

2. Component II – Historical Land Use Report in the Lower Raritan Basin

The impacts of anthropogenic activities following the industrial revolution are well known. Pollution histories for various metals are so well-studied that the timing of their impact can be used to date sediments (Kemp *et al.*, 2013). Researchers in various locations meticulously recorded the degradation on their waterways due to increased industrial activity and trash disposal (Marshall, 2004). We have records from various local and regional rivers of increasing industrial pollutants, increasing nutrients from farming and detergent use, and increased loads of sediment from runoff (Church, 2006; Cooper and Brush, 1993; others). In the Raritan River, recreational use and a strong fishery exist until the First World War, after which pollution reduced or destroyed these uses (Jeffries, 1962). Improvements in environmental legislation, such as the Clean Water Act, have greatly reduced the amount of pollution entering the Raritan River; however, because of storage of pollutants in sediments, many of the tidal marshes surrounding the river need extensive remediation as they will continue to contribute pollution to the river as sediment becomes resuspended (Christiansen, *et al.*, 2000).

Considerably less is known about the pre-industrial history of the Raritan River. Understanding pre-industrial pollution levels, and in particular, establishing base-line conditions prior to European settlement, is imperative if remediation is to take place. Knowledge of base-line conditions allows us to better understand how the health of the river has changed and how best to remediate it. We also establish reasonable standards for remediation.

Here, we present our findings on the pollution history of the Raritan River from pre-European settlement through the present. By collecting sediment cores along the sediment gradient and from areas with differing amounts of anthropogenic influence, we are able to see how humans have impacted the water quality of the Raritan River through time. We measured changes in pollutants such as metals and organics and analyzed the change in nutrient impacts by observing changes in diatom communities. These changes were placed into historic context by using a composite chronology to create an age-depth model. Changes were compared within each core in order to see how pollution changed through time. We also compared changes among sites so that we could better understand how areas with greater or smaller amounts of anthropogenic influence were impacted by industrialization and urbanization of the region.

Overall, we found that nutrients increased at the time of colonization. A second increase occurred around the time of industrialization. Metal and organic pollution generally increased around the time of industrialization. Among the study sites, the site with the greatest amount of anthropogenic impact was found to have the greatest increases in pollution loads. This is consistent with the surface water sampling, in that this region of the river had a much higher amount of most pollutants than anywhere else in the study area.

Overall, we were able to reconstruct the pollution history of the Raritan River from pre-European settlement through the present. These findings allow a comprehensive look at how anthropogenic activities have impacted the Raritan River, and allow us to make better-informed decisions regarding restoration.

2.2 Methods

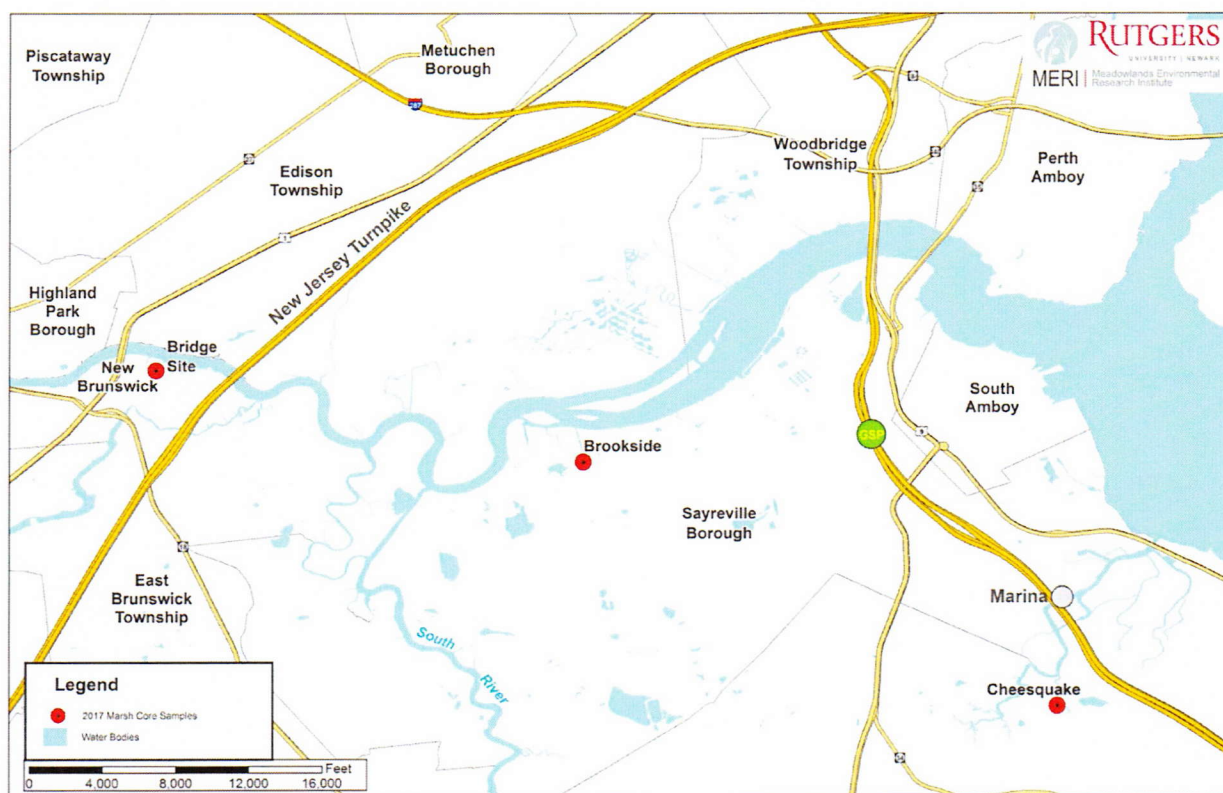
2.2.1 Coring and Sample Selection

Three sites were chosen along the Raritan River for coring (Figure 42). The sites were chosen with consideration to the following:

1. Sites should cover a range of salinities, and
2. Sites should cover a range of pollution levels.

We initially planned to include both high and low marshes, however, in early investigations, little difference was seen between them with regards for historical pollution levels. A much greater difference was seen when comparing among salinities and pollution levels, and so these characteristics were the focus of this study.

Figure 42: Location of the coring sites



The first site, located near New Brunswick between the New Jersey Turnpike Bridge and the Route 1 Bridge (40.49° , -74.41°), will hereafter be called “Bridge” site. This site is located in a

freshwater tidal marsh, with a salinity of 0.1 ppt. Very dense *Phragmites australis* (common reed) dominates the site in low-lying areas which are inundated twice daily. Some sparse trees live in areas at a slightly higher elevation, which are less frequently inundated. The Bridge site had a moderate amount of anthropogenic disturbance.

The second site is located near Sayresville close to Brookside Avenue (40.48°, -74.34°) and will hereafter be referred to as “Brookside” site. Here, the site is tidally inundated by brackish water and is dominated by a mix of *Spartina patens* and *P. australis*. The surface salinity measured at this site was approximately 1.7 ppt. A former factory is located near this site, and many nearby marshes have a layer of crushed bricks coating them. This site was selected to avoid this issue. Additionally, water chemistry monitoring revealed this site as a hotspot for high levels of pollutants (see *Component I*). Brookside site had the highest amount of anthropogenic disturbance.

A third site in the Raritan Bay completed our transects of sites along the salinity gradient of the tidal Raritan River. In the low marsh *Spartina alterniflora* (long form) dominates and the high marsh is vegetated by *Spartina patens* and *Distichlis spicata*. This site, located in Cheesequake State Park (40.44°, -74.27°), will be referred to as “Cheesequake”. This site has a salinity of 12 ppm. Cheesequake was the site with the least amount of anthropogenic disturbance.

At each site, a Russian-type peat sampler was used to extract four replicate sets of cores in order to ensure that we had enough sediment for all analyses and for an archived core. For each core, two bore holes were used to collect alternating 50 cm intervals of sediment, with 10 cm overlaps to ensure complete sections (De Vleeschouwer, *et al.*, 2010). We cored at each site to refusal to ensure enough sample was collected to include pre-industrial materials.

2.2.2 Geochemistry

We collected samples every 4 to 8 cm in the top 80 cm of core material in order to assess the amount of pollutants in the sediments. Samples were collected from Replicate A from the Bridge Site and Replicate C from the Brookside Site. We based our sampling interval on the local accumulation rate of 3.1 cm/yr (Kemp, *et al.*, 2013). Samples weighed at least 10 g of sediment

in order to perform both organic pollutant analysis and metal analysis.

In order to assess the amount of organic pollution through time PAH, PCBs, and OCPs were extracted from the samples. To extract organics, we first used an 1:1 mixture of hexane and acetone in an accelerated solvent extractor (ASE 100, Dionex, USA). We then cleaned the samples using gel permeation chromatography (GPC, Autoprep 2000, O I Analytical, USA) and concentrated the extracts at 30 °C using rotary evaporation.

We separated PCBs and OPCs by fractioning using a florisil column. We analyzed sample extracts for 16 PAHs using Agilent 6890N gas chromatography and a 5975 inert mass spectrometer and quantified them using the internal standard method. Samples were analyzed for 109 PCB congeners and 18 OCPs. We identified congeners based on relative retention time. We spiked PCB and OCP surrogates in order to complete a QC recovery check.

We determined metal concentrations using EPA Method 200.8 (microwave-assisted acid digestion of sediment). Quality control was maintained by digesting a standard reference material 1944 (New York/New Jersey Waterway Sediment, NIST) alongside the samples. We analyzed the samples using an Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

Once pollutants were extracted, their concentrations were compared throughout the depth of the core. Metals in particular have well defined dates associated with their peaks, based on the timing of pollution regionally. The peaks and initial onsets of metal pollution were used to assign some of the dates included in the age-depth model. In this location, initial copper pollution occurred in 1875 ± 25 , initial lead pollution occurred in 1900 ± 5 , the cadmium peak occurred in 1963 ± 7 , the nickel peak occurred at 1969 ± 11 , and the lead peak occurred at 1974 ± 5 (Bricker-Urso et al., 1989; Donnelly et al., 2001; Metcalfe & Derwent, 2014; Kemp, et al., 2013; Hurst, 2002; Marcantonio, et al., 2002; Lima, et al., 2005).

