

## Division of Science, Research and Technology

### Research Project Summary

November, 2007

#### The New Jersey Toxics Reduction Workplan for New York - New Jersey Harbor: Phase One Ambient Water Quality Studies

*Joel A. Pecchioli<sup>1</sup>, Timothy Wilson<sup>2</sup>, K. Nadia Dimou<sup>3</sup>, and Jennifer Bonin<sup>2</sup>*

##### **Abstract**

The presence of toxic chemicals in water and sediments throughout New York-New Jersey Harbor has resulted in reduced water quality, fisheries restrictions/advisories, and general adverse impacts to the estuarine and coastal ecosystems. To help remediate the harbor, Phase One of the New Jersey Toxics Reduction Workplan for NY-NJ Harbor (NJTRWP) included a set of ambient water quality studies designed to provide the NJ Department of Environmental Protection the information it needs to identify sources of the toxic chemicals of concern, and to prioritize these sources for appropriate action. Samples were collected at the heads-of-tide and within the tidal reaches of the five major New Jersey tributaries to the harbor (the Passaic, Hackensack, Elizabeth, Rahway, and Raritan Rivers), and within the estuarine areas of Newark Bay, the Kill van Kull, and the Arthur Kill. Large-volume samples were collected using a Trace Organics Platform Sampler (TOPS), which used glass fiber filters to collect suspended sediments (and associated organic contaminants), and XAD-2 resin columns to collect dissolved fraction PCBs and pesticides. The TOPS samples were analyzed using high resolution methods for PCBs, dioxins/furans (PCDD/Fs), PAHs, and pesticides. Grab and composite samples were also collected and analyzed for Cd, Pb, Hg, methyl-Hg, and dissolved PAHs. Median total Hg concentrations exceeded the New Jersey Saline Human Health Water Quality Criteria (NJ WQC; 51 ng/L) in the tidal Passaic, Hackensack, and Rahway Rivers. The applicable NJ WQC for total and dissolved Pb and Cd were not exceeded at any of the sampling locations. The highest median 2,3,7,8-TCDD (353 pg/g sed) and total PCDD/F Toxic Equivalency concentrations (TEQ; 457 pg/g sed) were found in the lower tidal Passaic River. Elevated median 2,3,7,8-TCDD (> 70 pg/g sed) and total PCDD/F TEQ (> 120 pg/g sed) concentrations were observed in the tidal Passaic and Hackensack Rivers, in upper Newark Bay, and in the Elizabeth River. The NJ Saline Human Health WQC for 2,3,7,8-TCDD (0.0051 pg/L) was exceeded by the median concentration at all of the tidal tributary and estuarine sampling locations; the Freshwater Human Health WQC was not exceeded at any of the tributary heads-of-tide. The highest median total PCB concentrations were found at the head-of-tide of the Elizabeth River (67 ng/L) and in the tidal Rahway River (46 ng/L), which were the only locations where the applicable NJ Aquatic Chronic WQC were exceeded. However, the New Jersey Saline and Freshwater Human Health WQC for total PCBs (0.064 ng/L) were exceeded by the median concentration at all of the head-of-tide and tidal sampling locations. The median total DDT (sum of DDT, DDD, and DDE; 26 ng/L), total chlordane (10.1 ng/L), and dieldrin (1.26 ng/L) concentrations were elevated in the tidal Rahway River. Elevated median total DDT concentrations (> 6.2 ng/L) were also found in the lower tidal Passaic River, Elizabeth River, and lower Arthur Kill. The NJ Human Health WQC for the individual 4,4'-DDT, 4,4'-DDD, and 4,4'-DDE compounds were exceeded at the heads-of-tide and in the tidal reaches of the Rahway, Passaic, and Elizabeth Rivers, and in the Arthur Kill. The NJ Saline and Freshwater Aquatic Chronic WQC for total 4,4'-DDT (1.0 ng/L) were also exceeded in the tidal Rahway River, at the head-of-tide and in the tidal Elizabeth River, and in the upper Arthur Kill. The NJ Human Health WQC for total chlordane and dieldrin were exceeded by the median concentration at all of the sampling locations. Median total chlordane concentrations greater than the NJ Freshwater Aquatic Chronic WQC (4.3 ng/L) were found at the heads-of-tide of the Hackensack, Elizabeth, and Rahway Rivers (4.5 to 6.2 ng/L). The median dieldrin concentrations were highest at the heads-of-tide of the Elizabeth and Rahway Rivers (2.14 ng/L), Hackensack River (1.73 ng/L), and in the upper-tidal Passaic River (1.47 ng/L). The highest median total (7,050 ng/L) and total dissolved (5,840 ng/L) PAH concentrations were found at the Elizabeth River head-of-tide. The median concentration for benzo(a)pyrene exceeded the NJ Freshwater Human Health WQC (3.8 ng/L) at all of the head-of-tide locations, and the NJ Saline Human Health WQC (18 ng/L) in the tidal Passaic, Hackensack, Elizabeth, and Rahway Rivers, and in upper Newark Bay and the upper Arthur Kill. In addition, the WQC for other individual PAH compounds were exceeded by the median concentration at various sampling locations. Ratios of the concentrations of various individual PAH compounds indicate that the combustion of petroleum and gas/wood/coal are the main sources of PAHs to the harbor. The contaminant concentration data collected as part of this study were combined with historic river discharge data from 1975-2000 to calculate the annual average load of sediment, organic carbon, and associated contaminants delivered to the harbor system at the heads-of-tide of each of the rivers. The largest loads were contributed by the Passaic and Raritan Rivers; but compared to its relatively small size, the loads of some of the contaminants at the Elizabeth River head-of-tide were substantial. Based on the analyses completed to date, the following areas of the harbor estuary have been identified as the most contaminated for the indicated compounds: Hackensack River – Hg, Passaic River – 2,3,7,8-TCDD and total PCDD/F TEQ, Elizabeth River - total PCBs (and potentially PAHs), Rahway River - total PCBs, DDT and metabolites, chlordanes, and dieldrin. The Phase One NJTRWP data and analyses will be used, together with other CARP data and the CARP Model results, to develop the NJTRWP Implementation Plan.

## Introduction

The New York-New Jersey Harbor estuary system is of enormous and interdependent ecological and economic importance. The Port of New York and New Jersey is central to the economy of the region, and is the largest port on the East Coast of the United States. The presence of toxic chemicals in water and sediments throughout the harbor results in reduced water quality, fisheries restrictions/advisories, reproductive impairments in some coastal species, and general adverse impacts to the estuarine and coastal ecosystems. Problems associated with the management of contaminated dredged material have resulted in uncertainty regarding construction and future maintenance of the maritime infrastructure that supports shipping in the Harbor.

The New York-New Jersey Harbor Estuary Program Comprehensive Conservation and Management Plan (HEP CCMP; March 1996) has identified at least fifteen chemicals of concern, including polychlorinated biphenyls (PCBs), dioxins/furans (PCDD/Fs), chlorinated pesticides, polycyclic aromatic hydrocarbons (PAHs), and metals. The HEP CCMP includes a number of actions to achieve its goals and objectives related to the "Management of Toxic Contamination":

- (1) reduce continuing discharges of the chemicals of concern to the estuary;
- (2) remediate selected contaminated sediments;
- (3) minimize human health risks due to the consumption of fish and shellfish;
- (4) better understand the problem and take additional actions as more is learned.

