

Availability of Chemical Sediment and Water Quality Data for the Tidal Raritan River

A report to the Edison Wetlands Association

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2012

1. Introduction

The Raritan River is the largest river system contained entirely within the state of New Jersey. It supplies water, recreation, and transportation for more than one million residents in seven counties. The Raritan flows predominantly eastward. The tidal reach of the Raritan extends from the head of tide at the Calco Dam in Bound Brook to Raritan Bay (figure 1.1). The dividing line between the River and the Bay is often arbitrarily drawn at the NJ Transit railroad bridge, which crosses the river between South Amboy and Perth Amboy. Given the importance of the River and its history of contamination, Rutgers, in partnership with the Mushett Foundation and Edison Wetlands Association, has developed a Raritan River Initiative. As part of this initiative, Rutgers has conducted various campaigns on the River using the Class of 1914 Boathouse as a primary access point. This area remains accessible to the Rutgers research vessel, the Caleta. Upstream of the Boathouse, the river becomes too shallow to navigate. Thus our forays into the River have focused on the stretch between the Boathouse and the NJ Transit Bridge, and we have designated 11 sampling sites that are used for water quality monitoring (figure 1.2).

The sediments of the River are generally sand and gravel from Bound Brook to roughly Crab Island, and then transition into black mud with a high organic content from there to the Bay. Thus in the upper reaches of the River, the sediment has a relatively low capacity to sorb and therefore serve as a reservoir for contaminants. The zone of highly organic sediments is caused by the presence of estuarine turbidity maximum (ETM), where the salt water from the ocean and Raritan Bay mixes with the fresh water from upstream. In this region, the water column is often stratified, with the heavier salt water lying below the lighter fresh water. This is a region of strong currents due to the interplay of the salt and fresh water and the tides, which can resuspend sediment. Also in this region, dissolved material in the river water flocculates (forms ever larger particles) when it comes into contact with the salt wedge. The combination of these two processes form the highly organic sediment bed and also keep the total suspended solids (TSS) high (hence the name, estuarine turbidity maximum). In the ETM, contaminants that are bound to the organic matter in sediments tend to be resuspended and moved back and forth with the tides, but the particles have a difficult time escaping completely. Because of this, the contaminant load remains trapped in the ETM, often until a large storm event produces sufficient freshwater flow to flush a large amount of sediment out of the River and into the Bay. Hurricane Irene in August of 2011, followed by Tropical Storm Lee a few weeks later, provided this type of

system flushing. This reach of the river, roughly from our sampling sites 7 to 10, is also sometimes referred to as the Keasbey Reach.

The Raritan has a long history of urbanization, industrialization, and contamination. There are at least 6 Superfund sites in the region, and hundreds of smaller sites that may release contamination into the river directly or via groundwater. Several of the most contaminated sites are located in Keasbey Reach. It is unfortunate that these sites happen to be located on the ETM, where contaminants can become trapped in the system.

For purposes of 303(d) classification, the tidal Raritan is divided into the following sections (see figure 1.1 for locations of the points of reference): (1) below Lawrence Brook, (2) Lawrence Brook to Mile Run, (3) Mile Run to the I-287 Bridge in Piscataway, (4) I-287 Piscataway to the Millstone River. Each section of the tidal Raritan is listed on the most recent (2008) 303(d) for impairment due to several contaminants[1]:

(1) below Lawrence Brook - arsenic, benzo[a]pyrene, cadmium, chlordane, DDD, DDE, DDT, dieldrin, dioxins, dissolved oxygen, heptachlor epoxide, mercury, and PCBs

(2) Lawrence Brook to Mile Run - arsenic, benzo[a]pyrene, cadmium, chlordane, DDD, DDE, DDT, dieldrin, dioxins, heptachlor epoxide, mercury, total phosphorus, PCBs, total suspended solids (TSS), and zinc

(3) Mile Run to the I-287 Bridge in Piscataway - arsenic, benzene, total phosphorus, PCBs, TSS

(4) I-287 Piscataway to the Millstone - arsenic, benzene, mercury, total phosphorus, and TSS

Due to these impairments, all four of these river segments are listed as needing TMDLs by the EPA.[1] The tidal portion of the river is considered to be part of the New York/New Jersey Harbor system. TMDLs are being developed for the NY/NJ Harbor for nutrients and benzo[a]pyrene, PCBs, chlordane, DDT (and its metabolites, DDE and DDD), 2,3,7,8-tetrachlorodibenzo-p-dioxin (the most toxic dioxin congener) as well as the sum of all polychlorinated dibenzo-p-dioxins and -furans (Σ PCDD/Fs). These efforts depend largely upon data gathered as part of the Contamination Assessment and Reduction Project (CARP).[2, 3] However, the CARP concluded in 2004 and the associated TMDLs for the Harbor have not yet been promulgated.

Given the level of water quality impairment, the Mushett Foundation and the Edison Wetlands Association have advocated a regional approach to water quality for the Raritan. In order to develop a comprehensive water quality management plan, it is important to assess the amount of information already available for the Raritan and to identify any data gaps. The purpose of this report is to assess the amount of water quality data available for the tidal Raritan. In addition, we will attempt to assess whether sufficient data exists for the construction of mass balances on

contaminants and for source apportionment of contaminants. This report will focus on three classes of contaminants: nutrients, metals, and organics.

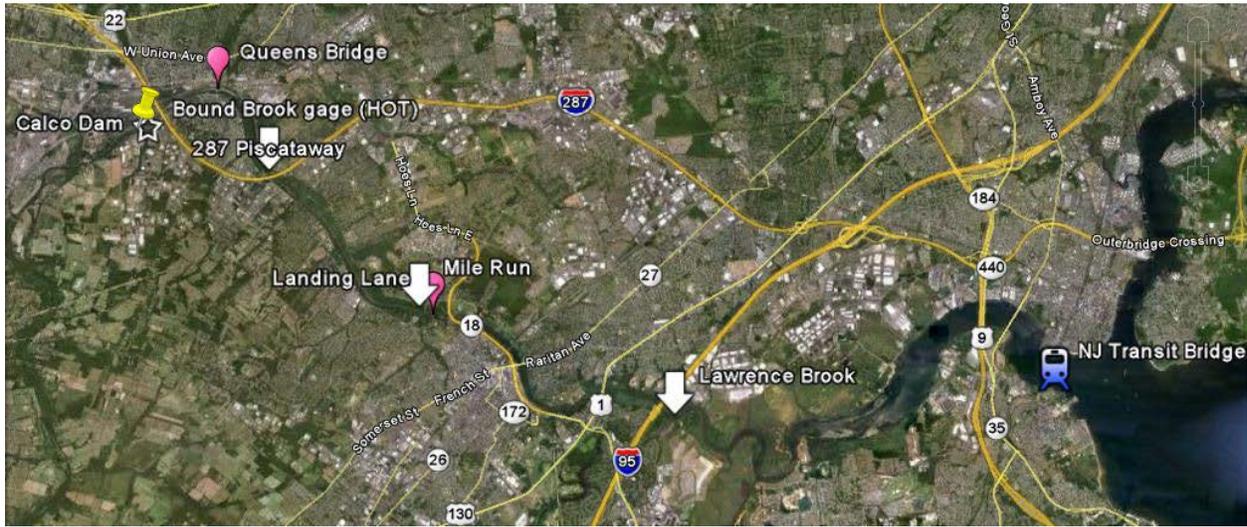


Figure 1.1. The tidal Raritan River, which runs from the Calco Dam (star) to the NJ Transit Bridge. The water quality zones of the river are delineated by the white arrows. Pink bubbles denote sampling stations of the New Jersey Bureau of Freshwater and Biological Monitoring (BFBM). Map courtesy of Google Earth.



Figure 1.2. Closeup of the tidal Raritan River, showing Rutgers sampling sites (yellow pins) as well as CARP sites RAR-1 and RAR-2 (blue bubbles). Map courtesy of Google Earth.

2. A word about data sources

Several types of sources were investigated to compile this report. It is useful to consider the strengths and weaknesses of each type of data source.

NJHDG – The New Jersey Harbor Dischargers Group is made up of 10 sewerage agencies that operate 12 wastewater treatment plants in New Jersey that discharge to the Harbor. NJHDG has been monitoring water quality at 33 sites in the New Jersey portion of the Harbor since 2003. This monitoring is required as part of their NPDES permits. As a result, this data source has the enormous advantage that it is an on-going program that has a long data history (since 2003). Another result of the association with permitting is that the NJHDG monitoring program is conducted under a Quality Assurance Project Plan (QAPP) that is approved by both NJDEP and the EPA, allowing the resulting data to be entered into the EPA’s STORET database (<http://www.epa.gov/storet/>) and NJDEP’s data mine (<http://datamine2.state.nj.us/>). This data is presented in Appendix A.

NJDEP HazSites data base. This database is maintained by the NJDEP and contains all data on contaminants from Hazardous Waste Sites in New Jersey. In order for data to be entered into this database, it must meet the NJDEP quality assurance criteria. Data in this database comes from a multitude of projects which have a variety of different contaminants of concern. Thus there is no consistent list of analytes. Sampling locations are determined by the location of contaminated sites. NJDEP queried this database at the author’s request for sediment results in Middlesex and Somerset counties, then selected from these all the results from all sampling locations within 1000 feet of the banks of the Raritan. In other words, they found all of the records in the database for which the field “Matrix” was “sediment”. Unfortunately, the “Matrix” field is not always consistent with the “Sample Type” field. In the present case, the sample types returned are of three types: “Surface Soil”, “Subsurface Soil”, and “Other”. It is not always clear that these really are sediment samples. According to Janine MacGregor at NJDEP, who provided this information, the HazSite database does little to enforce these fields, and there has been little incentive for responsible parties submitting data to pay close attention to the combination of these two fields. Nevertheless, this query returned 4494 records. This data set was further filtered to present only those measurements that were above detection (Appendix B).