We used ^{210}Pb ($t_{1/2} = 22.3$ years) and ^{137}Cs ($t_{1/2} = 30.2$ years) to establish a portion of the chronology. ^{137}Cs activity was analyzed by direct gamma counting on a low-background, high-efficiency Germanium detector coupled with a multi-channel analyzer. We packed samples into standardized vessels and placed them in the counters for approximately 24 hours. We calibrated the detectors using natural matrix standards (IAEA-300, 312, 314) at the energy of interest (661 keV) in the standard counting geometry for the associated detector.

We measured total ^{210}Pb using alpha spectroscopy following the methodology of Nitttrouer *et al.* (1979). We spiked 1.5 g of sample with ^{209}Po , as a yield determinant, and then partially digested them with 8 N nitric acid (HNO_3) by microwave heating. Polonium-209 and ^{210}Po in solution was then electroplated onto nickel planchets in a dilute acid solution (modified from Flynn, 1968). We subtracted the ^{210}Pb activity supported by ^{226}Ra from the total ^{210}Pb activity in order to determine the amount of excess ^{210}Pb . This assumes that supported ^{210}Pb activity for a given core is equal to the uniform background activity found at depth (Nitttrouer *et al.*, 1979). We calculated sediment accumulation rates using the constant flux–constant sedimentation (CF–CS) model (Appleby and Oldfield, 1992). Down-core ^{137}Cs activities were used to substantiate the ^{210}Pb -determined accumulation rates.

Finally, we selected three samples from each core in the bottom 50 cm to send for radiocarbon dating at NOSAMS. Samples were individual rhizomes from *Spartina alterniflora* and *Spartina patens* at Cheesequake and Brookside, and single roots or other plant material from Bridge as this site was freshwater rather than marine and *Spartina* species were not present. At NOSAMS, AMS dating was used to get the most precise date with the least amount of sediment used. Standard radiocarbon calibration (intcal13) was used to determine the age before present at the time of deposition.

2.2.3 Pollen Analysis

Pollen samples were collected every 4 cm in the region of the cores anticipated to include the start of settlement based on other dating methods. Samples were processed by Dr. Vaughn M. Bryant using the methods of Faegri and Iverson (1964), in which samples are exposed to a series of acid washes in order to remove extraneous materials, such as organics and silicates. Once the pollen grains were extracted and concentrated, we preserved them in glycerol. We placed preserved samples on slides and identified and identified and counted 100 pollen grains. Analyses were completed using a magnification of 400x.

We used pollen counts to identify changes in vegetation related to land-clearance, which occurred when the Europeans settled in New Jersey. For example, in this region shifts from an

abundance of *Quercus* to *Ambrosia* indicate deforestation in 1795 (Russell, 1980). An additional pollen horizon was observed in the Bridge Site: Chestnut Blight, a decrease in *Castanea* pollen due to the widespread death of chestnut trees in 1920 (Brugam, 1978; Clark and Patterson, 1984).

2.2.4 Constructing of an Age-Depth Model

Bchron is an extension for R which uses Bayesian models to analyze age-depth relationships (Haslett & Parnell, 2008). Bchron is able to take a composite chronology and associated methodological and depth errors and determine a best-fit age depth model with 95% confidence intervals. We used Bchron to create our age-depth model. To do so, we input the chronohorizons from metal pollution, radiocarbon dating, pollen, and ^{137}Cs and ^{210}Pb analysis. We also included the core extraction year. Bchron used these dated depths to construct a model of age vs. depth for each site, as well as a confidence interval associated with it.

2.2.5 Diatom Analysis

We collected diatom samples every 10 cm in the top 100 cm of core in order to encompass pre-colonial (background) nutrient load through the present. This allows us to see what nutrient levels in the river were like prior to European settlement, how it changed during the industrial revolution, and how it fares in the present. Samples were weighed and placed in 50 mL Falcon Tubes. Once in the Falcon Tubes, samples were exposed to 35% hydrogen peroxide overnight, until the amount of bubbling reduced. We then placed the tubes in a warm water bath for two to three days, depending on the organic content of the samples. We allowed the samples to cool before placing them in the centrifuge to spin at 3500 rpm for 3 minutes then decanted. Fresh DI water was added to the tubes and they were centrifuged again. We completed the centrifugation procedure three times, each time decanting and replacing the water in order to wash the hydrogen peroxide from the samples.

Once the samples were clean, we added DI water up to 10 mL. We then placed water on a coverslip and used a micropipette to add a known amount of sample slurry. Coverslips dried overnight and were adhered to slide using NAPHRAX. We kept extra sample in order to make additional slides if needed.

We identified to species level and counted at least 100 valves from each sample under 1000x. Relative abundances were determined for each species. Species were grouped based on their nutrient preferences and the percentage in each group was traced through time. This allowed us to determine how the nutrient load in the Raritan River has change from pre-European settlement through the present.

2.3 Results

2.3.1 Age-Depth Models

In order to construct a composite age-depth model, we used a suite of methods: radionuclides, pollen, and metal pollution history. Cadmium, copper, nickel, and lead were measured downcore (Figures 43-45). At Brookside, we found that copper pollution, which designates 1875 ± 25 years began at 70 cm (Bricker-Urso et al., 1989; Donnelly et al., 2001). Initial lead pollution (1900 ± 5 years) occurred at 60 cm, and the lead peak (1974 ± 5 years) occurs at 34 cm (Hurst, 2002). The cadmium peak (1963 ± 7 years) was present at 40 cm (Metcalf & Derwent, 2014; Kemp, et al., 2013). Finally, the nickel peak (1969 ± 11 years) occurred at 34 cm (Kemp, et al., 2013). At Bridge Site, the start of copper pollution was located at 55 cm. We found the start of lead pollution and the lead peak at 55 and 34 cm respectively. The cadmium and the nickel peaks both occurred at 36 cm. Finally, at Cheesequake, the initial copper pollution was found at 33 cm. The initial lead pollution occurred at 40 cm and the lead peak at 12 cm. We found the cadmium peak at 9 cm, and the nickel peak at 4 cm.

In addition to metals, we also looked at radionuclide, specifically ^{14}C , ^{137}Cs , and ^{210}Pb . ^{210}Pb was generally used to corroborate the sedimentation rate established using ^{137}Cs . We were able to identify a ^{137}Cs peak at all three sites. This peak corresponds with the peak in atmospheric nuclear weapons testing in 1963 (He and Walling, 1996). The ^{137}Cs peak was found in Brookside at 27 cm and at Cheesequake at 13 cm. At Bridge Site, we were unable to use ^{137}Cs due to large errors in measurement. We were able to calculate sedimentation rate based on the CSCF model for ^{210}Pb at both Bridge Site and Brookside. To include this information in the model, we determined the age of the deepest sample using the sedimentation rate. At Bridge Site, the sedimentation rate was 0.43 ± 0.03 cm/year, the deepest reliable age was 43 cm and the age determined for this sample was 1913 ± 2 years. We found a sedimentation rate of 0.42 ± 0.03 cm/year at Brookside, with a deepest reliable date at 37 cm, with an age of 1932 ± 5 years. We also used radiocarbon dating for older sediments. We were able to date three samples at Brookside. The shallowest site we dated was located at 55 cm and returned a date of 273 ± 15 years before present. We dated a second sample at 85 cm which returned a date of 453 ± 15 years before present. Our third sample at 110 cm returned a date of 173 ± 15 years before present, attesting to the high degree of mixing which occurred at these sites. We sent three dates from

Bridge Site as well, located at depths of 47 cm, 63 cm, and 83 cm. All three samples returned dates indicating that the samples were likely deposited post-1950, which is inconsistent with other chronometers and likely represents mixing. At Cheesequake, three samples were sent for radiocarbon dating within our study depth: 62 cm, 81 cm, and 93 cm. These samples returned dates of 155 ± 15 years, 380 ± 15 , and 605 ± 20 years, respectively.

Finally, we used pollen horizons to determine the age of sediments. We looked for a shift in the ratio of oak to ragweed pollen to less than 1, which indicates that deforestation has occurred and it is 1795 ± 55 years (Russell, 1980). We also looked for the decline or elimination of chestnut pollen, which corresponds to the Chestnut Blight which occurred at 1920 ± 10 years (Brugam, 1978; Clark and Patterson, 1984). The settlement peak was found at 58 cm at Brookside, 58 cm at Bridge Site, and 60 cm at Cheesequake. We found the Chestnut Blight horizon in Bridge site only, at 54 cm.

Figure 43. Brookside Metals, colors in figure represents pre-land clearance (green), post-land clearance, but pre-industrial (yellow), and post-industrial (red) land uses.