The Joint Dredging Plan for the Port of New York and New Jersey (October 7, 1996) stresses the economic importance of the port, and the associated need to dredge navigation channels and maintain port facilities. The Joint Dredging Plan has two major objectives:

- (1) to promote greater certainty and predictability in the dredging project review process, and dredged material management;
- (2) to facilitate effective long-term environmentally sound management strategies for addressing dredging and disposal needs for the region.

As part of the commitments included in the Joint Dredging Plan, the States of New Jersey and New York agreed to implement the HEP CCMP as it relates to a number of sediment and toxic contamination concerns. In response, the HEP Contaminant Assessment and Reduction Program (CARP) was developed and implemented. The New Jersey Toxics Reduction Workplan for NY-NJ Harbor (NJTRWP) is the New Jersey component of CARP.

The NJTRWP includes a series of studies designed to provide the NJ Department of Environmental Protection (NJDEP) with the information it needs to identify sources of the toxic chemicals of concern, and to prioritize these sources for appropriate action. In addition, the data from these studies have been compiled with the CARP data collected by the New York State Department of Environ-

mental Conservation in the CARP Database. Finally, the CARP data collected by the two states has been used to develop the CARP sediment and contaminant fate, transport and bioaccumulation model. The CARP Database and CARP Model can be accessed at [www.carpweb.org](http://www.carpweb.org).

Phase One of the NJTRWP included a set of ambient water quality studies. Samples were collected at the heads-of-tide (Study I-C) and within the tidal reaches (Study I-D) of the five major New Jersey tributaries to the harbor (the Passaic, Hackensack, Elizabeth, Rahway, and Raritan Rivers), and within the estuarine areas of Newark Bay, the Kill van Kull, and the Arthur Kill (Study I-E water quality component). Together with hydrodynamics studies (summarized in Pecchioli, et al., 2006) and sampling of the discharges from municipal wastewater treatment plants, combined sewer overflows, and stormwater outfalls (NJTRWP Study I-G), these sampling activities comprised Phase One of the NJTRWP (NJDEP, 2001). This is by far the most comprehensive sampling for toxic contaminants ever to occur in this economically important and complex estuarine system.

The major objective of NJTRWP Study I-C (undertaken by the U.S. Geological Survey) is to determine the loadings of sediment and selected organic and inorganic toxic contaminants originating above the heads-of-tide of the major New Jersey tributaries to NY-NJ Harbor. The primary goal of the water quality components of NJTRWP Studies I-D and I-E (undertaken by Stevens Institute of Technology) is to determine the relative importance of the discharges of the toxic contaminants originating within the tidal watersheds of these tributaries.

A key program goal was the development of sampling and analytical protocols that would provide significantly lower detection limits than those achieved in routine environmental sampling work. Large-volume ambient river and estuary samples were collected using a Trace Organics Platform Sampler (TOPS), which used glass fiber filters to collect organic contaminants associated with suspended sediments, and XAD-2 resin columns to collect dissolved fraction PCBs and pesticides. The TOPS samples were analyzed using high resolution methods for PCBs, dioxins/furans, PAHs, and pesticides. Grab and composite samples were analyzed for Cd, Pb, Hg, methyl-Hg, and dissolved PAHs.

The following NJTRWP workplan and project reports detail the objectives, sampling and analytical methods, quality assurance protocols, and results of the NJTRWP studies:

- ◆ NJDEP NJTRWP Workplan – Volume I (Revised/Version 2 – February 2, 2001)
- ◆ NJDEP NJTRWP Workplan – Volume II/QAPP (Version 2.3 – June 2007[Final])
- ◆ Study I-C: Concentrations and Loads of Organic Compounds and Trace Elements in Tributaries to Newark and Raritan Bays, New Jersey (Wilson and Bonin, 2007)
- ◆ Study I-C: Organic Compounds, Trace Elements, Suspended Sediment, and Field Characteristics at the Heads-of-Tide of the Raritan, Passaic, Hackensack, Rahway, and Elizabeth Rivers, New Jersey, 2000-03. (Bonin and Wilson, 2006)

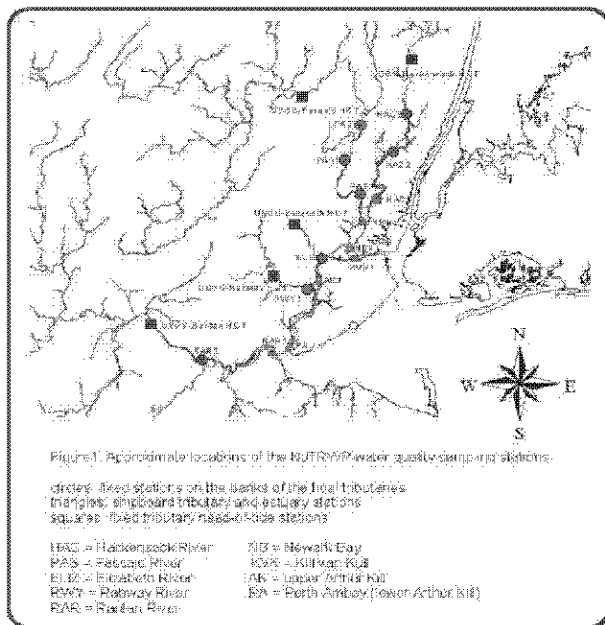
- ◆ Study I-D/E: The New Jersey Toxics Reduction Workplan for NY-NJ Harbor – Ambient Monitoring of Water Quality Within Major Tributaries and the Estuary, Final Report – April 2007 (Stevens Institute of Technology, 2007)
- ◆ Study I-G: The New Jersey Toxics Reduction Workplan Study I-G Project Report (2007)

These documents are/will be available in electronic format at <http://www.state.nj.us/dep/dsr/njtrwp/>.

## Methods and Data Analysis

Sampling was conducted from June 2000 to June 2003 at five (5) fixed sampling sites located on the banks of the tributary rivers at their head-of-tide, ten (10) fixed sampling sites located on the banks within the tidal reach of the tributary rivers, and five (5) ship-board locations in the estuarine areas of the harbor (Figure 1). Sampling targeted defined dry weather/low river flow and wet weather/high river flow hydrologic conditions in the tributaries, and was conducted over a minimum time period of 4-5 hours. Study I-C sampling activities were coordinated with the hydrograph at the sampling station during wet weather/high river flow condition events. Study I-D and I-E sampling began approximately at slack high tide and continued for 4-5 hours during the following ebb tide.