NJDEP data mine. This is a database of all water quality measurements that meet NJDEP quality assurance criteria. This database has a web-based query system (<http://datamine2.state.nj.us>). We queried this database for data collected in the four water quality zones of the River (described in the introduction) from January 1, 2000 to the present. We assumed that data older than that was of questionable quality. This query returned data on a variety of parameters, including nutrients and other water quality measures, metals, and organics. The raw data obtained from these queries, including the locations of the samples, sampling dates, methods, etc., is provided in Appendix C. The NJHDG data was also returned by this query, but it was removed from Appendix C to avoid duplication and to minimize file size.

The Contamination Assessment and Reduction Project (CARP) was a collaborative effort of the NJDEP, the NY State Department of Environmental Conservation (NYSDEC) and the US Geological Survey.[2, 3] Conducted from 1998-2001, CARP collected hundreds of samples of

surface water, sediment, biota, and treated wastewater effluents for measurement of metals (cadmium, lead, mercury and methylmercury) and a variety of organics, including polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), organochlorine pesticides, and polycyclic aromatic hydrocarbons (PAHs). CARP used the newest and most sensitive analysis methods and collected a wealth of data on contaminants in the NY/NJ Harbor. Unfortunately, the CARP was never intended to be a long-term monitoring program, so its temporal resolution is minimal. Also, the CARP only included two sampling stations within the tidal Raritan River (figure 1.2) and one at the Head of Tide (HOT). This data can be found in Appendix D.

Peer-reviewed publications. Many of the scientific studies of water quality in the Raritan River have been conducted outside the purview of NJDEP and/or EPA and have been published in peer-reviewed journals. The data from these studies was included in this report. Despite the fact that these studies are peer-reviewed, they often use methodology that is not acceptable to EPA and/or NJDEP. The authors have attempted to verify the quality of the data in the peer-reviewed articles cited here.

Site investigations. There are many contaminated sites on the tidal Raritan River. Some are Superfund sites that fall under federal (EPA) jurisdiction, while others are managed under the state (NJDEP) programs. In order to assess the possible impacts of contaminated sites on the water and sediment quality of the river, potentially responsible parties (PRPs) are typically required to conduct sampling of water and/or sediment near the contaminated site. These sampling campaigns are conducted under the oversight of the state and/or federal agencies, and all phases of data gathering, including sample collection, storage, handling, analysis, and data reporting are conducted under the guidelines provided in the New Jersey Field Sampling Procedures Manual, which was most recently updated in 2005 (<http://www.nj.gov/dep/srp/guidance/fspm/>). As a result, the data collected by these site investigations is usually of high quality. However, detection limits are often a problem, as the PRP has no incentive to use the most sensitive testing methods available, but instead chooses the least expensive method (usually with the highest detection limits) that is acceptable to the relevant authorities. Also, site investigations offer little or no temporal resolution, as the data gathering is usually done only once. Spatial resolution is limited to the area immediately adjacent to the site, although it may include a small number of samples collected upstream as a control.

2. Nutrients

The generic term ‘nutrients’ generally refers to the elements nitrogen and phosphorus. These elements can be present in the water column in various forms, some of which are easier to measure than others. Nitrate, nitrite, and ammonia are inorganic forms of nitrogen that are relatively easy to measure. More difficult to measure are the organic forms of nitrogen, which occur when living things use the inorganic forms of nitrogen to grow. One way to measure

organic nitrogen is to measure Total Kjeldahl Nitrogen (TKN), which is the sum of organic nitrogen plus ammonia (NH₃) and ammonium (NH₄⁺). The amount of organic nitrogen can then be calculated by measuring ammonia+ammonium separately and subtracting this amount from TKN. This can be problematic if either (or both) of these measurements are uncertain. Another approach is to measure Total Dissolved Nitrogen (TDN), which includes all forms of nitrogen, including nitrate, nitrite, ammonia/ammonium, and organic nitrogen. As with TKN, TDN can be used to calculate the amount of organic nitrogen by measuring nitrate, nitrite, and ammonia/ammonium separately and subtracting these from TDN. Again, any flaws in any of the measurements can introduce uncertainty in to the calculation of organic nitrogen. For example, in some cases, TDN may be less than the sum of nitrate, nitrite, and ammonia/ammonium, in which case organic nitrogen is assumed to be negligible.

Phosphorus can also have inorganic as well as organic forms. The inorganic form, PO₄³⁻ (which may be called either phosphate or orthophosphate) is relatively easy to measure. As with nitrogen, it is common to also measure total phosphorus (TP) and then subtract the phosphate concentration to derive the concentration of organic phosphorus.

Monitoring for nutrients in the tidal Raritan is carried out by the New Jersey Harbor Dischargers Group (NJHDG). Their data and reports are available on the website of the Passaic Valley Sewerage Commission (<http://www.pvsc.com/>) and are summarized in Table 1. Note that in our query of the STORET database (<http://www.epa.gov/storet/index.html>), the NJHDG data is the only data that comes up within the tidal Raritan. The NJHDG is made up of 10 sewerage agencies that operate 12 wastewater treatment plants in New Jersey that discharge to the Harbor. NJHDG has been monitoring water quality at 33 sites in the New Jersey portion of the Harbor since 2003. Three of these sites are in the tidal Raritan River: NJHDG site 25 in bound Brook near the Calco Dam, NJHDG site 26 (near Rutgers site 3), and NJHDG site 27 (near Rutgers site 6). In addition, NJHDG has one monitoring site (NJHDG site 28) in Raritan Bay at the mouth of the Raritan River about 1 km east of the NJ Transit bridge. NJHDG measures temperature, pH, dissolved oxygen (DO), salinity, secchi depth, total suspended solids (TSS), 5-day carbonaceous biological oxygen demand (CBOD-5), total kjeldahl nitrogen (TKN), nitrite, nitrate, ammonia, total phosphorous, orthophosphate, dissolved organic carbon (DOC), chlorophyll-a, Fecal coliform bacteria, and Enterococcus bacteria. Monitoring is performed for all parameters at each station weekly from May through September, and twice per month from October through April. NJHDG follows a Quality Assurance Project Plan (QAPP) that is approved by the NJ Department of Environmental Protection (NJDEP) and Region II of the Environmental Protection Agency (EPA).

The NJHDG provides good temporal coverage of the river's water quality by monitoring monthly. In order to provide more information on the spatial trends in water quality, the authors with funding from the Edison Wetlands Association and the Mushett Foundation measured temperature, salinity, DO, pH, Secchi depth, TSS, TDN, nitrate, nitrite, ammonia, CBOD-5, orthophosphate, DOC, and Chlorophyll-a at the eleven stations shown in figure 1. We measured

these parameters seasonally (i.e. four times per year) in 2011. This data is available in a separate report.[4]

The NJDEP data mine contains data on water quality parameters including alkalinity; organic and inorganic forms of nitrogen, including ammonia, nitrate, and TKN; calcium; chloride; chlorophyll-a; DO; hardness; magnesium; phosphate; potassium; specific conductance; and sulfate. These are summarized in table 2.2. Despite the fact that we queried the data mine for data from 1/1/2000 to present, the oldest data on nutrients returned was from February of 2007. Generally, the data mine data is in reasonable agreement with the data from the NJHDG for ammonia, nitrate, TKN, DO, and phosphate.

The US Geological Survey (USGS) conducts some measurements of nutrients on the river. Their report “Evaluation of Streamflow, Water Quality, and Permitted and Nonpermitted Loads and Yields in the Raritan River Basin, New Jersey, Water Years 1991-98” [5] describes measurements of alkalinity, ammonia, total ammonium plus organic nitrogen, BOD, chloride, DO, total dissolved solids (TDS), fecal coliform, hardness, nitrate+nitrite, TOC, pH, total phosphorus, sodium, sulfate, TSS, and temperature. More recent USGS data is available via the USGS web site. According to their web site, they conducted water quality monitoring at the Calco Dam (USGS 01403060) from 1952 to 2000. However, nitrate was only measured 5 times at this location between 1952 and 2000. The USGS also collects water quality information at the Manville site (USGS 01400500), where they measure temperature, pH, specific conductance, and DO in real time. In addition, they occasionally take field samples here for measurement of temperature, specific conductance, DO, pH, TSS, TDN, nitrate, nitrite, ammonia, CBOD-5, orthophosphate, and DOC. The USGS occasionally collects samples for measurement of this same list of parameters in the Lawrence Brook at USGS 01404302 and USGS 01405003.

Some peer-reviewed publications have reported nutrient concentrations in the Raritan. Maest et al. [6] measured phosphate and nitrate along with a variety of metals (discussed below) and silicon, DOC, pH, TSS, and dissolved inorganic carbon (DIC) at 20 sites in the River and Bay in 1982. These researchers note that for dissolved phosphate, nitrate and inorganic carbon, the Raritan estuary can be divided into two mixing zones, with the Raritan River controlling nutrient concentrations in the lower salinity stretches and the South River controlling their distributions at intermediate and higher salinities.

We conclude that data availability for nutrients in the tidal Raritan River is good. The available data provide adequate coverage of both spatial and temporal trends. They reveal that the tidal Raritan experiences periods of low dissolved oxygen in the summer. Hypoxia is generally defined as a DO level less than 30% of saturation, below which most fish cannot live. The NJHDG data shows no periods when the Raritan exhibited hypoxic conditions since 2003. However, on several occasions, usually in July, the DO levels in the Raritan have been in the 30-40% range. The state of NJ has a freshwater surface water quality standard for nitrate of 10 mg/L. This level was exceeded in only one sample collected at NJHDG 25 on March 4, 2009.