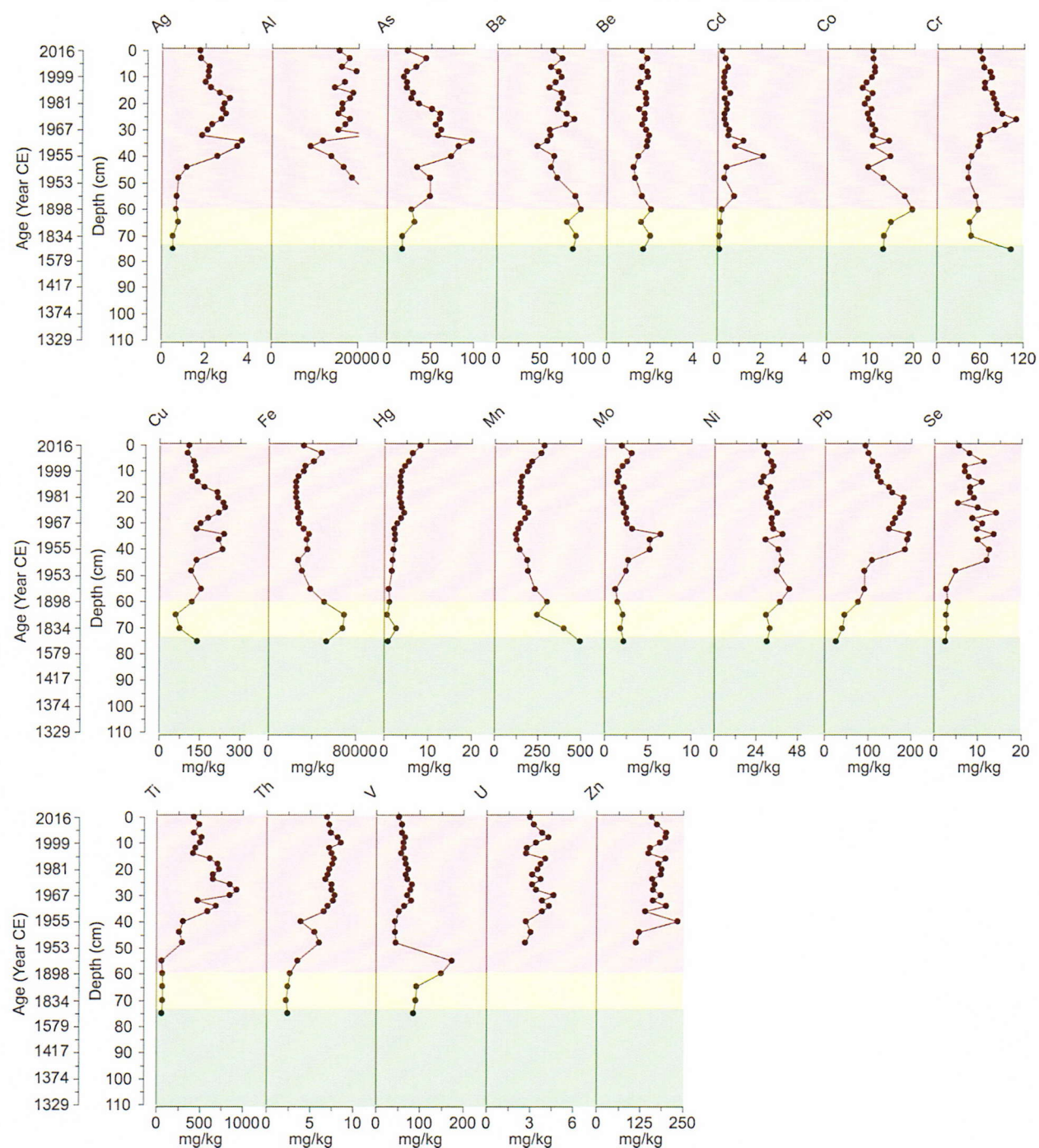


Figure 44. Bridge Site Metals, colors in figure represents pre-land clearance (green), post-land clearance, but pre-industrial (yellow), and post-industrial (red) land uses.

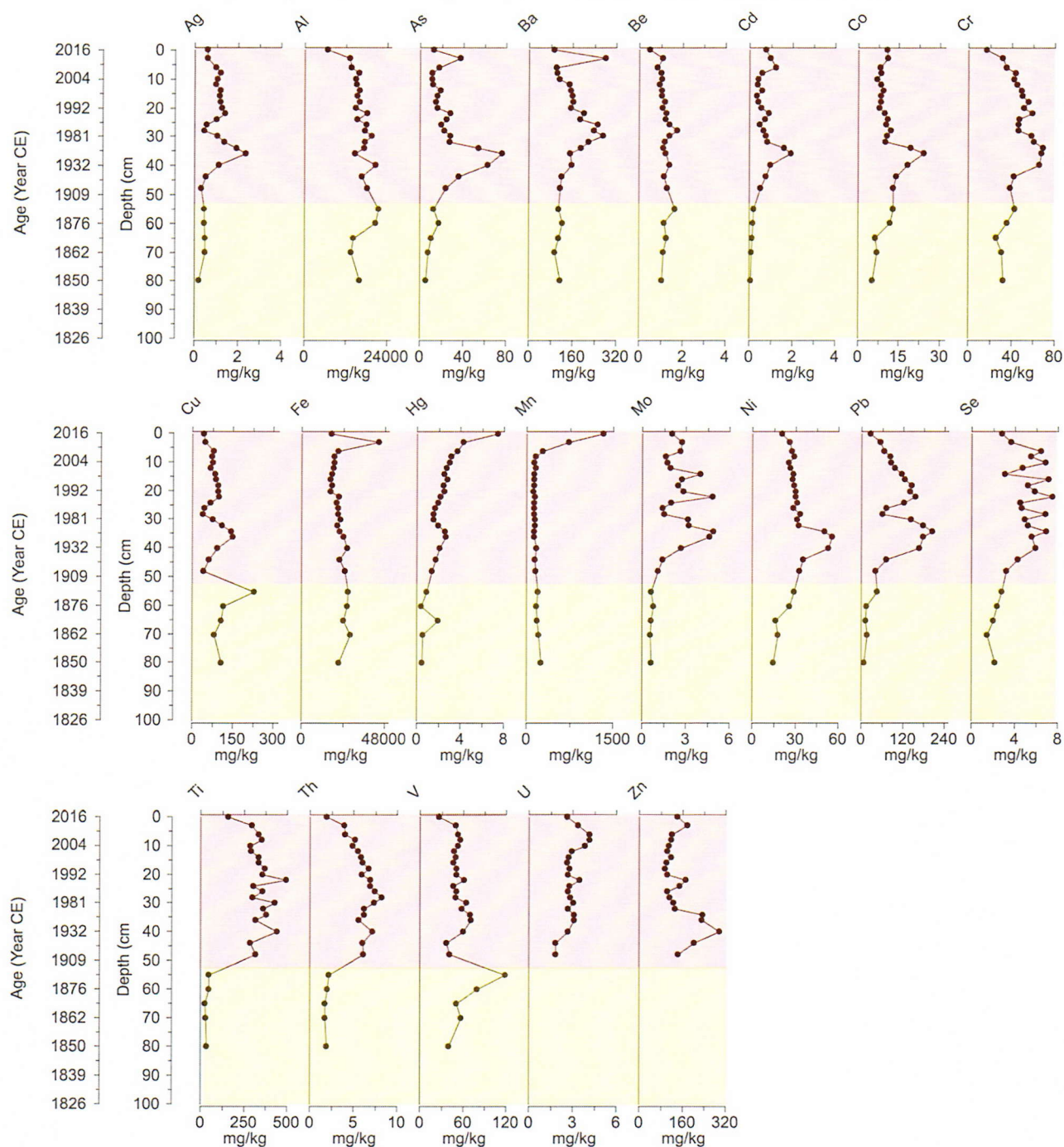
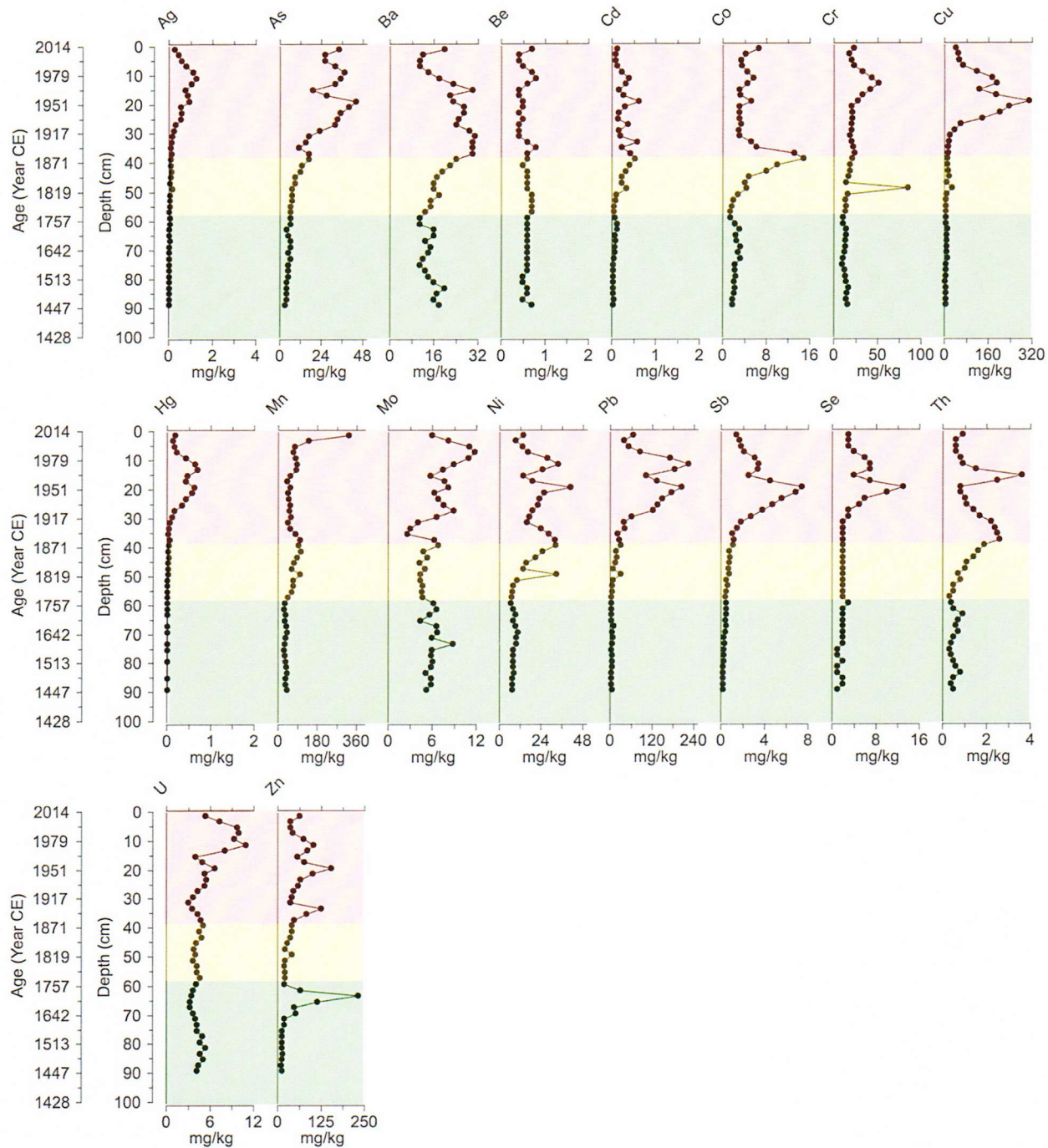


Figure 45. Cheesequake Site Metals, colors in figure represents pre-land clearance (green), post-land clearance, but pre-industrial (yellow), and post-industrial (red) land uses.