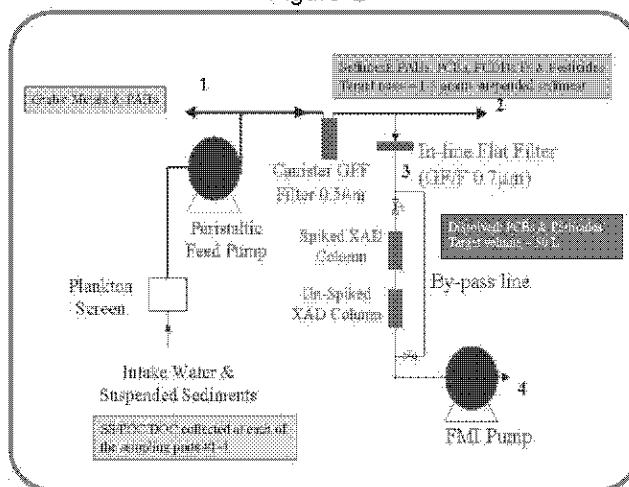
Figure 1



Water quality sampling was performed using the Stevens Modified Trace Organics Platform Sampler (SIT-TOPS; Figure 2). The advantage of the SIT-TOPS is its ability to process large volumes of water, and thus obtain large samples of both the dissolved and suspended sediment fractions in the water column. Combined with high-resolution analytical methods, this allows for the consistent detection of trace levels of the toxic contaminants.

The TOPS samples were analyzed using high-resolution methods for PCBs (modified USEPA Method 1668a), diox-

Figure 2



ins/furans (modified USEPA Method 1613b), PAHs (low-resolution [LR] GC/MS), and pesticides (HR GC/MS). Grab and composite samples were analyzed for Cd and Pb (USEPA Method 1638), Hg (modified USEPA Method 1631b), methyl-Hg (modified USEPA Method 1630), and dissolved PAHs.

Because of the number and nature of the samples and associated blanks collected, a "maximum blank" approach was developed to assess the impact of blank contamination on the usability of the sample data. In this "maximum blank" approach, the Method, Equipment, and Field Blanks associated with a sample are evaluated for each target analyte. Of the three blank results, that having the largest value – i.e. the "maximum blank" – is used to assess the effects of blank contamination on the sample result. In order for a sample result to be usable, it must be at least five times (5x) greater than the "maximum blank" (3x for PCBs). No other blank correction/subtraction is performed on the sample result prior to use.

The raw data for these studies, as reported by the analytical laboratories, are available in the CARP Database.

## Results and Discussions

The major advantage of the Trace Organics Platform Sampler (TOPS) is its ability to process large volumes of water. Since it can process water at a much greater rate through the filters than through the XAD resin columns, significant amounts of suspended solids may be captured even in waters with low suspended sediment (SS). A 0.5µm Cartridge GFF (C-GFF), followed by a 0.7µm 142mm AE in-line flat filter, is the optimal solution to minimize the amount of SS passing into the XAD columns, and thus reducing the error in the measured "dissolved concentrations".

The design and implementation of the NJTRWP Phase One studies focused on the collection of samples under two conditions: dry weather/low river flow and wet weather/high river flow. As a result, the variability in contaminant concentrations was large at most of the sampling locations. This was particularly true at the head-of-tide and tidal tributary locations, where the standard deviation equaled or exceeded the mean concentration for many contami-

nants. Although in most cases the mean and median concentrations were very similar, there were exceptions to this. In most of these cases, the mean value was substantially higher than the median, indicative of potential sample outliers. Thus, for descriptive purposes and comparison to New Jersey Water Quality Criteria (NJ WQC), the median values are used in this report, as – overall - they appear to better represent central tendency in the concentration data.

In summary, Table 1 lists those locations where the median concentration for a chemical of concern exceeded an applicable NJ WQC. Except for total Cd, total Pb, dissolved Hg, and some of the individual PAH compounds, one or more of the NJ WQC for a given contaminant were exceeded by the median concentration observed in at least one sampling

Table 1: Summary of exceedances of New Jersey State Water Quality Criteria (WQC) by the median contaminant concentrations at the NJRWQP sampling locations.

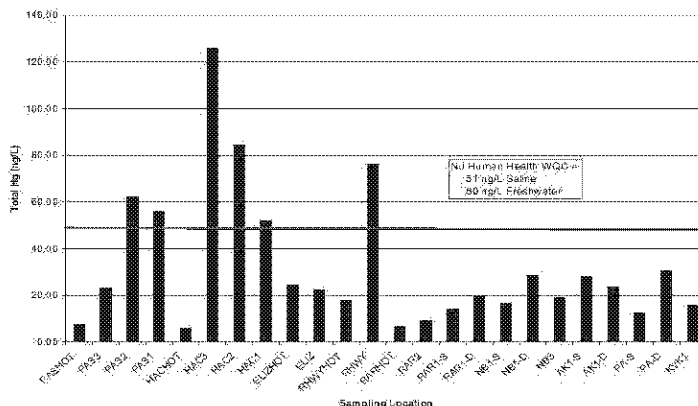
Contaminant	Human Health WQC	Aquatic Chronic WQC	Aquatic Acute WQC
total Hg	Tidal Passaic, Hackensack, & Rahway Rivers	No WQC	No WQC
dissolved Hg	No WQC	None	None
total Pb	Freshwater: None Saline – No WQC	No WQC	No WQC
dissolved Pb	No WQC	None	None
total Cd	None	No WQC	No WQC
2,3,7,8-TCDD	all tidal tributary & estuarine locations; no tributary head-of-tide locations	No WQC	No WQC
total PCBs	all tidal tributary & estuarine locations and all tributary head-of-tide locations	tidal Rahway River & Elizabeth River head-of-tide	No WQC
4,4-DDD Saline & Fresh Human WQC: 0.31 ng/L	all tidal tributary & estuarine locations; Passaic, Elizabeth, and Rahway River head-of-tide locations	No WQC	No WQC
4,4-DDE Saline & Fresh Human WQC: 0.22 ng/L	all tidal tributary & estuarine locations; Passaic, Elizabeth, and Rahway River head-of-tide locations	No WQC	No WQC
4,4-DDT Saline & Fresh Human WQC: 0.22 ng/L	tidal Elizabeth, Passaic, and Rahway Rivers & Arthur Kill, Elizabeth, Rahway, and Raritan River head-of-tide locations	tidal Elizabeth, lower Passaic, and Rahway Rivers & upper Arthur Kill, Elizabeth River head-of-tide	None
total chlordane	all tidal tributary & estuarine locations and all tributary head-of-tide locations	tidal Rahway River & Elizabeth, Rahway, and Hackensack River head-of-tide	None
dieldrin	all tidal tributary & estuarine locations and all tributary head-of-tide locations	tidal Elizabeth, Passaic, Hackensack & Rahway Rivers	None
PAHs - various	various exceedances – see text	No WQC	No WQC

location. Widespread exceedances of the WQC were found for 2,3,7,8-TCDD, total PCBs, 4,4'-DDD/DDE/DDT, total chlordane, dieldrin, and a few of the PAH compounds. In addition, exceedances of the NJ WQC for some compounds were observed in individual samples collected at various sampling locations during the course of the study, even though the median concentrations at these locations did not exceed the NJ WQC.