The NJHDG station 25 is at the Calco Dam, so it measures outflow from the non-tidal portion of the Raritan River. A nutrient TMDL for this portion of the River is currently under development. Promulgation and implementation of this Upper Raritan nutrient TMDL should decrease the nutrients inputs from the Upper Raritan into the Lower Raritan.

The amount of nutrient data currently available for the tidal Raritan is sufficient for the calculation of TMDLs. As noted above, there is a Harbor-wide nutrient TMDL under development.

Station		pH	DO (mg/L)	DO (%)	Salinity (ppt)	TSS (mg/L)	DOC (mg/L)	Ammonia- Nitrogen NH3-N (mg/L)	Nitrate- Nitrogen NO3-N (mg/L)	Nitrite- Nitrogen NO2-N (mg/L)	TKN (mg/L)	Ortho P (mg/L)	Total P (mg/L)
25	avg	7.6	12	113	0.20	11	4.7	0.18	2.5	0.021	0.99	0.34	0.34
	min	6.1	3.4	37	0.070	1.0	0.60	0.026	0.13	0.0080	0.050	0.050	0.043
	max	9.6	21	184	0.75	84	14	0.72	17	0.065	2.0	2.1	1.3
26 Upper	avg	7.5	9.2	91	1.6	15	5.1	0.14	1.7	0.025	1.2	0.19	0.22
	min	5.4	3.9	44	0.070	1.0	0.50	0.020	0.25	0.0080	0.33	0.070	0.078
	max	9.5	18	158	8.9	200	26	0.64	4.1	0.067	4.1	0.41	0.64
26 Lower	avg	7.6	8.8	88	2.4	20	5.0	0.14	1.6	0.027	1.3	0.20	0.22
	min	5.7	3.0	40	0.080	1.0	0.90	0.017	0.25	0.0090	0.46	0.070	0.063
	max	10	18	139	14	225	25	0.46	3.6	0.083	3.9	0.45	0.56
27 Upper	avg	7.3	8.1	84	8.5	21	4.8	0.22	1.2	0.038	1.2	0.16	0.18
	min	6.1	3.2	44	0.080	2.0	0.50	0.027	0.28	0.010	0.29	0.020	0.070
	max	8.8	19	174	22	159	16	2.2	2.1	0.11	3.7	0.35	0.69
27 Lower	avg	7.2	7.6	79	12	33	4.3	0.23	1.1	0.045	1.2	0.18	0.19
	min	6.2	3.2	39	0.090	6.0	0.50	0.036	0.38	0.011	0.32	0.070	0.090
	max	9.0	16	143	25	174	9.7	0.54	2.4	0.11	3.4	0.36	0.44
28 Upper	avg	7.5	7.8	86	21	23	4.2	0.29	0.70	0.063	1.1	0.15	0.16
	min	6.2	2.0	34	5.7	3.0	0.60	0.026	0.22	0.017	0.30	0.050	0.060
	max	8.5	20	182	29	59	21	0.68	2.5	0.39	2.9	0.33	0.48
28 Lower	avg	7.4	7.4	81	24	29	4.0	0.29	0.63	0.062	0.99	0.15	0.17
	min	6.2	2.6	35	11	10	0.60	0.028	0.13	0.018	0.30	0.050	0.040
	max	8.8	18	168	31	176	21	0.66	3.1	0.16	2.9	0.28	0.47

Table 2.1. Summary of NJHDG water quality data for sites in or near the Raritan River.

	Average	Min	Max	Stdev	n	unit
Alkalinity, total	40	3.0	75	19	28	mg/l
Ammonia-nitrogen	0.041	0.0036	0.11	0.032	17	mg/l
Calcium	22	9.8	33	8.0	19	mg/l
Calcium carbonate	38	3.0	75	19	13	mg/l
Chlorophyll a	51	46	56	5.1	5	ug/l
Chloride	57	21	157	30	17	mg/l
Dissolved oxygen (DO)	9.0	4.4	15	2.2	33	mg/l
Dissolved oxygen saturation	95	75	118	14	24	%
Hardness, carbonate	88	38	136	26	32	mg/l
Magnesium	8.4	3.5	13	2.9	19	mg/l
Nitrate	1.9	0.0030	21	1.9	748	mg/l
Organic carbon - dissolved	4.1	2.7	5.7	0.87	17	mg/l
Organic carbon - total	4.2	2.9	5.7	0.80	16	mg/l
Orthophosphate	0.20	0.034	0.45	0.16	7	mg/l
Phosphate-phosphorus - dissolved	0.20	0.050	0.47	0.14	14	mg/l
Phosphate-phosphorus - total	0.21	0.010	0.54	0.14	17	mg/l
Potassium	3.0	1.7	4.1	0.72	19	mg/l
Specific conductance	339	0.16	719	150	33	uS/cm
Sodium	31	14	88	15	19	mg/l
Sulfate	25	7.5	44	11	17	mg/l
Kjeldahl nitrogen - dissolved	0.42	0.27	0.80	0.14	16	mg/l
Kjeldahl nitrogen - total	0.57	0.28	1.1	0.23	19	mg/l

Table 2.2. Summary of data available in the NJDEP data mine, excluding data from the NJHDG, for the Lower Raritan River.

3. Metals

Measurement of nutrients is relatively straightforward, and the methods have not changed substantially in about 20 years. In contrast, measurement of metals, especially at the low concentrations exhibited in the water column, is more difficult. It requires careful collection and handling of samples to prevent contamination, and the use of very sensitive instruments to measure low concentrations of metals. In the sediment, concentrations of metals are much higher, so sample contamination and instrument sensitivity are less of a concern. The most sensitive EPA method for measurement of metals in sediment is method 6020A [7], which uses an inductively coupled plasma/mass spectrometer (ICP/MS). This method was published in 2007. EPA method 1638 [8], which uses ICP/MS to measure metals in water, was published in 1996. The widely used method for mercury in sediment (method 200.7) [9] was published in 1994, and the method for mercury in water (method 1631)[10] was published in 2002. Because the methods for measurement of metals are relatively new, older metals measurements may not yield comparable data and so their output should be viewed with caution.

The New York-New Jersey Harbor Estuary Program published TMDLs for copper, mercury, nickel, and lead in 1994 [11], but these were obviously based on older data. This report will focus on data collected since 1994.

For purposes of constructing mass balances and TMDLs, measurements of the metals of interest in both the water column and the sediment are needed. For source apportionment and forensics, it is often necessary to measure a wide variety of metals, including those that are not generally considered to be contaminants because they are not toxic. These metals can be used as tracers to establish the source of contamination. For many contaminated site investigations, the Target Analyte List (TAL) of inorganic species is measured: Cyanide, Al, Sb, As, Ba, Be, Cd, Cr, Co, Cu, Fe, Pb, Mn, Hg, Ni, Se, Ag, Tl, V, Zn, Ca, Mg, K, and Na. The TAL includes many species such as Fe and Mg that are not contaminants for exactly this reason. This broader list of analytes may be useful in determining the sources of arsenic in the tidal Raritan. Arsenic is a problem in all four segments of the Lower Raritan, but the sources are not clear. Although there are many contaminated sites on the river that may be releasing arsenic to the river, there are also natural sources of arsenic. Natural arsenic might enter the river along with many other naturally occurring metals such as manganese, so measuring manganese and arsenic together might indicate what fraction of the arsenic comes from natural sources and what comes from anthropogenic sources. Thus as we evaluate the available data on metals, we will consider what other parameters were measured along with the pollutant metals.

3.1. Metals in water

Measurement of metals in the water column is complicated by the fact that in some cases it is desirable to measure the dissolved and particle phase concentrations separately. In such cases, usually the metal is measured in the total (unfiltered) water column and then separately in the

dissolved phase by filtering the water. The particle-bound metal concentration is then calculated by subtracting the dissolved from the total.

Maest et al. [6] measured metals (Fe, Cr, Al, Mn, Cu, Pb, Co, Cd, Ni, and Zn) in the dissolved and particle phases using Graphite Furnace Atomic Absorption Spectroscopy (GFAAS) in samples collected in 1982. The particle phase data was presented in an earlier publication that is not readily available. This study used what are now considered to be obsolete methods of analysis, but the authors still reach some interesting conclusions. They note that although sediments are an important sink for trace metals in the system, the metals can be there released via oxidation of surface bottom sediment in the marsh and at the estuary mouth.

Battelle Ocean Sciences measured Ag, Cd, Cu, Ni, Pb, and Zn by graphite furnace atomic absorption spectrometry (GFAAS), and Hg by cold vapor atomic absorption spectrometry (CVAAS) in support of the 1994 TMDLs.[11] Although they report data for the Raritan River, their report [12] does not indicate exactly where these samples were collected. Given that this data was collected using older methods, we consider it to be obsolete.

The CARP [3] program measured total and dissolved cadmium, lead, mercury and methylmercury at two sites in the tidal Raritan, RAR1 and RAR2 (see figure 1.2). At RAR1, samples were taken from the top of the water column (RAR1-S) and the bottom (RAR1-D) due to stratification. In addition, samples were taken at the head of tide (HOT) at Bound Brook. The results are summarized in table 3.1. The NJ Saline Human Health Surface Water Quality Criteria for total mercury is 146 ng/L, well above the levels measured by CARP. This data has been synthesized into several reports by the NJ Toxics Reduction Workplan (<http://www.state.nj.us/dep/dsr/njtrwp/>). Here we have focused on the raw data, which is available by request to the Hudson River Foundation (for information on how to request this data, see <http://www.carpweb.org/main.html>). These measurements, although few, were adequate for the calculation of TMDLs for these metals in the Harbor. However, since only three metals were measured, this data is not particularly useful for forensics studies. In addition, there has been no attempt to follow up on the CARP project, so there is no data on time trends of metals in the water column of the Raritan.