By combining these methods, we constructed a composite chronology in Behron for each site. Based on these reconstructions, we were able to determine that the top 100 cm of Brookside dates from pre-European settlement to present, capturing major land use changes associated with the impacts of settlement, deforestation, and industry (Figure 48). At Bridge Site, the bottom of the 100 cm core pre-date the industrial revolution, thus enabling a comparison of pre-industrial conditions with pollution levels that occurred following the industrial revolution through the present (Figure 49). We found that the sediments at Cheesequake are deposited the most rapidly of the three sites, such that the bottom of the core greatly pre-dates settlement, allowing us to observe water quality far before European settlement, so that comparisons to post-settlement, and post-industrial conditions can be made (Figure 50). Cheesequake was also the least bioturbated site, resulting in the least amount of uncertainty in the age-depth model. Because sediments were very mixed at Bridge Site, the uncertainty is rather high; however, differentiation between pre- and post-industrial sediments can still be made. Brookside was intermediate, and a reliable age-depth model resulted from the sediment analysis there.

Figure 48. Brookside Site Age-Depth Model showing the various marker types that were used to determine the pre- and post-settlement as well as the post-industrial contamination levels

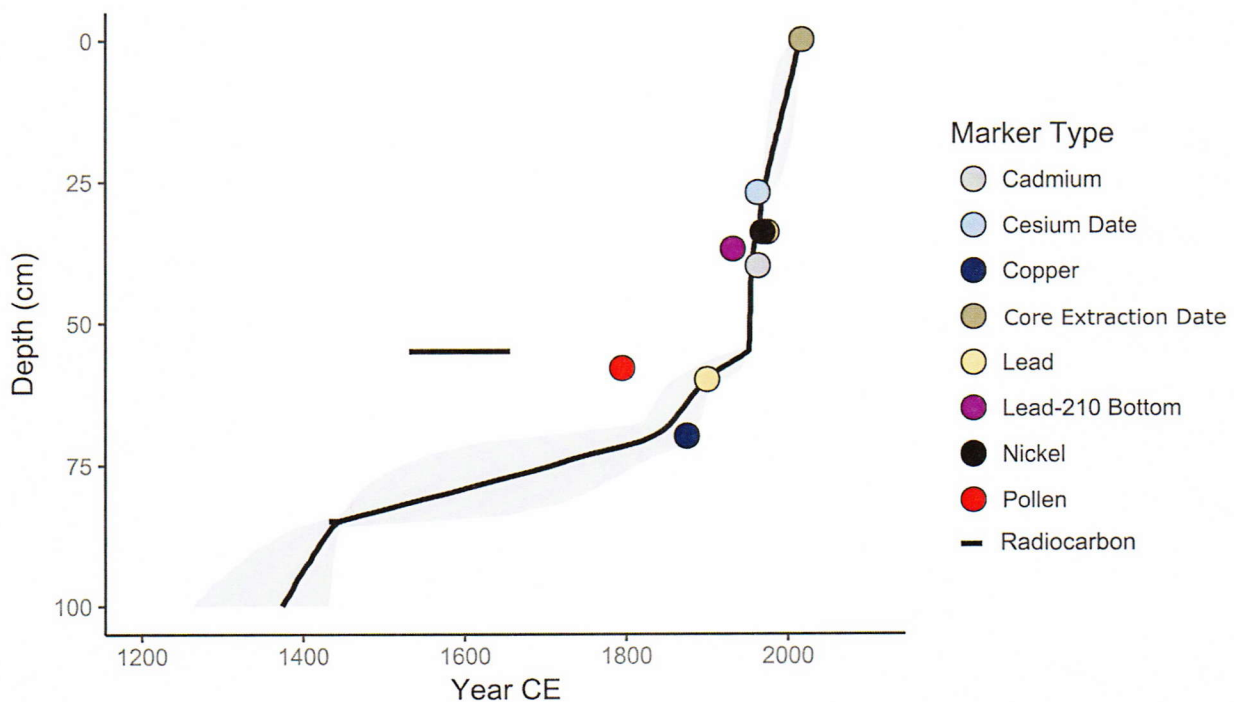


Figure 49. Bridge Site Age-Depth Model showing the various marker types that were used to determine the pre- and post-settlement as well as the post-industrial contamination levels

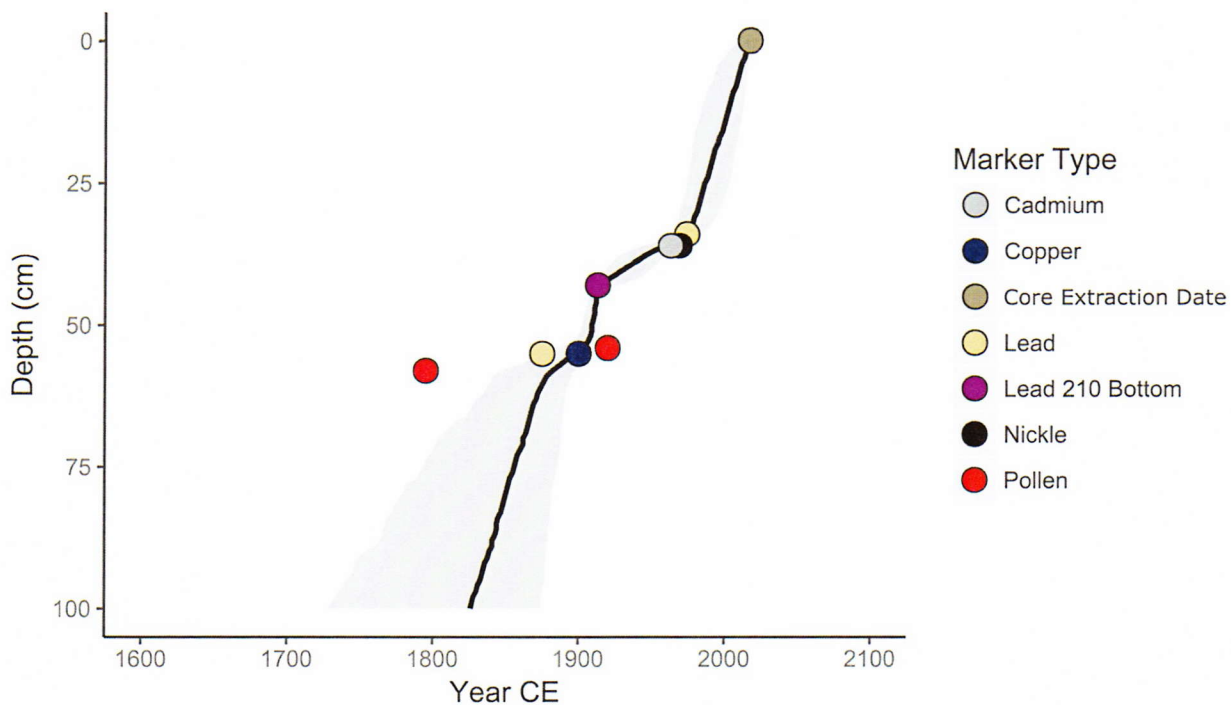
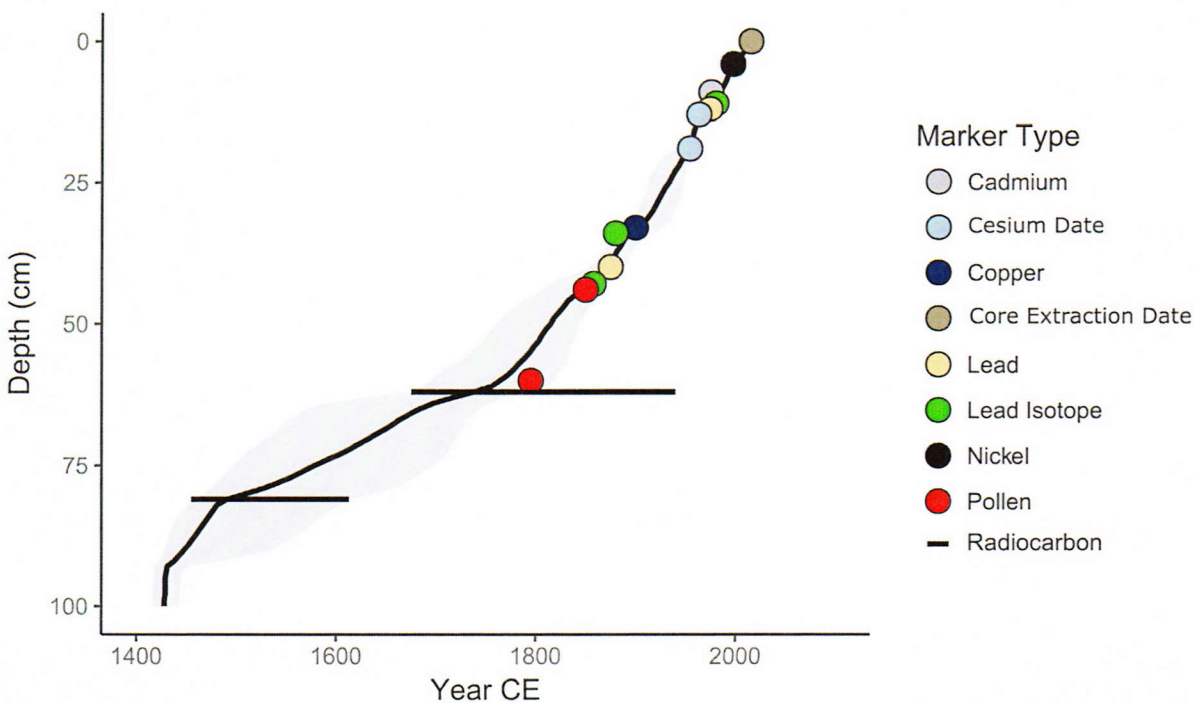


Figure 50. Bridge Site Age-Depth Model showing the various marker types that were used to determine the pre- and post-settlement as well as the post-industrial contamination levels



2.3.2 Pollution History

Metals, organic pollutants, and nutrient loads are all factors that influence water quality. We looked at these three aspects historically in our cores.