**Metals – Hg, methyl-Hg, Pb, and Cd**

Figure 3 shows the median total Hg concentration at each of the sampling locations. At the tidal tributary and estuary locations, median total Hg concentrations varied considerably, from a low of 9.1 ng/L (station RAR2) to high of 126 ng/L (station HAC3) – a factor of 14. Concentrations and variability were lower among the head-of-tide stations (5.9 to 24.4 ng/L, a factor of 4). Median dis-

Figure 3: Overall Median Total Hg



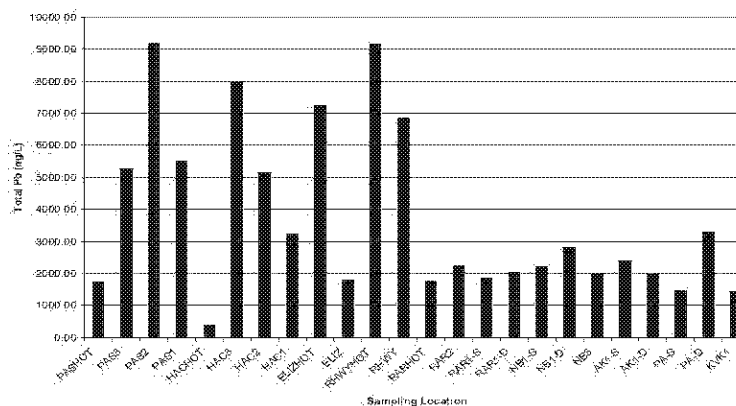
solved Hg concentrations (data not shown) also varied considerably, ranging from 0.31 to 8.34 ng/L (a factor of 27). Median dissolved Hg concentrations were highest at the Elizabeth River head-of-tide (8.34 ng/L) and tidal Elizabeth (5.9 ng/L) stations, elevated at the Rahway River head-of-tide (2.9 ng/L), and were less than 2.0 ng/L at the remaining locations.

The New Jersey Saline Human Health Water Quality Criteria (NJ WQC) for total Hg (51 ng/L) was exceeded by the median concentration in the tidal Passaic, Hackensack, and Rahway Rivers. The NJ Freshwater Human Health WQC for total Hg was not exceeded by the median concentration at any of the head-of-tide locations. The NJ Saline and Freshwater Aquatic WQC for dissolved Hg were not exceeded by the median concentration at any sampling location.

Median dissolved methyl-Hg concentrations (data not shown) at the tributary head-of-tide stations ranged from 0.0085 ng/L in the Hackensack River to approximately 0.05 ng/L in the Passaic, Elizabeth, and Raritan Rivers, with a high of 0.103 ng/L in the Rahway River. In the tidal tributaries, median dissolved methyl-Hg concentrations ranged between 0.007 and 0.09 ng/L. In the estuarine areas of the harbor median concentrations were lower and typically less than 0.017 ng/L. Only a limited number of samples were analyzed for total methyl-Hg.

Figure 4 shows the median total Pb concentration at each of the sampling locations. The median concentration was low at the

Figure 4: Overall Median Total Pb

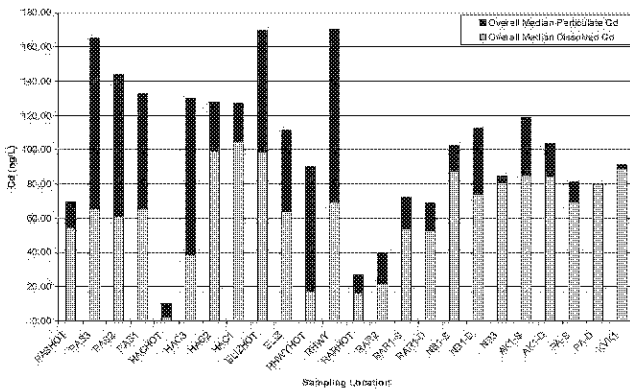


Hackensack River head-of-tide (396 ng/L), but was relatively high at the Rahway River head-of-tide (9,155 ng/L, a factor of 23 difference). The NJ Freshwater Human Health WQC for total Pb was not exceeded by the median concentration at any of the head-of-tide locations. The total Pb concentration was below 3,300 ng/L in the tidal Raritan and lower Hackensack Rivers (Station HAC1), and in the estuarine areas of the harbor, and ranged up to a maximum of 9,205 ng/L in the tidal mid-Passaic River (Station PAS2).

Median dissolved Pb concentrations (data not shown) ranged from 28 ng/L at the Hackensack River head-of-tide to a high of 1,400 ng/L in the lower Arthur Kill (Station PA-S). The NJ Saline and Freshwater Aquatic WQC for dissolved Pb were not exceeded by the median concentration at any sampling location.

Figure 5 shows the median total, particulate, and dissolved Cd concentrations at each of the sampling locations. In contrast to Hg and Pb, where the overall median total concentrations were predominantly associated with the particulate fraction (Hg = 88%, Pb = 86%), the overall median total Cd concentration was distributed approximately 67% in dissolved fraction and only 33% in the particulate fraction.

Figure 5: Overall Median Dissolved and Particulate Cd



The median total Cd concentration was low at the Hackensack River head-of-tide (10.3 ng/L), and was typically greater than 60 ng/L (except at the Hackensack and Raritan River heads-of-tide, and at the upper Raritan River tidal station RAR2). The NJ Saline and Freshwater Human Health WQC for total Cd were not exceeded by the median concentration at any of the sampling locations.

The median dissolved Cd concentration was also low at the Hackensack River head-of-tide (2.4 ng/L), and was typically greater than 38 ng/L (except at the Hackensack, Rahway, and Raritan River heads-of-tide, and at Station RAR2). The NJ Saline Aquatic WQC were not exceeded by the median concentration at any sampling location.

The lowest median metals concentrations were consistently observed at the Hackensack River head-of-tide. Except for total Hg, the range of median concentra-

tions observed for each metal at the five head-of-tide sampling locations were generally similar to those seen at the ten tidal tributary and estuarine locations.

Dissolved and total metals concentrations did not consistently vary with river flow, except in the tidal Rahway River and above the head-of-tide, where total metal concentrations tended to be greater during wet weather/high river flow condition events. This is indicative of stormwater/runoff sources for these contaminants in the Rahway River.

**Dioxins/Furans (PCDD/Fs)**

Only the suspended particulate fraction of the TOPS samples was analyzed for dioxins/furans. Figure 6 shows the median total dioxin/furan (PCDD/F) and total PCDD/F minus OCDD (PCDD/F-OCDD) concentrations at each sampling location. Total PCDD/F concentrations were highest at the Elizabeth River stations (24 to 33 ng/g sed) and at the upper Raritan River tidal station (35 ng/g sed); total PCDD/F concentrations were less than 14 ng/g sed at all of the other locations. Total PCDD/F-OCDD concentrations were less than 5 ng/g sed throughout the harbor, with the highest levels (> 4 ng/g sed) at the Elizabeth River and lower/mid-tidal Hackensack River stations. Overall, OCDD accounted for 80% of the total PCDD/F at the sampling locations, with greater than 90% OCDD found at the heads-of-tide on the Passaic, Hackensack, and Raritan Rivers, and in the tidal Raritan River.