Table 3.1. Average concentrations (ng/L) of metals in the water column of the Raritan River as measured by CARP (2001-2002). The number of samples included in the average is n.

Site	Fraction	Cadmium	Lead	Mercury	Methylmercury	n
RAR1-D	DISS	37	102	1.2	0.0068	4
	TOTAL	51	1975	18	0.016	4
RAR1-S	DISS	73	834	1.3	0.0030	4
	TOTAL	53	1978	14	0.019	4
RAR2	DISS	16	322	2.7	0.042	4
	TOTAL	40	2283	9.5	0.024	4
HOT	DISS	17	250	1.7	0.22	1
	TOTAL	45	2655	10	0.11*	5

*Average represents only one sample above detection limit.

The only data on metals in the water column retrieved from the NJDEP data mine was from the New Jersey Bureau of Freshwater and Biological Monitoring (BFBM). They collected 10 samples during 2010 and 2011. Metals measured were total recoverable arsenic, cadmium, mercury, chromium, chromium(VI), copper, nickel, selenium, and zinc. Arsenic and selenium were measured using EPA method 200.9, which uses a graphite furnace atomic absorption instrument. Cadmium, chromium, copper, nickel and zinc were measured using EPA method 200.7 (ICP/MS). Mercury was measured using EPA method 245.1 (cold vapor atomic absorption), and chromium VI was measured by USGS method I1230 (a colorimetric method). These methods suggest that the BFBM data should be comparable to the CARP data. The BFBM data was collected at two sites, Landing Lane in Johnson Park in Piscataway, and at Queens Bridge in Somerset County (figure 1.1). These samples were therefore collected further upstream than the CARP samples. Influx of cleaner ocean water at the CARP stations may explain why the cadmium and lead concentrations measured by BFBM are so much higher; note that units in table 3.1 are ng/L, while in table 3.2 the units are ug/L. The arsenic and mercury concentrations measured at these two freshwater stations well exceed the NJ human health Surface Water Quality Standard (SWQS). Cadmium is dangerously close to the NJ freshwater human health SWQS of 3.4 ppb (ppb = ug/L). In contrast, copper, chromium, nickel, selenium, and zinc are well below the applicable SWQS.

Table 3.2. Total recoverable metal concentrations in ug/L measured in the tidal Raritan River by the New Jersey Bureau of Freshwater and Biological Monitoring (BFBM) in 2010 and 2011, as obtained from the NJ data mine.

	average	max	min	n*
Arsenic	1.1	2.1	0.3	10
Cadmium	3.1	3.2	3.0	2
Chromium	1.5	3.2	0.7	7
Chromium(VI)	5.4	6.1	4.8	2
Copper	3.7	6.1	2.2	10
Mercury	1.6	3.4	0.03	6
Nickel	2.3	3.4	0.5	8
Selenium	4.4	12.4	0.4	3
Zinc	6.9	12.4	4.2	10

* n indicates the number of samples above detection limit out of the ten collected.

Paulson [13] measured a variety of metals by ICP/MS throughout the Harbor in 1999 (i.e. during the CARP era), including 5 sites in the Raritan River roughly between RU sites 8 and 11. He reports dissolved Cd, Cu, Ni, and Pb as well as particle phase concentrations of Cu, Pb, Mn, Ni, Cd, Co, As, and Fe. He appears to have also measured Li, Be, Mg, Ti, V, Cr, Ag, Sn, Sb, Tl, Bi and U, but these data are not reported. We requested the raw data directly from the author (Appendix E). Paulson's measurements of dissolved concentrations of Pb are in good agreement with those of the CARP program. His measurements of Cd are somewhat higher than the CARP measurements. His range from about 80-150 ng/L, whereas the average concentration measured by CARP was just 37 ng/L. His particle phase measurements are presented as $\mu\text{mol per g}$ of particle, so we cannot make a direct comparison of his results with those of CARP. Paulson's data set is ideal for source apportionment of metals in the Harbor, and indeed, he conducted principal components analysis on his particle phase data. In this analysis, the elevated concentrations of As in the Raritan set it apart from the other Harbor locations. Paulson concluded that the Raritan signal is characterized by elevated levels of dissolved cobalt and particle phase arsenic, and that the influence of the arsenic signature of the Raritan River was limited to inner Raritan Bay (i.e. particles from the Raritan to do not travel very far into the Bay). Paulson made no attempt to determine whether the arsenic in the Raritan arises from natural or anthropogenic sources.

Some sampling of surface water was conducted in 1997 (3 samples) and 1999 (15 samples) as part of the ecological risk assessment for the Atlantic Resources Corporation (ARC) and the Horseshoe Road (HR) Superfund sites in Sayreville.[14] These two sites lie on the south bank of the River near our site 9 in the Keasbey Reach. In 1997, three water samples were collected near the bank of the Raritan River. In 1999, 15 water samples were collected from further out in the river. These 18 samples of unfiltered surface water were analyzed for the Target Analyte List (TAL) of inorganic species, as well as pesticides/PCBs, semivolatile organic compounds

(SVOCs), volatile organic compounds (VOCs), alkalinity, hardness, and total dissolved solids (TDS). Ancillary data such as dissolved oxygen, pH, temperature, salinity, turbidity, and specific conductance were measured *in situ* during the collection of most of these samples. Due to the location of their collection, the 1997 samples generally exhibited higher contaminant concentrations than the 1999 samples. (Note that in 1997, two samples of surface water from the Marsh were also collected. These are not considered here.) The major inorganic contaminants associated with the ARC/HR superfund sites are Hg and As. Given this, and the fact that As is known to be a problem in this stretch of the river, it is not surprising that As was detected in most samples at concentrations ranging from 2.2 to 20.3 ug/L, well above the salt water human health SWQS of 0.61 ug/L. Despite the concern about Hg at the ARC/HR site, Hg was not detected in any of the 1999 samples, but was detected at concentrations ranging from 0.45 to 0.86 ug/L in the 1997 samples, above the human health saline SWQS of 0.146 ug/L (146 ng/L). Cd, Cr, Cu, Mn, and Zn were also detected in some of the water samples, but all measured concentrations were below the applicable SWQS. This data set might be useful for forensics investigations, since it measured 23 elements in about 20 samples (including the 2 marsh samples). Unfortunately, many of the elements were below detection limit in the majority of samples, and the geographical area over which sampling was conducted is small. However, this data set is useful in providing an end member that describes the metal contamination emanating from the ARC/HR site.

Surface water sampling was also conducted as part of the Raritan Arsenal Baseline Ecological Risk Assessment.[15] The Raritan Arsenal superfund site lies on the north bank of the River near our site 9 in the Keasbey Reach. During water and sediment sampling, basic water quality parameters were measured, such as pH, turbidity, dissolved oxygen, temperature, conductivity, and salinity. Seven surface water samples were collected (one of these in duplicate) in 2005 in the River within 50 feet of the shoreline in front of the Raritan Arsenal site. TAL metals were measured in the total and dissolved phases. Of these, antimony and mercury were always below detection limit. Manganese and selenium exceeded their Lowest Ecological Benchmark in all samples, while cadmium, copper, nickel, and zinc sometimes exceeded this benchmark.

Surface water sampling associated with the National Lead (NL Industries) site in Sayreville on the south bank of the Keasbey Reach was conducted in 2000 and 2002. In 2000, 19 surface water samples were collected near the site and analyzed for arsenic and lead. Two of these samples were analyzed for radiological parameters (gross alpha, gross beta, gamma spec, radium-226, radium-228, thorium-232, uranium-238, and uranium-234). Although we have not been able to obtain this raw data, a 2003 report states that these samples “did not indicate an impact to the Raritan River from the [NL Industries] site.” [16]

In summary, several data sets have measured metals in the water column in the Keasbey Reach portion of the Raritan River. Only one data set, the BRBM, measured metals above the Keasbey Reach. Unfortunately, these various projects used different analyte lists and different methods, such that the data are not comparable. Thus both the spatial and temporal coverage are limited.

3.2. Metals in sediment

The Regional Environmental Monitoring and Assessment Program (REMAP) conducted a survey of sediment quality in the New York/New Jersey Harbor in 1993-1994 and again in 1998 (<http://www.epa.gov/emap/remap/html/docs/two.html>). [17, 18] REMAP measured a variety of metals as well as organics, but samples were not collected in the Raritan River. The closest samples were collected at the mouth of the River in Raritan Bay.

Maest et al. [6] also measured metals in the sediments of the Raritan River in 1982 using what are now considered to be obsolete methods. As noted above, Maest et al. considered the dynamics of metals in the estuary and concluded that the sediments serve as an important sink for metals. This is in agreement with the discussion above, which notes that much of the contamination in the River becomes trapped in the ETM. However, Maest et al. also note that metals in the sediment can be released back to the water via oxidation of surface bottom sediment in the marsh and at the estuary mouth.

Most of the contemporary measurements of metals in sediment were conducted in the Keasbey Reach. A selection of the Keasbey Reach data is provided in table 3.3 so that the results of various studies can be easily compared. There is surprisingly good agreement between the four studies that measure the TAL of metals, suggesting that these data sets can be combined into a larger data matrix for forensics studies to determine the sources of metals in the tidal Raritan.