Brookside was the most disturbed site. In Brookside, metals were lowest prior to European settlement. Following settlement, metals generally increased very slightly (Figure 43). Around 1900, metal levels increased drastically. During the 1960s and 1970s, metal levels decreased slightly, possibly as a result of environmental legislation which was prevalent during this time. This can be seen in the changes in the average concentrations of select metals. In the four metals we used for chronology, there is an increase in concentration from pre-deforestation to post-deforestation in cadmium, nickel, and lead (Table 5).

Table 5 Summary of the metal and organics concentration values from the core samples

		mg/kg																				ug/kg		%			
	Brookside	Ag	Al	As	Ba	Be	Cd	Co	Cr	Cu	Fe	Hg	Mn	Mo	Ni	Pb	Sb	Se	Ti	Th	V	U	Zn	PCB	OPC	Low Nutrient Diatoms	High Nutrient Diatoms
All Samples	Mean	2.04	17970	42.7	72.2	1.70	0.47	11.5	68.5	160	35961	3.34	207	2.55	33.0	129	0.11	8.09	470	6.29	74.2	3.51	173	101	26.3	18.3	5.55
	Median	2.16	17493	35.4	70.8	1.74	0.33	10.6	65.1	143	32317	3.57	184	2.20	32.3	127	0.06	8.27	486	7.16	67.5	3.46	175	83.5	22.7	15.0	6.00
	std dev	0.94	3950	21.5	12.1	0.20	0.41	2.82	17.9	52.9	12517	1.76	87.2	1.25	3.80	48.1	0.11	3.50	261	2.00	29.1	0.57	27.9	50.6	15.6	11.4	3.91
Pre-deforestation	Mean	0.52	24000	17.8	89.4	1.86	0.12	13.1	75.7	110	60512	1.85	450	2.03	31.2	33.6	NA	2.74	66.7	2.39	88.1	NA	NA	NA	NA	28.8	3.75
	Median	0.52	24000	17.8	89.4	1.86	0.12	13.1	75.7	110	60512	1.85	450	2.03	31.2	33.6	NA	2.74	66.7	2.39	88.1	NA	NA	NA	NA	27.5	3.00
	std dev	0.01	1206	0.42	2.2	0.21	0.00	0.20	39.0	46.5	10463	1.38	64.6	0.24	1.11	9.23	NA	0.25	4.14	0.10	3.63	NA	NA	NA	NA	9.32	3.10
Post-deforestation Pre-Industrial	Mean	0.48	17326	14.1	117	1.21	0.15	9.21	31.3	111	25165	1.20	180	0.73	21.1	14.3	NA	2.25	37.7	1.87	65.4	NA	NA	NA	NA	12.0	18.0
	Median	0.72	24385	30.4	88.7	1.82	0.18	17.2	51.4	92.3	60545	0.99	276	1.83	33.7	62.4	NA	3.02	68.0	2.61	121.19	NA	NA	NA	NA	19.0	6.00
	std dev	0.09	2790	2.5	10.8	0.33	0.04	3.59	8.56	43.7	12793	0.46	40.0	0.47	5.39	22.8	NA	0.29	1.48	0.21	40.6	NA	NA	NA	NA	NA	NA
Post-Industrial	Mean	2.29	16838	46.1	69.1	1.67	0.53	10.9	69.4	171	31494	3.68	179	2.66	33.0	143	0.11	9.04	543	6.98	68.7	3.51	173	101	26.3	11.2	6.67
	Median	2.23	16679	46.7	69.0	1.74	0.40	10.4	65.8	155	30104	3.73	166	2.33	32.6	148	0.06	8.99	514	7.28	65.5	3.46	175	83.5	22.7	9.50	6.00
	std dev	0.78	3068	21.5	10.2	0.19	0.42	2.25	16.6	48.4	6135	1.65	43.0	1.33	3.92	34.9	0.11	2.91	211	1.23	25.9	0.57	27.9	50.6	15.6	7.57	4.55
Bridge Site																											
All Samples	Mean	0.95	16101	24.2	159	1.18	0.67	10.9	46.0	89.4	22243	2.32	227	2.27	30.4	93.6	0.03	4.70	282	5.16	55.6	2.95	148	82.6	15.6	13.7	22.3
	Median	1.02	15963	18.3	153	1.16	0.61	10.2	46.0	83.0	21335	2.12	144	2.01	29.2	84.1	0.01	4.85	318	5.95	51.1	2.81	129	77.2	14.7	13.0	21.0
	std dev	0.51	2974	17.2	56.1	0.24	0.45	4.23	13.1	40.6	5550	1.40	253	1.30	9.77	58.1	0.03	1.77	136	2.05	17.0	0.60	53.8	35.0	6.08	6.86	8.12
Pre-deforestation	Mean	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	Median	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
	std dev	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Post-deforestation Pre-Industrial	Mean	0.42	17091	10.9	111	1.25	0.14	8.73	34.0	128	25317	0.86	206	0.66	20.8	20.1	NA	2.20	37.8	1.92	69.6	NA	NA	NA	NA	20.0	13.3
	Median	0.47	15927	10.8	110	1.16	0.13	7.07	32.6	109	26252	0.53	193	0.63	17.9	16.1	NA	2.18	34.8	1.91	57.4	NA	NA	NA	NA	17.5	15.5
	std dev	0.12	3654	4.6	10.3	0.23	0.04	3.34	6.38	57.9	2514	0.64	32.8	0.08	6.26	14.3	NA	0.51	9.75	0.17	31.2	NA	NA	NA	NA	6.93	3.88
Post-Industrial	Mean	1.07	15865	27.4	170	1.17	0.79	11.4	48.9	80.1	21511	2.67	232	2.65	32.7	111	0.03	5.30	340	5.93	52.2	2.95	148	82.6	15.6	9.80	28.0
	Median	1.06	16000	22.7	158	1.16	0.74	10.3	47.2	76.4	20997	2.50	141	2.62	30.0	116	0.01	5.25	337	6.08	50.6	2.81	129	77.2	14.7	11.0	27.0
	std dev	0.49	2843	17.6	56.5	0.25	0.41	4.32	12.7	30.3	5858	1.31	283	1.14	9.10	50.0	0.03	1.39	68.2	1.42	10.3	0.60	53.8	35.0	6.08	4.09	5.83
Cheesequake																											
All Samples	Mean	0.29	NA	15.7	18.8	0.57	0.18	3.99	20.9	50.8	NA	0.17	65.2	6.34	16.1	50.7	1.63	3.11	NA	1.04	NA	5.06	52.0	42.1	13.9	6.67	9.41
	Median	0.09	NA	9.0	17.0	0.60	0.12	3.10	18.0	11.8	NA	0.05	55.0	5.97	13.7	17.8	0.81	2.00	NA	0.80	NA	4.50	41.0	38.9	9.87	2.00	8.50
	std dev	0.35	NA	12.5	6.2	0.11	0.15	2.80	13.1	75.3	NA	0.21	46.9	1.96	9.18	64.4	1.83	2.45	NA	0.75	NA	1.85	43.6	18.0	10.7	8.37	5.25
Pre-deforestation	Mean	0.05	NA	5.0	14.5	0.60	0.06	2.28	13.2	6.58	NA	0.02	38.1	5.91	8.25	5.91	0.35	1.78	NA	0.53	NA	4.27	40.4	42.3	8.01	18.0	3.57
	Median	0.05	NA	5.0	14.5	0.60	0.06	2.20	13.0	6.20	NA	0.02	37.0	5.92	7.90	5.45	0.33	2.00	NA	0.50	NA	4.23	19.0	42.3	8.01	14.8	4.00
	std dev	0.01	NA	0.97	2.5	0.06	0.03	0.55	1.8	1.94	NA	0.00	7.81	1.00	1.02	1.53	0.11	0.55	NA	0.16	NA	0.61	55.1	8	7.04	9.22	1.80
Post-deforestation Pre-Industrial	Mean	0.10	NA	10.5	20.2	0.64	0.26	6.55	24.0	12.5	NA	0.04	84.1	4.88	20.6	17.5	0.82	2.00	NA	1.33	NA	4.35	37.6	29.4	8.53	6.45	13.5
	Median	0.09	NA	9.0	18.0	0.60	0.22	4.80	19.0	11.6	NA	0.03	83.0	4.76	21.0	17.8	0.81	2.00	NA	1.10	NA	4.29	38.0	29.5	8.87	2.00	16.0
	std dev	0.04	NA	3.9	5.6	0.08	0.15	4.47	20.5	6.54	NA	0.02	16.2	1.08	9.99	9.31	0.23	0.00	NA	0.75	NA	0.43	18.6	7	1.51	8.35	6.16
Post-Industrial	Mean	0.67	NA	30.8	21.7	0.50	0.23	3.92	27.1	126	NA	0.37	83.0	7.92	21.0	122	3.57	5.38	NA	1.31	NA	6.50	68.5	47.8	17.5	3.30	9.96
	Median	0.60	NA	32.0	23.0	0.45	0.18	3.40	22.0	123	NA	0.40	58.0	7.66	19.0	128	3.27	4.50	NA	0.95	NA	5.43	62.5	45.7	14.4	1.67	9.33
	std dev	0.33	NA	7.3	6.8	0.13	0.14	1.10	10.2	84.7	NA	0.21	68.8	2.08	8.15	60.3	1.84	2.96	NA	0.83	NA	2.46	31.8	20.6	12.4	4.48	4.19

Copper decreased slightly, but this likely resulted from a low number of samples in pre-deforestation sediments, and mixing. The average concentration of all four metals increased following industrialization. PAHs we also observed at this site. We found that both PCBs and OPCs increased in the 1950s through the 1970s (Figure 51). We did not capture pre-industrial PAHs at this site. Nutrients were observed by categorizing diatoms by their preference for high nutrient concentrations or low concentrations (Potapova *et al.*, 2015). At Brookside, we found that diatoms preferring low nutrient concentrations decreased following deforestation in 1795 (Figure 52). Concurrently, the abundance of diatoms preferring high nutrient concentrations increased slightly during this time. Diatoms that prefer low nutrient conditions stay generally low in abundance following industrialization, while diatoms that prefer high nutrient concentrations continue to increase after industrialization.