Figure 6: Median Total Dioxin/Furan Concentrations

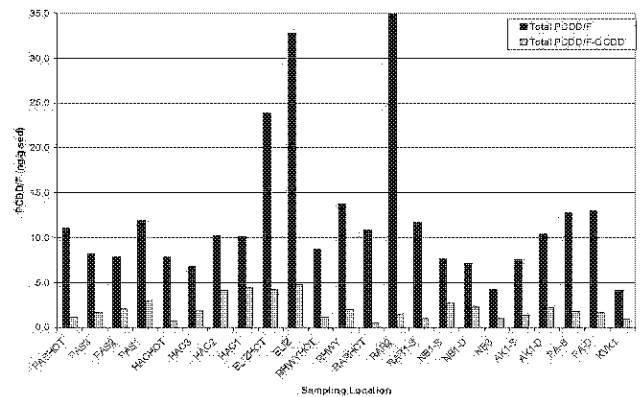


Figure 7: 2,3,7,8-TCDD and Total PCDD/F TEQ

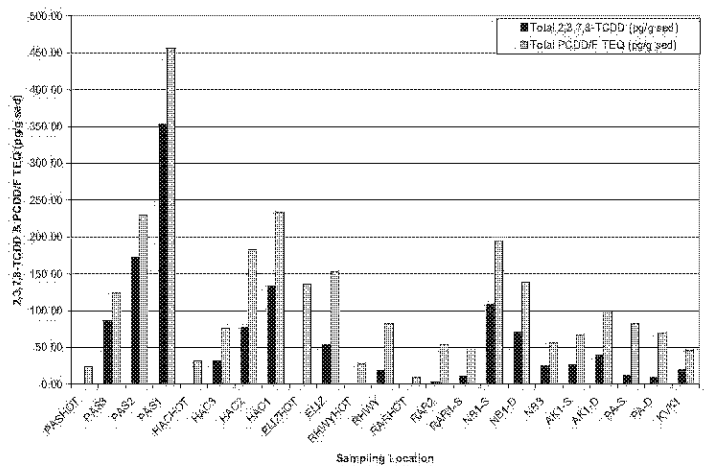


Figure 7 shows the median 2,3,7,8-TCDD and total PCDD/F Toxic Equivalency (TEQ) concentrations at each sampling location. The highest 2,3,7,8-TCDD (353 pg/g sed) and total PCDD/F TEQ (457 pg/g sed) concentrations were found at the lower tidal Passaic River Station PAS1. Median 2,3,7,8-TCDD concentrations greater than 70 pg/g sed were observed in the tidal Passaic and Hackensack Rivers, and in upper Newark Bay. Median total PCDD/F TEQ concentrations were also elevated (> 120 pg/g sed) at these locations, as well as in the Elizabeth River. 2,3,7,8-TCDD accounted for 70-77% of the total PCDD/F TEQ in the tidal Passaic River, and 40-57% in the tidal Hackensack River, Newark Bay, upper Arthur Kill, and Kill van Kull. Although the median total PCDD/F TEQ was elevated at the Elizabeth River head-of-tide (136 pg/g sed), none of this TEQ was due to 2,3,7,8-TCDD; in the tidal Elizabeth River, only 35% of the total PCDD/F TEQ (152 pg/g sed) was due to 2,3,7,8-TCDD (53 pg/g sed).

The NJ Saline Human Health WQC for 2,3,7,8-TCDD (0.0051 pg/L) was exceeded by the median concentration at all of the sampling locations (data not shown). 2,3,7,8-TCDD was not detected in any of the samples collected at the Hackensack and Rahway River heads-of-tide. The Freshwater Human Health WQC for 2,3,7,8-TCDD (0.0050 pg/L) was not exceeded by the median concentrations at the Passaic, Elizabeth, and Raritan River heads-of-tide.

The highest 2,3,7,8-TCDD and total PCDD/F TEQ concentrations were observed at the lower Passaic River Station PAS1, and there was very little variability in the PCDD/F congener distribution patterns for each sampling event at this station (data not shown). This is indicative of a single source of dioxins/furans. In addition, the 2,3,7,8-TCDD concentration distribution pattern among the sampling sites in Newark Bay and the Passaic and Hackensack Rivers points to the existence of a source along the Passaic River, probably between stations PAS1 and PAS2. The major source of this 2,3,7,8-TCDD has been attributed to the Diamond Alkali (Lister Avenue, Newark) site located on the banks of the lower Passaic River.

The median total PCDD/F (23.9 ng/g sed) and total PCDD/F TEQ (136 pg/g sed) concentrations were elevated at the Elizabeth River head-of-tide, but none of the TEQ was due to 2,3,7,8-TCDD. In the tidal Elizabeth River, the median total PCDD/F (32.7 ng/g sed) and total PCDD/F TEQ (152 pg/g sed) concentrations were about 35% higher than at the head-of-tide, and about 35% of the median total PCDD/F TEQ (53 pg/g sed) was due to 2,3,7,8-TCDD. The PCDD/F congener distribution patterns were more variable among the sampling events in the tidal Elizabeth River. The lower chlorinated PCDD/Fs (tetra through hexa, including 2,3,7,8-TCDD) consistently comprised a higher percentage of the tPCDD/Fs during the low river flow/dry weather surveys compared with the high river flow/wet weather surveys. This was not the case with the head-of-tide samples; however total PCDD/F, total PCDD/F-OCDD, and total PCDD/F TEQ concentrations at the head-of-tide were consistently higher (by factors of 15 -24, data not shown) during high river flow/wet weather conditions compared to low river flow/dry weather conditions. This indicates at least two different and signifi-

cant sources of PCDD/Fs to the lower Elizabeth River: one located above the head-of-tide (which is potentially a stormwater/runoff source), and the second (which is also a source of 2,3,7,8-TCDD) located below the head-of-tide.

### Polychlorinated Biphenyls (PCBs)

Figure 8 shows the median total PCB concentration at each of the sampling locations. The highest concentrations were found at the head-of-tide of the Elizabeth River (67 ng/L) and in the tidal Rahway River (46 ng/L); concentrations were less than 25 ng/L at the other sampling locations. Median concentrations tended to be lower at the heads-of-tide (0.7 to 5.6 ng/L), except in the Elizabeth River (67 ng/L), compared to the tributary and estuary locations (3.7 to 46 ng/L). The NJ Saline and Freshwater Human Health WQC for total PCBs (0.064 ng/L) were exceeded by the median concentration at all of the sampling locations. The NJ Saline Aquatic Chronic WQC (30 ng/L) was exceeded by the median total PCB concentration in the Rahway River. The NJ Freshwater Aquatic Chronic WQC (14 ng/L) was exceeded by the median total PCB concentration at the Elizabeth River head-of-tide.

Median dissolved total PCB concentrations ranged between 0.4 and 5.8 ng/L. Median concentrations tended to be lower at the heads-of-tide (0.4 to 1.9 ng/L), except in the Elizabeth River (4.7 ng/L), compared to the tributary and estuary locations (1.3 to 5.8 ng/L). Overall, about 29% of the total PCBs were found in the dissolved fraction and 71% in the suspended particulate fraction. However, higher percentages of the total PCBs were found in the suspended particulate phase at the Elizabeth River head-of-tide (93%) and in the tidal Rahway River (90%).