The CARP measured the TAL metals as well as methylmercury in one sample collected at RAR1 (figure 1.2). The raw data are provided in Appendix D. The US Army Corps of Engineers (USACE) characterized the sediments at locations just east of the NJ Transit Bridge in 2008 in preparation for dredging. They collected several sediment cores and then composited these into 10 samples for TAL metals analysis. Complete data is available at <http://www.blueraritan.org/data/dredge.php>.

Table 3.3. Comparison of metals concentrations in the sediments of the Keasbey Reach portion of tidal Raritan River as measured by various projects. All values are averages, except for the CARP, which is a single sample. ND = not detected.

	CARP	USACE	ARC/HR		Raritan Arsenal
			River	Reference	
Aluminum	16200	15800	12569	14868	15073
Antimony	ND	0.34	12	13	1.9
Arsenic	27	20	91	43	33
Barium	88	71	63	65	61
Beryllium	1.3	1.3	0.80	0.82	1.1
Cadmium	1.2	0.64	0.82	1.0	1.0
Calcium	4370	5680	2221	3120	3971
Chromium	68	70	161	80	48
Cobalt	13	11	6.9	8.9	12
Copper	128	132	229	203	133
Iron	43100	35470	41700	35320	35346
Lead	125	117	114	132	87
Magnesium	7480	8090	4239	4780	6034
Manganese	455	431	217	263	292
Mercury	1.2	1.4	1.6	1.3	0.79
Nickel	32	31	6.8	41	32
Potassium	3630	3055	1809	2201	2515
Selenium	ND	1.5	3.2	4.5	3.8
Silver	2.1	2.7	7.4	2.9	1.8
Sodium	10600	13640	4132	4038	5715
Thallium	ND	ND	0.19	0.24	0.42
Vanadium	57	46	100	64	47
Zinc	281	264	208	232	228

The Edison Wetlands Association recently commissioned Chapin Engineering to conduct a survey of sediment data in the Keasbey Reach.[19] The study consisted of assembling data on sediment quality from existing studies, collection and analysis of sediment samples from the Keasbey Reach, assembling all this data into a Geographic Information System (GIS) data base and using the GIS data base to prepare contaminant distribution maps. This report is available by request to the Edison Wetlands Association. The new data collected as part of this study included 23 samples from 16 locations, which were analyzed for a variety of organics (described below) and four total metals (arsenic, mercury, lead and titanium). A second sampling event occurred and collected sediments at 8 additional locations, four of which were also analyzed for arsenic, mercury, lead and titanium. The sediment samples were collected using a coring apparatus, and some of the samples were divided into upper and lower 1-foot sections in order to

provide a rough determination of the depth of contamination. Metal concentrations were compared to the ER-L and ER-M concentrations (4. NJDEP, “Guidance for Sediment Quality Evaluation” http://www.nj.gov/dep/srp/guidance/sediment/03_screen.htm). The ER-L (Effects Range-Low) is the contaminant concentration at which adverse impacts to benthic organisms were found in 10% of studies. The ER-M (Effects Range-Median) is the contaminant concentration at which a greater than 50% incidence of adverse impacts to sensitive species and/or life stages. Arsenic concentrations exceed the ER-L of 8.2 mg/kg at essentially all locations at both depths and the majority of the study area has arsenic concentrations above its ER-M of 70 mg/kg. Mercury exceeded its ER-M of 0.71 mg/kg in both sediment layers nearly everywhere. Lead exceeded its ER-L of 47 mg/kg throughout the study area at both sediment depth intervals evaluated. However, there were limited locations where the ER-M (218 mg/kg) was exceeded. Titanium was measured as a tracer for contamination from the former N.L. Industries site. It is non-toxic and therefore has no established sediment criteria. However, the distribution of titanium measured in the Chapin study was consistent with a source at the North Ditch’s discharge from the N.L. Industries site, which historically manufactured titanium products. Thus Chapin concluded that titanium in the study area could be attributed to the former operations of N.L. Industries. This study provided valuable information about contaminant distributions in the Keasbey Reach. Since only four metals were measured, the data cannot be used for factor analysis forensics studies, but the conclusions reached, especially the conclusion that titanium can be used as a tracer for contamination from N.L. Industries, will inform future forensics studies.

In addition to the new data collected, the Chapin study also evaluated the available information on contaminants in the sediments of the Keasbey Reach. This study identified four sources of sediment data associated with investigations of contaminated sites in the area: (1) A Baseline Ecological Risk Assessment that was conducted for the Raritan Arsenal; (2) A Baseline Ecological Risk Assessment that was conducted for the Atlantic Resources Corp.[14]; (3) a Feasibility Study conducted for the Atlantic Resources Corp.; and (4) a Remedial Investigation Report for the N.L. Industries site. These studies will be discussed in more detail below.

The NL Industries investigation collected 31 sediment samples at 25 locations in June 2000. Based on the results of this sampling, an additional 27 sediment samples from 16 locations were collected in the summer of 2002. Unfortunately, this data has proven difficult to obtain. We filed an Open Public Records Act (OPRA) to obtain the report entitled: Remedial Investigation Report Supplemental Raritan River Sediment Sampling Results NL Industries, Inc. Sayrevill, New Jersey Site ISRA Case No. E88768.[16] Unfortunately, this report was only available in hard copy form, and although the hard copy states that several CDs containing data are part of the report, these were not made available. In addition, the hard copy we received did not include any of the figures. We have scanned the hard copy into a pdf and made it available on the Sustainable Raritan River website (<http://www.raritan.rutgers.edu/>). This report contains only

the raw data from the 2002 sampling, but it does discuss the data from the 2000 sampling campaign.

The sampling in 2000 collected sediment at 25 locations. At six of these locations, sediment was sampled at two depths, giving rise to 31 samples. Priority pollutant metals were measured in all samples, and two samples were tested for radiological parameters (gross alpha, gross beta, gamma spec, radium-226, radium-228, thorium-232, uranium-238, and uranium-234). Based on this sampling, it was determined that concentrations of radionuclides in the sediment were below the levels of any significant concern.

The 2002 sampling included 27 sediment samples from 16 locations. At 11 of the locations, samples were collected from 0-6" depth as well as from 18-24" depth. Five metals were measured in these samples: arsenic, copper, nickel, lead, and zinc. In nine of the samples, radiological parameters were measured (gamma spec and alpha spec for thorium and uranium). The raw data for these measurements are available in the 2003 DPR report.[16] Arsenic, copper, lead, nickel and zinc were almost always above the ER-L and often above the ER-M.[16]

Sediment from the Raritan River was sampled as part of the remedial investigation and ecological risk assessment for the ARC/HR site.[14] Marsh sediment was also sampled for this effort but will not be discussed here. Sediment sampling campaigns were conducted in 1997 (four samples), 1998 (2 samples), 1999 (20 samples). The 1999 samples were sectioned into 0-6, 6-18, 18-30, and 30-42 in. intervals. In 2004, surface (0-6 in. interval) sediments were collected from 10 stations in the marsh, 10 stations in the river, three marsh reference stations, and five river reference stations. (Note that in table 3.3 averages for both the river and river reference stations are provided.) In 2004, TAL metals were measured in all samples, as well as Target Compound List (TCL) SVOCs, VOCs, pesticides/PCBs, and PCDD/Fs. At select locations, TOC, pH, grain size, and percent moisture were measured. Data from these four sampling campaigns should be fully comparable, giving rise to a data set of about 23 elements in about 200 samples (if we include samples from the marsh and upland soil). This data set is of sufficient size that it may be useful for forensic investigations. In addition, most of the analytes were above detection limits in nearly all samples. The geographical range of the data is of useful size due to the inclusion of five river reference stations. As was noted above with respect to the surface water sampling conducted for the ARC/HR sites, the concentrations of contaminants is greater in the marsh than in the adjacent river. The metals of most concern in the ARC/HR investigations are As, Cr, Cu, and Hg. Of these, As was found to always exceed the ER-L and frequently exceed the ER-M. Cr and Hg frequently exceeded the ER-L and ER-M values. Cu usually exceeded the ER-L and frequently exceeded the ER-M. In all cases, it must be noted that these metals frequently exceeded the ER-L value even at the river reference stations, i.e. in locations where the ARC/HR contamination is not thought to be significant.

Some sediment sampling was conducted in 2005 as part of the Raritan Arsenal Baseline Ecological Risk Assessment.[15] A total of 36 locations were sampled (3 of these in duplicate). In the report, these are listed as "estuarine sediment", although only 13 of these locations fall within the main stem of the river (table 3.4). The TAL metals were measured. In the main stem

sediment samples, arsenic, cadmium, chromium, copper, lead, mercury, nickel, silver, and zinc exceeded the Lowest Ecological Benchmark in some or all samples.

Table 3.4. Concentrations (mg/kg) of metals in Raritan River sediments collected near the Raritan Arsenal in 2005 as part of the Baseline Ecological Risk Assessment.[15] Values in bold exceed the Lowest Ecological Benchmark.

	Lowest Ecological Benchmark	average	min	max	n*
Aluminum	none	15,073	2,630	21,100	13
Antimony	none	1.9	0.93	4.0	13
Arsenic	8.2	33	6	98	13
Barium	none	61	16	104	13
Beryllium	none	1.1	0.32	1.7	13
Cadmium	1.2	1.0	0.18	2.0	11
Calcium	none	3,971	1,820	18,500	13
Chromium	81	48	14	90	13
Cobalt	none	12	3.7	16	13
Copper	34	133	13	352	13
Cyanide	none	0.64	0.36	1.0	6
Iron	none	35,346	16,800	45,900	13
Lead	46.7	87	12	189	13
Magnesium	none	6,034	1,810	7,740	13
Manganese	none	292	87	456	13
Mercury	0.15	0.79	0.036	2.4	12
Nickel	20.9	32	10	59	13
Potassium	none	2,515	304	4,100	13
Selenium	none	3.8	0.40	11	10
Silver	1	1.8	0.24	4.5	10
Sodium	none	5,715	1,660	9,510	13
Thallium	none	0.42			1
Vanadium	none	47	13	66	13
Zinc	150	228	70	508	13

*number of samples above detection limit (out of 13).