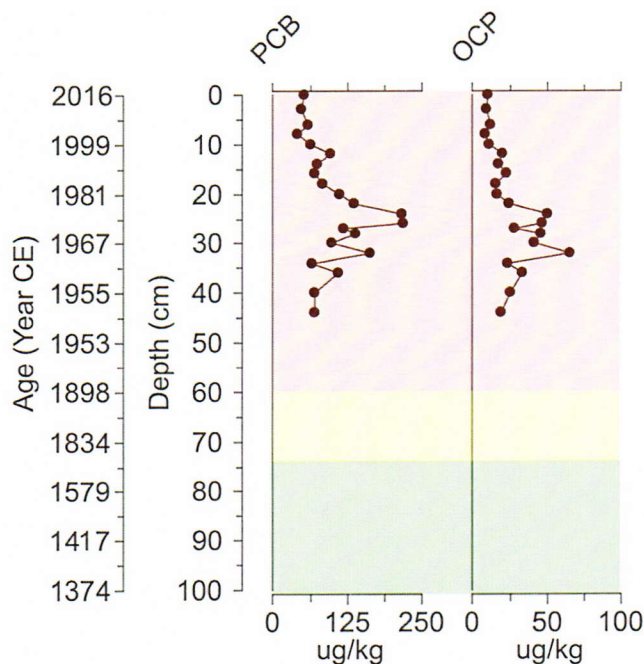


Figure 51. Brookside Organics, colors in figure represents pre-land clearance (green), post-land clearance, but pre-industrial (yellow), and post-industrial (red) land uses.

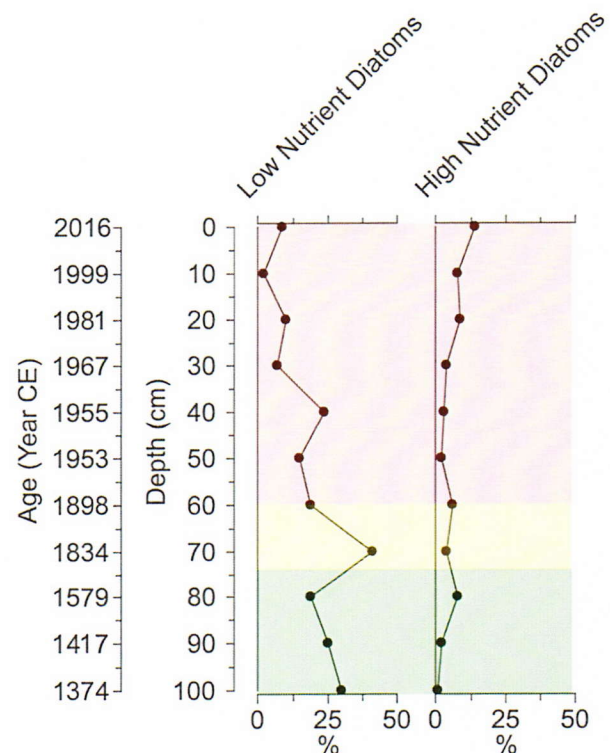


Figure 52. Results of Diatom Analysis at the Brookside Site, showing distribution of Low and High Nutrient Diatoms over time.

The Bridge Site was moderately disturbed. At Bridge Site, we were unable to sample pre-deforestation sediments. We did find, however, that metals increased in sediment concentration following industrialization (Figure 44). Copper decreased slightly in average concentration, again likely due to mixing and a smaller sample size prior to industrialization (Table 5). The other three metals, cadmium, nickel, and lead, all show an increase in concentration following industrialization. PCBs and OPCs were not sampled prior to industrialization. PCBs and OPCs were both found to be very variable at this site, however, and generally show an increase during the 1920s (Figure 53). The wide variations of PCBs and OPCs here may be related to mixing, which was found to be very problematic at this site. Diatom reconstructions of nutrient levels showed a near complete loss of diatoms preferring low nutrients after industrialization occurred (Figure 54) (Potapova and Charles, 2007). We found that diatoms with a preference for moderate nutrient levels became very variable after industrialization. Finally, we found that diatoms which are tolerant of or prefer high nutrient levels increased following industrialization.

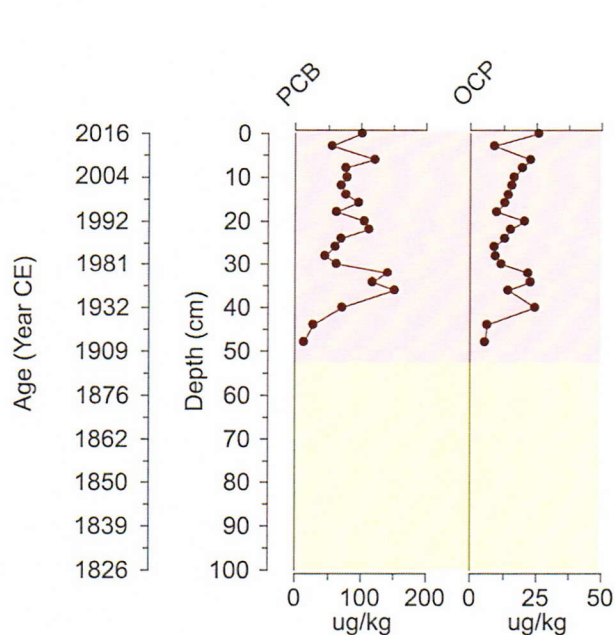


Figure 53. Bridge Site, colors in figure represents pre-land clearance (green), post-land clearance, but pre-industrial (yellow), and post-industrial (red) land uses.

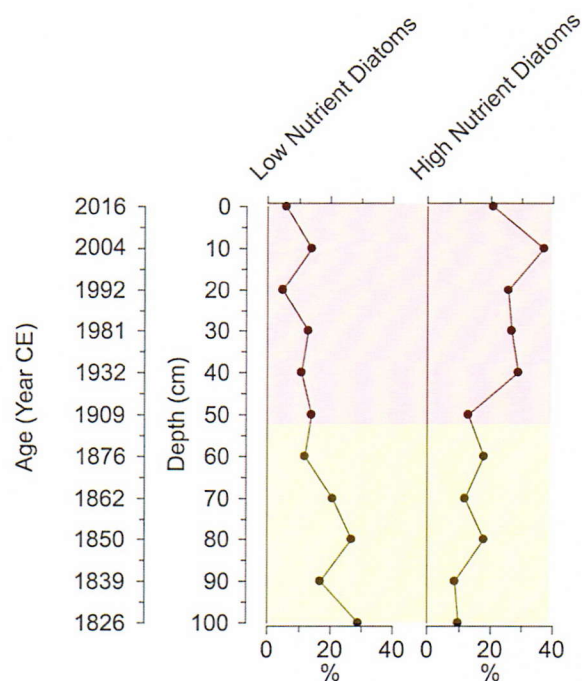


Figure 54. Results of Diatom Analysis at the Bridge Site, showing distribution of Low and High Nutrient Diatoms over time.

At Cheesequake, our least disturbed site, we found that cadmium, copper, nickel, and lead increased slightly following deforestation (Figure 45). Following industrialization, all four metals increase greatly. The average of all four metals reflects this, with the post-industrial average being 3 to 17 times higher than the pre-deforestation average. PCBs and OPCs also increased following industrialization (Figure 55). PCBs increased only slightly, from 42.3 ug/kg prior to deforestation to 44.5 ug/kg following industrialization (Table 5). OPCs however doubled following industrialization (Table 5). Both were variable. Here, diatoms showed a similar pattern to the other two sites. Diatoms which prefer low nutrient concentrations decreased following settlement, and particularly following industrialization (Figure 56) (Potapova *et al.*, 2015). Concurrently, diatoms which prefer high nutrient concentration increased following settlement and industrialization.

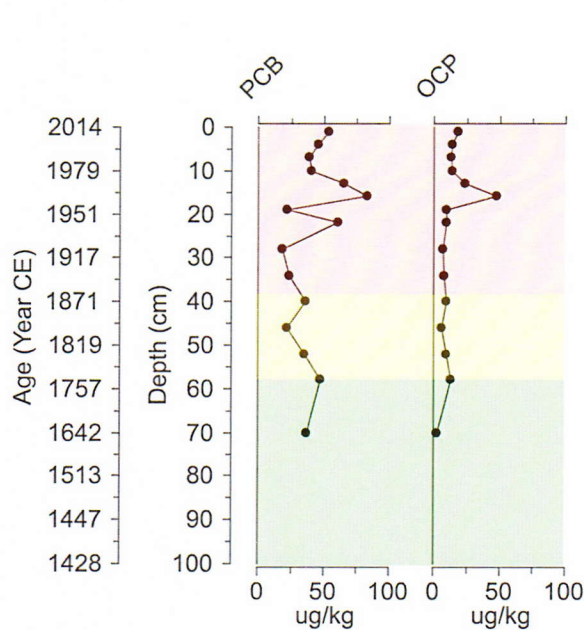


Figure 55. Cheesequake Site, colors in figure represents pre-land clearance (green), post-land clearance, but pre-industrial (yellow), and post-industrial (red) land uses.