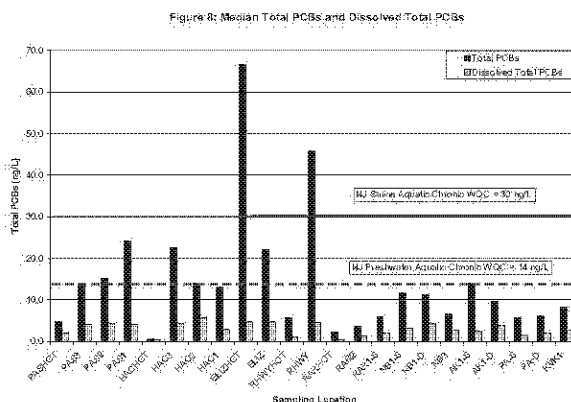


Figure 9 shows the median total PCB concentration in the suspended particulate phase at each of the sampling locations. As with the total PCB (ng/L) concentrations, the suspended particulate phase concentrations (expressed as ng/g sed) were highest at the head-of-tide of the Elizabeth River (2,740 ng/g sed) and in the tidal Rahway River (1,620 ng/g sed), as well as in the tidal Elizabeth River (1,610 ng/g sed). Median concentrations at the other tidal tributary and estuarine sampling locations ranged between 283 and 955 ng/g sed, and were also lower at the other head-of-tide locations (57 to 334 ng/g sed).



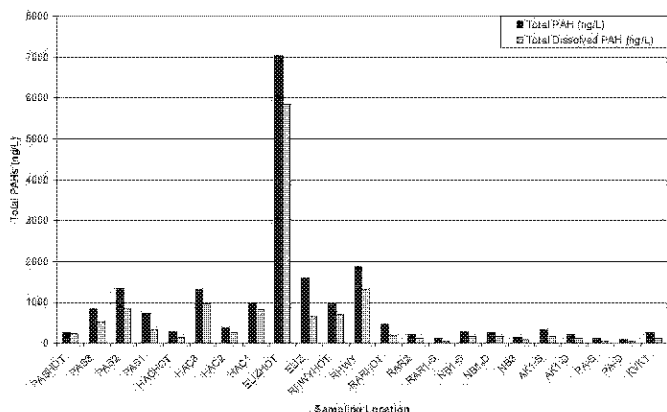


Along the rivers with more than one sampling station along their tidal stretches (the Passaic, Hackensack, and Raritan Rivers), there was a tendency for the median dissolved total DDT concentration to decrease in the upstream direction. In contrast, the median dissolved total chlordane and dieldrin concentrations tended to increase in the upstream direction.

### Polyaromatic Hydrocarbons (PAHs)

Figure 12 shows the median total (dissolved + suspended particulate fractions) and total dissolved PAH concentrations at each of the sampling locations. The highest median total (7,050 ng/L) and total dissolved (5,840 ng/L) PAH concentrations were found at the Elizabeth River head-of-tide. Total concentrations were less than 1,900 ng/L, and total dissolved concentrations were less than 1,310 ng/L, at all of the other sampling locations.

Figure 12: Median Total and Dissolved Total PAHs



New Jersey Saline and Freshwater Human Health WQC have been promulgated for various individual PAH compounds. The NJ Saline Human Health WQC for dibenz(a,h)anthracene (18 ng/L) was exceeded by the median concentration in the tidal Rahway River, while the Freshwater WQC (3.8 ng/L) was exceeded at the heads-of-tide of the Raritan and Elizabeth Rivers. The NJ Saline Human Health WQC for benzo(a)pyrene (18 ng/L) was exceeded at all of the sampling locations in the tidal Passaic, Hackensack, Elizabeth, and Rahway Rivers, and at sampling Stations NB1-S and AK1-S. The median concentration for benzo(a)pyrene at all of the heads-of-tide exceeded the Freshwater Human Health WQC (3.8 ng/L). In addition, the median concentration at the heads-of-tide of the Passaic, Rahway, and Elizabeth Rivers exceeded the Freshwater WQC for benz(a)anthracene, benzo(b)fluoranthene, and benzo(k)fluoranthene (each 38 ng/L). The median concentration at the heads-of-tide of the Rahway and Elizabeth Rivers exceeded the Freshwater WQC for indeno(1,2,3-cd)pyrene (38 ng/L).

Parent and alkyl-substituted PAHs have both natural sources (coal, oil seeps, forest and prairie fires) and anthropogenic sources (fossil fuels and combustion). Ra-

tios of the concentrations of various individual PAH compounds can potentially be used to identify the types of sources for the PAHs found in environmental samples. Based on the NJTRWP sample data, combustion of petroleum and gas/wood/coal are the main sources of PAHs to the harbor; this is to be expected for this urbanized region.

### Sediment and Contaminant Loads at the Tributary Heads-of-Tide

Using the contaminant concentration data collected as part of this study and historic river discharge data from 1975-2000, the USGS calculated the annual average load of sediment, organic carbon, and associated contaminants for each of the rivers. These estimated loads are presented in Table 2, and represent the loads discharged at the heads-of-tide of each of the rivers into their downstream tidal watersheds.

The annual discharge of water (and DOC) are approximately the same for the Passaic (251,000 Mgal) and Raritan (279,000 Mgal) rivers, and account for 44.6% and 49.6%, respectively, of the total flow from the five major New Jersey tributaries to NY-NJ Harbor. However, the estimated load of sediment (and POC to a lesser degree) is much larger in the Raritan River (93.1 Mkg; 79.2% of the total) compared to the Passaic River (22.7 Mkg; 19.3% of the total). The Hackensack and Rahway Rivers each contribute about 2.5% of the total flow and DOC, while the Elizabeth River accounts for only 1% of the flow and DOC.

Table 2: Estimated annual average loads of sediment and associated contaminants at the heads-of-tide of the Passaic, Hackensack, Elizabeth, Rahway, and Raritan Rivers for the period 1975-2000.