The EPA is currently working with its contractors to measure contaminants at the ARC/HR site, and has collected some data in the river. This sampling is on-going, and the data from this investigation is not yet fully available.

Fewer measurements are available outside of the Keasbey Reach. The NJDEP HazSites data base was queried for us for concentrations in sediment samples within 1000 ft of the tidal portion of the River. This resulted in 4494 records. We further limited our search to records for which the result was greater than the detection limit. This resulted in about 500 records for metals,

summarized in table 3.5 and presented in detail in Appendix B. Due to the problems with field conformity in the HazSites data base, we cannot be sure that all of these samples represent sediment rather than soil or other material from contaminated sites.

In March and September of 2011, our research group collected 42 samples of surficial sediment in the Raritan from New Brunswick to the NJ Transit Railroad Bridge. TAL metals plus titanium were measured in these samples by a certified contract lab. Some samples exceeded the holding times for metals, and all of them exceeded the holding times for mercury. The results of this sampling are provided in a separate report.[4] This is one of the only data sets that provides spatial resolution of metals across a long stretch of the tidal Raritan. Arsenic, mercury, and copper exceeded the Ecological Screening Criteria. Arsenic exceeded the ER-L in 16 out of 42 samples. Copper exceeded the ER-L in 24 of 42 samples and exceeded the ER-M in one sample. Mercury exceeded the ER-L in 26 samples and exceeded the ER-M in 3 samples. PCBs were also measured in these samples (see below).

Table 3.5. Concentrations (ppm) of various metals in sediment within 1000 ft of the Raritan River from the NJDEP HazSites data base.

	average	min	max	n
Aluminum	19390	11500	31900	10
Arsenic	30	1.0	551	77
Barium	184	121	300	5
Beryllium	1.378	1.1	1.6	5
Cadmium	0.36	0.035	2.9	55
Chromium	0.14	0.035	1900	55
Calcium	2898	1900	4370	5
Chromium	185	7.0	2530	18
Cobalt	13	9.0	19	10
Copper	67	1.7	535	78
Iron	30190	19500	54800	10
Lead	53	2.4	359	73
Magnesium	3251	360	6810	10
Mercury	0.099	0.0035	2.0	65
Methyl Mercury	1.6	1.3	1.9	2
Nickel	32	3.0	67	24
Potassium	2286	1920	2540	5
Selenium	385	1.4	1920	5
Silver	2.5	1.0	4.6	9
Sodium	1527	1300	1630	4
Thallium	0.27	0.22	0.32	4
Vanadium	40	27	64	10
Zinc	236	14	739	29

In summary, several data sets have measured metals in sediment in the Keasbey Reach section of the Raritan River. Several of these used the TAL, which is fortuitous because it allows the data from several studies to be compared. It may be possible to combine the various TAL data sets into one data set for factor analysis so that sources of metals to the Keasbey Reach can be identified. The HazSite data base provides the only data on metals in sediment outside of the Keasbey Reach, and this data is not thought to be reliable.

4. Organics

Organic chemicals are any chemicals that contain carbon. This definition includes an enormous range of chemicals, most of which are naturally occurring. Thus environmental scientists focus on organic chemicals that are anthropogenic and have the capacity to cause harm to organisms. Also, since organic chemicals can often be broken down by living things, only those chemicals that are persistent are likely to cause harm to ecosystems. Thus we focus on persistent organic pollutants (POPs). Of specific interest are organic chemicals that are on the priority pollutant (PP) list (<http://water.epa.gov/scitech/methods/cwa/pollutants.cfm>). These include polycyclic aromatic hydrocarbons such as acenaphthene, fluoranthene, naphthalene, benzo(a) anthracene, benzo(a)pyrene, benzo(b) fluoranthene, benzo(b) fluoranthene, chrysene, acenaphthylene, anthracene, benzo(ghi) perylene, fluorene, phenanthrene, dibenzo(a,h)anthracene, indeno(1,2,3-cd)pyrene, and pyrene. The PP list also contains a wide range of chlorinated compounds, including chlorinated pesticides (DDT and its breakdown products DDD and DDE; chlordane, alpha-endosulfan, beta-endosulfan, endosulfan sulfate, endrin, endrin aldehyde, heptachlor, heptachlor epoxide, the various isomers of hexachlorocyclohexanes including lindane, and toxaphene), polychlorinated biphenyls (PCBs under their trade name “Aroclor”) and 2,3,7,8-tetrachloro dibenzo-p-dioxin (2,3,7,8-TCDD). 2,3,7,8-TCDD is one of a class of polychlorinated dibenzo-p-dioxins and –furans, which are often simply referred to as “dioxins” although the more proper abbreviation is “PCDD/Fs”.

Measurement of these organic compounds is difficult, especially in the water column. As with metals, the methods for measurement of these compounds have been developed relatively recently. Method 1668 for measurement of PCBs and method 1613 for measurement of PCDD/Fs both use a high resolution mass spectrometer for detection of the analytes. These instruments are expensive both to buy (about \$1 million) and to maintain. Revision A of method 1668 was approved in 1999 [20] and has undergone two revisions since then. The most recent, method 1668C, was published in April of 2010.[21] Method 1613 was published in 1994.[22]

PCBs represent a unique analytical challenge, since the class of chemicals referred to as PCBs includes 209 separate compounds (“congeners”) that are structurally very similar. Because they are so similar, it is often difficult to measure each one independently. Even the most sophisticated method (1668C) still reports some congeners as the sum of two or more congeners that cannot be measured separately. Older methods got around this problem by reporting Aroclors, which are the mixtures of PCBs manufactured and sold in the US. The Aroclors are

each described by a number in which the last two digits usually describe the % chlorine content of the mixture. Thus Aroclor 1242 contained 42% chlorine by weight. Heavier Aroclors, such as Aroclor 1260 contained as much as 60% chlorine by weight. (A few Aroclors were named using a different system. Most notably, Aroclor 1016 is a formulation that is very similar to Aroclor 1242, and the number 1016 has no relevant meaning.)

Methods that measure PCBs as Aroclors are less precise than those that measure individual congeners. In addition, methods that measure only Aroclors may miss some important contributors to the total PCB burden in surface waters. The first is dechlorination of congeners with many chlorines to form congeners with fewer. This can occur in anaerobic environments, such as deep sediments. By detecting the products of dechlorination, it is sometimes possible to determine the source of the PCBs. The second is PCB 11 (3,3'-dichlorobiphenyl). This one specific congener is produced inadvertently during the production of many pigments that are used in printing inks.[23] In this way, PCB 11 becomes dispersed throughout the environment. In surface water, PCB 11 can be an indicator of PCB sources from wastewater treatment and storm water runoff.[23] PCB 11 is routinely found in urban environments. The third possible non-Aroclor PCB source is the production of titanium tetrachloride (TiCl_4). During this process, titanium ore is chlorinated in the presence of fuel oil, leading to a variety of highly chlorinated organics, including PCB 209 (decachlorobiphenyl). This process is only used at a small number of facilities in the US, notably at the DuPont EdgeMoor plant near Wilmington, Delaware. The Delaware River contains high levels of PCB 209 because of this facility.[24-26] To our knowledge, there are no current or former TiCl_4 production facilities in the Raritan basin. However, another by-product of this process is ferric chloride, which was often sold to wastewater and drinking water treatment plants as a flocculant.[27] The PCB 209 contamination can be transported to other watersheds by this route. Thus it is possible that the Raritan may contain some traces of PCB 209 associated with TiCl_4 production. For these reasons, it is important to measure individual PCB congeners, preferably via method 1668, in the Lower Raritan.

Because the measurement of organics is expensive and difficult, there is relatively little data available on organics in the Lower Raritan.

4.1. Organics in water

Measurement of organics in water is particularly difficult due to the relatively low concentrations and the desire to measure the dissolved- and particle-phase concentrations separately. The CARP measured a wide variety of POPs in the Raritan using the Trace Organics Platform Sampler, or TOPS, in which the water was filtered through a 0.7 μm filter and the filtrate was sent through a column containing XAD-2, a resin that absorbs the organics in the water. Since large volumes of water must be processed in this manner in order to have enough mass of contaminants to be above the detection limits, the filter often clogs before enough sample can be collected. Also, if the concentrations of organic contaminants in the dissolved phase are

relatively high, the XAD-2 resin can become overloaded. Thus it was often necessary to use more than one filter and/or more than one XAD-2 column to collect each water sample in the CARP program. Unfortunately, very hydrophobic chemicals such as PCBs and PCDD/Fs sorb extensively to particles in the water column, such that their freely dissolved concentrations are very low. Some of the smaller particles are able to get through the filter, carrying their contaminant burden with them. In such cases, much of what is measured as being dissolved is really sorbed to small particles. Thus the contaminants measured in the XAD-2 column are sometimes referred to as being in the “apparent” dissolved phase, since they may actually be sorbed to very small particles. Currently there is no good way to avoid this sampling artifact.