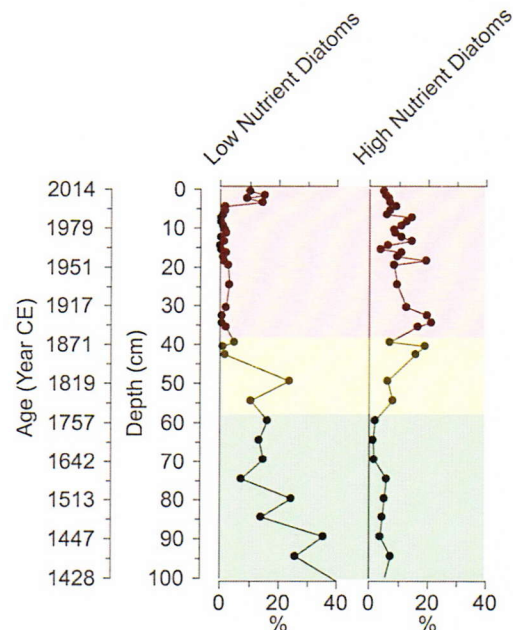


Figure 56. Results of Diatom Analysis at the Cheesquake Site, showing distribution of Low and High Nutrient Diatoms over time.

When the three sites are compared, Cheesequake, for the most part, has the lowest pollution levels, which Brookside has the highest (Table 5). Bridge Site is intermediate. Considering the post-industrial concentrations of metals, with the exception of copper, Cheesequake has the lowest concentrations. Brookside has the highest concentration of all metals. Similarly, Cheesequake has the lowest levels of PCBs and is similar to Bridge Site in OPCs concentrations. Brookside has nearly twice the concentration of PAHs as Cheesequake. This is consistent with surface water samples documented elsewhere in this report. Water samples taken near Brookside tend to be much higher in all pollutants than any other location in the river.

2.4 Conclusions

Overall, we were able to show that pollution levels including metals, organic pollutants, and nutrients all increased following industrialization throughout the Raritan River. In some cases, we were also able to show an increase following deforestation. We found that sites with a greater amount of anthropogenic impact showed the highest increases in pollution levels. These changes were consistent with finding that the site with the greatest anthropogenic impact, Brookside, also had the highest surface water contamination.

We found mixing to be an issue, particularly in Brookside and Bridge Site. Mixing results from the activities of burrowing animals such as worms or crabs, or the growth of plant roots, and is also referred to as bioturbation. Bioturbation can make establishing an age-depth model difficult because signals may be smeared over several centimeters. Bridge site was the most bioturbated, and thus age markers near the bottom were both noted as pre-deforestation (in the case of pollen), and modern/1950. Additionally, pollution such as PAHs and markers such as diatoms are similarly smeared. This resulted in larger errors on ages and less obvious pollution patterns. Despite this, we were able to interpret many of the expected environmental changes at these sites.

Previous studies in various locations have helped identify the behavior of organic and inorganic pollutants in wetland systems. Sanger *et al.* (1999) compared industrial and urban watersheds to suburban and forested watersheds in North Carolina. Like our results, the areas with greater anthropogenic impact, specifically the urban and industrialized areas had much higher concentrations of organic pollutants such as PCBs and PAHs than forested and suburban areas. Additionally, in our study, the increased amount of pollution in the river is near our most polluted site, Brookside. This may imply that historically deposited pollutants can be remobilized and redeposited onto the surface. In the study by Sanger *et al.* (1999) core samples contained both historical and contemporary sources, likely representing a remobilization of historical sediments and that because organic pollutants bind tightly to organics in wetland sediments, these environments can be historical sinks, but potential contemporary sources.

Metals also tend to adhere more closely to finer grains in sediments, resulting in the potential for greater contamination of wetlands and surface water (Gambrell, 1994). However, the marshes studied here are consistently wet, which reduced the potential for metal contamination to

contribute to decreased water quality through surface runoff. Because sediments that drain and dry out are frequently prone to oxidation, and thus they are at increased risk for metals to become less firmly adhered to grains, and more prone to contaminating runoff (Gambrell, 1994).

These findings can help us set realistic and achievable goals for restoration. Additionally, they help point to additional considerations, such as sediment resuspension. Because sediments are often resuspended as marshes are reworked, contaminants stored in sediments may re-enter the waterway, causing surface water pollution. Contaminant can also leach through groundwater. Because sediment can be stored for a very long time, this means that contaminant stored in marshes may be a problem for a long time, however, because metals bind tightly to wetland soils, causing them to be immobilized by capping them under additional sediment is possible (McKee *et al.*, 2005; Gambrell, 1994).

Several solutions are possible for this sort of problem. Because wetland sediments are frequently good sinks of contaminants, they could be capped to prevent the loss of contaminants from surface layers (Gambrell, 1994; Sanger *et al.* 1999). If the pollution levels are incompatible with bringing back vegetation, or there is concern that it might re-enter the system through vegetation or runoff, removal and disposal could also be considered (Zedler & Leach, 1998). Additionally, studies have shown that vegetation can effectively move contaminants farther below ground. In Weis and Weis (2003), *Phragmites* was shown to uptake more metals and store more of them below ground, where they are less accessible, than *Spartina*. Because *Spartina* stored the metals in its leaves, they were more frequently excreted via the salt gland and additionally, more likely to be present in leaf litter, which can be consumed by detritus feeder and enter the food chain (Weis & Weis 2003). Because of this, careful consideration would be needed in determining which plants could best serve the remediation efforts while still allowing the environment to be as close to natural as possible.

Overall, it is important to consider several additional studies when planning how to best proceed with remediating the Raritan River and the marshes surrounding them. There are several studies we recommend. First, additional historical sites should be identified and sampled, particularly in marshes adjacent to portions of the river with higher bed-sediment contamination. This would help establish the location of the most impacted sites and identify potential sources. We would also improve our knowledge of the timing of impacts by sampling back to pre-European

conditions. Secondly, additional bed sediment samples should be taken to monitor changes in the bedload contamination levels. Ideally, these samples would be taken annually for several years to monitor what changes are occurring in the river. Pairing them with surface water samples would assist in understanding how the contaminants in the sediments are impacting water quality. Collecting multiple sets of water quality samples throughout tidal cycles and throughout the year would allow us to observe how pollution from contaminated marshes might move through the river. Third, once a site is selected to be remediated, studies on its hydrology and the prevalence of erosion at the site are needed to establish which remediation method is appropriate. A groundwater hydrology study would help establish how much contamination is escaping from the marsh and entering the river. Because deeper sediments are from time with less environmental regulation, they may have increased contamination. If water flows through them and picks up contamination, they may still contribute to poor water quality. On the other hand, if they are not contributing to water quality in this way, removing overlying, cleaner sediments may re-expose them and allow them to leach contaminants into the system even more easily. During and after remediation, the site should be monitored to ensure remediation efforts are effective (Spencer & Harvey, 2012). Multiple aspects, including physical and biogeochemical processes as well as ecological and morphological indicators, should be considered to identify the effectiveness of any plan put into place (Spencer & Harvey, 2012). By monitoring multiple aspects of the remediation effort and its outcome, we can ensure that the water quality and environmental health of the site is improving as expected and that pollutants have been effectively sequestered or fully removed.

3. Discussion

To assess a river's environmental past and present we used a multidisciplinary approach where biology, chemistry, statistics and computer modelling were combined to gain a greater understanding into the spatial and temporal distribution of priority pollutants and contaminants in the lower Raritan River .

Water quality analysis revealed that at the time of sampling there's considerable mixing of the water column as shown by measurements of salinity, temperature and dissolved oxygen. Figure 23 sums up the findings of the sediment chemistry analysis. Metal accumulation in the sediment tends to be higher at the first bend in the river, around the GSP bridge as well as further upriver around Crab Island and around the sand bar island on the southern bank. When compared to natural metal accumulation (Figures 26-38) only Arsenic, Copper, Mercury, Selenium, and Silver showed considerable enrichment in the sediment. Those metals along with Nickel, Lead and Zinc all exceeded the ERL thresholds. Mercury concentrations on the other hand were above the ERM levels in almost all sampling locations (Table 3). Overall organics and metals coincided on the same hotspots.

When comparing earlier sediment contamination records to our findings (Figure 40-41) the possibility of natural attenuation emerged for Chromium, Nickel and Antimony, while the rest of the metals showed no change in contamination levels between 2000 and 2006. In 2017 the metal concentration of Silver, Arsenic, Chromium and Selenium peak slightly upriver compared to measurements in 2000-2006. A similar slight attenuation pattern was found for most of the PCB congeners but they still exceeded the ERL criteria. Among the OCP's Endrin showed a marked increase between 2000 and 2006. Our results suggest active sources of Mercury and OCP's still exist and are having an impact in the Lower Raritan. ERL criteria levels and the hotspots showed concentrations higher than the ERM criteria.

When looking at the surrounding wetlands of the river we found that industrialization led to increased pollution due to anthropogenic activity in the tidal Raritan River. These changes were most pronounced in the sites closer to anthropogenic influences and were least pronounced at the more undisturbed site. This is consistent with findings in surface water pollution, which showed that a greater amount of metals and organic pollutants were present in the water near Brookside, our most polluted site, than anywhere else in the study reach. This may imply that these

pollutants are continuing to be put into the waterway by resuspension. These findings can help to identify the timing of pollution in the tidal Raritan River. Additionally, they could also be used to establish reasonable standards for restoration and remediation efforts.