	Passaic	Hackensack	Elizabeth	Rahway	Raritan
Discharge (Mgal)	251,000	13,900	6,120	22,900	279,000
Sediment (Mkg)	22.7	0.285	0.447	0.882	93.1
POC (kg)	589,000	113,000	16,300	64,200	666,000
DOC (kg)	4,200,000	215,000	89,000	205,000	4,190,000
SS-PCBs (g)	5,800	35	1,000	370	4,100
Diss-PCBs (g)	1,500	39	120	67	323
Total PCBs (g)	7,290	74	1,120	437	5,020
SS-PCDD/Fs (g)	268	2.1	12	10	1,970
BCDD/F TEQ (g)	0.62	0.009	0.056	0.032	1.3
PCB TEQ (g)	0.25	0.002	0.028	0.017	0.52
SS-Total PAHs (kg)	490	5.6	54	25	1,900
Diss-Total PAHs (kg)	630	9.5	220	45	340
Total PAH (kg)	1,050	15.3	274	70	1,380
SS-Total DDTs (g)	1,460	35	180	210	4,900
Diss-Total DDTs (g)	299	12	22	51	340
Total DDTs (g)	1,890	47	202	261	5,240
SS-Total chlordane <sup>1</sup> (g)	1,690	108	245	316	1,130
Diss chlordane <sup>1</sup> (g)	340	91	49	165	480
Total chlordane <sup>1</sup> (g)	2,330	199	297	481	1,610
SS-Dieldrin <sup>2</sup> (g)	150	15	35	23	210
Diss-Dieldrin <sup>2</sup> (g)	170	64	49	85	430
Total Dieldrin <sup>2</sup> (g)	320	79	83	108	640
Total Hg (g)	8,000	78	2,290	1,200	15,000
Total Pb (g)	2,100	29	1,890	450	5,400
Total Cd (g)	64,000	260	17,000	4,500	54,000

<sup>1</sup> estimated using a POC concentration of 1 mg/L  
<sup>2</sup> estimated using a DOC concentration of 3.8 mg/L  
<sup>3</sup> total chlordane + nonachlor  
<sup>4</sup> dieldrin + dieldrin



The loads of the various contaminants are greatest in the Passaic and Raritan Rivers. However, note the relatively large loads of suspended sediment PCBs, dissolved total PAHs, and total Cd at the Elizabeth River head-of-tide.

### Conclusions and Recommendations

Table 3 summarizes the NJTRWP Phase One ambient water quality data based on comparisons to the applicable New Jersey Water Quality Criteria (WQC), with a "secondary level" comparison to the available Long et al. (1995) sediment effects range median (ERM) guideline values (i.e. NJTRWP suspended sediment concentrations were compared to ERM values). Based on this analysis, those areas identified with an "XZ\*" (or "X\*" where there is no ERM) in this table can be considered to be the most contaminated for the indicated compound:

- ◆ Hackensack River – Hg
- ◆ Passaic River – 2,3,7,8-TCDD (and total PCDD/F TEQ)
- ◆ Elizabeth River – total PCBs (and potentially PAHs)
- ◆ Rahway River – total PCBs, DDT and metabolites, chlordanes, and dieldrin

However, it should be stressed that contamination of the study area by the hydrophobic contaminants of concern – dioxins/furans (2,3,7,8-TCDD), PCBs, and various organochlorine pesticides and PAHs – is widespread.

In addition, based on the data collected and analyses conducted to date, note the following conclusions and recommendations:

(1) Due to their sizes, the largest loads of the contaminants of concern from the upper freshwater watersheds of the NJ tributaries to the tidal/estuarine areas of the harbor originate in the Raritan and Passaic Rivers. The ultimate fate of these contaminant loads as they are transported downstream into the harbor estuary will be evaluated by the CARP Model.

(2) Compared to its size, relatively large loads of total PCBs, total PAHs, total DDTs, dieldrin, and the metals Hg, Pb, and Cd are discharged at the head-of-tide on the Elizabeth River. A NJTRWP Phase II trackdown study has been implemented above the head-of-tide on this river (Wilson and Bonin, 2007a) and should be followed up with additional trackdown work.

(3) The NJ Human Health WQC and Long et al. (1995) ERM values for mercury were consistently exceeded in the tidal Passaic, Hackensack, and Rahway Rivers. A NJTRWP Phase II Hg trackdown study has been implemented in the Hackensack River (to be described in a future NJTRWP report); additional Hg work is needed in this river.

(4) Additional study is needed to evaluate Pb contamination in both the upper watershed and tidal reaches of the Rahway River, where there may be stormwater/runoff sources of this contaminant.

(5) The 2,3,7,8-TCDD WQC was exceeded in every sample collected throughout the tidal tributary and estuarine areas of the harbor. It appears that the harbor can be separated into five sub-areas, with potential "sources" of dioxins/furans, as follows:

- ◆ Passaic River, Upper Newark Bay, and the Hackensack River: elevated levels of 2,3,7,8-TCDD (particularly in the lower Passaic River) and high total PCDD/F TEQ. Significant "sources" of 2,3,7,8-TCDD, with the lower Hackensack River also a source of furans.
- ◆ Elizabeth River: elevated total PCDD/Fs, 2,3,7,8-TCDD, and total PCDD/F TEQ. Two different "sources" of tetra-through hexa- PCDD/Fs, including 2,3,7,8-TCDD.
- ◆ Rahway River: elevated total PCDD/Fs and 2,3,7,8-TCDD, but total PCDD/F TEQ is not elevated.
- ◆ Raritan River: the upper tidal Raritan River has elevated levels of total PCDD/Fs due to relatively high concentrations of OCDD. Total PCDD/F in the lower tidal Raritan River

Table 3: Comparisons of Contaminant Water Column Concentrations from NJTRWP Data to NJ Water Quality Criteria and Long et al. (1995) ERM values.

Contaminant	Passaic R.		Hackensack R.		Elizabeth R.		Rahway R.		Raritan R.		Newark Bay	Arthur Kill
	HOT	Tidal	HOT	Tidal	HOT	Tidal	HOT	Tidal	HOT	Tidal		
2,3,7,8-TCDD	X	X*		X	?	X		X	?	X	X	X
Total PCBs	XZ	XZ	X	XZ	X-Z*	XZ	XZ	X-Z*	X	XZ	XZ	XZ
DDTs	XZ	X-Z		XZ	X-Z	X+Z	XZ	X-Z*	X	XZ	XZ	X+Z
Chlordanes	X	X	X	X	X-	X	X+	X*	X	X	X	X
Dieldrin	X	X	X	X	X	X	X	X*	X	X	X	X
Benzo(a)pyrene	X	X	X	X	X*	XZ	X	X	X			?
Total PAHs					Z*							
Mercury		XZ		XZ*			Z?	XZ				
Lead					Z?		Z*	Z?				

X = large number of exceedances of NJ Human Health WQC observed

+ = large number of exceedances of NJ Aquatic Chronic WQC also observed

Z = large number of exceedances of Long et al. (1995) ERM observed (Hg, Pb, Total PCBs, and Total DDTs only)

? = additional study needed to determine if contaminant is of significant concern

\* = highest median concentrations observed in NJTRWP data

Note: integration of NYSDEC CARP data, CARP model results, and other information (for example, biota and sediment data) during development of the NJDEP Implementation Plan may result in future revisions to this table.

is similar to the lower Arthur Kill. 2,3,7,8-TCDD concentrations are relatively low. Total PCDD/F TEQ at the Raritan River sites were among the lowest in the harbor.

- ◆ Arthur Kill, Kill Van Kull, and Lower Newark Bay: relatively low/moderate total PCDD/Fs, and low 2,3,7,8-TCDD and total PCDD/F TEQ.

The most significant source of 2,3,7,8-TCDD to the harbor contamination is being evaluated through the Lower Passaic River Restoration Project and the Newark Bay Superfund RI/FS. However, it appears that additional 2,3,7,8-TCDD source trackdown work is needed in the Elizabeth and lower Hackensack Rivers.