Organic contaminants in the water column (whole water) were measured as part of the ARC/HR site investigations in 1997 and 1999.[14] Pesticides, PCBs, SVOCs and VOCs were measured in these samples. Most of these measurements were below the detection limits, which were high due to the methods used. This leads us to question the validity of the results. For example, PCBs were detected in only one sample, but at a concentration of 8.8 ug/L. This concentration is extremely high. Even in the Hudson River, which is heavily contaminated with PCBs, concentrations rarely exceed about 50 ng/L, or 0.05 ug/L.[3] The analytes that were occasionally above detection limit were PCBs (as noted above), β -hexachlorocyclohexane, γ -hexachlorocyclohexane, bis(2-ethylhexyl)phthalate, di-*n*-butylphthalate, chlorobenzene, 1,3-dichlorobenzene, 1,4-dichlorobenzene, cis-1,2-dichloroethene, and vinyl chloride.

Organics in the water column were also measured as part of the Raritan Arsenal Baseline Ecological Risk Assessment.[15] A suite of explosives was analyzed (mono-, di-, and trinitrobenzenes, aminodinitrobenzenes, HMX (also known as Octogen or octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine), RDX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine), and Tetryl (2,4,6-trinitrophenylmethylnitramine). All of these were below detection in all samples.

The NJ data mine contains some information on organics in the water column. Compounds measured were: alpha-endosulfan, 1,1,1-trichloroethane, 1,1,2,2-tetrachloroethane, 1,1,2-trichloroethane, 1,1-dichloroethylene, 1,2-dichloroethane, 1,2-dichloropropane, 2-chloroethyl vinyl ether, carbon tetrachloride, CFC-11, chlorobenzene, chlorodibromomethane, chloroethane, chloroform, chloromethane, cis-1,3-dichloropropene, dichlorobromomethane, ethylbenzene, m-dichlorobenzene, meta & para xylene mix, methyl bromide, methyl tert-butyl ether, methylene chloride, naphthalene, o-dichlorobenzene, o-xylene, p-dichlorobenzene, tert-butanol, tetrachloroethylene, toluene, trans-1,2-dichloroethylene, trans-1,3-dichloropropene, tribromomethane, trichloroethylene, and vinyl chloride. Of the 370 records in the data set, only 8 were above detection limit. Compounds that were measured above detection limit were 1,1-dichloroethylene (1 measurement out of 16), chloroform (4 out of 8), and o-dichlorobenzene (3 out of 8). The one measurement of 1,1-dichloroethylene that was above detection limit was 0.14 ug/L. Chloroform averaged 0.76 ug/L (max = 2.0 ug/L) and o-dichlorobenzene averaged 0.49 ug/L (max = 0.81 ug/L). All of these levels are well below the applicable SWQS.

The only data set to use modern methods to measure organics in the water column is the CARP.[3] As conducted by the NJDEP, the CARP measured 114 PCB congeners, the 17 2,3,7,8-substituted PCDD/F congeners, 27 organochlorine pesticides, and 26 PAH compounds. The PCDD/Fs were only measured in the particle phase, because their dissolved concentrations were expected to be negligible. The CARP measured these parameters at RAR-1 (surface only) and RAR-2 as well as at the head of tide (HOT). These data are summarized in Table 4.1, which lists only those organics which have applicable SWQS. Most of the average values reported in table 4.1 are averages of 4 or 5 samples. For the dioxins and some pesticides (aldrin, endosulfan, endrin, endrin aldehyde), detection limits were a problem. For example 2,3,7,8-TCDD was above detection limit in only one of five samples collected at the HOT.

Because the CARP data is the only high-quality data set on organic contaminants in the water column of the Raritan River, spatial resolution is weak and there is no temporal resolution. There is not enough data on organics in the water column to conduct source apportionment studies unless the CARP data from other parts of the Harbor is included in the data set. Rodenburg and Fennell [28, 29] performed a source apportionment analysis of organic contaminants in the NY/NJ Harbor using CARP data under a grant from the Hudson River Foundation; however, their analysis was limited to data from New York because data from New Jersey was not available at the time this project was conducted.

Table 4.1. Average concentrations of organic contaminants measured in the whole water (dissolved plus particulate) phase by the CARP and comparison with human health water quality standards (WQS).[30] Values in red exceed the applicable WQS.

Analyte	unit	Average concentration			Human Health WQS	
		HOT	RAR1-S	RAR2	fresh	saline
ΣPCBs	pg/L	3308	5221	4614	64	64
2,3,7,8-TCDD	pg/L	0.041	0.083	0.044	0.005	0.005
4,4'-DDD	ng/L	0.88	0.58	0.36	0.31	0.31
4,4'-DDE	ng/L	0.36	0.40	0.60	0.22	0.22
4,4'-DDT	ng/L	0.14	0.46	0.67	0.22	0.22
Aldrin	ng/L	0.010	0.0038	0.018	0.049	0.05
BHC, alpha	ng/L	0.55	0.067	0.076	2.6	4.9
BHC, beta	ng/L	0.073	0.10	0.096	9.1	17
BHC, gamma	ng/L	0.24	0.42	0.39	980	1800
Chlordane (sum)	ng/L	0.33	0.61	0.59	0.1	0.11
Dieldrin	ng/L	0.35	0.56	0.49	0.052	0.054
Endosulfan sulfate	ng/L	0.087	0.14	0.18	62000	89000
Endosulfan (α+β)	ng/L	0.041	0.16	0.017	62000	89000
Endrin	ng/L	BDL	BDL	0.010	59	60
Endrin aldehyde	ng/L	BDL	BDL	0.046	59	60
Heptachlor	ng/L	0.020	0.023	0.022	0.079	0.079
Heptachlor epoxide	ng/L	0.10	0.34	0.18	0.039	0.039
Methoxychlor	ng/L	0.029	0.049	0.072	40	
Mirex	ng/L	0.0025	0.0033	0.0072	0.001*	
Acenaphthene	ng/L	1.0	5.5	4.5	670000	990000
Anthracene	ng/L	8.3	5.6	15	8300000	40000000
Benzo(a)anthracene	ng/L	7.8	13	33	38	180
Benzo(a)pyrene	ng/L	8.4	15	45	3.8	18
Benzo(b)fluoranthene	ng/L	8.0	16	41	38	180
Benzo(k)fluoranthene	ng/L	7.2	16	42	380	1800
Chrysene	ng/L	14	26	56	3800	18000
Dibenz(a,h)anthracene	ng/L	2.7	6.3	11	3.8	18
Fluoranthene	ng/L	26	42	93	130000	140000
Fluorene	ng/L	1.6	3.4	4.5	1100000	5300000
Indeno (1,2,3-cd)pyrene	ng/L	8.1	20	35	38	180
Pyrene	ng/L	26	42	84	830000	4000000

*Aquatic chronic criterion (salt and fresh).

4.2. Organics in sediment

More data is available on organics in sediment because sediment is somewhat easier to sample and analyze for organics and because sediment analysis is often required as part of a remedial site investigation. In contrast to the water column, there are no applicable standards for sediment quality, only guidelines. In New Jersey, these take the form of the NJDEP's Ecological Screening Criteria (<http://www.nj.gov/dep/srp/guidance/ecoscreening/>). This is in part because the toxicity of various contaminants in sediment depends heavily on the characteristics of the sediment, which control the bioavailability of the contaminant. For organics, the primary characteristic of the sediment that can affect contaminant concentrations and bioavailability is organic carbon content: sediments with high levels of organic carbon will tend to have higher concentrations of organic contaminants, but these may not be bioavailable. As described above, the sediments of the Raritan River generally consist of sand and gravel with very low organic carbon content from Bound Brook to about Crab Island. Below Crab Island, the sediments contain much more organic carbon. Because the sandy sediment contains little organic carbon and therefore low levels of organic contaminants, measurement of organics in these sediments is likely to encounter problems with detection limits.

Organics were measured in sediment samples taken from the Keasbey Reach as part of the ARC/HR investigation.[14] Surface (0–6 in. interval) sediment was collected from four stations in the Raritan River in 1997 and two stations in 1998. In 1999, 20 stations in the Raritan River were sampled, including two upstream reference stations and two downstream reference stations. The 1999 samples included 0–6, 6–18, 18–30, and 30–42 in. intervals. Additional measurements of organics in sediment were performed in 2004 at the ARC/HR site. Fifteen locations in the intertidal zone of the Raritan were sampled at 0-6 in. depth. The full TCL and TAL compounds were measured in these samples along with pH, grain size, TOC, acid volatile sulfide and simultaneously extracted metals (AVS/SEM), and percent moisture. At a subset of these sites, PCDD/Fs were also measured. VOCs and SVOCs were usually below detection limits, with the exception of many of the PAHs. Most of the PAHs were above detection limit in most of the ~180 samples (including marsh and upland samples), resulting in a large data set that may be useful for forensics investigations. Among the pesticides, 4,4'-DDT and 4,4'-DDE and α -chlordane were frequently detected. The PCBs, which were measured as Aroclors, were usually below detection limit in the 1997 and 1999 data sets, but were frequently detected in the 2004 data set. Although the 17 2,3,7,8-substituted PCDD/Fs were measured in only a sub-set of samples, the high-resolution method 1613 was used, such that most congeners were detected in most of the samples. As a result, this data set can be used to in establish an end member or fingerprint for any dioxin contamination that might be emanating from the ARC/HR site.

Additional sediment sampling was performed as part of the Raritan Arsenal Baseline Ecological Risk Assessment.[15] Semivolatiles (SVOCs by method 8270C), organochlorine pesticides (by method 8081A using GC/MS), Aroclor-1260 (by method 8082 using gas chromatography with an electron capture detector), and explosives (by method 8330) were measured in the same 13

sediment samples that were described in the metals section above. As with the surface water, the explosives were all below detection limit in all samples. About 70% of the measurements of all of the other analytes were below detection limit. This limits the utility of this data set for source apportionment. Only 4,4'-DDE and 4,4'-DDT were found at levels above the Lowest Ecological Benchmark.