Overall, it is important to consider several additional studies when planning how to best proceed with remediating the Raritan River and the marshes surrounding them. There are several studies we recommend. First, additional historical sites should be identified and sampled, particularly in marshes adjacent to portions of the river with higher bed-sediment contamination. This would help establish the location of the most impacted sites and identify potential sources. We would also improve our knowledge of the timing of impacts by sampling back to pre-European conditions. Secondly, additional bed sediment samples should be taken to monitor changes in the bedload contamination levels. Ideally, these samples would be taken annually for several years to monitor what changes are occurring in the river. Pairing these samples with surface water samples would assist in understanding how the contaminants in the sediments are impacting water quality. Collecting multiple sets of water quality samples throughout tidal cycles and throughout the year would allow us to observe how pollution from contaminated marshes might move through the river. Third, once a site is selected to be remediated, studies on its hydrology and the prevalence of erosion at the site are needed to establish which remediation method is appropriate. A groundwater hydrology study would help establish the amount of contaminants escaping from the marsh and entering the river. Since deeper sediments are from times with no environmental regulation, they may be an active source of contaminants. On the other hand if they are not contributing to water quality in this way, removing overlying, cleaner sediments may re-expose them and allow them to leach contaminants into the system even more easily. During and after remediation, the site should be monitored to ensure remediation efforts are effective (Spencer & Harvey, 2012). Multiple aspects, including physical and biogeochemical processes as well as ecological and morphological indicators, should be considered to identify the effectiveness of any plan put into place (Spencer & Harvey, 2012). By monitoring multiple aspects of the remediation effort and its outcome, we can ensure that the water quality and environmental health of the site is improving as expected and that pollutants have been effectively sequestered or fully removed.

4. References

- Appleby, P., & Oldfield, F. (1992). Application of ^{210}Pb to sedimentation studies. In M. Ivanovich, & R. Harmon (Eds.), *Uranium-Series Disequilibrium: Applications to Earth, Marine, & Environmental Studies* (pp. 731-778). Oxford, UK: Oxford University Press.
- Bricker-Urso, S., Nixon, S., Cochran, J., Hirschberg, D., & Hunt, C. (1989). Accretion rates and sediment accumulation in Rhode Island salt marshes. *Estuaries*, 12, 300-317.
- Brugam, R. (1978). Pollen indicators of land-use change in southern Connecticut. *Quaternary Research*, 9, 349-362.
- Christiansen, T., Wilberg, P., & Milligan, T. (2000). Flow and Sediment Transport on a Tidal Salt Marsh Surface. *Estuarine, Coastal and Shelf Science*, 50, 315-331.
- Church, T., Sommerfield, C., Velinsky, D., Point, D., Benoit, C., Amouroux, D., . . . Donard, O. (2006). Marsh sediments as records of sedimentation, eutrophication and metal pollution in the urban Delaware Estuary. *Marine Chemistry*, 102, 72-95.
- Clark, J., & Patterson, W. (1984). Pollen, Pb-^{210} , and opaque spherules; an integrated approach to dating and sedimentation in the intertidal environment. *Journal of Sedimentary Research*, 54, 1251-1265.
- Cooper, S., & Brush, G. (1993). A 2,500-year history of anoxia and eutrophication in Chesapeake Bay. *Estuaries*, 16, 617-626.
- De Vleeschouwer, F., Chambers, F., & Swindles, G. (2010). Coring and sub-sampling of peatlands for palaeoenvironmental research. *Mires and Peat*, 7, 1-10.
- Donnelly, J., Bryant, S., Butler, J., Dowling, J., Fan, L., Hausmann, N., . . . Webb III, T. (2001). A 700-year sedimentary record of intense hurricane landfalls in southern New England. *Geological Society of America Bulletin*, 113, 714-727.
- Fægri, K., & Iversen, J. (1964). *Textbook on Pollen Analysis*. New York, New York: Hafner.
- Flynn, W. (1968). The determination of low levels of polonium-210 in environmental materials. *Analytical Chimica Acta*, 43, 221-227.
- Forstner U., Muller G. (1981). Concentrations of Heavy Metals and Polycyclic Aromatic Hydrocarbons in River Sediments: Geochemical Background, Man's Influence and Environmental Impact. *GeoJournal*, Vol. 5, No. 5: *Water Pollution*, p. 417-432
- Gallagher, F.J., Pechmann, I., Grabosky, J., Bogden, J., Weis, P., 2008. Soil metal concentrations and vegetative assemblage structure in an urban brownfield. *Environmental Pollution* 153 (2), 257-496

- Gambrell, R. (1994). Trace and toxic metals in wetlands - A review. *Journal of Environmental Quality*, 23, 883-891.
- Haslett, J., & Parnell, A. (2008). A simple monotone process with application to radiocarbon-dated depth chronologies. *Journal of the Royal Statistical Society*, 3, 399-418.
- He, Q., & Walling, D. (1996). Rates of Overbank Sedimentation on the Floodplains of British Lowland Rivers Documented Using Fallout ¹³⁷Cs. *Geografiska Annaler. Series A, Physical Geography*, 78, 223-234.
- Hurst, R. (2002). Lead isotopes as age-sensitive genetic markers in hydrocarbons. 3. Leaded gasoline, 1923-1990 (ALAS model). *Environmental Geosciences*, 9, 43-50.
- Jeffries, H. (1962). Environmental characteristics of Raritan Bay, a polluted estuary. *Limnology and Oceanography*, 7, 21-31.
- Juang, K.W., Lee, D.Y., Ellsworth, T.R., 2001. Using rank-order geostatistics for spatial interpolation of highly skewed data in heavy-metal contaminated site. *Journal of Environmental Quality* 30, 894-903.
- Kemp, A., Horton, B., Vane, C., Bernhardt, C., Corbett, D., Engelhart, S., . . . Cahill, N. (2013). Sea-level change during the last 2500 years in New Jersey, USA. *Quaternary Science Reviews*, 81, 90-104.
- Lima, A., Bergquist, B., Boyle, E., Reuer, M., Dudas, F., Reddy, C., & Eglinton, T. (2005). High-resolution historical records from Pettaquamscutt River basin sediments: 2. Pb isotopes reveal a potential new stratigraphic marker. *Geochimica et Cosmochimica Acta*, 69, 1813-1824.
- Long, E.R., MacDonald, D.D., Smith, S.L., and Calder, F.D. 1995. Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments. *Environmental Management* 19(1):81-97
- Marcantonio, F., Zimmerman, A., Xu, Y., & Canuel, E. (2002). A Pb isotope record of mid-Atlantic US atmospheric Pb emissions in Chesapeake Bay sediments. *Marine Chemistry*, 77, 123-132.
- Marshall, S. (2004). The Meadowlands Before the Commission: Three Centuries of Human Use and Alteration of the Newark and Hackensack Meadows. *Urban Habitats*, 4-27.
- McKee, L., Ganju, N., & Shoellhamer, D. (2006). Estimates of suspended sediment entering San Francisco Bay from Sacramento and San Joaquin Delta, San Francisco Bay, CA. *Journal of Hydrology*, 323, 335-352.
- Metcalfe, S., & Derwent, D. (2014). *Atmospheric Pollution and Environmental Change*. Routledge.

- Nittrouer, C., Sternberg, R., Carpenter, R., & Bennett, J. (1979). The use of Pb-210 geochronology as a sedimentological tool: Application to the Washington coast shelf. *Marine Geology*, 31, 297-316.
- Potapova, M., & Charles, D. (2007). Diatom metrics for monitoring eutrophication in rivers of the United States. *Ecological Indicators*, 7, 48-70.
- Potapova, M., Desianti, N., & Velinsky, D. (2015). *Barnegat Bay Nutrient Inference Model*. Philadelphia, PA: Academy of Natural Sciences of Drexel University.
- Russell, E. (1980). Vegetational Change in Northern New Jersey from Precolonization to the Present: A Palynological Interpretation. *Bulletin of the Torrey Botanical Club*, 107, 432-446.
- Sanger, D., Holland, A., & Scott, G. (1999). Tidal creek and saltmarsh sediments in South Carolina Coastal estuaries: II. Distribution of Organic Contaminents. *Archives of Environmental Contamination and Toxicology*, 37, 458-471.
- Spencer, J., & Harvey, K. (2012). Understanding system disturbance and ecosystem services in restored saltmarshes: integrating physical and biogeochemical processes. *Estuarine, Coastal, and Shelf Science*, 106, 23-32.
- Weis, J., & Weis, P. (2004). Metal uptake, transport and release by wetland plants: implications for phytoremediation and restoration. *Environment International*, 30, 685-700.
- Zedler, J., & Leach, M. (1998). Managing urban wetlands for multiple use: research, restoration, and recreation. *Urban Ecosystems*, 2, 189-204.

5. Acknowledgements

This study was sponsored by the Mushett Family Foundation. We would like to thank Hank and Mark Daaleman and the Foundation for trusting MERI with this task and their continuous support throughout the study.

We would like to acknowledge Margaret Christie, Benjamin Horton, Jennifer Walker and Jennifer Clear from RU Marine & Coastal Sciences for their work in the assessment of wetland core samples and historical anthropogenic influence, as well as Margaret Christie as the author of Component II - Historical Land Use Report in the Lower Raritan Basin. We would like to thank the staff of the Marine & Coastal Sciences Department for their professionalism and continued support of the study.

We would like to thank Chip Haldeman, captain of the Rutgers Research Vehicle to make our field outing seamless and effective.

Great thanks goes to the MERI staff for the endless hours of mucky field work of Francisco Artigas, Joe Grzyb, Michael Stepowyj and Brian Wlodawski, for the infinite patience of Cheryl Yao, Yefim Lewinsky and Joe Grzyb while running the sample analysis, the countless screen time from Michael Stepowyj and Ildiko C. Pechmann spent on the computer modelling, and Sandy Speers for taking care of the business end of it and getting the group organized throughout the study.