(6) The NJ Human Health WQC and Long et al. (1995) ERM values were consistently exceeded for total PCBs throughout the entire study area. The highest total PCB concentrations were observed in the tidal Rahway River and above the head-of-tide on the Elizabeth River, where exceedances of the NJ Aquatic Chronic WQC were also frequently observed. NJTRWP Phase II trackdown studies for PCBs should be implemented in these two rivers.

(7) Consistent and widespread exceedances of the NJ Human Health and Aquatic Chronic WQC for various pesticides were observed throughout most of the harbor, with certain pesticides particularly problematic in the following areas:

- ◆ DDT - Passaic, Elizabeth, and Rahway Rivers, and the Arthur Kill
- ◆ Chlordane – above the heads-of-tide of the Hackensack, Elizabeth, and Rahway Rivers, and in the tidal Rahway River
- ◆ Dieldrin - above the heads-of-tide of the Passaic, Elizabeth, and Hackensack Rivers, and in the tidal Elizabeth River.

In the rivers with more than one sampling station along their tidal stretches (the Passaic, Hackensack, and Raritan Rivers), there was a tendency for the median dissolved total DDT concentration to decrease in the upstream direction; this is indicative of DDT sources located in the tidal tributary and estuarine areas of the harbor. In contrast, the median dissolved total chlordane and dieldrin concentrations tended to increase in the upstream direction; this is further evidence of notable sources of these pesticides above the heads-of-tide on these rivers.

(8) The highest total PAH concentrations were observed above the Elizabeth River head-of-tide. In addition, exceedances of NJ WQC were observed for individual PAH compounds in the upper watersheds of the tributaries:

- ◆ benzo(a)pyrene – all rivers
- ◆ dibenz(a,h)anthracene – Raritan and Elizabeth Rivers (and tidal Rahway River)
- ◆ benz(a)anthracene, benzo(b)fluoranthene, and benzo(k)fluoranthene - Passaic, Rahway, and Elizabeth Rivers
- ◆ indeno(1,2,3-cd)pyrene – Rahway and Elizabeth River.

Benzo(a)pyrene concentrations exceeded the NJ Human Health WQC in both the upper watersheds and the tidal reaches of the tributaries (except for the Raritan River), and

in upper Newark Bay and the upper Arthur Kill.

Many contaminants were found largely in the suspended sediment fraction - for example, dioxins/furans (99+ % in the suspended sediment fraction), PCBs (71%), Hg (88%), and Pb (86%). Thus, whole water (total) concentrations of these contaminants were strongly influenced by the amount of suspended sediment in the water column at the time of sample collection. In addition, this suggests that future trackdown and source reduction/eliminations actions that focus on one of these toxic contaminants may also result in reductions in the other contaminants.

Overall, no consistent patterns were found between contaminant concentrations and dry weather/low flow and wet weather/high flow river conditions. However, in the tidal Rahway River and above this river's head-of-tide, PCB and metals concentrations did appear to consistently increase during wet weather/high river flow conditions, which is indicative of stormwater/runoff sources of these contaminants.

Results of NJTRWP Study I-G, which sampled the discharges from municipal wastewater treatment plants (POTWs), combined sewer overflows (CSOs), and stormwater outfalls (SWOs), will be summarized in a companion NJDEP-DSRT Research Project Summary.

The Phase One NJTRWP data and analyses will be used, together with other data and information - including the New York State CARP data, the CARP modeling results, and other studies - to develop the NJTRWP Implementation Plan. This plan will integrate and evaluate the available information for each toxic contaminant and recommend a future course of action for source trackdown and reduction/elimination. However, based on the data and analyses completed to date - and the ongoing Passaic River and Newark Bay RI/FS work - it is recommended that future NJTRWP trackdown activities in ambient waters be prioritized as follows:

- #1 – Elizabeth River above the head-of-tide (PCBs, PAHs, and potentially 2,3,7,8-TCDD and pesticides)
- #2 – tidal Rahway River (PCBs, pesticides, and Hg)
- #3 – tidal Hackensack River (Hg)

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### References

Bonin, J.L. and T.P. Wilson, 2006. Organic Compounds, Trace Elements, Suspended Sediment, and Field Characteristics at the Heads-of-Tide of the Raritan, Passaic, Hackensack, Rahway, and Elizabeth Rivers, 2000-03. U.S. Geological Survey Data Series 123, 32 pp. + CD.

Long, E.R., D.D. MacDonald, S.L. Smith, and F.D. Calder 1995. Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments. *Environmental Management* 19(1):81-97.

New Jersey Department of Environmental Protection, 2001. New Jersey Toxics Reduction Workplan, Volume I, Revised/Version 2 – February 2, 2001, 111 pp + attachments.

New Jersey Department of Environmental Protection, 2007. New Jersey Toxics Reduction Workplan, Volume II – Quality Assurance Project Plan, Version 2.3 – May 2007 [Final], 93 pp. + attachments.

New York-New Jersey Harbor Estuary Program, 1996. Final Comprehensive Conservation and Management Plan, March 1996.

Pecchioli, J.A., M.S. Bruno, R. Chant, A. M. Pence, A.F. Blumberg, D. Fugate, B. J. Fullerton, S. Glenn, C. Haldeman, E. Hunter, and K. L. Rankin, 2006. The New Jersey Toxics Reduction Workplan for New York-New Jersey Harbor: Study I-E – Hydrodynamic Studies in the Newark Bay Complex, NJDEP-DSRT Research Project Summary, December 2006, 10 pp.

Stevens Institute of Technology, 2007. The New Jersey Toxics Reduction Workplan for NY-NJ Harbor – Ambient Monitoring of Water Quality Within Major Tributaries and the Estuary, Final Report – April 2007, 292 pp.

Wilson, T.P. and J.L. Bonin, 2007. Concentrations and Loads of Organic Compounds and Trace Elements in Tributaries to Newark and Raritan Bays, New Jersey. Scientific Investigations Report 2007-5059, 192 pp.

Wilson, T.P. and J.L. Bonin 2007a. Occurrence of organic compounds and trace elements in the upper Passaic and Elizabeth Rivers and their tributaries in New Jersey, July 2003 to February 2004: Phase II of the New Jersey Toxics Reduction Workplan for New York-New Jersey Harbor. Scientific Investigations Report 2007-5136.

### Prepared By

- 1 Joel A. Pecchioli, Project Manager, NJDEP, DSRT
- 2 Timothy Wilson and Jennifer Bonin, U.S. Geological Survey, New Jersey Field Office
- 3 K. Nadia Dimou, Stevens Institute of Technology

STATE OF NEW JERSEY  
*Jon S. Corzine, Governor*

Department of Environmental Protection  
*Lisa P. Jackson, Commissioner*

Division of Science, Research & Technology  
*Dr. Eileen Murphy, Director*

Please send comments or requests to:  
Division of Science, Research and Technology  
P.O.Box 409, Trenton, NJ 08625  
Phone: 609 984-6070  
Visit the DSRT web site @ [www.state.nj.us/dep/dsr](http://www.state.nj.us/dep/dsr)



## RESEARCH PROJECT SUMMARY

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