The CARP [3] measured 114 PCB congeners, the 17 2,3,7,8-substituted PCDD/F congeners, and 26 PAH compounds in one sample from site RAR-1. Pesticides were not measured in this sample. Most of the measured parameters are above the Effects Range-Low NJDEP Ecological Screening Criteria (Table 4.2).

Table 4.2. Concentrations (mg/kg d.w.) of organics measured in one sample of sediment from the RAR-1 location by CARP compared to the NJDEP Ecological Screening Criteria (Effects Range-Low (ER-L) and Effects Range-Medium (ER-M)). Values above the ER-L are in purple; values above the ER-M are in red.

	Concentration	ER-L	ER-M
ΣPCBs	0.43	0.023	0.18
2,3,7,8-TCDD	7.5		3.6
2-Methylnaphthalene	0.14	0.07	0.67
Acenaphthene	0.051	0.016	0.5
Acenaphthylene	0.15	0.044	0.64
Anthracene	0.29	0.085	1.1
Benzo(a)anthracene	1.6	0.261	1.6
Benzo(a)pyrene	1.1	0.43	1.6
Benzo(b)fluoranthene	1.7		1.8
Benzo(g,h,i)perylene	0.6	0.17	320
Benzo(k)fluoranthene	0.42	0.24	1340
Chrysene	1.5	0.384	2.8
Dibenz(a,h)anthracene	0.22	0.063	0.26
Fluoranthene	1.4	0.6	5.1
Fluorene	0.27	0.019	0.54
Indeno (1,2,3-cd)pyrene	0.56	0.2	320
Naphthalene	0.34	0.16	2.1
Phenanthrene	1	0.24	1.5
Pyrene	1.2	0.665	2.6

We collected 42 samples of surficial sediment at sites ranging from New Brunswick to the NJ Transit Railroad Bridge. PCBs were measured in 34 of these samples using tandem-quadrupole mass spectrometry. Method details and the full data are available in a separate report.[4] All 209 PCB congeners were measured, allowing an estimate of the Aroclor composition of the

PCBs. The results indicated that the background PCB signal in the Raritan River consists primarily of Aroclor 1254 (about 58% of the total PCBs), followed by Aroclors 1242 and 1260, each comprising about 20% of the total. Aroclor 1248 is generally not very abundant, averaging about 3% of the total PCB signal. However, in six samples collected on the north bank of the River in the Keasbey Reach, Aroclor 1248 was markedly more abundant, averaging 26% of the total PCB signal.

Table 4.3. Concentrations (ppm) of various organic compounds above detection limit in sediment samples taken within 1000 ft of the tidal Raritan River from the NJDEP HazSites data base.

Analyte	average	min	max	n
1,3-Dichlorobenzene	0.072	0.072	0.072	1
1,4-Dichlorobenzene	0.13	0.12	0.13	2
2-Methylnaphthalene	0.036	0.022	0.050	2
4,4'-DDT	0.0045	0.00046	0.023	16
Acenaphthene	0.044	0.020	0.096	4
Acenaphthylene	0.056	0.038	0.068	4
Acetone	2.8	2.0	3.0	4
Aldol Condensation Product	210	150	310	7
Aldrin	0.0027	0.00083	0.0084	7
alpha-Chlordane	0.0048	0.00015	0.023	21
Anthracene	0.091	0.060	0.12	4
Benzo[a]anthracene	0.30	0.066	0.57	9
Benzo[a]pyrene	0.29	0.068	0.49	5
Benzo[b]fluoranthene	0.25	0.061	0.44	5
Benzo[g,h,i]perylene	0.21	0.16	0.28	4
Benzo[k]fluoranthene	0.22	0.066	0.32	5
bis(2-Ethylhexyl)phthalate	1.9	0.44	3.4	4
Butyl benzyl phthalate	0.042	0.031	0.051	4
Carbazole	0.026	0.019	0.039	4
Chrysene	0.33	0.076	0.50	5
Dibenz[a,h]anthracene	0.068	0.055	0.083	4
Dieldrin	0.0039	0.00012	0.026	15
Dimethyl phthalate	0.020	0.020	0.020	1
Di-n-octyl phthalate	0.020	0.0055	0.034	2
Diesel range organics	302	90	695	4
Fluoranthene	0.55	0.15	0.93	5
Fluorene	0.047	0.024	0.085	4
gamma-Chlordane	0.0047	0.00013	0.024	21
Indeno[1,2,3-cd]pyrene	0.17	0.15	0.23	4
Naphthalene	0.031	0.027	0.037	3
Phenanthrene	0.28	0.076	0.52	5
Pyrene	0.51	0.13	0.85	5
Toluene	0.094	0.085	0.11	3
Total petroleum hydrocarbons, Recoverable	410	15	848	7
Xylenes (Total)	0.12	0.12	0.12	1

The NJDEP HazSites data base contains about 200 records in which organics were above detection limit in the sediments taken within 1000 ft of the Raritan. These are summarized in table 4.3. Due to the problems with field conformity in the HazSites data base, we cannot be sure that all of these samples represent sediment rather than soil or other material from contaminated sites.

In summary, the data on organics in sediment is limited, and comparability among the various data sets is poor due to different analyte lists, different methods, and poor detection limits.

5. Conclusions and Recommendations

Much less data on contaminants in the sediments and water column exists for the Raritan than for other major waterways in New Jersey such as the Delaware, Passaic, and Hudson Rivers. In assessing the data gaps, we focus on three issues: the spatial resolution of the existing data, the temporal resolution of the existing data, and the degree to which the different data sets are comparable with each other, such that several data sets can be combined to create an accurate assessment of the health of the River and to track down and identify sources of contamination. These three issues are assessed in Table 5.1.

For nutrients, data availability is judged to be good, with both temporal and spatial resolution adequate for most purposes. The monitoring performed by the NJHDG as part of their NPDES permit process has created a data set with excellent temporal resolution back to 2003. The sampling conducted by Rutgers with funding from the Edison Wetlands Association has filled in the gaps in spatial resolution in the NJHDG data set, and the two data sets are judged to be comparable.

For metals, the spatial resolution is merely fair. Between CARP [3], NJ BFBM, and the studies of Paulson [13] and Maest et al. [6], metals have been measured in the water column at several locations in the River. Investigations of metals in the sediment have generally ignored the portion of the river above the Keasbey Reach, due to the sandy sediments encountered there. Investigations regarding the Kin-Buc Landfill (near our site 4) will fill in some of these data gaps. Nevertheless, the spatial resolution of the various metals data sets are merely fair, and their temporal resolution is poor, since each of these studies captured only one snapshot in time. Moreover, the comparability of these studies is judged to be poor as they used a variety of different methods for measuring metals. Comparability of the metals data for the sediments is better than the data for the water column, primarily due to the problem of accurately separating the dissolved and particle phase and the low detection limits required to measure metals in the water column. We recommend a campaign to measure the Target Analyte List of metals plus titanium in the water column at a minimum of four locations in the tidal stretch of the river. Each of these four locations should represent one of the water quality zones of the river, as described in the introduction. Measurements in the water column should be conducted seasonally (4 times per year). This sampling program should ideally be directed by the NJDEP,

and would support the 303(d) requirements as well as monitoring the effectiveness of the existing TMDLs for copper, mercury, nickel, and lead. Complimentary measurements in the sediments should be conducted annually or biennially.

For organics, data availability is even worse. Due to the expense and difficulty of measuring organics, very little information on their concentrations in the sediments and/or water column exists. What does exist is for the most part limited to two types of sources: CARP and the investigations concerning the various contaminated sites on the River. Although it employed the best analytical techniques then available, the CARP collected samples at an extremely limited number of locations (two for water, one for sediment). The only other data sets to measure organics in the water column comes from the ARC/HR and Raritan Arsenal sites, but this data is virtually useless due to the use of methods differing from CARP, high detection limits, and questionable results. Thus the temporal and spatial coverage of the data sets for organics in the water column are minimal. In the sediments the situation is somewhat better. A larger number of measurements exist, although these are mostly concentrated in the Keasbey Reach. The data comparability between the CARP and contaminated site measurements is questionable, however. Thus the spatial resolution of the data sets on organics in sediment are fair (except in areas above the Keasbey Reach), but the temporal resolution is poor because the various data sets are not comparable. We recommend a campaign to measure PCBs (by method 1668C or equivalent) and pesticides (including all those currently exceeding the WQS) as well as benzene and PCDD/Fs in the water column and the sediments at the same locations as the metals. Again, sampling in the water column should be conducted seasonally while sediment sampling could be conducted annually. This sampling program should ideally be directed by the NJDEP, and would support the 303(d) requirements as well as supporting the TMDLs for ΣPCBs, PCDD/Fs, and various PAHs that is under construction for the Harbor. This data set should be collected using the same methods as the CARP to provide data comparability and temporal resolution.

Table 5.1. Summary of the availability of data for the Raritan River

Class	Compartment	Spatial	Temporal	Data comparability
Nutrients	water column	good	good	good
Metals	water column	fair	poor	poor
	sediment	fair	poor	good
Organics	water column	fair	poor	poor
	sediment	fair	poor	poor

Despite this grim picture of data availability in the Raritan River, there are a few data sets currently available that could be used to track down and apportion sources of contaminants in the river. These mostly concern metals in the sediment. Any projects that measured the TAL can be combined and used for source apportionment. If these data sets also include titanium they can be

used to trace contamination from N.L industries site. Conducting factor analysis on these data sets may also shed light on the sources of arsenic in the river, since arsenic may be natural or anthropogenic.

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