA 71. National Oceanic and Atmospheric Administration, Silver Spring, MD.